

Oxidative addition of different electrophiles with rhodium(I) carbonyl complexes of unsymmetrical phosphine–phosphine monoselenide ligands

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Dimeric chlorobridge complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ reacts with two equivalents of a series of unsymmetrical phosphine–phosphine monoselenide ligands, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{Se})\text{Ph}_2$ ($n = 1(\text{a}), 2(\text{b}), 3(\text{c}), 4(\text{d})$) to form chelate complex $[\text{Rh}(\text{CO})\text{Cl}(\text{P}\eta\text{Se})]$ (1a) $\{\text{P}\eta\text{Se} = \eta^2\text{-(P,Se)}$ coordinated $\}$ and non-chelate complexes $[\text{Rh}(\text{CO})_2\text{Cl}(\text{P}\sim\text{Se})]$ (1b–d) $\{\text{P}\sim\text{Se} = \eta^1\text{-(P)}$ coordinated $\}$. The complexes 1 undergo oxidative addition reactions with different electrophiles such as CH_3I , $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and I_2 to produce Rh(III) complexes of the type $[\text{Rh}(\text{COR})\text{ClX}(\text{P}\eta\text{Se})]$ $\{\text{where R} = -\text{C}_2\text{H}_5$ (2a), $\text{X} = \text{I}$; $\text{R} = -\text{CH}_2\text{C}_6\text{H}_5$ (3a), $\text{X} = \text{Cl}$), $[\text{Rh}(\text{CO})\text{ClI}_2(\text{P}\eta\text{Se})]$ (4a), $[\text{Rh}(\text{CO})(\text{COCH}_3)\text{ClI}(\text{P}\sim\text{Se})]$ (5b–d), $[\text{Rh}(\text{CO})(\text{COH}_3)\text{ClI}(\text{P}\sim\text{Se})]$ (6b–d), $[\text{Rh}(\text{CO})(\text{COCH}_2\text{C}_6\text{H}_5)\text{ClI}_2(\text{P}\sim\text{Se})]$ (7b–d) and $[\text{Rh}(\text{CO})\text{ClI}_2(\text{P}\sim\text{Se})]$ (8b–d). The kinetic study of the oxidative addition (OA) reactions of the complexes 1 with CH_3I and $\text{C}_2\text{H}_5\text{I}$ reveals a single stage kinetics. The rate of OA of the complexes varies with the length of the ligand backbone and follows the order $1\text{a} > 1\text{b} > 1\text{c} > 1\text{d}$. The CH_3I reacts with the different complexes at a rate 10–100 times faster than the $\text{C}_2\text{H}_5\text{I}$. The catalytic activity of complexes 1b–d for carbonylation of methanol is evaluated and a higher turnover number (TON) is obtained compared with that of the well-known commercial species $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: rhodium carbonyl complexes; phosphine-phosphine monoselenide; oxidative addition reaction (OA); kinetic study; carbonylation of methanol; IR and NMR spectroscopy

INTRODUCTION

The unsymmetrical potential polydentate phosphine based ligands bearing N, O, S and Se donor atoms have the focus of several investigations in connection with the coordination chemistry, catalytic properties and structural novelties of their complexes. Particular attention has been paid to the ligands with PN ,^{1–4} $\text{PO}^{3–11}$ and $\text{PS}^{6,7,11–18}$ donor sets, in part because of the interesting hemilabile nature¹⁹ displayed by these type of ligands. Amongst these, the chemistry of phosphorus–sulfur ligands is rich and a large number of sulfur-containing functionalities like phosphine thiolate,^{20,21} phosphine thioethers^{22,23} and alkyl-backboned phosphine–phosphine monosulfides^{6,7,11–18} as well as the phosphine–phosphine aminemonosulfides like $\text{Ph}_2\text{PNHP}(\text{S})\text{Ph}_2$, $\text{Ph}_2\text{PNPhP}(\text{S})\text{Ph}_2$ and $\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2$ ^{24–26} were reported. As a

part of our interest in investigating the structural chemistry of metal–phosphine chalcogenides interactions, particularly with *bis*-(tertiaryphosphine chalcogenides), we have reported^{27,28} a few ruthenium carbonyl complexes with the ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$, $n = 1–4$. In contrast, a few reports exist on phosphine–phosphine monoselenide complexes.^{11,15,29–34} Recently, Dutta *et al.*³⁵ reported on the rhodium carbonyl complexes of the types $[\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2)]$ and $[\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_2\text{PN}(\text{CH}_3)\text{P}(\text{Se})\text{Ph}_2)]$ and their catalytic activity.

Substantial activity has been aroused on the synthesis of rhodium carbonyl complexes because of their versatile application in homogeneous catalysis, such as carbonylation of alcohols. The oxidative addition (OA) reactions of different electrophiles like CH_3I , $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, I_2 etc. to square planar transition metal centers such as Rh(I) complexes is a fundamental process in organometallic chemistry with significant implications in catalytic carbonylation of alcohols. The OA of various organic halides, particularly methyl iodide to neutral rhodium(I) carbonyl phosphine complexes of monodentate and bidentate ligands, have been extensively

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studied.³⁶ In our previous report,³⁷ the details of possible intermediates through an OA reaction have been described. It is of interest how the steric and electronic properties as well as length of ligand backbone affect the rates of the OA reactions.

In view of the above, we have carried out the synthesis and characterization of neutral rhodium(I) carbonyl complexes with phosphine–phosphine monoselenide ligands, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{Se})\text{Ph}_2$, $n = 1-4$ and also studied the OA reactions of these complexes with the electrophiles CH_3I , $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and I_2 . The effect of chain-length of ligand backbones on the rate of OA reactions of the complexes particularly with methyl iodide and ethyl iodide along with catalytic activity of the complexes for the carbonylation of methanol are also included in the present communication.

EXPERIMENTAL

Materials

All the solvents used were distilled under nitrogen prior to use. Chlorides were analyzed using a standard analytical method.³⁸ $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from M/s Arora Matthey Ltd, Kolkata, India. Analytically pure $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) and elemental selenium were purchased from M/s Aldrich, USA and used without further purification. The ligands, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{Se})\text{Ph}_2$ were prepared by refluxing a solution of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) in toluene with one molar equivalent of elemental selenium for 3 h under nitrogen and purified by chromatographic techniques.^{16,31}

Starting material

The starting dimeric rhodium moiety $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared by passing CO gas over $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ powder at 100°C in the presence of water.³⁹

Instrumentation

FT-IR spectra of range $400-4000\text{ cm}^{-1}$ were recorded using Perkin-Elmer 2000 spectrophotometer in KBr disk. Carbon and hydrogen analyses were carried out on a Perkin-Elmer 2400 elemental analyzer. NMR data were recorded on a Bruker DPX 300 MHz spectrometer and the ^1H and ^{31}P NMR chemical shifts were quoted relative to SiMe_4 and 85% H_3PO_4 as internal and external standard respectively using CDCl_3 and d_6 -acetone as solvent. The carbonylation reactions of methanol were carried out in a 100 cm^3 teflon coated high pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gage and the reaction products were analyzed by GC (Chemito 8510, FID).

Synthesis of complexes

$[\text{Rh}(\text{CO})\text{Cl}(\text{P}\cap\text{Se})]$ (**1a**) and $[\text{Rh}(\text{CO})_2\text{Cl}(\text{P}\sim\text{Se})]$ (**1b-d**); $\text{P}\cap\text{Se} = \eta^2-(\text{P},\text{Se})$ coordinated **a**, $\text{P}\sim\text{Se} = \eta^1-(\text{P})$ coordinated **b-d**

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (50 mg, 0.129 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and was added drop wise to the 10 cm^3 CH_2Cl_2

solution of 0.257 mmol corresponding ligands **a-d** with constant stirring under nitrogen atmosphere. The reaction mixtures were stirred at room temperature (r.t.) for about 1 h and the solvent was evaporated under reduced pressure in a rotavapor to obtain yellow solid compounds which were washed with diethyl ether. All the complexes were stored in the dark.

$[\text{Rh}(\text{COR})\text{ClX}(\text{P}\cap\text{Se})]$; $\text{R} = -\text{C}_2\text{H}_5$ (**2a**), $\text{X} = \text{I}$ and $\text{R} = -\text{CH}_2\text{C}_6\text{H}_5$ (**3a**), $\text{X} = \text{Cl}$; $\text{P}\cap\text{Se} = \eta^2-(\text{P},\text{Se})$ coordinated **a**

A 0.0318 mmol (20 mg) aliquot of complex **1a** was dissolved in 10 cm^3 dichloromethane. To this solution 6 cm^3 **RX** (**RX** = $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) were added. The reaction mixtures were then stirred at r.t. for about 4 and 12 h for $\text{C}_2\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, respectively, and the solvent was evaporated under vacuum. Reddish-black compounds so obtained were washed with diethyl ether and stored in the dark.

$[\text{Rh}(\text{CO})\text{ClI}_2(\text{P}\cap\text{Se})]$ (**4a**); $\text{P}\cap\text{Se} = \eta^2-(\text{P},\text{Se})$ coordinated **a**

A 0.0159 mmol aliquot of the complex **1a** (10 mg) was dissolved in 20 cm^3 CH_2Cl_2 and 4.033 mg of I_2 (0.0318 mmol) were added. The reaction mixture was stirred for 0.5 h. The solvent was evaporated under reduced pressure to obtain a reddish-black solid compound. After washing with diethyl ether, the compound was kept in the dark.

$[\text{Rh}(\text{CO})(\text{COCH}_3)\text{ClI}(\text{P}\sim\text{Se})]$ (**5b-d**); $\text{P}\sim\text{Se} = \eta^1-(\text{P})$ coordinated **b-d**

To a solution of the complexes **1b-d** prepared by dissolving 0.0149 mmol of the corresponding complexes in 40 cm^3 CH_2Cl_2 , about 6 cm^3 of CH_3I were added and stirred for 1.5 h. The reddish-black compounds so obtained were washed with diethyl ether and dried *in vacuo* and stored in the dark.

$[\text{Rh}(\text{CO})(\text{COC}_2\text{H}_5)\text{ClI}(\text{P}\sim\text{Se})]$ (**6b-d**); $\text{P}\sim\text{Se} = \eta^1-(\text{P})$ coordinated **b-d**

A 6 cm^3 aliquot of $\text{C}_2\text{H}_5\text{I}$ was added to the 10 cm^3 CH_2Cl_2 solution of the corresponding complexes **1b-d** (0.0149 mmol). The reaction mixture was stirred for 4 h at r.t. during which time the color of the solution changes from red to reddish-black. On evaporating the solvent and washing with diethyl ether reddish-black colored solid compounds were obtained, which were stored in the dark.

$[\text{Rh}(\text{CO})(\text{COCH}_2\text{C}_6\text{H}_5)\text{ClI}_2(\text{P}\sim\text{Se})]$ (**7b-d**); $\text{P}\sim\text{Se} = \eta^1-(\text{P})$ coordinated **b-d**

A 0.0149 mmol aliquot of $[\text{Rh}(\text{CO})_2\text{Cl}(\text{P}\sim\text{Se})]$ (**1b-d**) was dissolved in 20 cm^3 CH_2Cl_2 to which 6 cm^3 of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ were added and the reaction mixture was stirred for about 12 h. The resulting solutions were dried in vacuum and the solid compounds were washed with diethyl ether to obtain reddish-black compounds which were kept in the dark.

$[Rh(CO)ClI_2(P\sim Se)]$ (**8b-d**); $P\sim Se = \eta^1-(P)$ coordinated **b-d**

A 3.78 mg (0.0298 mmol) aliquot of I_2 was added to a 20 cm³ CH_2Cl_2 solution containing $[Rh(CO)_2Cl(P\sim S)]$ (**1b-d**) (0.0149 mmol) and the reaction mixtures were stirred for 0.5 h at r.t. The resulting solutions were dried *in vacuo* and the solid compounds were washed with diethyl ether to obtain reddish-black compounds, which were stored in the dark.

Kinetic experiment

FT-IR spectroscopy was employed to monitor the kinetic experiments of OA reactions of the complexes **1b-d** with CH_3I and **1a-d** with C_2H_5I in a solution cell of 1.0 mm path length. Ten milligrams of complexes were added to (i) 1 cm³ (16×10^{-3} mol) neat CH_3I , (ii) 0.75 cm³ (11.92×10^{-3} mol) CH_3I and 0.25 cm³ dichloromethane, (iii) 0.50 cm³ (8×10^{-3} mol) CH_3I and 0.50 cm³ dichloromethane or (iv) 1 cm³ (12.25×10^{-3} mol) neat C_2H_5I at 25 °C. An aliquot of the reaction mixtures were transferred by a syringe into the IR cell. Then kinetic measurements were made by monitoring the simultaneous decay of lower energy terminal $\nu(CO)$ band of the complexes and increasing the intensity of the acyl $\nu(CO)$ band of the corresponding acyl complexes. A series of spectra were recorded at regular time intervals.

Carbonylation of methanol using complexes

1b-d as catalyst precursors

In the reactor CH_3OH (4 ml, 0.099 mol), CH_3I (1 ml, 0.016 mol), H_2O (1 ml, 0.056 mol) and complexes **1b-d** (0.054 mmol) were taken and then pressurized with CO (18 bar at r.t., 0.072 mol). The reaction vessel was then placed into the preheated jacket of the autoclave and the reactions were carried out at 130 ± 5 °C (corresponding pressure 35 ± 2 bar) for 1 h. The products were collected and analyzed using GC.

RESULTS AND DISCUSSION

Synthesis and characterization of Rh(I) complexes

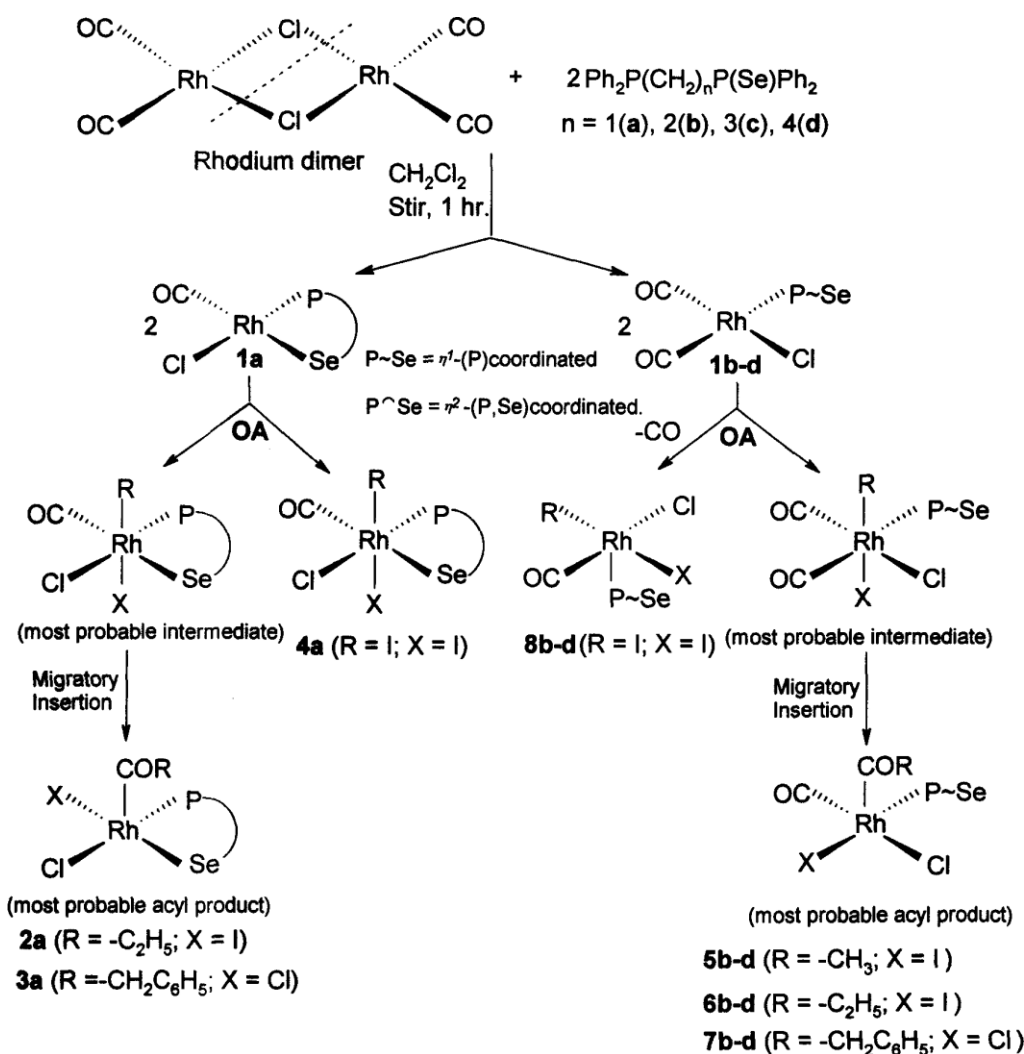
The reactions of two equivalent of the ligands $Ph_2P(CH_2)_n P(Se)Ph_2$ ($n = 2-4$ (**b-d**)) with the chloro bridge dimeric complex $[Rh(CO)_2Cl]_2$ lead to the formation of dicarbonyl non-chelate complexes of the type $[Rh(CO)_2Cl(P\sim Se)]$ (**1b-d**) { $P\sim Se = \eta^1-(P)$ coordinated}(Scheme 1) while the ligand $Ph_2PCH_2P(Se)Ph_2$ (**a**) yields the monocarbonyl chelate complex $[Rh(CO)Cl(Ph_2PCH_2P(Se)Ph_2)]$ (**1a**) (Scheme 1) as reported in our earlier work.³⁵ The elemental (C, H, Cl) analysis data of the complexes **1a-d** match well with the calculated ones (Table 1). The monocarbonyl complex **1a** shows a $\nu(CO)$ band at around 1977 cm⁻¹ (Table 2), while **1b-d** exhibit two equally intense $\nu(CO)$ bands in the range 1984–2067 cm⁻¹, indicating *cis* disposition of the two terminal carbonyl groups.^{37,40} The $\nu(PSe)$ band of **1a** occurs at

Table 1. Elemental analyses of the complexes **1-8**

Complex	Yield (%)	Elemental analysis: found (calcd) in %		
		C	H	Cl
1a ^a	92	49.12(49.60)	3.42(3.49)	5.67(5.64)
1b	89	50.00(50.01)	3.54(3.57)	5.30(5.28)
1c	96	50.72(50.74)	3.77(3.79)	5.15(5.18)
1d	94	51.41(51.44)	4.03(4.00)	5.04(5.07)
2a	90	42.71(42.76)	3.40(3.44)	4.49(4.52)
3a	96	52.33(52.36)	3.82(3.83)	9.37(9.39)
4a	93	35.34(35.30)	2.47(2.49)	3.98(4.02)
5b	94	42.75(42.76)	3.33(3.38)	4.40(4.36)
5c	94	43.45(43.49)	3.52(3.50)	4.30(4.29)
5d	87	44.20(44.19)	3.65(3.68)	4.19(4.22)
6b	91	43.48(43.49)	3.53(3.50)	4.27(4.29)
6c	88	44.21(44.19)	3.64(3.68)	4.18(4.22)
6d	90	44.85(44.87)	3.83(3.85)	4.12(4.15)
7b	89	52.58(52.61)	3.86(3.88)	8.87(8.89)
7c	87	53.20(53.18)	4.03(4.06)	8.76(8.74)
7d	97	53.75(53.73)	4.25(4.23)	8.57(8.59)
8b	87	36.07(36.09)	2.63(2.67)	3.91(3.95)
8c	94	36.81(36.85)	2.84(2.85)	3.90(3.89)
8d	92	37.57(37.59)	3.00(3.02)	3.80(3.83)

^a Our earlier report.³⁵

513 cm⁻¹, which is significantly lower than the free ligand **a** ($\nu(PSe) = 527$ cm⁻¹) and thus indicates the chelate formation in the complex **1a** through the Rh–Se bond. In contrast, the ligands **b-d** in the complexes **1b-d** coordinate to the metal center through their tertiary phosphorus atom only, which is corroborated by the IR spectra (Table 2) of the $\nu(PSe)$ stretchings which are close to the corresponding free ligand bands.^{27,33} The ¹H NMR spectra of **1a** (Table 2) show a triplet resonance at δ 4.3 ppm ($-CH_2-$) along with the Ph protons in the range δ 7.19–7.69 ppm. Similarly, the complexes **1b-d** display two multiplet resonances in the range δ 7.19–7.50 and δ 7.63–7.84 ppm attributed to two non-equivalent phenylic protons and another two multiplet resonances at around δ 2.10–2.84 ppm for methylene protons. The methylene protons of the complexes show little downfield shift compared with the corresponding free ligands, which further substantiates the non-chelating mode of the ligands. The ³¹P{H} NMR spectra (Table 2) of **1a** exhibit doublet of doublets centered at $\delta = 51.1$ ppm for the tertiary phosphorus atom (P_1) bonded to the metal center and a doublet at $\delta = 35.2$ ppm for the pentavalent phosphorus atom (P_2) bonded to the selenium. The remarkable downfield shifts of these two resonances compared with the free ligand **a** further substantiate the chelation in the complex. Similarly, for the complexes **1b-d**, the P_1 phosphorus atoms resonate as a doublet of doublets at relatively lower field (δ 37.24–57.59 ppm; $J_{Rh-P} = 131-137$ Hz, $J_{P-P} = 26-59$ Hz) than the P_2 phosphorus atoms, which appear as a doublet resonance in the range δ 35.24–37.76 ppm



Scheme 1. Synthesis of Rh(I) and Rh(III) carbonyl complexes containing P–Se donor ligands.

($J_{\text{P-P}} = 26\text{--}59$ Hz). The positions of the P₂ resonances are close to that of the corresponding free ligands, whilst large downfield shifts of about 52–71 ppm are observed for the P₁ resonances compared with the free ligands. Thus the ³¹P{H} NMR spectra are also consistent with monodentate coordination nature of the **b–d** ligands through the tertiary phosphorus (P₁) atom.³³

Oxidative addition reactions of Rh(I) complexes with different electrophiles

One of the most important industrial processes utilizing homogeneous transition-metal catalysis is the rhodium- and iodide-promoted carbonylation of methanol to acetic acid. In this respect, OA reaction of alkyl halides with metal complexes is a very important reaction as it is the key step in the carbonylation catalysis.⁴¹ Therefore, oxidative reactivities of **1a–d** towards various electrophiles were evaluated.

The preliminary OA reaction of **1a** with CH₃I, as reported by us,³⁵ has now been extended and evaluated thoroughly with other electrophiles like C₂H₅I, C₆H₅CH₂Cl and I₂. With the alkyl halide **RX** (R = C₂H₅, C₆H₅), the chelate complex **1a** forms the Rh(III) acyl chelate complexes like [Rh(COR)ClX(P ∩ Se)] {R = -C₂H₅ (**2a**); X = I and R = -CH₂C₆H₅ (**3a**), X = Cl} (Scheme 1), displaying a new ν(CO) band at 1693 and 1712 cm⁻¹, respectively. The ν(PSe) bands of the complexes **2a** and **3a** occur at 507 and 508 cm⁻¹, respectively, indicating chelate formation. The ¹H NMR spectra of the complex **2a** consist of one triplet at δ 1.80 ppm for the methyl protons and one quartet at δ 3.52 ppm for the methylene protons of the ethyl group in addition to the characteristic ligand signals. The methylene protons of the -CH₂C₆H₅ group in the complex **3a** show a singlet at around δ 3.72 ppm, which is due to deshielding effect of the electron withdrawing phenyl group.⁴² The I₂ adds oxidatively to the complex **1a** to form the monocarbonyl chelate complex [Rh(CO)ClI₂(P ∩ Se)] (**4a**; Scheme 1), which exhibits only

Table 2. IR (cm⁻¹), ¹H and ³¹P NMR (δ, ppm; J, Hz) spectroscopic data of the complexes **1a–d** and oxidized products **2–8**

Complex	IR (cm ⁻¹)		³¹ P-{H} NMR				¹ H NMR			
	ν(CO)	ν(PSe)	δ _P	δ _{P=Se}	J _{Rh-P}	J _{P-P}	C ₆ H ₅	-(CH ₂) _n -	CH ₂	CH ₃
1a ^a	1977	513	51.10dd	35.20d	164	56	7.19–7.43m, 7.60–7.69m	4.32t	—	—
1b	1988, 2067	531	57.59dd	37.76d	131	59	7.19–7.50m, 7.68–7.84m	2.49m, 2.84m	—	—
1c	1984, 2062	532	57.59dd	37.76d	132	59	7.19–7.50m, 7.67–7.81m	2.49m, 2.83m	—	—
1d	1992, 2067	526	37.24dd	35.24d	137	26	7.24–7.44m, 7.63–7.77m	2.10m, 2.57m	—	—
2a	1693	507	51.45dd	35.07d	150	56	7.24–7.46m, 7.57–7.65m	4.25t	3.52q	1.80t
3a	1712	508	53.40dd	37.08d	154	63	7.22–7.49m, 7.60–7.75m	4.32t	3.72s	—
4a	2072	506	56.32dd	41.30d	161	58	7.29–7.65m, 7.75–8.09m	4.20t	—	—
5b	2071, 1713	528	50.76dd	37.78d	140	99	7.24–7.47m, 7.61–8.06m	2.39m, 2.82m	—	3.16s
5c	2075, 1702	527	48.55dd	37.76d	105	59	7.24–7.48m, 7.61–8.06m	2.40m, 2.83m	—	3.16s
5d	2063, 1707	522	34.85dd	32.56d	135	17	7.24–7.44m, 7.71–7.77m	2.07m, 2.57m	—	3.45s
6b	2022, 1701	528	49.48dd	37.60d	100	90	7.26–7.51m, 7.68–7.82m	2.20m, 2.85m	3.48q	1.50t
6c	2022, 1697	528	57.59dd	38.29d	132	55	7.26–7.45m, 7.70–8.05m	2.52m, 2.85m	3.35q	2.17t
6d	2057, 1694	531	34.50dd	32.49d	137	20	7.19–7.40m, 7.64–7.74m	2.10m, 2.65m	3.40q	1.66t
7b	2023, 1714	528	52.52dd	34.73d	110	86	7.20–7.53m, 7.73–7.98m	2.44m, 2.80m	3.65s	—
7c	2022, 1711	529	44.90dd	36.52d	102	62	7.29–7.51m, 7.69–7.89m	2.56m, 2.88m	3.86s	—
7d	2068, 1714	531	39.28dd	36.28d	134	23	7.20–7.49m, 7.61–7.98m	2.06m, 2.65m	3.98s	—
8b	2076	529	49.58dd	37.77d	122	78	7.18–7.52m, 7.65–7.82m	2.47m, 2.80m	—	—
8c	2076	529	55.50dd	37.75d	114	52	7.20–7.53m, 7.66–7.84m	2.51m, 2.81m	—	—
8d	2073	520	43.38dd	34.24d	140	30	7.22–7.44m, 7.60–7.81m	2.13m, 2.60m	—	—

^a Our earlier report.³⁵

Free ligands (**a–d**): IR, ν(PSe): 527(**a**), 530(**b**), 531(**c**), 531(**d**); ³¹P NMR, δ_P and δ_{P=Se}, -26.4, 31.3d [²J_{P-P} = 85 Hz] (**a**); -12.71, 36.55d [³J_{P-P} = 50 Hz] (**b**); -12.34, 36.75d [⁴J_{P-P} = 50 Hz] (**c**); -15.30, 34.47d [⁵J_{P-P} = 15 Hz] (**d**); ¹H NMR: -(CH₂)_n- : 3.49d (**a**), 2.10m, 2.86m (**b**); 2.15m, 2.53m (**c**); 2.01m, 2.54m (**d**); s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet.

one terminal characteristic ν(CO) band of Rh(III) complex at 2072 cm⁻¹. The ν(PSe) band for the complex appears at 506 cm⁻¹, suggesting the retention of a chelate ring.

The non-chelate complexes **1b–d** are coordinately unsaturated and like **1a** undergo OA reactions with the different electrophiles like CH₃I, C₂H₅I, C₆H₅CH₂Cl and I₂ to afford Rh(III) complexes (Scheme 1). The OA of CH₃I with complexes **1b–d** give penta coordinated rhodium (III) acyl complexes of the type [Rh(CO)(COCH₃)Cl(P ~ Se)] (**5b–d**), which may form through non-isolable hexa-coordinated intermediates. The IR spectra (Table 2) of the complexes **5b–d** show two different types of ν(CO) bands in the range 2063–2075 and 1702–1713 cm⁻¹ assignable to terminal and acyl carbonyl groups respectively.^{37,40} The higher values of the terminal ν(CO) band indicate the formation of the oxidized products. The ν(PSe) bands for the complexes **5b–d** appear at around 522–528 cm⁻¹, corroborating the monodentate nature of the ligands. Apart from the characteristic resonances of the ligands, the ¹H NMR spectra of complexes **5b–d** (Table 2) show a singlet in the region δ 3.16–3.45 ppm, indicating the formation of a -COCH₃ group. In a similar manner, OA reactions of the alkyl halide C₂H₅I and C₆H₅CH₂Cl with the complexes **1b–d** afford penta coordinated complexes, viz. [Rh(CO)(COC₂H₅)Cl(P ~ Se)] (**6b–d**) and [Rh(CO)(COCH₂C₆H₅)Cl₂(P ~ Se)] (**7b–d**) (Scheme 1). The IR spectral values (Table 2) of the ν(PSe) bands of

these complexes clearly imply the tertiary P coordination of the ligands to the metal. The ν(CO) bands of the complexes occur in the range 2022–2068 and 1694–1714 cm⁻¹ and are attributable to terminal and acyl carbonyl groups, respectively. The ¹H NMR spectra of the complexes **6b–d** show one triplet in the range δ 1.50–2.17 ppm for the methyl protons and one quartet signal at around δ 3.35–3.48 ppm for the methylene protons of the ethyl group in addition to the characteristic ligand bands. The methylene protons of the -CH₂C₆H₅ groups in the complexes **7b–d** appear as a singlet at around δ 3.65–3.98 ppm along with the other characteristic signals. The OA reactions of I₂ with the dicarbonyl complexes **1b–d** occur very rapidly, affording monocarbonyl complexes [Rh(CO)Cl₂(P ~ Se)] (**8b–d**) substantiated by a single terminal ν(CO) band in the range 2073–2076 cm⁻¹. As I₂ adds oxidatively to Rh(I) dicarbonyl complexes **1b–d**, both the iodides pull electron density towards them from the metal center oxidizing it to Rh(III) state. The Rh–CO bonds become destabilized as a result of decrease in π-back bonding due to insufficient electron on the metal center⁴³ and, consequently, one of the CO groups is eliminated to form a stable monocarbonyl Rh(III) acyl compound. The decrease in π-back bonding is evidenced from the higher shifting (6–14 cm⁻¹) of the terminal ν(CO) band in the oxidized complexes **8b–d** compared with the parent complexes **1b–d**.⁴⁴ The ν(PSe) values are consistent with the non-chelating behavior of the ligands.

The ^1H NMR spectra (Table 2) of these oxidized complexes show that there is not much change in the chemical shift compared with the parent complexes. The ^{31}P {H}NMR data of all the oxidized complexes (Table 2) show the similar pattern of spectral data with the corresponding parent complexes.

Depending on the stereochemical arrangement of the ligands **R** and **X** of the alkyl halides **RX**, several hexa-coordinated alkyl intermediates are possible during OA reactions. As most of the penta-coordinated carbonyl–Rh(III)–acyl complexes reported are square pyramidal in nature,^{45,46} it is likely that all the acyl complexes would also have a similar geometry. The presence of a single high terminal $\nu(\text{CO})$ value is consistent with CO group *trans* to a weak *trans* influencing chloride.⁴⁵ On the other hand, in view of high *trans* influencing nature, the acyl group favors apical position *trans* to the vacant coordination site.^{6,13} Thus, the most probable structure of the intermediates and the acyl complexes are represented in Scheme 1. In the complexes **4a** and **8b–d**, iodine prefers to coordinate to the metal centers at *trans* to each other.⁴⁷

The literature⁴⁵ reveals that such OA reactions may lead to the formation of different isomeric, oligomeric or halide-exchanged species, which are difficult to establish even with sophisticated analytical tools. However, in our study the $\nu(\text{CO})$ bands in the IR spectra, the NMR data and elemental analyses do not indicate the presence of any such isomeric or halide-exchanged species, but the possibility of the existence of these cannot be ruled out. Substantiation of the structures of different rhodium(I) and rhodium(III) carbonyl complexes/isomers by X-ray crystal structure determination was not possible because no suitable crystals could be developed despite several attempts.

Kinetics of OA reactions of Rh(I) complexes with CH_3I and $\text{C}_2\text{H}_5\text{I}$

The dicarbonyl rhodium(I) complexes $[\text{Rh}(\text{CO})_2\text{Cl}(\text{P} \sim \text{Se})]$ (**1b–d**) are coordinately unsaturated and undergo rapid OA reactions with CH_3I similar to our preliminary report³⁵ on the kinetics of the complex **1a** with CH_3I where a single stage kinetics was observed ($k_{\text{obs}} = 2.467 \times 10^{-3} \text{ s}^{-1}$). The reactivities of the complexes vary with the chain-length of the ligand backbones. To determine the rate of OA, *in situ* IR was taken during the course of the reaction. The reaction kinetics were monitored by following the simultaneous decay of the lower $\nu(\text{CO})$ absorption of the complexes **1b–d** in the region $1984\text{--}1992 \text{ cm}^{-1}$ and the formation of acyl $\nu(\text{CO})$ band of the corresponding acyl complexes **5b–d** in the range $1702\text{--}1713 \text{ cm}^{-1}$. During the course of the OA reactions of the complexes with CH_3I , a series of IR spectra were recorded at different time intervals and a typical set of spectral pattern for complex **1b** is shown in Fig. 1. It is clear that, out of the two terminal $\nu(\text{CO})$ bands, the intensity of the lower $\nu(\text{CO})$ band occurring at 1988 cm^{-1} decreases while the higher $\nu(\text{CO})$ band at 2067 cm^{-1} shifts to 2071 cm^{-1} .

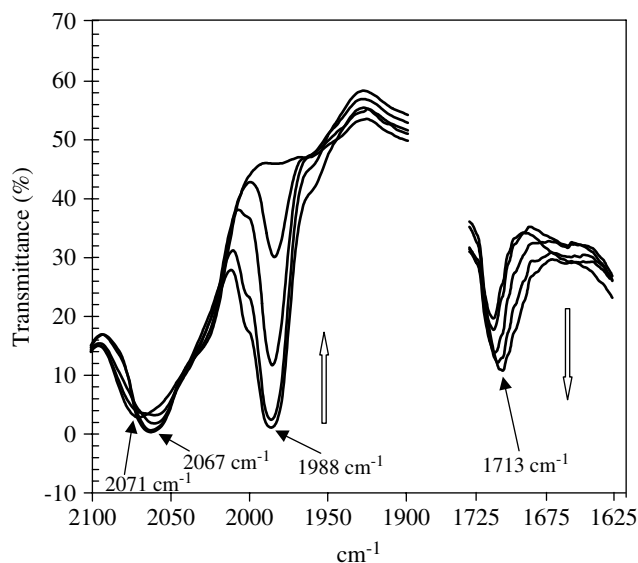


Figure 1. Series of IR spectra ($\nu(\text{CO})$ region) showing the OA reaction of **1b** with CH_3I at room temperature. The arrows (\uparrow) and (\downarrow) indicate the decrease and increase in intensity of the terminal and acyl $\nu(\text{CO})$ bands, respectively, with the progress of the reaction.

The rate of the OA reaction was found to be dependent on both the concentration of complexes **1b–d** and CH_3I . The rate was evaluated by applying pseudo-first-order condition, i.e. at high concentration (neat) of CH_3I (1 cm^3 , $16 \times 10^{-3} \text{ mol}$). The formations of acyl complexes from the parent complexes **1b–d** as a function of time are shown in Fig. 2. The decaying curves of the parent complexes **1b–d** indicate that the entire course of the OA reactions proceeds in an exponential manner and is completed at around 30, 35 and 40 min, respectively. Applying the pseudo-first-order condition, the plot of $\ln(A_0/A_t)$ vs t (Fig. 3), where A_0 and A_t are the concentrations of the complexes at time $t = 0$ and t , respectively, shows a good linear fit for the entire course of the reaction. The slopes of the plots give the pseudo-first-order rate constants $k_{\text{obs}} = 2.34 \times 10^{-3}$, 2.30×10^{-3} and $1.67 \times 10^{-3} \text{ s}^{-1}$ for the complexes **1b–d** respectively (Table 3). Thus the reactivity of the complexes follows the order **1a** > **1b** > **1c** > **1d** and the trend may be due to steric hindrance of the ligands where it increases with increase of the chain-length of the backbone. To find out the dependence of reaction rate on concentration of CH_3I , in addition to measurements in neat CH_3I (1 cm^3 , $16 \times 10^{-3} \text{ mol}$), reactions were also carried out in (i) 0.5 cm^3 ($8 \times 10^{-3} \text{ mol}$) CH_3I and 0.5 cm^3 dichloromethane and (ii) 0.75 cm^3 ($11.92 \times 10^{-3} \text{ mol}$) CH_3I and 0.25 cm^3 dichloromethane solution of complexes **1b–d** at 25°C . The k_{obs} values at different concentrations are evaluated (Table 3) from the plot of $\ln(A_0/A_t)$ vs t (Fig. 3). The plots indicate, as the concentration of CH_3I decreases, the time required to complete the OA reaction increases. The plots (not shown) of k_{obs} vs concentration of

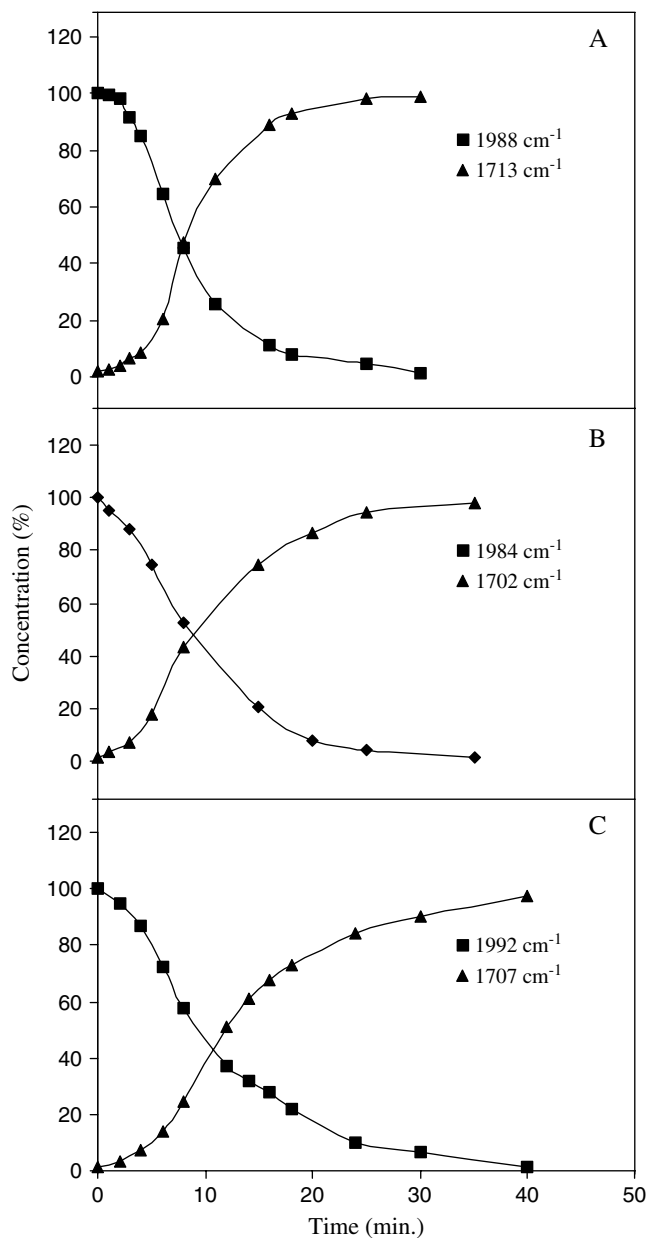


Figure 2. Simultaneous decay (■) of terminal $\nu(\text{CO})$ bands in complexes **1b** (A), **1c** (B) and **1d** (C) and increase in intensity (▲) of acyl $\nu(\text{CO})$ bands of the corresponding acyl complexes **5b–d** during the OA reaction with CH_3I against time.

CH_3I shows a good linear fit, revealing that the reactions are of first order in CH_3I as well as complexes **1b–d** concentrations. Therefore, the overall OA reaction is second order and $k_{\text{obs}} = k_2 [\text{CH}_3\text{I}]$, where k_2 is the second-order rate constant.

In order to compare the reactivity (OA) of CH_3I , the OA reactions of neat $\text{C}_2\text{H}_5\text{I}$ (1 cm^3 , $12.25 \times 10^{-3} \text{ mol}$) with complexes **1a–d** were also carried out. Applying the same conditions as above, similar types of kinetics were observed from the decay of lower $\nu(\text{CO})$ bands of the complexes

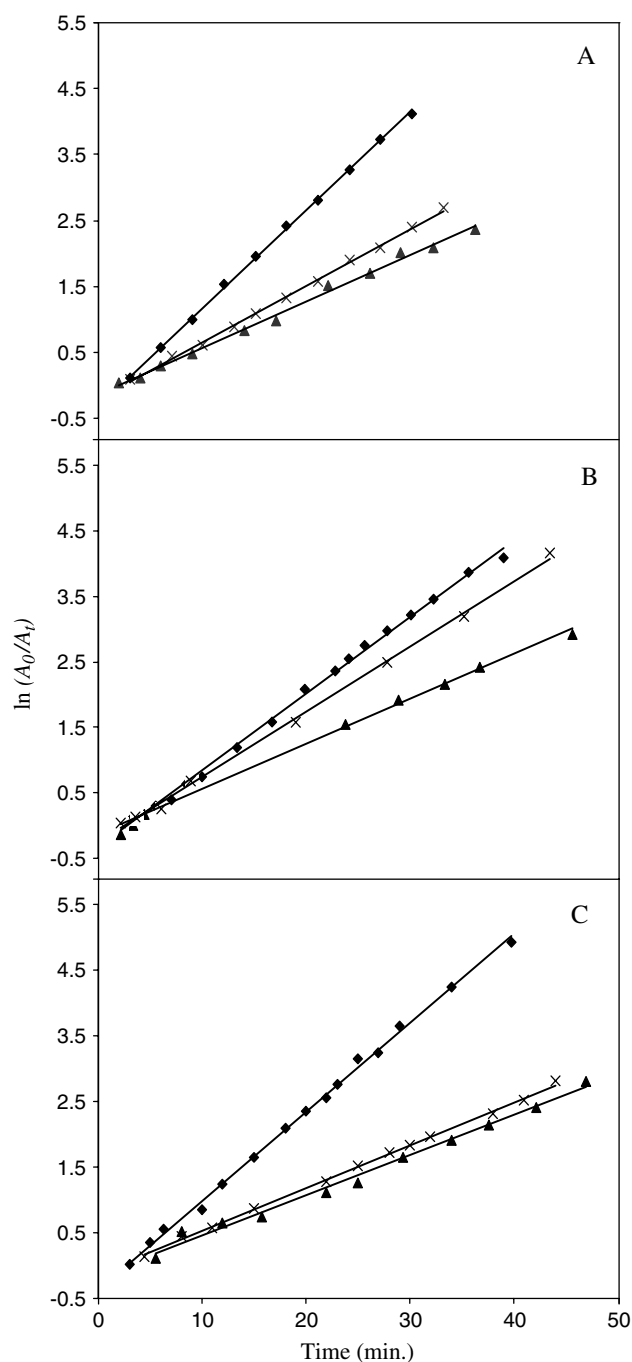


Figure 3. Plot of $\ln(A_0/A_t)$ against time (min): OA of each complexes **1b** (A), **1c** (B) and **1d** (C) in (♦) 1, (×) 0.75 and (▲) 0.5 cm^3 of CH_3I .

1a–d and an increase of intensity of the corresponding acyl complexes. It was found that OA reaction of the complexes with $\text{C}_2\text{H}_5\text{I}$ is slower than with CH_3I . The reaction follows the single-stage kinetics and k_{obs} values (Table 3) for the complexes **1a–d** were found to be 2.07×10^{-4} , 1.4×10^{-4} , 9.33×10^{-5} and $8.50 \times 10^{-5} \text{ s}^{-1}$ which is about 10–100 times slower than the corresponding k_{obs} of the complexes with

Table 3. k_{obs} values for the OA reactions of the complexes **1a–d** with CH_3I and $\text{C}_2\text{H}_5\text{I}$

Complexes	k_{obs} (s^{-1}) ([RI] mol)	
	CH_3I	$\text{C}_2\text{H}_5\text{I}$
[Rh(CO)Cl(P \cap Se)] (1a)	$2.467 \times 10^{-3\text{a}}$	2.07×10^{-4} (12.25×10^{-3})
[Rh(CO) ₂ Cl(P \sim Se)] (1b)	1.23×10^{-3} (8×10^{-3})	1.40×10^{-4} (12.25×10^{-3})
[Rh(CO) ₂ Cl(P \sim Se)] (1c)	1.78×10^{-3} (11.92×10^{-3})	9.33×10^{-5} (12.25×10^{-3})
	2.34×10^{-3} (16×10^{-3})	
	1.10×10^{-3} (8×10^{-3})	
[Rh(CO) ₂ Cl(P \sim Se)] (1d)	1.65×10^{-3} (11.92×10^{-3})	8.50×10^{-5} (12.25×10^{-3})
	2.30×10^{-3} (16×10^{-3})	
	1.02×10^{-3} (8×10^{-3})	
	1.34×10^{-3} (11.92×10^{-3})	
	1.67×10^{-3} (16×10^{-3})	

^a Our earlier report.³⁵

CH_3I . The trend of reactivity (OA) of $\text{C}_2\text{H}_5\text{I}$ with complexes **1a–d** follows the order **1a** > **1b** > **1c** > **1d**, which was also observed in the case of CH_3I reactivities.

Catalytic activity of the complexes **1b–d** for carbonylation of methanol

The results of carbonylation of methanol to acetic acid and its ester in the presence of the complexes **1b–d** as catalyst precursors are shown in Table 4. GC analyses of the products reveal that complexes **1b–d** respectively show 36.21, 35.90 and 35.54% total conversions of methanol, with the corresponding turnover numbers (TON) 812, 690 and 683. Under the same experimental conditions, the well-known catalyst precursor $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, generated *in situ*⁴⁸ from added $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ shows only 34.08% total conversion with TON 648. On the other hand, total conversions of 38.80% with TON 870 were reported under the same experimental conditions for the complex **1a** by our group.³⁵ Thus, the efficiency trend of the complexes follows the order **1a** > **1b** > **1c** > **1d** >

Table 4. Results of carbonylation of methanol in the presence of complexes **1a–d** as catalyst precursors at $130 \pm 5^\circ\text{C}$ and 35 ± 2 bar CO pressure for 1 h

Catalyst	Acetic acid ^a (%)	Methyl acetate ^a (%)	Total conversion (%)	TON ^b
$[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ^c	3.34	30.74	34.08	648 ^d
1a	9.60	29.20	38.80	870 ^d
1b	8.16	28.05	36.21	812
1c	4.26	31.64	35.90	690
1d	4.22	31.32	35.54	683

^a Yield of methyl acetate and acetic acid were obtained from GC analyses.

^b TON = [amount of product (mol)]/[amount of catalyst (Rh mol)].

^c Formed from added $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ under catalytic condition.

^d Our earlier report.³⁵

$[\text{Rh}(\text{CO})_2\text{I}_2]^-$. Therefore, the advantage of the complexes **1a–d** as catalysts over the species $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is obvious. The observed trend of the complexes can be well explained on the basis of rate of OA reactions with CH_3I . In carbonylation of methanol, the OA of CH_3I is the rate-determining step, and the higher the rate of OA reaction, the higher is the catalytic activity. From the kinetic study of OA reaction of CH_3I with complexes **1a–d**, it has been observed that the rate of OA reaction also follows the same order as mentioned above. Therefore, the described difference in reactivity is due to the observed difference in rate of OA reaction. The chelate complex **1a** shows higher catalytic activity than the non-chelate complexes **1b–d** and this higher activity may be due to higher electron density on the central metal atom gain by the chelate formation through Se donor of the ligand. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reaction, multiple $\nu(\text{CO})$ bands are obtained that match well with the $\nu(\text{CO})$ values of solution containing a mixture of the parent rhodium(I) carbonyl complexes **1b–d** and rhodium(III) acyl complexes **5b–d**. Thus, it may be inferred that the ligands remained bound to the metal center throughout the entire course of the catalytic reactions.

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