APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 258–264
Materials, Nanomaterials and Synthesis AOC
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.293

Carbonylrhodium complexes of pyridine ligands and their catalytic activity towards carbonylation of methanol

Nandini Kumari, Manab Sharma, Pankaj Das and Dipak Kumar Dutta*

Material Science Division, Regional Research Laboratory (CSIR), Jorhat 785 006, Assam, India

Received 4 June 2001; Accepted 4 December 2001

The *cis*-[Rh(CO)$_2$ClL] (1) complexes, where L = 2-methylpyridine (a), 3-methylpyridine (b), 4-methylpyridine (c), 2-phenylpyridine (d), 3-phenylpyridine (e), 4-phenylpyridine (f), undergo oxidative addition reactions with various electrophiles, like CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ or I_2, to yield complexes of the types [Rh(CO)(COR)ClXL] (2) (where R = CH_3 (i), C_2H_5 (ii), X = I; R = $C_6H_5CH_2$ (iii), X = Cl) or [Rh(CO)ClI_2L] (3) and [Rh(CO)$_2$ClI_2L] (4). The pseudo-first-order rate constants of CH_3I addition with complexes 1 containing pyridine (g) and 2-substituted pyridine (a and d) ligands were found to follow the order pyridine >2-methylpyridine >2-phenylpyridine. The catalytic activity of complexes 1 containing different pyridine ligands (a–g) on carbonylation of methanol was studied and, in general, a higher turnover number was obtained compared with that of the well-known species [Rh(CO)$_2$$I_2$]$^-$. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: carbonylrhodium(I); pyridine ligands; reactivity; kinetics; catalytic activity; carbonylation of methanol

INTRODUCTION

Rhodium(I) complexes are of great interest because of their reactivity and potential applications as catalysts in organic synthesis.[1,2] One of the important industrial applications of rhodium(I) complexes as a catalyst precursor is the species [Rh(CO)$_2$$I_2$]$^-$ for the carbonylation of methanol.[3] Research activities continue to modify the catalyst for enhancement of its activity by incorporating different types of ligand in the complex.[4–6] It is well known that the catalytic activity can be improved by increasing the nucleophilicity of the rhodium centre. One way to achieve this is by introducing strong electron donor ligands, like pyridines, that have a 'hard' nitrogen donor in the coordination sphere of the rhodium complexes. A literature survey reveals that nitrogen donor ligands have a great impact on catalysis.[7–10] So far, only a few rhodium(I) complexes containing pyridine and substituted pyridine ligands have been reported.[11–17] Moreover, studies relating to their reactivity and catalytic reactions, particularly for carbonylation, have not been investigated. In the present work, we carried out oxidative addition (OA) reactions of the complexes [Rh(CO)$_2$ClL] (**1**), where L = 2-methylpyridine (**a**), 3-methylpyridine (**b**), 4-methylpyridine (**c**), 2-phenylpyridine (**d**), 3-phenylpyridine (**e**), 4-phenylpyridine (**f**) with various electrophiles, such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2. In the carbonylation of methanol, the OA reaction of CH_3I with the rhodium metal centre is the key rate-determining step,[18] which, among other factors, depends upon the electronic and steric effects of the ligands. In view of this, a kinetic study on such addition reactions between the electrophilic CH_3I and complexes **1** containing ligands **a, d** and pyridine (**g**) has been carried out. The catalytic activity of complexes **1** on the carbonylation of methanol was evaluated.

*Correspondence to: D. K. Dutta, Material Science Division, Regional Research Laboratory (CSIR), Jorhat 785 006, Assam, India.
E-mail: dipakkrdutta@yahoo.com
Contract/grant sponsor: Department of Science and Technology (DST) New Delhi.
Contract/grant sponsor: Oil Industry Development Board (OIDB), Ministry of Petroleum & Natural Gas, New Delhi.

EXPERIMENTAL

All the solvents used were distilled under nitrogen prior to use. Carbon, hydrogen and nitrogen analyses were done on a Perkin–Elmer 2400 elemental analyser. Halide analyses were performed by standard methods.[19] IR spectra (4000–400 cm^{-1}) were recorded using a Perkin–Elmer 2000 in $CHCl_3$ and KBr discs. ^{1}H NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer and the ^{1}H chemical shifts are quoted relative to $SiMe_4$ as an internal standard in $CDCl_3$. The carbonylation of methanol was carried out in a 150 cm^3 Teflon-coated pressure reactor fitted with a pressure gauge (M/S Berghof Type-Heizung 75–150, Germany). $RhCl_3 \cdot 3H_2O$ was purchased from M/S Arrora Matthey Ltd,

Calcutta. All the ligands were purchased from Aldrich, USA, and used as received.

Starting material

All the complexes were prepared from $[Rh(CO)_2Cl]_2$ as the starting material, which was prepared by passing CO gas over $RhCl_3{\cdot}3H_2O$ at 100 °C.[20]

General procedure for the synthesis of the complexes $[Rh(CO)_2ClL]$ (1)

0.0257 mmol of $[Rh(CO)_2Cl]_2$ was dissolved in 10 ml of CH_2Cl_2 and to this solution 0.0514 mmol of the respective ligands, **d–f**, was added. The reaction mixture was stirred at room temperature (r.t.) for 10 min and the solvent was evaporated under vacuum. The compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. The complexes **1a**,[11] **1b**,[17] **1c**[15] and **1g**[11] were prepared by the literature methods.

Synthesis of $[Rh(CO)(COR)ClXL]$ (2), where L = a–f; R = CH_3 (i), C_2H_5 (ii), X = I; R = $C_6H_5CH_2$ (iii), X = Cl

$[Rh(CO)_2ClL]$ (100 mg) was dissolved in CH_2Cl_2 (10 cm^3) and RX (6 cm^3) was added. The reaction mixture was then stirred at r.t. for about 2 h, 4 h and 6 h for CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ respectively and the solvent was evaporated under vacuum. The yellow–orange-coloured compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

Synthesis of $[Rh(CO)ClI_2L]$ (3)/$[Rh(CO)_2ClI_2L]$ (4), where L = a–f

$[Rh(CO)_2ClL]$ (100 mg) was dissolved in CH_2Cl_2 (20 cm^3) and to this I_2 (50 mg) was added. The reaction mixture was stirred at r.t. for about 4 h. Then the solvent was evaporated under vacuum and the compound was stored and purified as above.

Carbonylation of methanol using $[Rh(CO)_2ClL]$ (1), where L = a–g as catalyst precursors

0.099 mol of methanol (4 cm^3), 0.016 mol of CH_3I (1 cm^3), 0.055 mol of H_2O (1 cm^3) and 0.054 mmol of complex **1** were placed in the reactor, which was then pressurized with CO gas (20 bar at r.t, 0.080 mol). The reaction vessel was then placed into the heated jacket of the reactor and the reactions were carried out at 130 °C for 1 h. The products were collected and analysed by gas chromatography (Cihemito GC 8510, FID).

Kinetic experiment

The reactions of complexes **1** containing ligands **a, d** and **g** with CH_3I were monitored by using IR spectroscopy in a solution cell (1.0 mm path length). 10 mg of complex **1** was added to 1 cm^3 of neat CH_3I at r.t. An aliquot (0.5 ml) of the reaction mixture was transferred by a syringe into the IR cell. Then the kinetic measurement were made by monitoring the simultaneous decay of the low terminal ν(CO) of complex **1** in the range 2008–2035 cm^{-1} and growth of the acyl ν(CO) of $[Rh(CO)(COCH_3)ClIL]$ (**2i**) in the range 1715–1720 cm^{-1}. A series of spectra were taken at regular intervals. The pseudo first-order rate constant was obtained from the slope of the plot of $\ln(A_0/A_t)$ against time t, where A_0 and A_t are the concentrations of complex **1** at time $t = 0$ and t respectively. The same pseudo-first-order rate is also observed from the concentration of the complex **2i**.

RESULTS AND DISCUSSION

Synthesis and characterization of $[Rh(CO)_2ClL]$

The chloro-bridged dimeric complex $[(CO)_2Rh(\mu{-}Cl)_2Rh(CO)_2]$ undergoes a bridge splitting reaction with two equivalents of substituted pyridine ligands to yield complexes of the type $[Rh(CO)_2ClL]$ (**1**), where L = 2-methylpyridine (**a**), 3-methylpyridine (**b**), 4-methylpyridine (**c**), 2-phenylpyridine (**d**), 3-phenylpyridine (**e**), 4-phenylpyridine (**f**). The microanalysis values are given in Table 1. The IR spectra of complexes **1a–f** (Tables 2 and 3) show two almost equally intense terminal ν(CO) bands in the range 2003–2090 cm^{-1}, attributable to the *cis* disposition of the carbonyl groups. Among the two ν(CO) groups, the one that exhibits the lower ν(CO) value is *trans* to the coordinating ligand.[21] Such *trans* CO groups have gained much interest because of their involvement in the migratory CO insertion reaction. The ^{1}H NMR spectra of complexes **1a, 1b, 1d** and **1e** (Tables 2 and 3) exhibit a doublet in the range δ 8.28–8.96 ppm for H_1, and two multiplets in the regions δ 6.86–8.06 ppm and δ 7.74–8.76 ppm for the H_2 and H_3 protons respectively of pyridine. On the other hand, complexes **1c** and **1f** show two doublets in the range δ 8.40–9.04 ppm and δ 7.17–8.75 ppm for H_1 and H_2 respectively of the pyridine. Complexes **1a, 1b** and **1c** exhibit a singlet in the region δ 2.27–2.95 ppm for the substituted methyl protons, and complexes **1d, 1e** and **1f** show a multiplet in the range δ 6.86–7.66 ppm for the substituted phenyl protons of the pyridine. The ^{1}H NMR values of complexes **1**, in general, show a downfield shift compared with that of the free ligands. Such a chemical shift is more prominent in the case of H_1 compared with H_2 and H_3, as they are remote from the coordinating N-donor atom of the pyridines.

OA reaction of $[Rh(CO)_2ClL]$ complexes with various electrophiles

Rhodium(I) complexes are coordinatively unsaturated[22] and undergo OA reactions with various electrophiles, such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2. The OA reactions of complexes **1a–f** with CH_3I yield a five-coordinated rhodium(III) acyl complex, $[Rh(CO)(COCH_3)ClIL]$ (**2i**). The IR spectra of the oxidized products show a single terminal ν(CO) band in the range 2055–2075 cm^{-1} and an acyl ν(CO) band in the range 1705–1720 cm^{-1} (Tables 2 and 3). Such

Table 1. Elemental analyses of the complexes

Complex	Found (Calc:) (%)				
	C	H	N	Cl	I
1a	34.2 (33.4)	2.5 (2.4)	4.7 (4.9)	11.9 (12.2)	–
1b	32.8 (33.4)	2.3 (2.4)	5.0 (4.9)	12.1 (12.2)	–
1c	33.9 (33.4)	2.5 (2.4)	5.1 (4.9)	12.0 (12.2)	–
1d	44.1 (44.6)	2.5 (2.6)	4.1 (4.0)	10.1 (10.0)	–
1e	45.2 (44.6)	2.5 (2.6)	3.9 (4.0)	10.2 (10.0)	–
1f	45.0 (44.6)	2.7 (2.6)	4.1 (4.0)	10.2 (10.0)	–
2ia	25.4 (25.2)	2.4 (2.3)	3.4 (3.3)	8.0 (8.2)	29.3 (29.6)
2iia	27.4 (27.1)	2.6 (2.7)	3.3 (3.2)	7.7 (7.9)	28.4 (28.7)
2iiia	42.6 (43.5)	3.3 (3.4)	3.5 (3.4)	16.6 (16.9)	–
2ib	25.7 (25.2)	2.4 (2.3)	3.4 (3.3)	8.3 (8.2)	29.2 (29.6)
2iib	27.4 (27.1)	2.6 (2.7)	3.1 (3.2)	7.6 (7.9)	28.3 (28.7)
2iiib	43.2 (43.5)	3.6 (3.4)	3.3 (3.4)	16.7 (16.9)	–
2ic	25.5 (25.2)	2.2 (2.3)	3.4 (3.3)	8.0 (8.2)	29.3 (29.6)
2iic	27.4 (27.1)	2.6 (2.7)	3.3 (3.2)	7.7 (7.9)	28.5 (28.7)
2iiic	43.9 (43.5)	3.3 (3.4)	3.5 (3.4)	16.6 (16.9)	–
2id	34.8 (34.2)	2.5 (2.4)	2.9 (2.8)	6.9 (7.1)	25.6 (25.9)
2iid	35.7 (35.6)	2.9 (2.8)	2.7 (2.8)	7.1 (6.9)	25.4 (25.2)
2iiid	50.3 (50.4)	3.3 (3.4)	3.0 (2.9)	14.5 (14.7)	–
2ie	34.9 (34.2)	2.5 (2.4)	2.9 (2.8)	7.3 (7.1)	25.7 (25.9)
2iie	35.2 (35.6)	2.9 (2.8)	2.9 (2.8)	6.6 (6.9)	25.1 (25.2)
2iiie	50.2 (50.4)	3.3 (3.4)	3.0 (2.9)	14.4 (14.7)	–
2if	34.8 (34.2)	2.3 (2.4)	2.7 (2.8)	6.9 (7.1)	25.7 (25.9)
2iif	35.9 (35.6)	2.9 (2.8)	2.7 (2.8)	6.6 (6.9)	24.9 (25.2)
2iiif	51.1 (50.4)	3.5 (3.4)	3.0 (2.9)	14.6 (14.7)	–
3a	16.8 (16.4)	1.4 (1.4)	2.8 (2.7)	6.6 (6.8)	48.9 (49.5)
3c	16.8 (16.4)	1.4 (1.4)	2.8 (2.7)	6.5 (6.8)	48.6 (49.5)
3d	24.8 (25.0)	1.7 (1.6)	2.5 (2.4)	5.8 (6.1)	43.8 (44.2)
3f	25.2 (25.0)	1.7 (1.6)	2.3 (2.4)	6.0 (6.1)	44.0 (44.2)
4b	17.4 (17.7)	1.2 (1.3)	2.5 (2.6)	6.3 (6.5)	46.5 (46.9)
4e	25.8 (25.9)	1.4 (1.5)	2.2 (2.3)	5.6 (5.8)	41.9 (42.1)

high values of the terminal ν(CO) band indicate the formation of the oxidized products. Apart from the characteristic resonances of the ligands, the ^{1}H NMR spectra of complexes **2ia–if** (Tables 2 and 3) show a singlet in the region δ 1.60–2.27 ppm, indicating the formation of $-COCH_3$. In a similar manner, OAs of C_2H_5I and $C_6H_5CH_2Cl$ with complexes **1a–f** also yield five-coordinated complexes, viz. [Rh(CO)(COC_2H_5)ClIL] (**2ii**) and [Rh(CO)($COCH_2C_6H_5$)Cl_2L] (**2iii**) respectively. IR spectra show two different types of ν(CO), in the ranges 2055–2080 cm^{-1} and 1705–1725 cm^{-1} and attributed to terminal and acyl ν(CO) values respectively. The ^{1}H NMR spectra of the complexes **2ii** show a triplet at around δ 0.98–1.87 ppm for $-COCH_2CH_3$ and a quartet in the region δ 2.26–3.33 ppm for $-COCH_2-$ protons. The $-COCH_2-$ proton in the complexes **2iii** show deshielded resonance in the range δ 3.98–4.70 ppm due to the presence of an electron-withdrawing phenyl group. The OAs of complexes **1b** and **1e** with I_2 yield hexa-coordinated [Rh(CO)$_2$ClI_2L] (**4**) species that exhibit two terminal ν(CO) values in the range 2014–2084 cm^{-1}. On the other hand, complexes **1a, 1c, 1d** and **1f** undergo OA with I_2 to yield products that show a single ν(CO) value in the range 2080–2085 cm^{-1}, indicating formation of a mono carbonyl penta-coordinated [Rh(CO)ClI_2L] (**3**) species. The ^{1}H NMR spectra of these oxidized complexes show that there is not much change in the chemical shift values compared with the parent complexes (**1a–f**). The literature[23] indicates that such OA reactions sometimes may lead to the formation of different types of isomeric, oligomeric or halide-exchanged species, which are difficult to establish even with sophisticated analytical tools. However, in our study the ν(CO) bands in the IR spectra, the NMR data and elemental analyses do not indicate the presence of any such oligomeric or halide-exchanged species, but the possibility of the existence of isomers cannot be ruled out.

Table 2. IR and ^{1}H NMR data of rhodium complexes containing substituted methyl pyridines

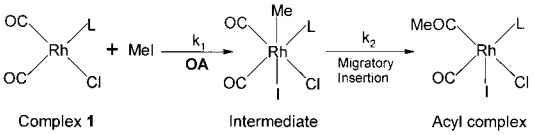
Complex or ligand	IR ν(CO) (cm^{-1})	^{1}H NMR (δ/ppm; J/Hz)				
		H_1 [J_{HH}]	H_2 [J_{HH}]	H_3 [J_{HH}]	CH_3 [J_{HH}]	CH_2 [J_{HH}]
a	–	8.48d [4.65]	7.04–7.13m	7.51–7.56m	2.54s	–
b	–	8.89d [5.55]	6.25–6.70m	7.57–7.68m	1.63s	–
c	–	8.07d [6.00]	6.67d [6.00]	–	2.05s	–
1a	2081, 2009	8.63d [5.64]	7.26–7.31m	7.74–7.80m	2.95s	–
1b	2080, 2003	8.28d [6.00]	6.86–7.24m	7.91–8.18m	2.27s	–
1c	2082, 2013	8.40d [6.60]	7.17d [6.00]	–	2.40s	–
2ia	2060, 1720	9.16d [7.05]	7.60–7.69m	8.26–8.31m	3.04s, 2.17s	–
2ib	2055, 1705	9.07d [8.40]	6.85–7.15m	8.36–8.43m	2.79s, 2.27s	–
2ic	2068, 1720	8.18d [6.00]	7.18d [6.00]	–	2.48s, 1.60s	–
2iia	2055, 1725	8.63d [5.70]	7.29–7.39m	7.74–7.79m	2.95s, 1.87t [7.50]	3.23q [7.45]
2iib	2075, 1715	8.79d [5.80]	6.76–7.18m	7.67–7.87m	2.68s, 1.87t [4.63]	2.28q [7.12]
2iic	2068, 1722	8.58d [5.95]	6.90d [6.16]	–	2.57s, 1.42t [5.34]	2.26q [7.03]
2iiia	2080, 1725	9.01d [5.04]	7.30–7.40m	7.87–8.02m	2.85s	3.98s
2iiib	2078, 1720	8.80d [4.20]	6.79–7.33m	7.93–8.13m	2.29s	4.40s
2iiic	2080, 1721	9.07d [6.13]	7.27d [6.78]	–	2.24s	4.33s
3a	2085	8.63d [5.58]	7.26–7.31m	7.71–7.79m	2.95s	–
3c	2082	8.30d [5.95]	7.15d [6.85]	–	2.32s	–
4b	2081, 2018	9.49d [5.40]	6.84–7.21m	8.20–8.47m	2.30s	–

Kinetics of the OA reaction

Kinetic studies of the OA reaction of complexes **1a, 1d** and **1g** were carried out with neat CH_3I and the course of the reaction was monitored by IR spectroscopy. The reaction is found to be first-order in both CH_3I and the complexes. At high concentrations of CH_3I a pseudo-first-order condition is applicable. In all the OA reactions, the five-coordinated acyl species is believed to be formed through an unstable six-

Table 3. IR and ^{1}H NMR data of rhodium complexes containing substituted phenyl pyridines

Complex or ligand	$IR_{\nu(CO)}$ (cm^{-1})	^{1}H NMR (δ/ppm; J/Hz)					
		H_1^a [J_{HH}]	H_2^a [J_{HH}]	H_3^a	C_6H_5	CH_2 [J_{HH}]	CH_3 [J_{HH}]
d	–	8.61d [4.05]	7.49–7.53m	7.95–7.98m	6.99–7.38m	–	–
e	–	8.80d [4.13]	7.69–7.71m	8.51–8.53m	6.95–7.46m	–	–
f	–	8.66d [3.87]	7.64d [6.45]	–	6.90–7.51m	–	–
1d	2090, 2035	8.92d [5.64]	7.57–7.61m	7.93–7.98m	6.86–7.50m	–	–
1e	2080, 2009	8.96d [8.25]	7.62–8.06m	8.08–8.76m	7.26–7.54m	–	–
1f	2078, 2004	9.04d [6.21]	8.75d [6.54]	–	6.90–7.66m	–	–
2id	2072, 1720	9.61d [6.12]	7.68–7.85m	7.97–8.22m	7.04–7.66m	–	2.03s
2ie	2070, 1715	8.90d [5.55]	7.60–7.90m	7.99–8.78m	6.92–7.48m	–	2.08s
2if	2075, 1720	9.25d [6.96]	9.05d [6.57]	–	7.17–7.70m	–	2.21s
2iid	2068, 1720	8.91d [4.41]	7.52–7.74m	7.87–7.95m	6.92–7.47m	2.57q [7.23]	0.98t [7.32]
2iie	2065, 1710	9.10d [6.63]	7.62–8.04m	8.61–8.96m	6.81–7.48m	3.20q [7.49]	1.84 t [7.47]
2iif	2067, 1718	9.05d [6.45]	8.80d [6.06]	–	7.15–7.56m	3.33q [8.10]	1.03 t [7.29]
2iiid	2070, 1715	9.64d [5.58]	7.53–7.63m	7.85–7.95m	6.74–7.47m	4.59s	–
2iiie	2072, 1705	8.98d [5.79]	7.62–8.04m	8.75–8.78m	6.91–7.49m	4.59s	–
2iiif	2068, 1712	9.05d [6.27]	8.80d [6.03]	–	7.12–7.43m	4.70s	–
3d	2085	8.90d [5.87]	7.51–7.57m	7.72–7.94m	6.88–7.26m	–	–
3f	2080	9.05d [6.57]	8.86d [5.94]	–	7.25–7.65m	–	–
4e	2084, 2014	8.94d [5.40]	7.56–8.09m	8.66–8.68m	6.91–7.49m	–	–



Scheme 1. OA, migratory insertion and acyl complex formation reactions.

coordinated intermediate,[24–26] $[Rh(CO)_2(CH_3)ClIL]$, and, therefore, the route of the reaction may be proposed as in Scheme 1.

From Scheme 1, the differential rate equations are:

$$d[\text{Complex } \mathbf{1}]/dt = -k_1[\text{Complex } \mathbf{1}] \quad (1)$$

$$d[\text{Intermediate}]/dt = k_1[\text{Complex } \mathbf{1}] - k_2[\text{Intermediate}] \quad (2)$$

$$d[\text{Acyl complex}]/dt = k_2[\text{Intermediate}] \quad (3)$$

where k_1 and k_2 are the rate constants for the OA and the migratory insertion reactions respectively. The overall rate of the reaction will be the rate of formation of the acyl complex, which depends on the concentration of the intermediate. The maximum concentration of the intermediate is given by:

$$[\text{Intermediate}]_{max} = (k_1/k_2)^{k_1/(k_2-k_1)} \quad (4)$$

The clean formation of the acyl complex through the undetectable intermediate indicates that $k_2 \gg k_1$ and that the OA reaction will be the rate-determining step. Thus, from Equation (4), it is clear that the concentration of the intermediate will be very low. In practice also, we could not detect the intermediate by IR spectroscopy under the present reaction conditions. The formation of the acyl complexes from the parent complexes **1a, 1d** and **1g** as a function of time are shown in Fig. 1. A simultaneous decay in the terminal ν(CO) bands of the complexes **1a, 1d** and **1g** in the range 2008–2035 cm^{-1} with increase in intensity of the ν(CO) bands in the acyl complexes in the range 1715–1720 cm^{-1} is observed. Figure 1A indicates that, for the complex containing pyridine (**1g**), the entire course of the OA reaction proceeds in an exponential manner. In the cases of the complexes containing 2-methylpyridine (**1a**) and 2-phenylpyridine (**1d**) (Fig. 1B and C), however, the OA reaction proceeds in two stages, each with pseudo-first-order rate kinetics. It is believed that a critical concentration factor of the undetectable intermediate is responsible for such two-stage kinetic behaviour, and soon after attaining this critical concentration the rate of the reaction becomes very fast. In the case of reaction of complex **1g** with MeI, such two-stage kinetic, is not observed, which may be due to much less time being required to reach the critical concentration. It can be observed from Fig. 1 that up to a period of about 55 min (Fig. 1B) the reaction for complex **1a** proceeds in a steady exponential way; thereafter, the rate of the reaction is very fast until 85 min. For complex **1d** (Fig. 1C), however, the first

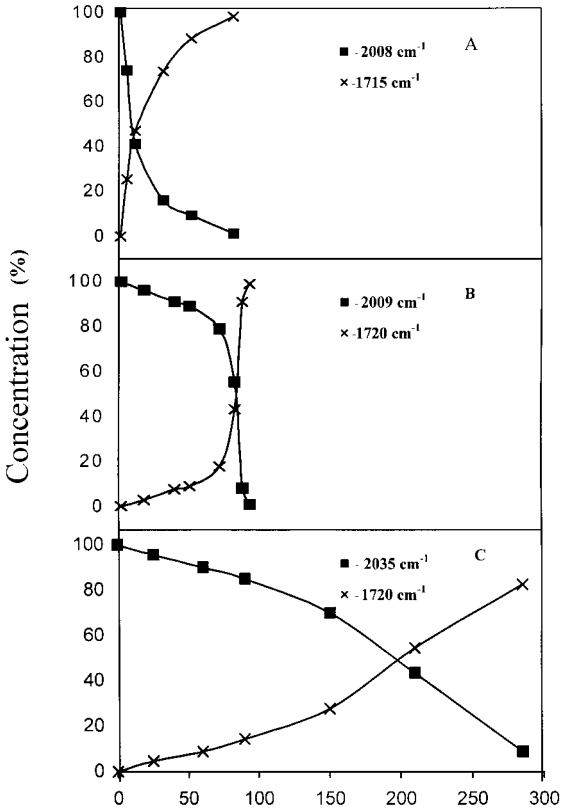


Figure 1. Simultaneous decay (■) of terminal ν(CO) bands in complexes **1g** (A), **1a** (B), **1d** (C) and increase in intensity (×) of ν(CO) bands of the corresponding acyl complexes against time (minutes).

stage of the reaction progresses in a steady exponential manner and takes a longer time period of about 90 min; in the second stage the rate of the reaction becomes faster, and is completed within 285 min. Therefore, it appears that the time required to attain the critical concentration of the intermediate in complex **1a** is far less than that for complex **1d**. Applying the pseudo-first-order condition, the plot of $\ln(A_0/A_t)$ versus t, where A_0 and A_t are the concentrations of complex **1g** at time $t = 0$ and t respectively, shows a good linear fit for the entire course of the reaction, whereas for complexes **1a** and **1d** it follows a two-stage linear fit. From the slope of the plots of $\ln(A_0/A_t)$ we obtained a rate constant $k_{obs} = 8.82 \times 10^{-4}$ s^{-1} for complex **1g**. For complex **1a** the rate constant k_{obs} for the first stage of the reaction is 5.67×10^{-5} s^{-1}; for the second stage it is 6.0×10^{-3} s^{-1}, which is about 100 times faster. Similarly, for complex **1d** the first-stage rate constant $k_{obs} = 3.0 \times 10^{-5}$ s^{-1} and the second-stage rate constant is 2.5×10^{-4} s^{-1}; hence, the second stage is about ten times faster than the first stage. It is worth indicating that the rate constant calculated from the concentration of the decaying complex **1** (rhodium (I) complexes) is found to be consistent with that calculated from the concentration of the growing complex **2i** (rhodium (III) acyl complexes). The

Table 4. Yields of carbonylation reactions of methanol

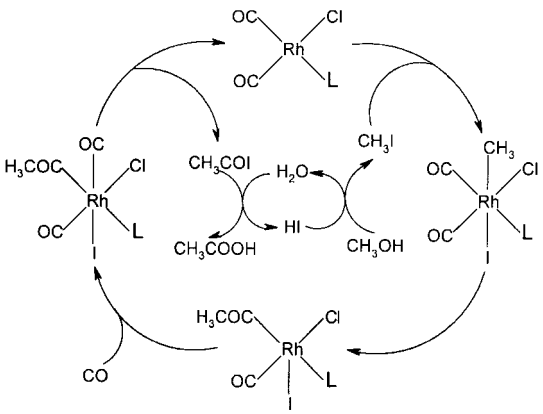
Catalyst	AcOH (%)	AcOMe (%)	Total conversion (%)	TON[a]
$[Rh(CO)_2Cl]_2$	4.07	37.45	41.52	760
1a	7.22	41.08	48.30	884
1b	12.35	53.55	65.90	1206
1c	10.72	48.68	59.40	1087
1d	3.42	36.73	40.15	735
1e	6.16	37.20	43.36	793
1f	5.54	40.33	45.87	840
1g	5.90	43.88	49.78	911

[a] Calculated for experiments carried out at 130 °C, 20 bar CO pressure for 1 h.

overall rates of the OA reactions of the complexes follow the order **1g** > **1a** > **1d**. As the OA reaction is believed to occur via nucleophilic attack by the rhodium centre at the carbon atom of CH_3I,[27] complex **1a** was expected to show a higher efficiency than **1g** because of the presence of electron-donating methyl groups in the ligand, but the reverse situation is observed. This may be due to steric hindrance caused by the 2-substituted methyl group in the pyridine. Further investigation on the rate of OA reaction with complexes containing different methyl-substituted pyridines (**1b** and **1c**) reveals an order **1a** ≈ **1c** > **1b**, which is as expected from the electronic point of view. The likely reason for complex **1d** exhibiting the lowest rate is due to the electron-withdrawing phenyl group in the pyridine ring with reduced electron density in the rhodium centre and a more sterically hindered situation.

Carbonylation of methanol in the presence of $[Rh(CO)_2ClL]$ complexes

The results of carbonylation of methanol to acetic acid and its ester in the presence of complexes **1a–g** as catalyst precursors are shown in Table 4. GC analyses of the products reveal that complexes **1a–g** respectively show about 48%, 66%, 59%, 40%, 43%, 46%, 50% conversions of methanol, with the corresponding turn over numbers (TONs) being 884, 1206, 1087, 735, 793, 840, 911. Under the same experimental conditions, the well-known catalyst precursor $[Rh(CO)_2I_2]^-$, generated *in situ* from $[Rh(CO)_2Cl]_2$,[28] shows only 42% conversion with TON 760. A carbonylation catalytic cycle for the pyridine-based rhodium system is proposed in Scheme 2, depending on the preliminary mechanistic study. Scheme 2 closely resembles the well-established cycle for the Monsanto catalyst,[29,30] $[Rh(CO)_2I_2]^-$. The overall rate of carbonylation is dependent on the rate-determining OA step of methyl iodide to the rhodium(I) centre.[18] Results indicate that the TON (Table 4) for the complexes containing phenylpyridine ligands are lower than that of the corresponding methylpyridines, which (except for **1a**), in general, show higher values compared with those containing the pyridine ligand. It is well known that increased nucleophilicity of the metal centre will increase the catalytic activity of the catalyst. Thus, the presence of electron-donating methyl groups on the pyridine ring facilitate carbonylation by increasing the nucleophilicity on the rhodium centre, whereas the electron-withdrawing phenyl group decreases it and retards carbonylation. However, the unexpected lower efficiency for complex **1a** may be due to the steric factor predominating over the electronic effect. This fact is well corroborated by the kinetic results, where the observed k value for complex **1a** is much lower than that of **1g**. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals, and at the end of the reaction, multiple ν(CO) bands were obtained that matched well with the ν(CO) values of a solution containing a mixture of the parent rhodium(I) carbonyl complexes **1** and the rhodium(III) acyl complexes **2**. Thus, it may be inferred that the ligands remain bound to the metal centre throughout the entire course of the catalytic reaction.



Scheme 2. Carbonylation reaction of methanol catalysed by rhodium(I)–pyridine complexes.

Acknowledgements

The authors are grateful to the Director, Regional Research Laboratory Jorhat, India, for his kind permission to publish the

work. The authors thank Dr P. C. Borthakur, Head Material Science Division, RRL Jorhat, for his encouragement and support. The Department of Science and Technology (DST) New Delhi, and the Oil Industry Development Board (OIDB), Ministry of Petroleum & Natural Gas, New Delhi, are acknowledged for their partial financial grant. One of the authors (PD) thanks CSIR, New Delhi, for the award of a Senior Research Fellowship (SRF). The authors are also grateful to the reviewers of the paper for their valuable comments and suggestions.

REFERENCES

1. Mullen A. Carbonylations catalyzed by metal carbonyls – Reppe reactions. In *New Synthesis with Carbon Monoxide*, Falbe J. (ed), Springer-Verlag, Heidelberg, New York, 1980; **11**, 286.
2. Cotton FA and Wilkinson G. In *Advanced Inorganic Chemistry, A Comprehensive Text*, 4th edn. Interscience: New York, 1980; 1262.
3. Howard MJ, Jones MD, Roberts MS and Taylor SA. *Catal Today* 1993; **18**: 325.
4. Wegman RW, Abatjoglou AG and Harrison AM. *J. Chem. Soc. Chem. Commun.* 1987; 1891.
5. Baker MJ, Giles MF, Orpen AG, Taylor MJ and Watt RJ. *J. Chem. Soc. Chem. Commun.* 1995; 197.
6. Dilworth JR, Miller JR, Wheatley N, Baker MJ and Sunley JG. *J. Chem. Soc. Chem. Commun.* 1995; 1579.
7. Linares C, Mediavilla M, Pardey AJ, Baricelli P, Longo-Pardey C and Moya SA. *Catal. Lett.* 1998; **50**: 183.
8. Pardey AJ, Mediavilla M, Canestrari M, Urbina C, Moronta D, Lujano E, Baricelli P, Longo C, Pastene R and Moya SA. *Catal. Lett.* 1998; **56**: 231.
9. Mediavilla M, Fernandez M, Pardey AJ, Baricelli P, Longo C, Sartori R and Moya SA. *Bol. Soc. Chil. Quim.* 1998; **43**: 359.
10. Pardey AJ, Fernandez M, Longo C, Lujano E, Baricelli P, Guerrero J and Moya SA. *React. Kinet. Catal. Lett.* 1998; **65**(2): 315.
11. Lawson DN and Wilkinson G. *J. Chem. Soc.* 1965; 1900.
12. Ugo R, Monica GLa, Cenini S and Bonati F. *J. Organomet. Chem.* 1968; **11**: 159.
13. Brodzki D and Pannetier G. *J. Organomet. Chem.* 1973; **63**: 431.
14. Denise B and Pannetier G. *J. Organomet. Chem.* 1973; **63**: 423.
15. Pribula AJ and Drago RS. *J. Am. Chem. Soc.* 1976; **98**: 2784.
16. Vallarino LM and Sheargold SW. *Inorg: Chim. Acta* 1979; **36**: 243.
17. Dutta DK and Singh MM. *Transition Met. Chem.* 1994; **19**: 290.
18. Haynes A, Mann BE, Morris GE and Maitlis PM. *J. Am. Chem. Soc.* 1993; **115**: 4093.
19. Vogel AR. In *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, 3rd edn. Longman Group Limited: London, 1962.
20. McCleverty JA and Wilkinson G. *Inorg. Synth.* 1966; **8**: 221.
21. Bandoli G, Clemente DA, Deganello G, Carturan G, Uguagliati P and Belluco U. *J. Organomet. Chem.* 1974; **71**: 125.
22. Faraone F. *J. Chem. Soc. Dalton Trans.* 1975; 541.
23. Adams H, Bailey NA, Mann BE, Manuel CP, Spencer CM and Kent AG. *J. Chem. Soc. Dalton Trans.* 1988; 489.
24. Steel DF and Stephenson TA. *J. Chem. Soc. Dalton Trans.* 1972; **19**: 2161.
25. Hayashi M, Takezaki H, Hashimoto Y, Takaoki K and Saigo K. *Tetrahedron Lett.* 1998; **39**: 7529.
26. Das P, Konwar D, Sengupta P and Dutta DK. *Transition Met. Chem.* 2000; **25**: 426.
27. Forster D and Singleton TA. *J. Mol. Catal.* 1982; **17**: 299.
28. Forster D. *J. Am. Chem. Soc.* 1976; **98**: 846.
29. Forster D. *Adv. Organomet. Chem.* 1979; **17**: 255.
30. Maitlis PM, Haynes A, Sunley GJ and Howard MJ. *J. Chem. Soc. Dalton Trans.* 1996; 2187.

