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Rhodium(I) carbonyl complexes of chalcogen functionalized tripodal phosphines, $[CH_3C(CH_2P(X)Ph_2)_3]$ {X = O, S, Se} and their reactivity

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ABSTRACT

The reaction of dimeric rhodium precursor $[Rh(CO)_2Cl]_2$ with two molar equivalent of 1,1,1-tris(diphenylphosphinomethyl)ethane trichalcogenide ligands, $[CH_3C(CH_2P(X)Ph_2)_3](L)$, where X = O(**a**), S(**b**) and Se(**c**) affords the complexes of the type $[Rh(CO)_2Cl(L)]$ (**1a–1c**). The complexes **1a–1c** have been characterized by elemental analyses, mass spectrometry, IR and NMR (^1H, ^{31}P and ^{13}C) spectroscopy and the ligands **a–c** are structurally determined by single crystal X-ray diffraction. **1a–1c** undergo oxidative addition (OA) reactions with different electrophiles such as CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ to give Rh(III) complexes of the types [Rh(CO)(COR)ClXL] {R = $-CH_3$ (**2a–2c**), $-C_2H_5$ (**3a–3c**); X = I and R = $-CH_2C_6H_5$ (**4a–4c**); X = Cl}. Kinetic data for the reaction of **a–c** with CH_3I indicate a first-order reaction. The catalytic activity of **1a–1c** for the carbonylation of methanol to acetic acid and its ester is evaluated and a higher turn over number (TON = 1564–1723) is obtained compared to that of the well-known commercial species $[Rh(CO)_2I_2]^-$ (TON = 1000) under the reaction conditions: temperature 130 ± 2 °C, pressure 30 ± 2 bar and time 1 h.

1. Introduction

The chemistry of phosphines and their derivatives have aroused much interest in the last few decades because of their reactivity, structural novelty and catalytic activity [1–5]. The tripodal polyphosphines such as $CH_3C(CH_2PPh_2)_3$ (triphos), have been employed in several metal complex systems [6–10] and there are a number of reports of five coordinate Rh(I) and Ir(I) complexes containing flexible η^2–P binding mode [10–15], which exhibit kinetic lability of M^I–P bonds (M = Rh, Ir) leading to structural and chemical variability. Metal complexes of multidentate phosphine chalcogen donor ligands play an important role on the stability and reactivity of the compounds. The most important feature of these ligands is that they can stabilize the metal complexes by chelate formation and may create vacant coordination sites at the metal centre by the cleavage of relatively weaker metal chalcogen bonds, which is a prerequisite criteria for catalytic reactions. The oxidative addition (OA) reactions of Rh(I) complexes containing labile ligands have a great impact in catalytic carbonylation of methanol. Since the introduction of the Monsanto's species i.e. $[Rh(CO)_2I_2]^-$ as an efficient catalyst for carbonylation of methanol to acetic acid, considerable efforts have been made to improve the catalysts by incorporating different ligands into its coordination sphere [16–21]. Though the Rh carbonyl complexes of mono- and ditertiary phosphine chalcogenides and their catalytic carbonylation of methanol are documented in the literature [5b,22], but to our best knowledge, there is no report of rhodium carbonyl complexes containing tripodal phosphine chalcogenides and their utilization as catalysts for carbonylation reaction. As a part of our continuing research activities [5,22,23], herein we report the synthesis, reactivity and catalytic carbonylation of rhodium(I) carbonyl complexes containing 1,1,1-tris(diphenylphosphino methyl)ethane trichalcogenide [P_3X_3, where X = O(**a**), S(**b**) and Se(**c**)] ligands. The X-ray structural characterization of the three P_3X_3 ligands (**a–c**) and their donor effects on the nucleophillicity of the metal centre have also been demonstrated.

2. Experimental

2.1. General definition

All solvents were distilled under N_2 prior to use. $RhCl_3{\cdot}xH_2O$ was purchased from M/S Arrora Matthey Ltd., Kolkota, India. $[CH_3C(CH_2PPh_2)_3]$, elemental sulfur and selenium powder were

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purchased from M/S Aldrich, USA and used without further purification. H_2O_2 was obtained from Ranbaxy, New Delhi, India and estimated before use.

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 FTIR spectrophotometer. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Bruker DPX-300 Spectrometer and chemical shifts were reported relative to $SiMe_4$ and 85% H_3PO_3 as internal and external standards respectively. 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).

2.2. Synthesis of the ligands, $[CH_3C(CH_2P(X)Ph_2)_3]$, where (X = O, S, Se)

The ligands, $[CH_3C(CH_2P(O)Ph_2)_3]$(**a**), $[CH_3C(CH_2P(S)Ph_2)_3]$(**b**) and $[CH_3C(CH_2P(Se)\text{-}Ph_2)_3]$(**c**) were synthesized as reported in our earlier paper [24].

2.3. Starting material

$[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3{\cdot}3H_2O$ at 100 °C in the presence of moisture [25].

2.4. Synthesis of the complexes $[Rh(CO)_2ClL]$ (**1**), L = $[CH_3C(CH_2P(O)Ph_2)_3]$(**a**), $[CH_3C(CH_2P(S)Ph_2)_3]$(**b**), $[CH_3C(CH_2P(Se)Ph_2)_3]$(**c**)

$[Rh(CO)_2Cl]_2$ (100 mg) was dissolved in dichloromethane (10 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:1) of the respective ligands were added. The reaction mixture was stirred at room temperature (r.t.) for about 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 a desiccator.

Analytical data for the complexes **1a–1c** and their free ligands **a–c** are as follows:

- **1a**: Yield: 85%; IR (KBr, cm^{-1}): 2075, 2069, 2010, 1996 [ν(CO)], 1168, 1165, 1174 [ν(P=O)]. ^1H NMR (CD_3OD, ppm): δ 0.91 (s, 3H, CH_3), δ 3.20–3.29 (6H, CH_2), δ 7.09–7.58, 7.75–8.06 (m, 30H, Ph). ^{13}C NMR (CD_3OD, ppm): δ 27.5 (q, CH_3), δ 40.9 (dt, $CH_2P{=}O$), δ 38.1 (q, C), δ 127.2–135.1 (m, Ph), δ 183.7 (s, CO). $^{31}P\{^1H\}$ NMR (CD_3OD, ppm): δ 32.5 [broad, P(V)]. Elemental analyses; Found (Calcd for $C_{43}H_{39}ClO_5P_3Rh$): C, 58.97 (59.50), H, 4.25 (4.49). Mass: 866.9 (m/z^+).
- **1b**: Yield: 88%; IR (KBr, cm^{-1}): 2074, 2067, 2004, 1991 [ν(CO)], 622, 609, 606 [ν(P=S)]. ^1H NMR ($CDCl_3$, ppm): δ 0.69 (s, 3H, CH_3), δ 3.72–3.90 (6H, CH_2), δ 7.03–7.48, 7.78–8.11 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 26.3 (q, CH_3), δ 41.8 (dt, $CH_2P{=}S$), δ 40.2 (q, C), δ 127.9–132.2 (m, Ph), δ 184.2 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 36.2 [broad, P(V)]. Elemental analyses; Found (Calcd for $C_{43}H_{39}ClO_2S_3P_3Rh$): C, 55.85 (56.36), H, 4.05 (4.26). Mass: 915.8 (m/z^+).
- **1c**: Yield: 91%; IR (KBr, cm^{-1}): 2072, 2066, 2001, 1989 [ν(CO)], 546, 543, 539 [ν(P=Se)]. ^1H NMR ($CDCl_3$, ppm): δ 0.62 (s, 3H, CH_3), δ 4.04–4.38 (d, 6H, CH_2), δ 7.08–7.39, 7.91–8.14 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 26.8 (q, CH_3), δ 41.5 (dt, $CH_2P{=}S$), δ 42.5 (q, C), δ 128.7–133.5 (m, Ph), δ 185.3 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 23.9 [broad, P(V)]. Elemental analyses; Found (Calcd for $C_{43}H_{39}ClO_2Se_3P_3Rh$): C, 48.11 (48.84), H, 3.26 (3.69). Mass: 1056.5 (m/z^+).
- **a**: Yield: 90%; IR (KBr, cm^{-1}): 1175 [ν(P=O)]. ^1H NMR ($CDCl_3$, ppm): δ 0.85 (s, 3H, CH_3), δ 3.19 (d, 6H, CH_2), δ 7.27–7.50, 7.65–7.85 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 29.1 (q, CH_3), δ 41.1 (dt, $CH_2P{=}S$), δ 39.7 (q, C), δ 128.8–134.5 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 31.3 [s, P(V)]. Elemental analyses; Found (Calcd for $C_{41}H_{39}O_3P_3$): C, 72.91 (73.13), H, 5.38 (5.80). Mass: 672.9 (m/z^+).
- **b**: Yield: 95%; IR (KBr, cm^{-1}): 625, 611 [ν(P=S)]. ^1H NMR ($CDCl_3$, ppm): δ 0.64 (s, 3H, CH_3), δ 3.8 (d, 6H, CH_2), δ 6.98–7.40, 7.95–8.02 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 26.4 (q, CH_3), δ 41.8 (dt, $CH_2P{=}S$), δ 42.3 (q, C), δ 128.3–134.2 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 35.5 [s, P(V)]. Elemental analyses; Found (Calcd for $C_{41}H_{39}S_3P_3$): C, 67.79 (68.26), H, 5.21 (5.41). Mass: 719.8 (m/z^+).
- **c**: Yield: 92%; IR (KBr, cm^{-1}): 548 [ν(P=Se)]. ^1H NMR ($CDCl_3$, ppm): δ 0.59 (s, 3H, CH_3), δ 4.02 (d, 6H, CH_2), δ 7.15–7.41, 7.98–8.06 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 26.1 (q, CH_3), δ 40.9 (dt, $CH_2P{=}S$), δ 42.9 (q, C), δ 128.3–132.8 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 23.1 [s, P(V)]. Elemental analyses; Found (Calcd for $C_{41}H_{39}Se_3P_3$): C, 56.93 (57.10), H, 4.35 (4.52). Mass: 861.5 (m/z^+).

2.5. Synthesis of $[Rh(CO)(COR)ClXL]$ (R = CH_3, X = I (**2**); R = C_2H_5, X = I (**3**); R = $C_6H_5CH_2$, X = Cl (**4**)

$[Rh(CO)_2ClL]$ (50 mg) was dissolved in dichloromethane (5 cm^3) and each of RX (3 cm^3) (RX = CH_3I, C_2H_5I, $C_6H_5CH_2Cl$) was added to it. The reaction mixture was then stirred at r.t. for about 4, 6 and 8 h for CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ respectively. 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.

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

- **2a**: Yield: 81%; IR ($CHCl_3$, cm^{-1}): 2065 [ν(CO)], 1745 [$\nu(CO)_{acyl}$], ^1H NMR ($CDCl_3$, ppm): δ 0.85 (s, 3H, CH_3), δ 3.22–3.35 (6H, CH_2), δ 7.14–8.06 (m, 30H, Ph), δ 2.16 (s, 3H, $CH_3)_{MeI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 122.2–135.1 (m, Ph), δ 184.4 (s, CO), δ 207.1 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 33.2 [broad, P(V)].
- **2b**: Yield: 85%; IR ($CHCl_3$, cm^{-1}): 2068 [ν(CO)], 1729 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.71 (s, 3H, CH_3), δ 3.78–3.92 (6H, CH_2), δ 7.08–8.03 (m, 30H, Ph), δ 2.29 (s, 3H, $CH_3)_{MeI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 124.2–134.1 (m, Ph), δ 185.1 (s, CO), δ 206.6 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 36.8 [broad, P(V)].
- **2c**: Yield: 84%; IR ($CHCl_3$, cm^{-1}): 2072 [ν(CO)], 1737 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.68 (s, 3H, CH_3), δ 3.98–4.25 (d, 6H, CH_2), δ 7.12–8.17 (m, 30H, Ph), δ 2.57 (s, 3H, $CH_3)_{MeI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 126.2–137.1 (m, Ph), δ 185.9 (s, CO), δ 204.8 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 24.6 [broad, P(V)].
- **3a**: Yield: 85%; IR ($CHCl_3$, cm^{-1}): 2066 [ν(CO)], 1728 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.89 (s, 3H, CH_3), δ 3.55–3.38 (6H, CH_2), δ 7.04–8.09 (m, 30H, Ph), δ 2.35 (q, 2H, $CH_2)_{EtI}$, δ 1.61 (t, 3H, $CH_3)_{EtI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 122.2–135.1 (m, Ph), δ 186.4 (s, CO), δ 204.1 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 33.4 [broad, P(V)].
- **3b**: Yield: 91%; IR ($CHCl_3$, cm^{-1}): 2071 [ν(CO)], 1720 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.78 (s, 3H, CH_3), δ 3.84–3.91 (6H, CH_2), δ 6.98–8.05 (m, 30H, Ph), δ 2.51 (q, 2H, $CH_2)_{EtI}$, δ 1.53 (t, 3H, $CH_3)_{EtI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 123.9–137.1 (m, Ph), δ 184.1 (s, CO), δ 203.6 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 36.7 [broad, P(V)].
- **3c**: Yield: 87%; IR ($CHCl_3$, cm^{-1}): 2060 [ν(CO)], 1735 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.72 (s, 3H, CH_3), δ 3.89–4.22 (6H, CH_2), δ 7.01–8.17 (m, 30H, Ph), δ 2.71 (q, 2H, $CH_2)_{EtI}$, δ 1.68 (t, 3H, $CH_3)_{EtI}$. ^{13}C NMR ($CDCl_3$, ppm): δ 123.2–137.1 (m, Ph), δ 184.9 (s, CO), δ

205.2 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 24.8 [broad, P(V)].

- **4a**: Yield: 78%; IR ($CHCl_3$, cm^{-1}): 2071 [ν(CO)], 1734 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.91 (s, 3H, CH_3), δ 3.42–3.61 (6H, CH_2), δ 6.94–8.16 (m, 35H, Ph), δ 4.26 (s, 2H, $CH_2)_{Bz}$ (Bz stands for $C_6H_5CH_2Cl$). ^{13}C NMR ($CDCl_3$, ppm): δ 124.8–133.3 (m, Ph), δ 185.3 (s, CO), δ 206.2 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 33.2[broad, P(V)].
- **4b**: Yield: 75%; IR ($CHCl_3$, cm^{-1}): 2066 [ν(CO)], 1736 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.78 (s, 3H, CH_3), δ 3.72–3.97 (6H, CH_2), δ 7.91–8.13 (m, 35H, Ph), δ 4.31 (s, 2H, $CH_2)_{Bz}$. ^{13}C NMR ($CDCl_3$, ppm): δ 122.8–136.2 (m, Ph), δ 184.2 (s, CO), δ 205.6 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 36.5 [broad, P(V)].
- **4c**: Yield: 79%; IR ($CHCl_3$, cm^{-1}): 2068 [ν(CO)], 1742 [$\nu(CO)_{acyl}$]. ^1H NMR ($CDCl_3$, ppm): δ 0.65 (s, 3H, CH_3), δ 3.94–4.15 (6H, CH_2), δ 7.01–8.17 (m, 35H, Ph), δ 4.58 (s, 2H, $CH_2)_{Bz}$. ^{13}C NMR ($CDCl_3$, ppm): δ 122.6–138.3 (m, Ph), δ 186.5 (s, CO), δ 206.4 (s, $CO)_{acyl}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 24.6 [broad, P(V)].

2.6. X-ray structural analysis

Single crystals of **a–c** were grown by layering a CH_2Cl_2 solution of **a–c** with n-pentane. Several different crystals of each sample were examined since the crystals were difficult to grow and of low quality. 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 structures were solved with SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 computer program [26]. Hydrogen atoms were idealized by using the riding models.

2.7. Kinetic experiment

The kinetic experiments of OA reaction of complexes **1a–1c** with CH_3I were monitored using FTIR spectroscopy in a solution cell (CaF_2 windows, 1.0 mm path length). In order to obtain pseudo-first-order condition, excess of CH_3I relative to metal complex was used. FTIR spectra (4.0 cm^{-1} resolution) were scanned in the ν(CO) region (2200–1600 cm^{-1}) and saved at regular time interval using spectrum software. After completion of experiment, absorbance versus time data for the appropriate ν(CO) frequencies were extracted by subtracting the solvent spectrum and analyzed off line using OriginPro 7.5 software. Kinetic measurements were made by following the decay of lower frequency ν(CO) band of the complexes in the region 1996–1989 cm^{-1}. The pseudo-first-order rate constants were found from the gradient of the plot of $\ln(A_0/A_t)$ versus time, where A_0 is the initial absorbance and A_t is the absorbance at time t.

2.8. Carbonylation of methanol using complexes *1a–1c* 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 carbonylation reactions were carried out at 130 ± 2 °C for 1 h under CO pressure (30 ± 2 bar). The products were collected and analyzed by GC.

3. Results and discussion

3.1. Single crystal X-ray structural determination of *a–c*

The single crystal X-ray structures (Fig. 1) of the reported [24] trichalcogen functionalized phosphine ligands **a–c** have been determined. The crystal information of **a–c** is summarized in Table 1. The compound **a** crystallizes in a triclinic system with space group $P\bar{1}$, while **b** and **c** crystallize in a monoclinic system with space group $P2_1/c$. Though both the asymmetric units in **b** and **c** contain two molecules, the X-ray crystallographic data show that these molecules are essentially identical in both molecular dimensions and conformations. The selected bond lengths of **a–c** are presented in Table 2. The P–O bond lengths (1.488(2)–1.490(3) Å) in **a** is similar to the P—O bond length in xantphos dioxide reported by Deb and Dutta [27] Similarly, the P–S (1.954(2)–1.971(2) Å) and P–Se (2.106(3)–2.124(3) Å) bond lengths are also in the expected ranges [28].

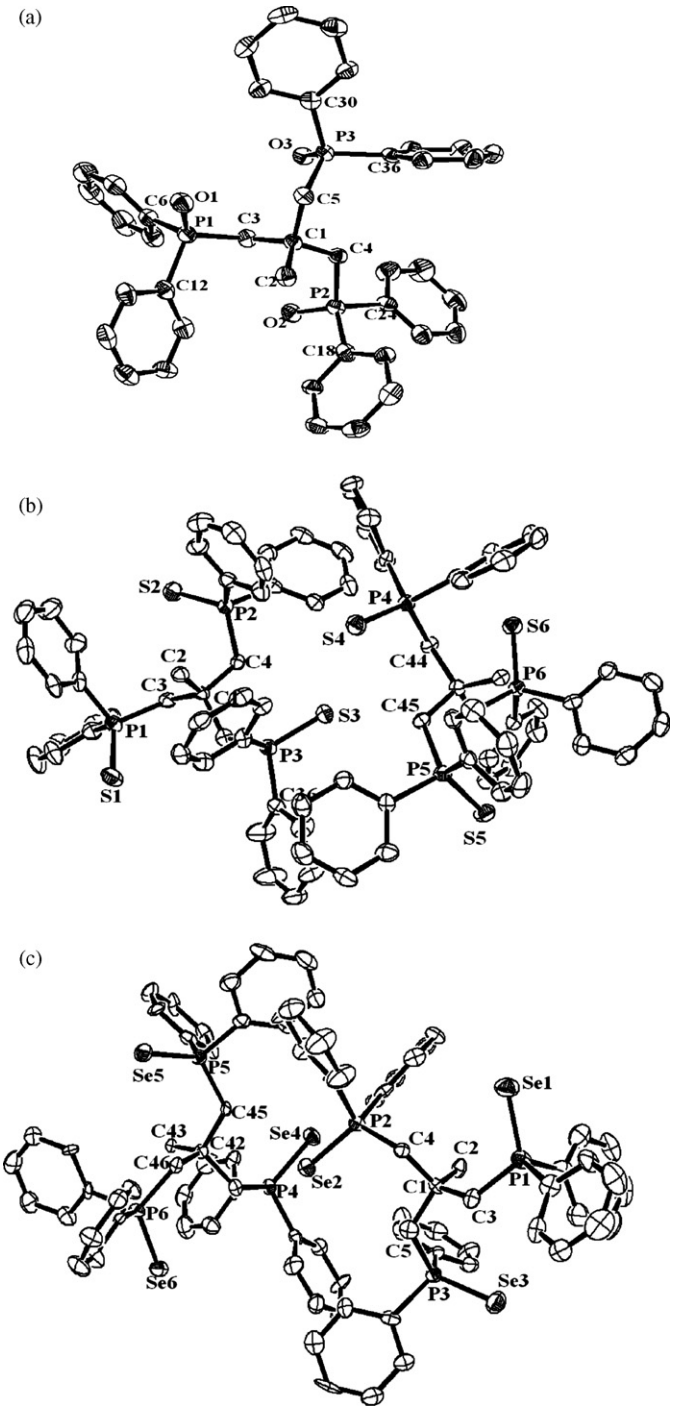


Fig. 1. X-ray crystal structures of **a–c**. Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data and structure refinement details for **a–c**.

	a	b	c
Empirical formula	$C_{41}H_{39}O_3P_3$	$C_{41}H_{39}S_3P_3$	$C_{41}H_{39}Se_3P_3$
Formula weight	672.68	720.86	861.56
Cryst. syst.	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P21/c$	$P21/c$
Z	2	8	8
a (Å)	11.2418 (15)	9.8624 (8)	9.9505 (8)
b (Å)	13.061 (2)	27.549 (2)	27.819 (2)
c (Å)	13.9967 (15)	27.387 (2)	27.556 (2)
α (°)	109.550 (13)		
β (°)	113.430 (13)	92.957 (2)	92.851 (2)
γ (°)	92.985 (18)		
μ (Mo Kα) (mm^{-1})	0.210	0.357	3.052
Reflections collected	6025	13,025	13,324
R (obs. data)	0.0786	0.1124	0.1240
wR2 (all data)	0.1996	0.1758	0.2037

Table 2
Selected bond distances (Å) and angles (°) for compounds **a–c**.

a					
P(1)–O(1)	1.488(2)	P(2)–O(2)	1.488(3)	P(3)–O(3)	1.490(3)
b					
P(1)–S(1)	1.954(2)	P(2)–S(2)	1.958(2)	P(3)–S(3)	1.970(2)
P(4)–S(4)	1.964(2)	P(5)–S(5)	1.962(2)	P(6)–S(6)	1.962(2)
c					
P(1)–Se(1)	2.106(3)	P(2)–Se(2)	2.135(3)	P(3)–Se(3)	2.108(3)
P(4)–Se(4)	2.124(3)	P(5)–Se(5)	2.118(3)	P(6)–Se(6)	2.115(3)

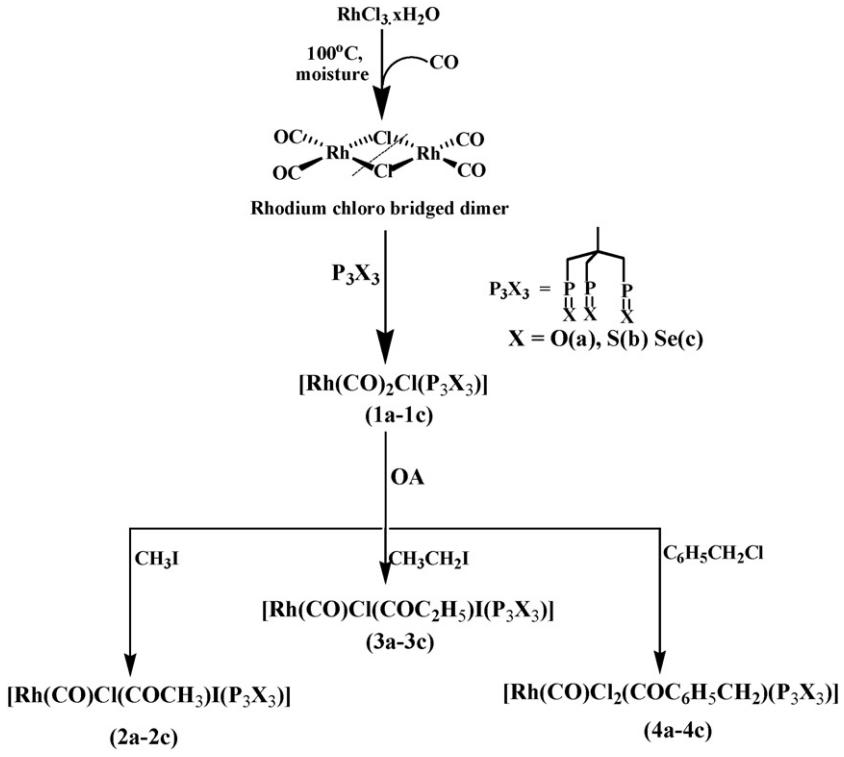
3.2. Synthesis and characterization of *1a–1c*

The reaction of the chloro-bridged dimer $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 with two molar equivalents of the ligands, **a–c** affords the complexes of the type $[Rh(CO)_2ClL]$ (**1a–1c**) [where L = **a–c**] (Scheme 1). Elemental analyses and mass spectrometric results of the complexes support the observed molecular composition of **1a–1c**. The IR spectra of **1a–1c** exhibit multiple ν(CO) bands in the range 1989–2075 cm^{-1} indicating the formation of a mixture of rhodium(I) carbonyl complexes of tripodal phosphine chalcogen donor ligands. The ν(P–X) bands of the complexes at around 1165, 1168 (**1a**), 606, 609 (**1b**) and 539, 543 (**1c**) cm^{-1} respectively are lower than that of the corresponding free ligands [ν(P–X) = 1175 (**a**); 625, 611 (**b**) and 548 (**c**) cm^{-1}] confirming the formation of Rh–X bonds. In addition, the occurrence of IR bands at around 1174, 622 and 546 cm^{-1} in the respective complexes **1a–1c** due to uncoordinated donors together with the observed peak intensity suggest the presence of dangling P–X bonds in the complexes indicating coordination to the metal centre either monodentate and/or bidentate coordination mode to generate a mixture of isomers. The presence of the mixture of isomers is also substantiated by the $^{31}P\{^1H\}$ NMR spectroscopy which shows broad singlets for the complexes **1a–1c** centred at δ = 32.5, 36.2 and 23.9 ppm respectively for three pentavalant P-atoms. The ^1H NMR spectra of **1a–1c** show characteristic resonances for methyl, methylene and phenylic protons. In the ^{13}C NMR spectra of **1a–1c**, only one weak signal for the two carbonyl carbons is appeared as broad singlet in the range 183.7–185.3 ppm. The phenyl and other carbon atoms are found in their respective ranges.

3.3. Reactivity of *1a–1c* towards various 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 [29]. Therefore, oxidative reactivities of **1a–1c** towards various electrophiles were evaluated.

The complexes **1a–1c** undergo OA reactions with CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ followed by migratory insertion reaction to generate Rh(III) complexes of the type [Rh(CO)Cl(COR)XL] {where R = $-CH_3$ (**2a–2c**), $-C_2H_5$ (**3a–3c**); X = I and R = $-CH_2C_6H_5$ (**4a–4c**),



Scheme 1. Syntheses of Rh(I) and Rh(III) complexes containing P_3X_3 ligands.

X = Cl} (Scheme 1). The IR spectra of the oxidized products show two broad ν(CO) bands in the range 2060–2072 cm^{-1} and 1720–1745 cm^{-1} characteristic of terminal and acyl carbonyl groups respectively. $^{31}P\{^1H\}$ NMR spectra of each of the oxidized products exhibit a broad singlet indicating the presence of a mixture of Rh(III) species formed after oxidative addition. The ^1H NMR spectra of the complexes **2a–2c** display singlet resonances in the range δ 2.16–2.57 ppm suggesting the formation of $-COCH_3$ group including other characteristic bands of the ligands. Similarly, the complexes **3a–3c** show the bands for methylene and methyl protons of $-COCH_2CH_3$ group as quartet and triplet in addition to characteristic bands for the ligands. The singlet resonances corresponding to methylene protons of $-COCH_2C_6H_5$ group in the complexes **4a–4c** appears in the range δ 4.26–4.58 ppm. The presence of electron withdrawing phenyl group deshields the $-COCH_2-$ proton resonances and the peaks are obtained at downfield [30]. The ^{13}C NMR spectra of **2a–2c**, **3a–3c** and **4a–4c** exhibit bands in the range 203–208 ppm characteristic to the acyl carbonyl group. Thus, it appears that the Rh(I) complexes **1a–1c** undergo oxidative addition with various alkyl halides to generate a mixture of isomers of Rh(III) species **2a–2c**, **3a–3c** and **4a–4c**, which could not be isolated.

Attempts to substantiate the structures of different rhodium(I) and rhodium(III) carbonyl complexes by X-ray crystal structure determination was not possible because no suitable crystals could be obtained in spite of numerous attempts.

Kinetic measurements for the OA reaction of the complexes **1a–1c** with methyl iodide were carried out using IR spectroscopy by monitoring the changes in the ν(CO). Fig. 2 shows a typical series of spectra of **1c** when reacts with MeI at 25 °C, in which the bands at around 1989 and 2066 cm^{-1} decay and new bands grow in the region 2070–2075 and 1720–1745 cm^{-1}. Finally, the two terminal ν(CO) bands at around 2066 and 1989 cm^{-1} are replaced by the terminal ν(CO) band at 2072 cm^{-1} and acyl ν(CO) band at 1737 cm^{-1}. Absorbance versus time plots for the decay of lower intensity ν(CO) bands at 1996, 1991 and 1989 cm^{-1} of **1a–1c** respectively are shown in Fig. 3. A linear fit of pseudo-first-order was observed for the entire course of the reaction of CH_3I with the complexes **1a–1c** as is evidenced from the plot of $\ln(A_0/A_t)$ versus time, where A_0 and A_t are the absorbance at time $t = 0$ and t respectively (Fig. 4). From the slopes of the plots, the rate constants were calculated and found as 7.19×10^{-5}, 1.95×10^{-4} and 2.68×10^{-3} s^{-1} for the complexes **1a**, **1b** and **1c** respectively. The observed values of the rate constants indicate that the rate of OA increases about tenfold on

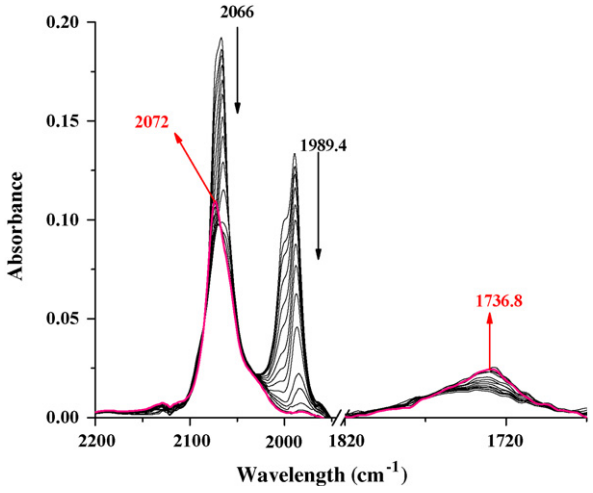


Fig. 2. Series of IR spectra {ν(CO) region} illustrating the reaction of **1c** with MeI at 25 °C. The arrows indicate the behavior of each band as the reaction progresses.

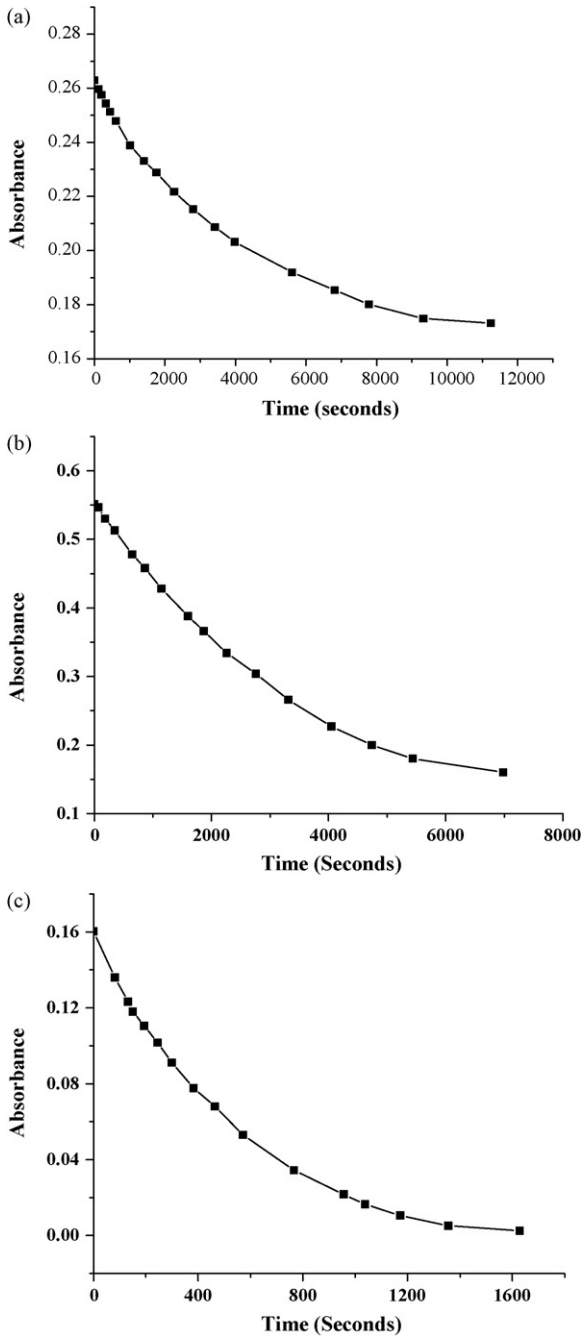


Fig. 3. Kinetic plot showing the decay of ν(CO) bands of **1a–1c** during the reaction with neat MeI at room temperature (~25 °C).

introducing the 'soft' donor ligand which is due to the higher nucleophilicity of the metal centre caused by higher electron donating capacity of the ligands. The softness of three chalcogens varies as O < S < Se and therefore, S and Se in complexes **1b** and **1c** respectively interact strongly with 'soft' rhodium(I) in contrast to 'hard' oxygen (O) donors in complex **1a**, which may be explained in terms of 'soft–hard' and 'soft–soft' interactions.

3.4. *Carbonylation of methanol to acetic acid and methyl acetate using the complexes **1a–1c** as the catalyst precursors*

The results of carbonylation of methanol to acetic acid and methyl acetate in the presence of **1a–1c** as catalyst precursors are shown in Table 3. The precursor complexes **1a–1c** show a total

Table 3
Results of carbonylation reaction of methanol.

Catalyst precursor	Time (h)	Total conv. (%)	Acetic acid[a] (%)	Methyl acetate[a]	TON[b]
$[Rh(CO)_2I_2]^-$[c]	1	52.1	10.3	41.8	1000
1a	1	81.3	42.2	39.1	1564
1b	1	87.4	45.6	41.8	1683
1c	1	89.6	53.2	36.4	1723

[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 $[Rh(CO)_2Cl]_2$ under catalytic condition.

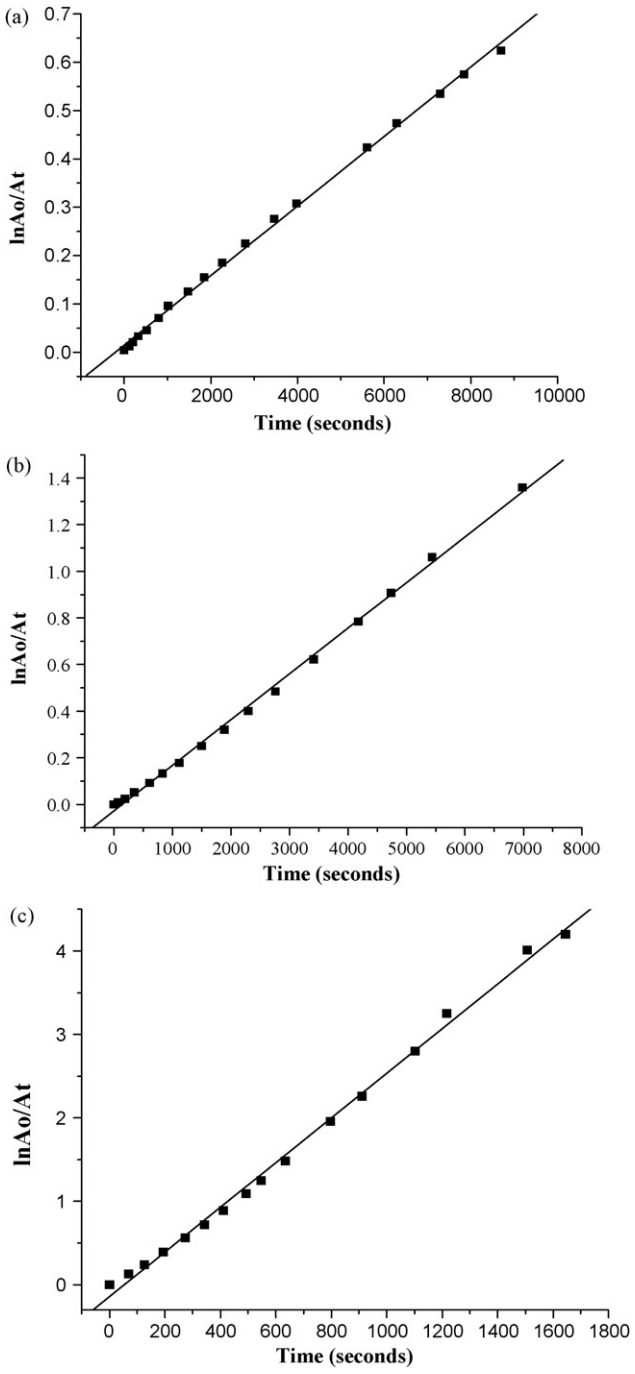


Fig. 4. Plot of $\ln(A_0/A_t)$ versus time for the OA reaction of the complexes **1a–1c** with neat MeI at ~25 °C. Rate constants: **1a**: 7.19×10^{-5} s^{-1}; **1b**: 1.95×10^{-4} s^{-1} and **1c**: 2.68×10^{-3} s^{-1}.

conversion of 81.3, 87.4 and 89.6% of CH_3OH at 130 ± 2 °C and 30 ± 2 bar CO pressure with corresponding TON of 1564, 1683 and 1723. Under the same experimental conditions, the well-known precursor $[Rh(CO)_2I_2]^-$ generated *in situ* from $[Rh(CO)_2Cl]_2$ [31] shows only 52.1% total conversion with a TON of 1000. Thus, the efficacy of the complexes depends on the nature of the ligands and follows the order **1c** > **1b** > **1a** > $[Rh(CO)_2Cl]_2$. The observed trend is also well supported by their kinetic experiments. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reaction, multiple ν(CO) bands are obtained that matched well with the ν(CO) values of solution containing a mixture of the parent rhodium(I) carbonyl complexes **1a–1c** and rhodium(III) acyl complexes **2a–2c**. Thus, it may be inferred that the ligands remained bound to the metal centre throughout the entire course of the catalytic reactions.

4. Conclusions

The new complexes of the type $[Rh(CO)_2Cl(L)]$(**1a–1c**) where L = 1,1,1-tris(diphenylphosphinomethyl)ethane trichalcogenide ligands, $[CH_3C(CH_2P(X)Ph_2)_3]$ [X = O(**a**), S(**b**) and Se(**c**)] have been synthesized and characterized and the structures of the ligands were determined by single crystal X-ray diffraction. The complexes **1a–1c** undergo oxidative addition (OA) reactions with different electrophiles like CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ to afford Rh(III) complexes of the type [Rh(CO)(COR)XL] {R = $-CH_3$ (**2a–2c**), $-C_2H_5$ (**3a–3c**); X = I and R = $-CH_2C_6H_5$ (**4a–4c**); X = Cl} and the kinetic data for the OA reactions with CH_3I indicate a first-order reaction. The catalytic activities of **1a–1c** for the carbonylation of methanol to acetic acid and its ester exhibit a higher turn over number (TON = 1564–1723) than that of the well-known commercial species $[Rh(CO)_2I_2]^-$ (TON = 1000).

Supplementary data

CCDC-711100(a), 711101(b) and 711102(c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033 e-mail: deposit@ccdc.cam.ac.uk.

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