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Rhodium(I) carbonyl complexes of quinoline carboxaldehyde ligands and their catalytic carbonylation reaction

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ABSTRACT

The dimeric rhodium precursor $[Rh(CO)_2Cl]_2$ reacts with quinoline (**a**) and its three isomeric carboxaldehyde ligands [quinoline-2-carboxaldehyde (**b**), quinoline-3-carboxaldehyde (**c**), and quinoline-4-carboxaldehyde (**d**)] in 1:2 mole ratio to afford complexes of the type *cis*-$[Rh(CO)_2Cl(L)]$ (**1a**–**1d**), where L = **a**–**d**. The complexes **1a**–**1d** have been characterised by elemental analyses, mass spectrometry, IR and NMR (^1H, ^{13}C) spectroscopy together with a single crystal X-ray structure determination of **1c**. The X-ray crystal structure of **1c** reveals square planar geometry with a weak intermolecular pseudo dimeric structure (Rh···Rh = 3.573 Å). **1a**–**1d** undergo oxidative addition (**OA**) with different electrophiles such as CH_3I, C_2H_5I and I_2 to give Rh(III) complexes of the type $[Rh(CO)(COR)Cl(L)I]$ {R = $-CH_3$ (**2a**–**2d**), R = $-C_2H_5$ (**3a**–**3d**)} and $[Rh(CO)Cl(L)I_2]$ (**4a**–**4d**) respectively. **1b** exhibits facile reactivity with different electrophiles at room temperature (25 °C), while **1a**, **1c** and **1d** show very slow reactivity under similar condition, however, significant reactivity was observed at a temperature ~40 °C. The complexes **1a**–**1d** show higher catalytic activity for carbonylation of methanol to acetic acid and methyl acetate [Turn Over Frequency (TOF) = 1551–1735 h^{-1}] compared to that of the well known Monsanto's species $[Rh(CO)_2I_2]^-$ (TOF = 1000 h^{-1}) under the reaction conditions: temperature 130 ± 2 °C, pressure 33 ± 2 bar, 450 rpm and time 1 h. The organometallic residue of **1a**–**1d** was also isolated after the catalytic reaction and found to be active for further run without significant loss of activity.

1. Introduction

The rhodium promoted catalytic carbonylation of methanol to acetic acid and methyl acetate is of great importance both academically and industrially [1–3]. The well known Monsanto's species $[Rh(CO)_2I_2]^-$ [4–6] used for carbonylation of methanol to acetic acid needs drastic reaction conditions. Attempts to develop new catalytic species have been hampered by the relatively harsh condition under which the reaction is conducted commercially (because under such conditions, virtually any source of rhodium will be converted to $[Rh(CO)_2I_2]^-$) [5]. Recently, considerable efforts have been made to improve the catalysts by incorporating different ligands into its coordination sphere to show comparable or better activity compared to Monsanto's species [7–12]. In this respect, phosphorus containing ligands are mostly studied since they can stabilize low valent metal centres by both σ-donation and π back bonding. Rhodium(I) complexes containing different types of N/N~O donor ligands have also aroused considerable interest because of their structural novelty and catalytic activity [13–22]. Since nitrogen atoms have no low lying vacant d-orbital available to accept back donation from the metal centre and thus, nitrogen donor ligands use only σ-donor electrons. This imparts more ionic character to the metal-ligand bonds [17] and hence makes the metal centre more susceptible to oxidative addition, which is the key step in carbonylation reaction [17–19]. The oxygen atom, being hard donor, confers stability to metal at high oxidation state in the oxidative addition reaction [17]. Thus, the different hardness and donor properties of ligands containing N and O donor sites may offer advantages in catalysis. Our group has recently contributed several publications particularly on rhodium carbonyl complexes of N/N~O donor ligands and their efficient catalytic carbonylation reaction [15–17,23–25] which prompted us to explore with some different types of N/N~O donor ligands like quinoline and its carboxaldehyde derivatives. In this paper, we report the synthesis of

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four new Rh(I) carbonyl complexes of quinoline and its carboxaldehyde derivatives, and their reactivity towards small molecules like CH_3I, C_2H_5I, and I_2. The catalytic activity of the synthesized complexes has also been demonstrated in carbonylation of methanol for the production of acetic acid and methyl acetate.

2. Results and discussion

2.1. Synthesis and characterization of *1a–1d*

The reaction of the chloro-bridged dimer $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 with two mole equivalents of the ligands, **a–d** affords the complexes of the type $[Rh(CO)_2Cl(L)]$ (**1a–1d**) [where L = **a–d**] (Scheme 1). Elemental analyses and mass spectrometric results of the complexes support the observed molecular composition of **1a–1d**. The IR spectra of **1a–1d** exhibit two equally intense ν(CO) vibrations in the range 2006–2087 cm^{-1} indicating the formation of *cis* dicarbonyl rhodium (I) complexes of ligands. The ^1H NMR spectra of **1a–1d** show multiple resonances (one doublet of doublet for **1a**, two doublets for **1b** and **1d** and two singlets for **1c**) in the range $\delta = 8.61–9.61$ ppm assigned to the H atoms of pyridyl ring, a singlet in the range $\delta = 10.25–11.69$ ppm for the –CHO group in **1b–1d** and a multiplet in the range $\delta = 7.45–8.88$ ppm for H atoms of phenyl ring. The ^1H NMR spectra of **1a–1d** show downfield chemical shifts for the pyridyl protons and almost similar resonances for –CHO protons in **1b–1d** compared to free ligands, which indicate the coordination in the complexes has taken place through the N-atom of the ligands. The ^{13}C NMR spectra of **1a–1d** show two singlet resonances in the range $\delta = 183–191$ ppm indicating the presence of CO and –CHO groups, while the resonance in the range 119–154 ppm are characteristic of the carbon atoms in the quinoline ring.

2.2. Single crystal X-ray structural determination of *1c*

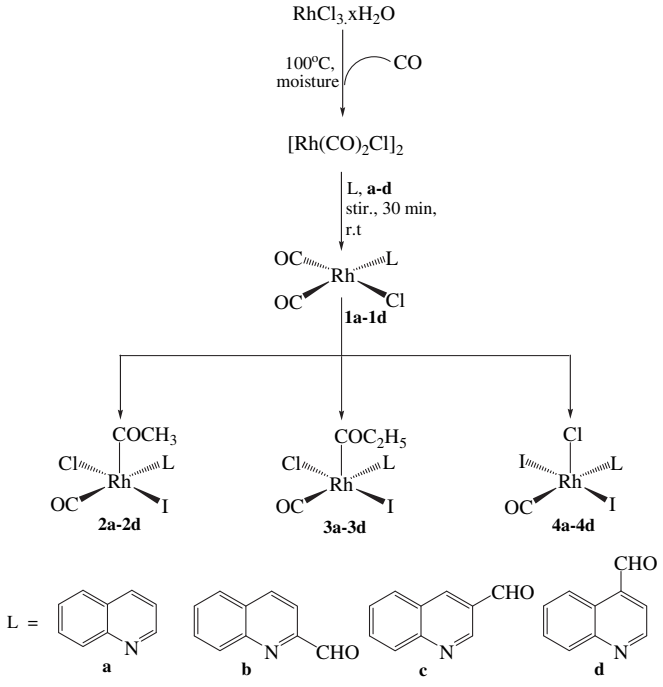
Compound **1c** crystallizes in a triclinic system with space group P –1 with two independent molecules in the asymmetric unit. The crystallographic data and important bond lengths and bond angles are shown in Tables 1 and 2 respectively. The rhodium centre of **1c** is situated in a square planar geometry coordinated by two *cis* CO groups, a Cl atom and the N-atom of the qunoline-3-carboxaldehyde ligand (Fig. 1). **1c** exhibits an interesting intermolecular Rh···Rh (3.573 Å) interaction between the two mononuclear units, which is ca. 0.4 Å shorter than the sum of van der Waals radii of two rhodium centres, indicating that the interaction is strong enough to hold the two molecular units together (Fig. 2). Assuming the centroides of the atoms Cl(1),C(12),C(13),N(1) and Cl(3),C(42),C(43),N(31) as C_{g1} and C_{g2} respectively (Fig. 3), the calculated distance between the two centroides (using mercury 2.2 crystallographic software) is found to be ca. 3.662 Å which is 0.089 Å longer than the distance between the two Rh centres of the complex **1c**. This slight distortion of square planar geometry may be due to the strong Rh···Rh intermolecular interaction which pulls the Rh metal slightly out of the molecular plane.

Table 1
Crystallographic data of **1c**.

Empirical formula	$C_{12}H_7ClNO_3Rh$
Formula Weight	351.55
T (K)	125
λ (Å)	0.71075
Cryst. Syst.	Triclinic
Space group	P–1
Z	4
a (Å)	7.4380(17)
b (Å)	9.085(2)
c (Å)	19.727(6)
α (°)	83.253(19)
β (°)	83.93(2)
γ (°)	67.325(17)
μ(MoKα) mm^{-1}	1.614
Reflections collected	4228
*R*1 (observed data)	0.0546(3820)
wR_2 (all data)	0.1817(4228)

2.3. Reactivity of *1a–1d* towards different electrophiles

The complexes **1a–1d** undergo oxidative addition (**OA**) with various electrophiles like CH_3I, C_2H_5I and I_2 to give complexes **2a–2d**, **3a–3d** and **4a–4d** respectively. The **OA** of CH_3I and C_2H_5I yields five coordinate rhodium acyl species $[Rh(CO)(COR)Cl(L)I]$ (R = $-CH_3$, $-C_2H_5$). It is likely that the **OA** of alkyl halides to the Rh (I) centre forms an octahedral rhodium(III) alkyl intermediate before forming the acyl complexes. These intermediates then undergo migratory insertion reaction to form five coordinate rhodium(III) acyl complexes **2a–2d** and **3a–3d** respectively. The IR spectra of the complexes **2a–2d** and **3a–3d** show only a single terminal ν(CO) band in the range 2019–2069 cm^{-1} and a broad band in the range 1680–1747 cm^{-1} due to the formation of the acyl carbonyl group. It is worth to mention here that the exact position of the $\nu(CO)_{acyl}$ band could not be assigned for the complexes **2b–2d** and **3b–3d** due to the overlapping with $\nu(CO)_{CHO}$ bands. The single high value of the terminal ν(CO) band indicates the formation of the oxidized products. Apart from the characteristics resonance for **2a–2d** and **3a–3d**, the ^1H NMR resonance in the range



Scheme 1. Synthesis and reactivity of **1a–1d**.

Table 2
Selected bond length (Å) and angles (°) of **1c**.

Rh(1)–Cl(1)	2.336(2)	Rh(1)–C(12)	1.847(10)
Rh(1)–C(13)	1.866(7)	Rh(1)–N(1)	2.132(5)
C(12)–O(12)	1.135(13)	C(13)–O(13)	1.110(9)
Cl(1)–Rh(1)–C(13)	87.7(3)	C(12)–Rh(1)–C(13)	89.3(2)
N(1)–Rh(1)–C(12)	92.9(3)	C(12)–Rh(1)–C(13)	90.0(3)
N(1)–Rh(1)–C(13)	177.0(3)	Cl(1)–Rh(1)–C(12)	177.7(2)

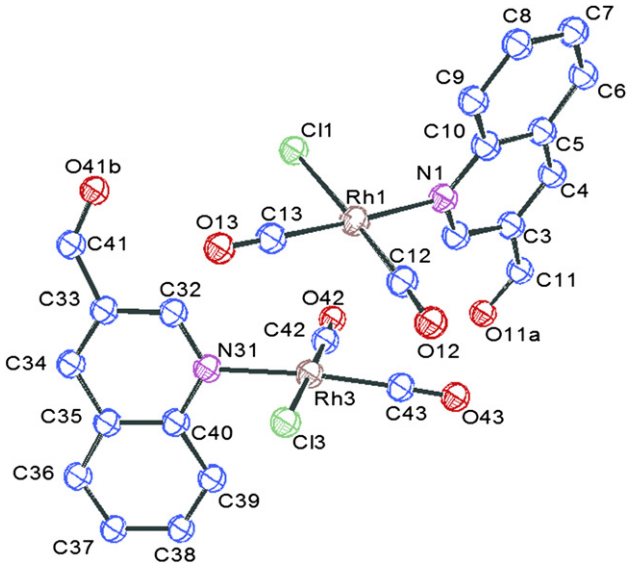


Fig. 1. Single crystal X-ray structure analysis of **1c** (Hydrogen atoms are omitted for clarity).

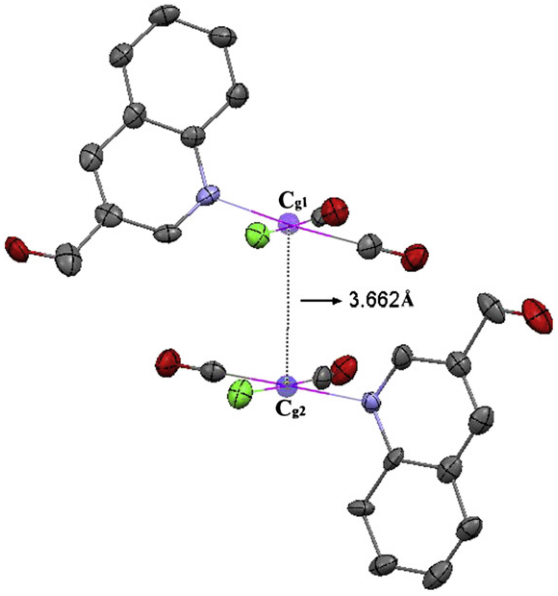


Fig. 3. The intermolecular distance of two centroids C_{g1} [Cl(1),C(12),C(13),N(1)] and C_{g2} [Cl(3),C(42),C(43),N(31)] (3.662 Å) in **1c**.

$\delta = 2.39–3.05$ ppm indicates the formation of acyl group. ^{13}C NMR for **2a**–**2d** and **3a**–**3d** show resonance in the range $\delta = 183–187$ ppm and a slightly broad resonance in the range $\delta = 204–210$ ppm for terminal CO and acyl group respectively. The ^{1}H and ^{13}C NMR of **4a**–**4d** show characteristic resonance of the quinoline ring and aldehydic group at slightly downfield compared to the parent compounds **1a**–**1d.** In addition, ^{13}C NMR spectra also show some characteristic resonances in the range $\delta = 185–187$ ppm attributable to the presence of terminal CO group. It is interesting to observe that **1b** shows facile reactivity with different electrophiles like CH_3I, C_2H_5I and I_2 at room temperature (25 °C), while **1a**, **1c** and **1d** exhibit very slow reaction under the similar condition, however, significant reactivity was observed when the reactions were conducted at ~40 °C. The higher reactivity of **1b** compared to **1a**, **1c**, and **1d** may be due the influence of the –CHO group at 2-position of the ligand (Scheme 2), which weakens the Rh–CO bond

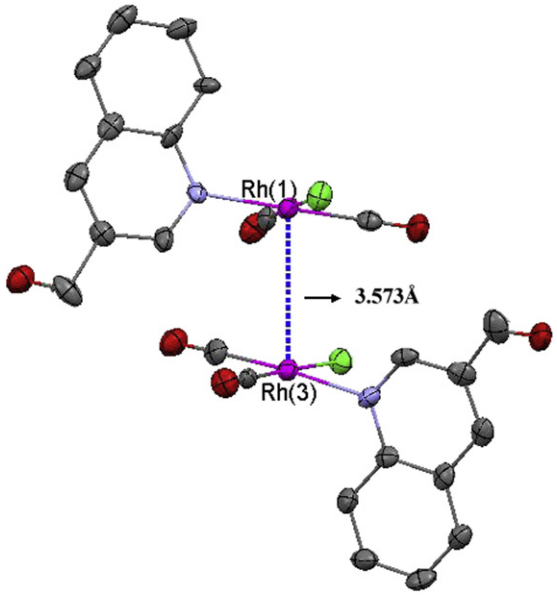


Fig. 2. The intermolecular distance of two Rhodium centres (3.573 Å) in **1c**.

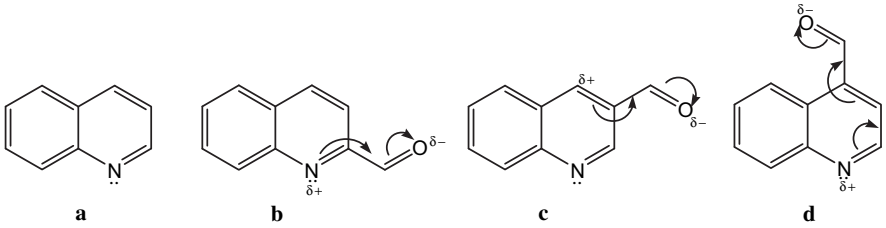
(substantiated by the higher ν(CO) values) leading to facile migratory insertion reaction. Further, the steric effect of the –CHO group may also destabilize the octahedral intermediate to facilitate the formation of acyl product [26,27].

2.4. Carbonylation of methanol to acetic acid and ester using the complexes *1a*–*1d* as the catalyst precursors

The results of carbonylation of methanol to acetic acid and methyl acetate in the presence of **1a**–**1d** as catalyst precursors are shown in the Table 3. The precursor complexes **1a**–**1d** show a total conversion of 88.9, 90.1, 80.6 and 89.2% of CH_3OH at 130 ± 2 °C and 30 ± 2 bar CO pressure with corresponding TOF of 1711, 1735, 1551 and 1719 h^{-1}. Under the similar experimental conditions, the well known precursor $[Rh(CO)_2I_2]^-$ generated *in situ* from $[Rh(CO)_2Cl]_2$ shows a total conversion of only 52.1% with corresponding TOF of 1000 h^{-1}. This indicates that the catalytic efficiency of the complexes is greatly enhanced by the incorporation of the ligands into the coordination sphere of the rhodium centre. The donor capacities of the N atoms of the ligands **a**–**d** follows the order **a** > **c** > **d** > **b** (Scheme 2). However, the catalytic efficiency of the complexes **1a**–**1d** follows a different order i.e. **1b** > **1d** ≈ **1a** > **1c**. Therefore, from the electron donation capacities of the ligands, the observed catalytic efficiency could not be interpreted. The marginal higher catalytic activity of **1b** over **1d** and **1a** may be due to the facile migratory insertion as mentioned earlier in the reactivity section. However, the factor responsible for the lowest catalytic activity of **1c** among the complexes has yet to be ascertained. The organometallic residue of **1a**–**1d** was recovered after the first catalytic run, which were mostly identified as rhodium(III) acyl complexes [IR ($CHCl_3$): 2021 – 2068 [ν(CO)], 1680 – 1750 [broad, $\nu(CO)_{acyl/CHO}$ cm^{-1}]. The recovered catalysts were still found active for further catalytic run showing TOF = 1437–1602 h^{-1}.

3. Conclusions

Four new complexes **1a**–**1d** have been synthesized and characterized. The molecular structure of **1c** has also been determined by single crystal X-ray diffraction, which exhibits a dimeric



Scheme 2. The electron density on the nitrogen atom of the ligands.

structure with a weak rhodium–rhodium interaction (Rh···Rh = 3.573 Å). **1a**–**1d** undergo **OA** with different electrophiles like CH_3I, C_2H_5I and I_2 to afford Rh(III) complexes of the type [Rh(CO)(COR)Cl(L)I] {R = $-CH_3$ (**2a**–**2d**), $-C_2H_5$ (**3a**–**3d**) and [Rh(CO)Cl(L)I_2] (**4a**–**4d**). The catalytic activities of **1a**–**1d** for the carbonylation of methanol to acetic acid and its ester exhibit a higher TOF (1551–1735 h^{-1}) compared to the well known commercial species $[Rh(CO)_2I_2]^-$ (TOF = 1000 h^{-1}).

4. Experimental

4.1. General information

All operations were carried out under N_2 environment. 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. Quinoline and quinoline carboxaldehyde 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 spectrophotometer. 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 $SiMe_4$. Mass spectra of the complexes were recorded on ESQUIRE 3000 Mass spectrometer. The carbonylation reactions of methanol were carried out in a high pressure reactor (Parr-4592, USA) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID).

4.2. Starting materials

$[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3 \cdot 3H_2O$ at 100 °C in the presence of moisture [28].

Table 3
Catalytic carbonylation data of **1a**–**d**.

Entry	Complexes	Total conversion (%)	Acetic acid[a] (%)	Methyl acetate[a] (%)	TOF[b] (h^{-1})
1	$[Rh(CO)_2I_2]^-$[c]	52.1	10.3	41.8	1000
2	**1a**	88.9	39.2	49.7	1711
3	Residue from entry 2	81.1	34.5	46.6	1556
4	**1b**	90.1	39.8	50.3	1735
5	Residue from entry 4	83.2	37.3	45.9	1602
6	**1c**	80.6	40.2	40.3	1551
7	Residue from entry 6	74.6	38.1	36.5	1437
8	**1d**	89.2	39.8	49.3	1719
9	Residue from entry 8	83.1	37.0	46.0	1601

[a] Yield of methyl acetate and acetic acid were obtained from GC analysis.
[b] TOF = [amount of product (mol)]/[amount of catalyst (Rh mol)]/Time (h).
[c] Formed from $[Rh(CO)_2Cl]_2$ under catalytic reaction condition.

4.3. Synthesis of the complexes $[Rh(CO)_2Cl(L)]$ (**1a**–**1d**), L = Quinoline (**a**), quinoline-2-carboxaldehyde (**b**), quinoline-3-carboxaldehyde (**c**), quinoline-4-carboxaldehyde (**d**)

About 0.257 mmol (0.10 g) $[Rh(CO)_2Cl]_2$ was dissolved in dichloromethane (10 cm^3) and to this solution, 0.514 mmol (0.066 g of **a** and 0.081 g of **b**–**d**) of the appropriate ligand was added. The reaction mixture was stirred at r.t. for ca. 30 min and the solvent was evaporated under vacuum. The yellowish red coloured compounds so obtained were washed with diethyl ether and stored over silica gel in desiccator.

1a: Yield: 0.138 g, 83%. IR (KBr): 2083, 2006 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.45–8.22 (6H, m, Ph, Py), δ = 9.61 (H-2, dd, J_{H-H} = 8.3, 4.3 Hz, Py) ppm. ^{13}C NMR ($CDCl_3$): δ = 119.9–152.5 (m, Ph, Py), 183 (CO) ppm. $C_{11}H_7NClO_2Rh$ (323.55): cald. C 40.79, H 2.17, N 4.32; found C 40.63, H 2.11, N 4.25. MS: m/z = 323.2 [M^+].

1b: Yield: 0.158 g, 88%. IR (KBr): 2087, 2014 [ν(CO)], 1712 [ν(–CHO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.86–8.32 (4H, m, Ph), 8.61 (H-3, d, J_{H-H} = 8.5 Hz, Py), δ 9.43 (H-4, d, J_{H-H} = 8.5 Hz, Py), δ 11.69 (CHO, s) ppm. ^{13}C NMR ($CDCl_3$): δ = 119.7–152.6 (m, Ph, Py), 189.5 (CHO), 185 (CO) ppm. $C_{12}H_7NClO_3Rh$ (351.55): cald. C 39.98, H 1.89, N 3.79; found C 39.73, H 1.81, N 3.71. MS: m/z = 350.8 [M^+].

1c: Yield: 0.153 g, 85%. IR (KBr): 2085, 2010 [ν(CO)], 1705 [ν(–CHO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.84–8.88 (3H, m, Ph), 9.08 (H-9, d, Ph), 8.82 (H-4, s, Py), 9.52 (H-2, s, Py), 10.25 (CHO, s) ppm. ^{13}C NMR ($CDCl_3$): δ = 128.3–153.0 (m, Ph, Py), 184 (CO), 188.2 (CHO) ppm. $C_{12}H_7NClO_3Rh$ (351.55): cald. C 39.98, H 1.89, N 3.79; found C 39.75; H 1.76, N 3.69. MS: m/z = 350.7 [M^+].

1d: Yield: 0.15 g, 83%. IR (KBr): 2086, 2011 [ν(CO)], 1707 [ν(–CHO)] cm^{-1}. ^1H NMR data ($CDCl_3$): δ = 7.92–8.07 (3H, m, Ph), 9.12 (H-9, d, J_{H-H} = 7.3 Hz, Ph), 9.22 (H-3, d, J_{H-H} = 8.6 Hz, Py), 9.36 (H-2, d, J_{H-H} = 8.6 Hz, Py), 10.58 (CHO, s) ppm. ^{13}C NMR ($CDCl_3$): δ = 124.8–154.0 (m, Ph, Py), 185.0 (CO), 191.0 (CHO). $C_{12}H_7NClO_3Rh$ (351.55): cald. C 39.98, H 1.89, N 3.79; found C 39.75, H 1.81, N 3.67. MS: m/z = 350.8 [M^+].

4.4. Synthesis of [Rh(CO)(COR)Cl(L)I] {R = $-CH_3$ (**2a**–**2d**), R = $-C_2H_5$ (**3a**–**3d**)}

$[Rh(CO)_2Cl(L)]$ (50 mg) (**1a**–**1d**) was dissolved in dichloromethane (5 cm^3) and each of RX (3 cm^3) (RX = CH_3I, C_2H_5I) was added to it. The reaction mixture of **1b** with alkyl halides was stirred at r.t. for about 6 and 12 h to yield **2b** and **3b** respectively. On the other hand, the reaction mixtures of **1a**, **1c** and **1d** with alkyl halides were refluxed for about 6 h to generate **2a**, **2c**, **2d** and **3a**, **3c**, **3d**. The colour of the solution changed from yellowish red to dark 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.

2a: Yield: 0.052 g, 73%. IR (KBr): 2021 [ν(CO)], 1720 [$\nu(CO)_{acyl}$] cm^{-1}. ^1H NMR (d_6–DMSO): δ = 2.39 (3H, s, CH_3), 7.87–8.43 (6H, m, Ph, Py), 9.56 (H-2, dd, J_{H-H} = 8.0, 4.1 Hz, Py) ppm. ^{13}C NMR (DMSO-D_6): δ = 45.0 (CH_3), 123.9–161.3 (m, Ph, Py), 186.3 (CO), 204.0 [$(CO)_{acyl}$] ppm.

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2b: Yield: 0.052 g, 74%. IR (KBr): 2065 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 2.51 (3H, s, CH_3), 7.93–8.45 (4H, m, Ph), 8.77 (H-3, d, J_{H-H} = 7.9 Hz, Py), 9.59 (H-4, d, J_{H-H} = 7.9 Hz, Py), 11.83 (CHO, s) ppm. ^{13}C NMR (DMSO-D_6): δ = 45.0 (CH_3), 123.9–161.3 (m, Ph, Py), 186.3 (CO), 192.9 (CHO), 204.0 [$(CO)_{acyl}$] ppm.

2c: Yield: 0.055 g, 79%. IR (KBr): 2065 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 2.49 (3H, s, CH_3), 7.91–8.91 (3H, m, Ph), 9.11 (H-9, d, J_{H-H} = 7.6 Hz, Ph), 8.94 (H-4, s, Py), 9.65 (H-2, s, Py), 10.39 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 46.0 (CH_3), 133.3–161.0 (m, Ph, Py), 187.0 (CO), 191.2 (CHO), δ 207.6 [$(CO)_{acyl}$] ppm.

2d: Yield: 0.051 g, 73%. IR (KBr): 2068 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 2.67 (3H, s, CH_3), 7.99–8.19 (3H, m, Ph), 9.28 (H-9, d, J_{H-H} = 6.9 Hz, Ph), 9.33 (H-3, d, J_{H-H} = 8.4 Hz, Py), 9.57 (H-2, d, J_{H-H} = 8.4 Hz, Py), 10.69 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 45.3 (CH_3), 129.1–161.3 (m, Ph, Py), 186.9 (CO), 194.2 (CHO), 209.9 [$(CO)_{acyl}$] ppm.

3a: Yield: 0.051 g, 69%. IR (KBr): 2019 [ν(CO)] cm^{-1} 1747 [ν $(CO)_{acyl}$] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 1.23 (3H, t, J_{H-H} = 6.3 Hz, CH_3), 2.89 (2H, q, J_{H-H} = 6.3 Hz, CH_2), 7.93–8.52 (6H, m, Ph, Py), 9.59 (H-2, dd, J_{H-H} = 7.9,4.0 Hz, Py) ppm. ^{13}C NMR (d_6-DMSO): δ = 22.7 (CH_3), 54.9 (CH_2), 121.5–161.0 (m, Ph, Py), 187.0 (CO), 205.1 [$(CO)_{acyl}$] ppm.

3b: Yield: 0.057 g, 79%. IR (KBr): 2069 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 1.21 (3H, t, J_{H-H} = 6.3 Hz, CH_3), 2.96 (2H, q, J_{H-H} = 6.3 Hz, CH_2), 7.89–8.44 (4H, m, Ph), 8.75 (H-3, d, J_{H-H} = 8.2 Hz, Py), 9.61 (H-4, d, J_{H-H} = 8.1 Hz, Py), 11.79 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 22.1 (CH_3), 56.3 (CH_2), 122.7–159.1 (m, Ph, Py), 186.0 (CO), 189.9 (CHO), 206.1 [$(CO)_{acyl}$] ppm.

3c: Yield: 0.051 g, 71%. IR (KBr): 2067 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 1.25 (3H, t, J_{H-H} = 6.3 Hz, CH_3), 3.05 (2H, q, J_{H-H} = 6.3 Hz, CH_2), 7.89–8.89 (3H, m, Ph), 9.10 (H-9, d, J_{H-H} = 7.9 Hz, Ph), 8.93 (H-4, s, Py), 9.67 (H-2, s, Py), 10.35 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 23.1 (CH_3), 57.6 (CH_2), 131.3–159.3 (m, Ph, Py), 186.3(CO), 190.7 (CHO), 208.1 [$(CO)_{acyl}$] ppm.

3d: Yield: 0.054 g, 75%. IR (KBr): 2067 [ν(CO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 1.28 (3H, t, J_{H-H} = 6.4 Hz, CH_3), 3.02 (2H, q, J_{H-H} = 6.4 Hz, CH_2) 8.00–8.29 (3H, m, Ph), 9.25 (H–9, d, J_{H-H} = 7.6 Hz, Ph), 9.35 (H-3, d, J_{H-H} = 8.4 Hz, Py), 9.55 (H-2, d, J_{H-H} = 8.4 Hz, Py), 10.68 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 22.8 (CH_3), 56.8 (CH_2), 128.9–160.8 (m, Ph, Py), 186.1 (s, CO), 193.7 (CHO), 208.5 [$(CO)_{acyl}$] ppm.

4.5. Synthesis of [Rh(CO)Cl(L)I_2](**4a**–**4d**)

[$Rh(CO)_2Cl(L)$] (0.05 g) (**1a**–**1d**) was dissolved in dichloromethane (5 cm^3). To that solution iodine was added (0.02 mmol, 0.025 g). The reaction mixture **1b** was stirred at r.t. for 6 h to yield **1b**. However, the reaction mixtures of **1a**, **1c** and **1d** with I_2 were refluxed for 6 h to yield **4a**, **4c** and **4d** respectively. The colour of the solution changed from yellowish red to dark reddish brown and the solvent was evaporated under vacuum. Excess iodine was removed by washing several times with hexane and stored over silica gel in a desiccator.

4a: Yield: 0.061 g, 68%. IR (KBr): 2059 [ν(CO)]. ^1H NMR (d_6-DMSO): δ = 7.81–8.49 (6H, m, Ph), 9.61 (H-2, dd, J_{H-H} = 8.1, 4.1 Hz, Py) ppm. ^{13}C NMR (d_6-DMSO): δ = 123.7–160.5 (m, Ph, Py) and 185.7 (CO) ppm.

4b: Yield: 0.056 g, 68%. IR (KBr): 2062 [ν(CO)], 1710[ν(−CHO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 7.86–8.41 (4H, m, Ph), 8.71(H-3, d, J_{H-H} = 7.2 Hz, Py), 9.62 (H-4, d, J_{H-H} = 7.2 Hz, Py), 11.71 (s, CHO) ppm. ^{13}C NMR (d_6-DMSO): δ = 123.7–160.5 (m, Ph, Py), 185.7 (CO) and 190.7 (CHO) ppm.

4c: Yield: 0.066 g, 81%. IR (KBr): 2066[ν(CO)], 1706 [ν(−CHO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 7.91–8.96 (3H, m, Ph), 9.12 (H-9, d, J_{H-H} = 7.1 Hz, Ph), 9.04 (H-4, s, Py), 9.69 (H-2, s, Py), 10.35 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 129.1–157.0 (m, Ph, Py), δ 185.7 (CO), δ 189.9 (CHO) ppm.

4d: Yield: 0.059 g, 72%. IR (KBr): 2067 [ν(CO)], 1707 [ν(−CHO)] cm^{-1}. ^1H NMR (d_6-DMSO): δ = 8.02–8.22 (3H, m, Ph), 9.27 (H-9, d, J_{H-H} = 6.9 Hz, Ph), 9.39 (H-3, d, J_{H-H} = 8.5 Hz, Py), 9.48 (H-2, d, J_{H-H} = 8.5 Hz, Py), 10.69 (CHO, s) ppm. ^{13}C NMR (d_6-DMSO): δ = 129.8–159.7 (m, Ph, Py), 187.1(CO), 193.7 (CHO) ppm.

4.6. X-ray structural analysis

Single crystals of **1c** were grown by slow diffusion of hexane into dichloromethane solution. The intensity data of the compounds were collected on a Rigaku Saturn CCD with Mo Kα radiation (λ = 0.71073 Å) at 125 K. The structure was solved with SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [29]. Hydrogen atoms were idealized using the riding models.

4.7. Carbonylation of methanol using complexes **1a**–**1d** 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 catalyst (0.0514 mmol) were taken into the reactor. The reactor was then purged with CO for about 5 min and then pressurized with CO gas (20 ± 1 bar at 25 °C). The sample vessel was placed in a heated jacket of the reactor and the reactions were carried out at 130 ± 2 °C for 1 h under CO pressure 33 ± 2 bar. After completion of the reaction, the reactor was allowed to cool upto room temperature. The products were collected and analyzed by GC (the species were verified by comparison with authentic sample). The recycle experiments were done by maintaining the same experimental conditions as described above with the dark brown solid mass as catalyst obtained by evaporating the carbonylation reaction mixture under the reduced pressure.

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Appendix A. Supplementary data

CCDC – 737945 (**1c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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