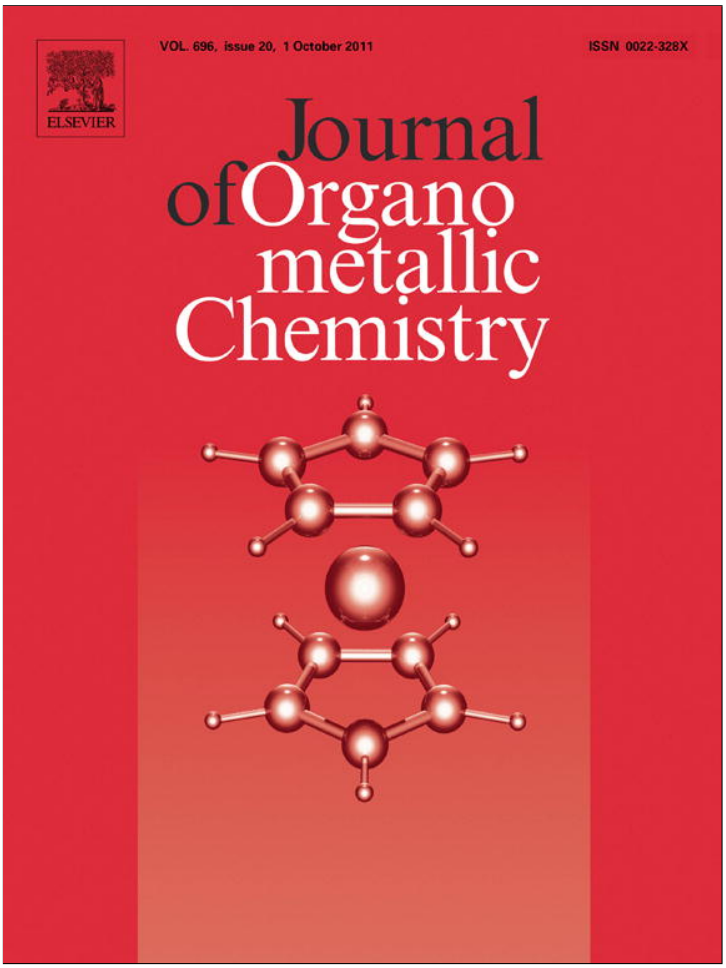

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Note

Rhodium(I) carbonyl complexes of tetradentate chalcogen functionalized phosphines, [P′(X)(CH$_2$CH$_2$P(X)Ph$_2$)$_3$] {X = O, S, Se}: Synthesis, reactivity and catalytic carbonylation reaction

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ABSTRACT

The reaction of [Rh(CO)$_2$Cl]$_2$ with 0.5 mol equivalent of the ligands [P′(X)(CH$_2$–CH$_2$P(X)Ph$_2$)$_3$](P′P$_3$X$_4$) {where X = O(**a**), S(**b**) and Se(**c**)} affords tetranuclear complexes of the type [Rh$_4$(CO)$_8$Cl$_4$(P′P$_3$X$_4$)] (**1a**–**1c**). The complexes **1a**–**1c** have been characterized by elemental analyses, mass spectrometry, IR and multinuclear NMR spectroscopy, and the ligands **b** and **c** are structurally determined by single crystal X-ray diffraction. **1a**–**1c** undergo oxidative addition (OA) reactions with CH$_3$I to generate Rh(III) oxidised products. Kinetic data for the reaction of **1a** and **1b** with excess CH$_3$I indicate a pseudo first order reaction. The catalytic activity of **1a**–**1c** for the carbonylation of methanol to acetic acid and its ester show a higher Turn Over Frequency (TOF = 1349–1748 h^{-1}) compared to the well-known species [Rh(CO)$_2$I$_2$]$^-$ (TOF = 1000 h^{-1}) under the similar experimental conditions. However, **1b** and **1c** exhibit lower TOF than **1a**, which may be due to the desulfurization and deselinization of the ligands in the respective complexes under the reaction conditions.

1. Introduction

Tertiary phosphines functionalized with chalcogen donors like oxygen [1–4], sulphur [5–9] and selenium [10,11] containing 'soft' phosphorus and 'hard' oxygen donors or 'soft' phosphorus and relatively less 'softer' sulphur and selenium donor ligands with distinctly different π-acceptor strength [1] form a variety of metal complexes due to their different bonding abilities. Recently, interest in phosphorus chalcogenides has increased significantly since ligands of these types may be effective in promoting catalysis at metal centres [1–16]. Following this interest, the potential polydentate phosphines such as tridentate, tetradentate or hexadentate have been synthesized and their coordination chemistry and reactivity are intensively examined [17–20]. Metal complexes of multidentate phosphine chalcogen donor ligands also play an important role on the stability and reactivity of the metal complexes [3,8,11–16,21–25].

The activation of small molecules by metal complexes through OA reactions has been extensively investigated in recent years due to their importance in catalytic reactions [26–30]. For instance, OA of CH$_3$I to a square planar d^8 complex is an important step in the rhodium catalyzed Monsanto's process for acetic acid production [31–33] and therefore the major focus has been made on the design of catalysts for the improvement of this reaction. For this purpose, considerable efforts have been made to improve the catalyst used in Monsanto's process i.e. [Rh(CO)$_2$I$_2$]$^-$ by incorporating different ligands into its coordination sphere [3,7,11–14,21,34–42]. Thus, as a part of our ongoing research activities [3,6,8,11,12,20–22,41–43], herein we report synthesis, reactivity and catalytic carbonylation of rhodium(I) carbonyl complexes containing P′P$_3$X$_4$, where X = O(**a**), S(**b**) and Se(**c**), as coordinating ligands. The X-ray structural characterization of [P′P$_3$S$_4$](**b**) and [P′P$_3$Se$_4$](**c**) and the donor effects of the ligands **a**–**c** on the nucleophillicity of the metal centre have also been demonstrated.

2. Results and discussion

2.1. Synthesis and characterization of *a*–*c*

Three chalcogen functionalized tetradentate ligands [P′(O)-(CH$_2$CH$_2$P(O)Ph$_2$)$_3$] (**a**), [P′(S)(CH$_2$CH$_2$P(S)Ph$_2$)$_3$] (**b**) and [P′(Se)-(CH$_2$CH$_2$P(Se)Ph$_2$)$_3$] (**c**) have been synthesized by oxidation of P′P$_3$

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with stoichiometric quantity of H_2O_2, elemental sulphur and elemental selenium respectively [21–23]. The IR spectra of **a**–**c** exhibit characteristic bands at around 1174, 611–621 and 533–540 cm^{-1} respectively, for the corresponding functional groups P═O, P═S and P═Se. The ^{31}P NMR spectra of **a**–**c** show chemical shifts in the range δ 35.3–45.09 and δ 42.69–55.44 ppm for P(V) and P′(V) respectively with relative intensity 3:1. The appearance of downfield shift of P(III) in ^{31}P NMR spectra, and methylene and phenylic protons in ^{1}H NMR spectra compared to the non-functionalized P′P_3 analogue indicating the formation of P′P_3X_4. In addition to the spectroscopic studies, the ligands **a**–**c** have also been characterized by elemental analyses and mass spectrometry along with the single crystal X-ray structure determination of **b** and **c** (Fig. 1). The P–S (1.9555(16)–1.9584(15) Å) and and P–Se (2.1055(15)–2.1112(14) Å) bond lengths (Fig. 1) are found in the range similar to literature values [8,21,44–46]. Attempts to substantiate the structure of **a** by single crystal X-ray structure determination were not possible because no suitable crystals could be obtained inspite of numerous attempts.

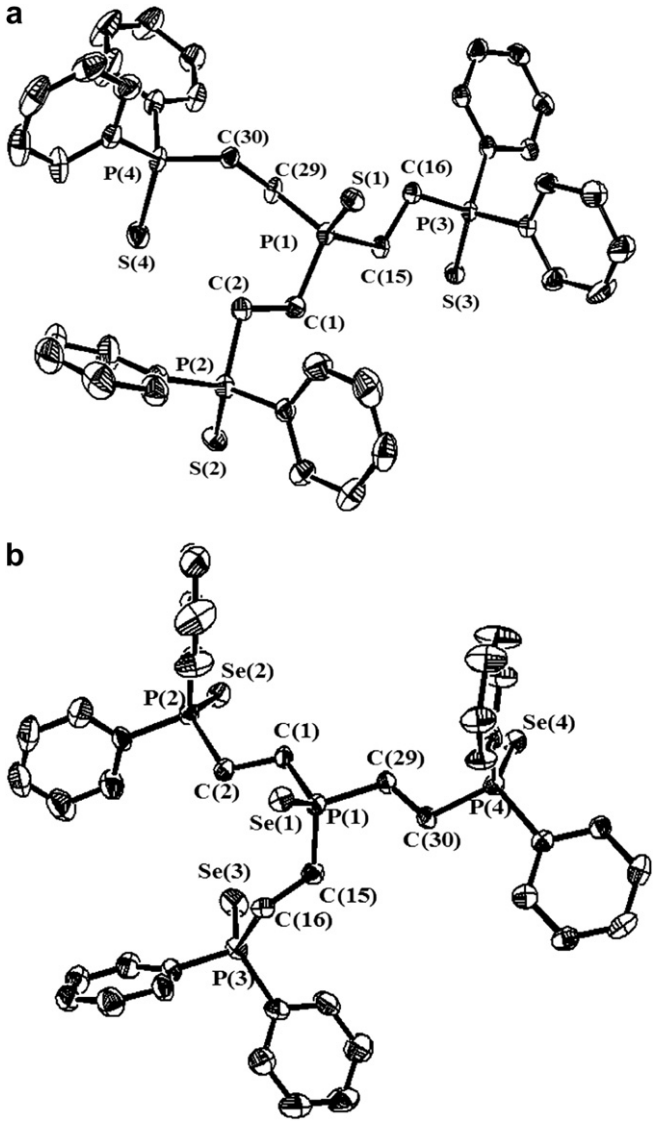


Fig. 1. X-ray crystal structures of **b** and **c**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), **b**: P(1)–S(1) 1.9555(16); P(2)–S(2) 1.9579(16); P(3)–S(3) 1.9584(15); P(4)–S(4) 1.9573(17). **c**: P(1)–Se(1) 2.1055(15); P(2)–Se(2) 2.1090(14); P(3)–Se(3) 2.1106(14); P(4)–Se(4) 2.1112(14).

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

The dimeric precursor $[Rh(CO)_2Cl]_2$ reacts with 0.5 mol equivalents of the ligands (**a**–**c**) [Rhodium : Ligand = 4:1] in CH_2Cl_2 to afford complexes of the type $[Rh_4(CO)_8Cl_4(P'P_3X_4)]$(**1a**–**1c**). The IR spectra of **1a**–**1c** exhibit multiple ν(CO) bands in the range 1988–2081 cm^{-1} indicating the formation of a multinuclear rhodium (I) carbonyl species of [P′P_3X_4] ligands. The ν(P–X) bands of the complexes at around 1149, 1186 (**1a**), 608, 582 (**1b**) and 522, 530 (**1c**) cm^{-1} are lower in frequency than those of the corresponding free ligands [ν(P–X) = 1174(**a**); 611, 621(**b**) and 533, 540 (**c**) cm^{-1}] confirming the formation of Rh–X bonds. The ^{31}P {^{1}H} NMR spectra of **1a**–**1c** show two distinct multiplets in the region δ = 37.2, 56.5; 46.3, 52.3 and 37.4, 42.2 ppm respectively for two different pentavalent P-atoms in the complexes. The intensity ratio of two ν(P–X) bands in the IR spectra and the P–X chemical shifts in ^{31}P {^{1}H} NMR spectra are found around 1:3, which indicate that out of four rhodium centres, three having similar chemical environment compared to the fourth one. The ^{1}H NMR spectra of **1a**–**1c** show characteristic resonances for methylene and phenylic protons in the range 2.04–2.80 and 7.48–8.04 ppm respectively. In the ^{13}C NMR spectra of **1a**–**1c**, weak signals for the carbonyl carbons appeared as broad singlet in the range 181.5–184.5 ppm. Elemental analyses, estimation of rhodium and mass spectrometric studies of the complexes support the observed molecular composition i.e. $[Rh_4(CO)_8Cl_4(P'P_3X_4)]$. The molecular structure of **1a**–**1c** could not be known as no suitable crystals for X-ray analysis could be developed after several attempts. The estimation of rhodium strongly supports the presence of four rhodium centres in a single molecular unit. The electrospray mass spectrometric results of **1a**–**1c** show a cluster of peaks of low intensity centred at m/z = 1512.5 (**1a**), 1576.2 (**1b**) and 1762.9 (**1c**), which may be assigned as $[Rh_4(CO)_8Cl_4(P'P_3O_4)]^+$, $[Rh_4(CO)_8\text{-}Cl_4(P'P_3S_4)]^+$ and $[Rh_4(CO)_8Cl_4(P'P_3Se_4)]^+$ respectively.

It is worth mentioning here that attempts to carry out the reaction between $[Rh(CO)_2Cl]_2$ and **a**–**c** with different Rh: ligand stoichiometric ratio, always results in the formation of $[Rh_4(CO)_8Cl_4(P'P_3X_4)]$ (Fig. 2) as evidenced by estimation of rhodium, mass spectrometric and spectroscopic studies. However, the reaction of $[Rh(CO)_2Cl]_2$ and non-functionalized phosphine, P′P_3 with variable Rh: ligand stoichiometric ratio generates different composition of rhodium(I) carbonyl complexes of P′P_3. This fact along with a detail investigation of the coordination behaviours of P′P_3X_4 ligands will be communicated in the form of a full paper [47].

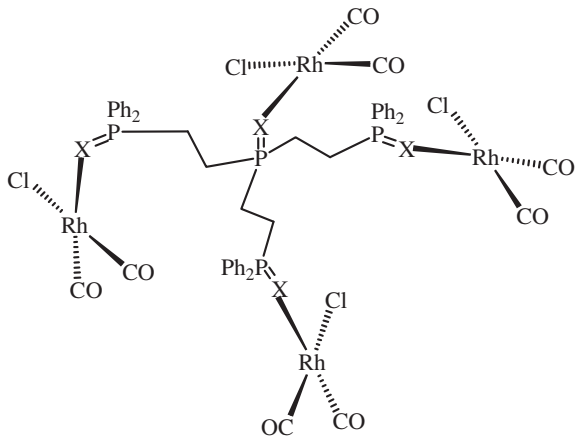


Fig. 2. Plausible structure of $[Rh_4(CO)_8Cl_4(P'P_3X_4)]$(**1a**–**1c**).

2.3. Reactivity of **1a**–**1c** with methyl iodide

The complexes **1a**–**1c** undergo OA reactions with CH_3I followed by migratory insertion reaction to generate Rh(III)-acyl complexes of the type $[Rh_4(CO)_4Y_4(COCH_3)_4I_4(P'P_3X_4)]$ (**2a**–**2c**) [Where, Y = Cl/I] (Scheme 1). The IR spectra of the oxidized products show two broad ν(CO) bands in the range 2063–2071 and 1703–1726 cm^{-1} characteristic of terminal and acyl carbonyl groups respectively. $^{31}P\{^1H\}$ NMR spectra of each of the oxidized products exhibit broad multiplets indicating the presence of a mixture of isomers of oxidative adducts. The possibility of different isomers may be due to the presence of both iodide and chloride ligands, which are expected to show some scrambling, giving the possibility of different isomeric species with I/I ligands instead of I/Cl. The ^1H NMR spectra of the complexes **2a**–**2c** display singlet resonances in the range δ 2.43–2.69 ppm suggesting the formation of $-COCH_3$ group including other characteristic bands of the ligands. The ^{13}C NMR spectra of **2a**–**2c** exhibit bands in the range 202–206 ppm characteristic to the acyl carbonyl group.

The kinetic measurement of OA reaction of the complexes **1a** and **1b** with excess CH_3I were monitored by following the decay of lower frequency of ν(CO) bands in the region 2006–2008 cm^{-1} by using FT-IR spectroscopy. The rate constants for the OA reaction of methyl iodide with **1a** and **1b** are measured and found as 2.3×10^{-4} and 4.5×10^{-4} s^{-1}, respectively. However, the kinetic study for the OA reaction of methyl iodide to **1c** could not be done due to the partial deselenisation of the ligand in the presence of excess CH_3I.

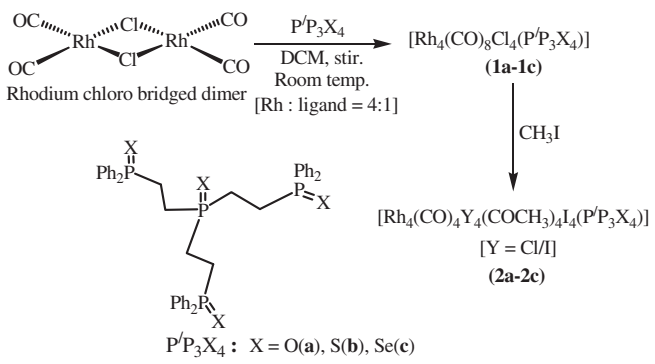
2.4. Carbonylation of methanol using **1a**–**1c** as the catalyst precursors

The results of carbonylation of methanol to acetic acid and methyl acetate in the presence of **1a**–**1c** as catalyst precursors are shown in the Table 1. The precursor complexes **1a**–**1c** show a total conversion of 91.1, 80.3 and 70.3% of CH_3OH at 130 ± 2 °C and 30 ± 2 bar CO pressure with corresponding TOF of 1748, 1541 and 1349 h^{-1}. Under the similar experimental conditions, the well-known catalyst, $[Rh(CO)_2I_2]^-$ generated *in situ* from $[Rh(CO)_2Cl]_2$ [48] shows only 52.1% total conversion with a TOF of 1000 h^{-1}. Thus, the efficiency of the complexes depends on the nature of the ligands and follows the order **1a** > **1b** > **1c** > $[Rh(CO)_2Cl]_2$. It is well-known that OA steps play a key role in enhancing the catalytic efficiency of such reaction. As expected from higher OA reaction rate of **1b** over **1a**, the former should act more efficiently than the latter in the carbonylation reaction. But in practice, the reversed situation was observed. In order to explain the above trend, each of the catalytic reaction mixtures was analyzed by FT-IR and NMR spectroscopy at the end of the catalytic reaction. The IR spectra of the reaction mixture show multiple ν(CO) bands indicating the presence of a mixture of Rh(I) carbonyl and Rh(III) acyl complexes. ^{31}P NMR spectra of the catalytic reaction mixture of **1b** and **1c** shows an interesting weak doublet at around 21.5 ppm (J_{P-Rh} = 81.8 Hz) corresponding to Rh–P bond along with other characteristic chemical shifts of Rh–X–P bonds. The appearance of peak at 21.5 ppm due to Rh–P bond substantiates the partial desulfurization and deselenization of ligands in the complexes **1b** and **1c** respectively. However, in the complex **1a**, the ligands remained bound to the metal centre throughout the course of the catalytic reactions. Thus, lower TOF of **1b** and **1c** over **1a** may be due to the partial desulfurization and deselenization of the ligands, respectively under the reaction conditions to generate less active Rh–P complexes.

Table 1
Results for carbonylation reaction of methanol.

Catalyst Precursor	Time/h	Total Conv.(%)	Acetic acid[a] (%)	Methyl acetate[a]	TOF[b] (h^{-1})
$[Rh(CO)_2I_2]^-$[c]	1	52.1	10.3	41.8	1000
1a	1	91.1	57.5	33.6	1748
1b	1	80.3	45.6	34.7	1541
1c	1	70.3	47.4	22.9	1349

[a] Yield of methyl acetate and acetic acid were obtained from GC analyses.
[b] TOF = [amount of product (mol)]/[amount of catalyst (Rh mol)]/time.
[c] Formed from added $[Rh(CO)_2Cl]_2$ under catalytic condition [48].



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

3. Conclusions

Three new rhodium(I) carbonyl complexes of the type $[\{Rh(CO)_2Cl\}_4(P'P_3X_4)]$ (**1a**–**1c**) have been synthesized and characterized, and the ligands **b** and **c** are structurally determined by single crystal X-ray diffraction. **1a**–**1c** undergo OA reactions with CH_3I to generate Rh(III) oxidized products. Kinetics data for the reaction of **1a** and **1b** 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 show a higher TOF (1349–1748 h^{-1}) than the well-known commercial species $[Rh(CO)_2I_2]^-$ (TOF = 1000 h^{-1}) under the similar experimental conditions. In addition, the coordination behaviour of $P'P_3$ and $P'P_3X_4$ ligands and catalytic activity by varying Rh/P = X or Rh/P ratio may lead to interesting results.

4. Experimental

4.1. General

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. The ligand, $[P'(CH_2CH_2PPh_2)_3]$ ($P'P_3$) elemental sulphur and selenium powder were obtained from M/S Aldrich, USA and used without further purification. H_2O_2 was purchased from Ranbaxy, New Delhi, India and the actual quantity of H_2O_2 was estimated before use.

Elemental analyses of C and H were performed on a Perkin–Elmer 2400 elemental analyzer. The analysis of rhodium was carried out by gravimetric method (For details see Supplementary materials). IR spectra (4000–400 cm^{-1}) were recorded in KBr discs and $CHCl_3$ on a Perkin–Elmer system 2000 FT-IR spectrophotometer. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature in $CDCl_3$ and CD_3OD 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).

4.2. Synthesis of the ligands, [P′(X)(CH$_2$CH$_2$P(X)Ph$_2$)$_3$], where [X = O(**a**), S(**b**), Se(**c**)]

The Ligands [P′(O)(CH$_2$CH$_2$P(O)Ph$_2$)$_3$](**a**), [P′(S)(CH$_2$CH$_2$P(S)Ph$_2$)$_3$](**b**) and [P′(Se)(CH$_2$CH$_2$P(Se)Ph$_2$)$_3$](**c**) were synthesized by literature methods [21–23].

Analytical data for **a**: Yield: 85%; IR (KBr, cm^{-1}): 1174 [br, ν(P–O)]. ^{1}H NMR (CDCl$_3$, ppm): δ 1.99, 2.42 (m, 12H, CH$_2$), δ 7.40, 7.66 (m, 30H, Ph). ^{13}C NMR (CDCl$_3$, ppm): δ 19.2, 21.9 (m, CH$_2$), δ 128.9–132.8 (m, Ph). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 35.3 [d, P^v, J_{P-P} = 50.30 Hz], δ 53.64 [q, (P′)^v, J_{P-P} = 50.8 Hz]. Elemental analyses; Found (Cald. for C$_{42}$H$_{42}$O$_4$ P$_4$): C, 67.98 (68.60), H, 5.48 (5.71). MS: m/z = 734.3 (M$^+$).

b: Yield: 92%; IR (KBr, cm^{-1}): 611, 621 [ν(P–S)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.12, 2.57 (m, 12H, CH$_2$), δ 7.42, 7.78 (m, 30H, Ph). ^{13}C NMR (CDCl$_3$, ppm): δ 23.08, 26.44 (m, CH$_2$), δ 128.9–132.03 (m, Ph). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 45.09 [d, P^v, J_{P-P} = 53.58 Hz], δ 55.44 [q, (P′)^v, J_{P-P} = 54.1 Hz]. Elemental analyses; Found (Cald for C$_{42}$H$_{42}$S$_4$ P$_4$): C, 62.58 (63.10), H, 5.08 (5.26). MS: m/z = 799.1 (M$^+$).

c: Yield: 88%; IR (KBr, cm^{-1}): 533, 540 [ν(P–Se)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.28, 2.72 (m, 12H, CH$_2$), δ 7.44, 7.93 (m, 30H, Ph). ^{13}C NMR (CDCl$_3$, ppm): δ 23.67, 26.94 (m, CH$_2$), δ 128.95–131.73 (m, Ph). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 37.34 [d, P^v, J_{P-P} = 55.8 Hz], δ 42.69 [q, (P′)^v, J_{P-P} = 55.3 Hz]. ^{77}Se NMR (CDCl$_3$, ppm): δ −352.2 [d, J_{P-Se} = 729 Hz], δ −368.1 [d, J_{P-Se} = 718 Hz]. Elemental analyses; Found (Cald for C$_{42}$H$_{42}$Se$_4$P$_4$): C, 50.58 (51.09), H, 4.11 (4.26). MS: m/z = 986.7 (M$^+$).

4.3. Synthesis of the complexes [Rh$_4$(CO)$_8$Cl$_4$(L)] (**1**), L = [P′(O)(CH$_2$CH$_2$P(O)Ph$_2$)$_3$](**a**), [P′(S)(CH$_2$CH$_2$P(S)Ph$_2$)$_3$](**b**) and [P′(Se)(CH$_2$CH$_2$P(Se)Ph$_2$)$_3$](**c**)

[Rh(CO)$_2$Cl]$_2$ (100 mg) was dissolved in dichloromethane (10 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:4) of the respective ligands were added. The reaction mixture was stirred at room temperature (25 °C) for about 30 min and the solvent was evaporated under vacuum. The yellowish to reddish brown coloured compounds so obtained were washed with pentane as well as diethyl ether and recrystallized from DCM solution. The compound was dried and stored over silica gel in a desiccator.

Analytical data for **1a**: Yield: 85%; IR (KBr, cm^{-1}): 2006 (br), 2081(sh) [ν(CO)], 1149, 1186 [ν(P–O)]. ^{1}H NMR (CD$_3$OD, ppm): δ 2.04, 2.55 (m, 12H, CH$_2$), δ 7.55, 7.85 (m, 30H, Ph), ^{13}C NMR (CD$_3$OD, ppm): δ 20.8, 22.8 (m, CH$_2$), δ 127.9–133.5 (m, Ph), δ 183.7 (br, CO). ^{31}P {^{1}H} NMR (CD$_3$OD, ppm): δ 37.2, 56.5 [m, P^V] Elemental analyses; Found (Cald for C$_{50}$H$_{42}$Cl$_4$O$_{12}$P$_4$Rh$_4$): Rh, 26.38 (27.21), C, 38.88 (39.67), H, 2.59 (2.78). MS: m/z = 1512.5 (M$^+$).

1b: Yield: 84%; IR (KBr, cm^{-1}): 2008 (br), 2079(sh) [ν(CO)], 608, 582 [ν(P–S)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.32, 2.80 (m, 12H, CH$_2$), δ 7.48, 7.84 (m, 30H, Ph), ^{13}C NMR (CDCl$_3$, ppm): δ 23.8, 27.1 (m, CH$_2$), δ 128.3–132.9 (m, Ph), δ 181.5 (br, CO). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 46.3, 52.3 [m, P^V]. Elemental analyses; Found (Cald for C$_{50}$H$_{42}$Cl$_4$O$_8$S$_4$P$_4$Rh$_4$): Rh, 26.28 (26.11), C, 36.89 (38.06), H, 2.81 (2.66). MS: m/z = 1576.2 (M$^+$).

1c: Yield: 80%; IR (KBr, cm^{-1}): 1988 (br), 2065 (sh) [ν(CO)], 522, 530 [ν(P–Se)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.26, 2.72 (m, 12H, CH$_2$), δ 7.44, 8.04 (m, 30H, Ph), ^{13}C NMR (CDCl$_3$, ppm): δ 23.9, 27.2 (m, CH$_2$), δ 129.3–133.8 (m, Ph), δ 184.5 (br, CO). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 37.4, 42.2 [m, P^V]. ^{77}Se NMR (CDCl$_3$, ppm): δ −352.8 [d, J_{P-Se} = 730 Hz], δ −402.2 [d, J_{P-Se} = 1299 Hz]. Elemental analyses; Found (Cald. for C$_{50}$H$_{42}$Cl$_4$O$_8$Se$_4$P$_4$Rh$_4$): Rh, 22.49 (23.33), C, 33.30 (34.01), H, 2.08 (2.38). MS: m/z = 1762.9 (M$^+$).

4.4. Synthesis of [Rh$_4$(CO)$_4$Y$_4$(COCH$_3$)$_4$I$_4$(P′P$_3$X$_4$)](**2**) [X = O(**a**), S(**b**) and Se(**c**); Y = Cl/I]

In 5 mL dichloromethane solution of **1a**–**1c** (50 mg), CH$_3$I (3 cm^3) was added drop by drop and the reaction mixture was stirred at r.t. (25 °C) for about 0.5–2 h. The colour of the solution changed from yellowish red to dark reddish brown and the solvent was evaporated under vacuum. The compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

2a: IR (KBr, cm^{-1}): 2071 [ν(CO)], 1726 [ν(CO)$_{acyl}$], 1159, 1176 [ν(P–O)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.09, 2.68 (m, 12H, CH$_2$), δ 2.43, 2.52 (s, 12H, CH$_3$), δ 7.45, 7.98 (m, 30H, Ph). ^{13}C NMR (CDCl$_3$, ppm): δ 22.8, 26.8 (m, CH$_2$), δ 44, 50 (CH$_3$), δ 129.9–138.5 (m, Ph), δ 180.7 (br, CO), 202.2 (br, CO$_{acyl}$). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 36.3–38.5, 54.2–56.5 [m, P^V]. Elemental analyses; Found (Cald. for C$_{54}$H$_{54}$Cl$_4$I$_4$O$_{12}$P$_4$Rh$_4$): Rh, 21.02 (19.79), C, 29.98 (31.15), H, 2.49 (2.60).

2b: IR (KBr, cm^{-1}): 2065 [ν(CO)], 1714 [ν(CO)$_{acyl}$], 607, 574 [ν(P–S)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.4, 2.9 (m, 12H, CH$_2$), δ 2.56, 2.61 (s, 12H, CH$_3$), δ 7.4, 8.05 (m, 30H, Ph), ^{13}C NMR (CDCl$_3$, ppm): δ 26, 29.4 (CH$_2$), δ 49, 53 (CH$_3$), δ 123.3–135.9 (Ph), δ 181.5 (br, CO), 203.5 (br, CO$_{acyl}$). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 47.1–48.9, 53.8–55.7 [m, P^V]. Elemental analyses; Found (Cald. for C$_{54}$H$_{54}$Cl$_4$I$_4$O$_8$S$_4$P$_4$Rh$_4$): Rh, 19.82 (19.20), C, 29.06 (30.22), H, 2.31 (2.51).

2c: IR (KBr, cm^{-1}): 2063 [ν(CO)], 1703 [ν(CO)$_{acyl}$], 520, 527 [ν(P–Se)]. ^{1}H NMR (CDCl$_3$, ppm): δ 2.3, 2.84 (m, 12H, CH$_2$), δ 2.49, 2.69 (s, 12H, CH$_3$), δ 7.3, 7.89 (m, 30H, Ph), ^{13}C NMR (CDCl$_3$, ppm): δ 25.5, 30.2 (CH$_2$), δ 46, 55 (CH$_3$), δ 124.3–134.9 (Ph), δ 182.5 (br, CO), 205.5 (br, CO$_{acyl}$). ^{31}P {^{1}H} NMR (CDCl$_3$, ppm): δ 38.4–39.3, 42.7–43.4 [m, P^V]. Elemental analyses; Found (Cald. for C$_{54}$H$_{54}$Cl$_4$I$_4$O$_8$Se$_4$P$_4$Rh$_4$): Rh, 15.62 (17.65), C, 28.03 (27.79), H, 2.85 (2.31).

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Appendix A. Supplementary material

CCDC-748443(**b**) and 737947(**c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.07.014.

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