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Rhodium(I) carbonyl complexes of mono selenium functionalized bis(diphenylphosphino)methane and bis(diphenylphosphino)amine chelating ligands and their catalytic carbonylation activity

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Abstract

The chelate complexes of the types $[\overline{Rh(CO)Cl(Ph_2PCH_2P(Se})Ph_2)]$ (**1**) and $[\overline{Rh(CO)Cl(Ph_2PN(CH_3)P(Se})Ph_2)]$ (**2**) have been synthesized and characterized by IR and NMR spectroscopy. The lower shift of the ν(P–Se) bands and downfield shift of the $^{31}P-\{^1H\}$NMR signals for both P(III) and P(V) atoms in **1** and **2** compared to the corresponding free ligands indicate chelate formation through selenium donor. **1** and **2** show terminal ν(CO) bands at 1977 and 1981 cm^{-1}, respectively, suggesting high electron density at the metal center. The molecular structure of **2** has been determined by single-crystal X-ray diffraction. The rhodium atom is at the center of a square planar geometry having the phosphorus and selenium atoms of the chelating ligand at *cis*-position, one carbonyl group *trans*-to selenium and one chlorine atom *trans*- to phosphorus atom. **1** and **2** undergo oxidative addition (OA) reaction with CH_3I to produce acyl complexes $[\overline{Rh(COCH_3)ClI(Ph_2PCH_2P(Se})Ph_2)]$ (**3**) and $[\overline{Rh(COCH_3)ClI(Ph_2PN(CH_3)P(Se})Ph_2)]$ (**4**), respectively. The kinetics of the OA reactions reveal that **1** undergoes faster reaction by about 4.5 times than **2**. The catalytic activity of **1** and **2** in carbonylation of methanol was higher than that of the well known species $[Rh(CO)_2I_2]^-$ and **2** shows higher catalytic activity compared to **1**.

Keywords: Rhodium(I) carbonyl complexes; Bis(diphenylphosphino)methane selenide; Bis(diphenylphosphino)amine selenide; Oxidative addition; Carbonylation

1. Introduction

Metal complexes of functionalized phosphines particularly potential chelating ligands like phosphine–phosphine monochalcogenides with different backbones have attracted much attention in the recent time because of their structural novelty, reactivity and catalytic activity [1–12]. Presence of two different types of donor sites makes the chemistry of these ligands more fascinating as they can coordinate to the metal center in bidentate or monodentate way [13,14]. Nature of backbone of these ligands plays an important role on the stability and reactivity of the complexes. The most promising feature of these ligands is that they can confer stability to the metal complexes by chelate formation and may create vacant coordination sites at the metal center by the cleavage of relatively weaker metal–chalcogen bond, which is a prerequisite for OA reactions. Thus, these types of hemilabile ligands have great impact on OA reactions [15–18], which is a key step in many catalytic reactions like carbonylation of methanol. Since the first introduction of the commercial species, i.e., $[Rh(CO)_2I_2]^-$ as an efficient catalyst for carbonylation of

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methanol to acetic acid [15,16,19–22], considerable efforts have been devoted to improve the catalyst by incorporating different ligands [15–18,23–27] into its coordination sphere. These prompted us to synthesize the Rh(I) carbonyl complexes containing P–Se donors ligands of the type $Ph_2PCH_2P(Se)Ph_2$ and $Ph_2PN(CH_3)P(Se)Ph_2$ which are expected to coordinate to the metal center through P and Se coordination sites with enhanced electron density on the metal center that might lower the activation energy for OA reactions. Moreover, chelate formation through least strained five-membered ring may increase the stability of the complexes. As a part of our continuing work [11,17c,25–30], we report here the synthesis and characterization of electron rich $[\overline{\mathrm{Rh(CO)Cl(Ph_2PCH_2P(Se}})\mathrm{Ph_2)}]$ (**1**) and $[\overline{\mathrm{Rh(CO)Cl(Ph_2PN(CH_3)P(Se}})\mathrm{Ph_2)}]$ (**2**) complexes including an X-ray study of **2**; their OA reactions with CH_3I; kinetic behavior and catalytic carbonylation of methanol.

2. Results and discussion

2.1. Synthesis and characterization

The reaction of the chloro-bridged dimer $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 with 2 molar equivalents of each of the ligands $Ph_2PCH_2P(Se)Ph_2$ and $Ph_2PN(CH_3)P(Se)Ph_2$ proceeds rapidly with the evolution of CO gas to yield the yellow chelated monocarbonyl complexes $[\overline{\mathrm{Rh(CO)Cl(Ph_2PCH_2P(Se}})\mathrm{Ph_2)}]$ (**1**) and $[\overline{\mathrm{Rh(CO)Cl(Ph_2PN(CH_3)P(Se}})\mathrm{Ph_2)}]$ (**2**), respectively. **1** and **2** show single terminal ν(CO) bands at 1977 and 1981 cm^{-1}, respectively, which is in the characteristic region for such rhodium(I) carbonyl complexes. The ν(CO) values of the complexes **1** and **2** are lower relative to the analogous rhodium phosphine complexes like $[\overline{\mathrm{Rh(CO)Cl(Ph_2PCH_2P(O}})\mathrm{Ph_2)}]$, $[\overline{\mathrm{Rh(CO)Cl(Ph_2PCH_2P(S}})\mathrm{Ph_2)}]$, etc. (Table 1) [14–17,28,31–34] indicating the metal center is rich in electron density and hence expected to show high nucleophilicity. Recently, Cole-Hamilton et al. [24] reported a few electron rich complexes of the type $[Rh(CO)X(PEt_3)_2]$ (X = Cl, Br, I) having ν(CO) ca. 1960 cm^{-1}, which showed high catalytic activity in the carbonylation of methanol, and postulated that electron rich centers play a significant role in improving the rate of the reaction. The ^{31}P–$\{^1H\}$NMR spectrum of **1** showed a doublet of doublet centered at $\delta = 51.1$ ppm and a doublet at $\delta = 35.2$ ppm for the tertiary and pentavalent P-atoms, respectively. These two resonances show a downfield shift compared to the free ligand $\{\delta = -26.4$ and $\delta = 31.3$ (d, $J_{PP} = 85$, $J_{PSe} = 725$ Hz) ppm$\}$ value which indicates chelate formation through metal phosphorus and selenium bonding. The complex **2** exhibits a downfield resonance at $\delta = 119.14$ ppm for the tertiary phosphorus and upfield resonance at $\delta = 66.42$ ppm for the pentavalent phosphorus atoms compared to the free ligand $\{\delta = 55.73$ and 76.08 (d, $J_{PP} = 96$, $J_{PSe} = 760$ Hz) ppm$\}$ while the $J_{PP} = 72$, $J_{PSe} = 481$ Hz values are lower than their corresponding free values similar to complex **1** indicating chelate formation. The ^1H NMR spectrum of **1** and **2** shows characteristic resonances $\delta = 4.3$ ppm ($-CH_2-$) and $\delta = 2.5$ ppm (CH_3-), respectively, along with their Ph protons in the range of 7.2–7.7 ppm. The ν(P–Se) bands of **1** and **2** occur at 513 and 543 cm^{-1}, respectively, which are considerably lower than the corresponding free ligands and thus substantiate further formation of chelate through Rh–Se bonds [4].

Table 1
Comparison of the ν(CO) cm^{-1} of the complexes [Rh(CO)Cl(P∩X)] for different hemilabile phosphine ligands

[Rh(CO)Cl(P∩X)] (X = O, S, N, Se)		
P∩X	ν(CO)[a]	Ref.
$Ph_2P(CH_2)_2SMe$	1990	[31]
$Ph_2P(CH_2)_2SEt$	1985	[28]
$Ph_2P(CH_2)_2SPh$	2000[b]	[14]
$2\text{-}Ph_2PC_6H_4SMe$	1998[c]	[15a]
$Ph_2P(CH_2)_2OEt$	1990[b]	[32]
$Ph_2PCH_2P(S)Ph_2$	1992[b]	[16a]
$Ph_2PCH_2P(O)Ph_2$	1985	[17]
$Ph_2P(CH_2)_2P(O)Ph_2$	1995	[17]
$Ph_2PCH_2P(O)(OPh)_2$	1990[b]	[32]
$Ph_2PCH_2P(O)(O\textit{i}\text{-}Pr)_2$	1990[b]	[32]
$2\text{-}Ph_2PC_6H_4N(Me)_2$	2005	[33]
$Ph_2P(CH_2)_2C_5H_4N$	1990	[34]
$Ph_2PCH_2P(Se)Ph_2$	1977	This work
$Ph_2PN(CH_3)P(Se)Ph_2$	1981	This work

[a] In KBr.
[b] In CH_2Cl_2.
[c] Medium not mentioned.

2.2. Single-crystal X-ray structure

Suitable crystals of **2** were grown by slow diffusion of diethyl ether into a solution of CH_2Cl_2 of the complex, however, attempts to develop suitable crystal from **1** were unsuccessful. The crystal structure (Fig. 1) was determined by single-crystal X-ray diffraction studies and the crystal data are given in Tables 2 and 3. The rhodium atom lies at the center of an approximately square planar environment

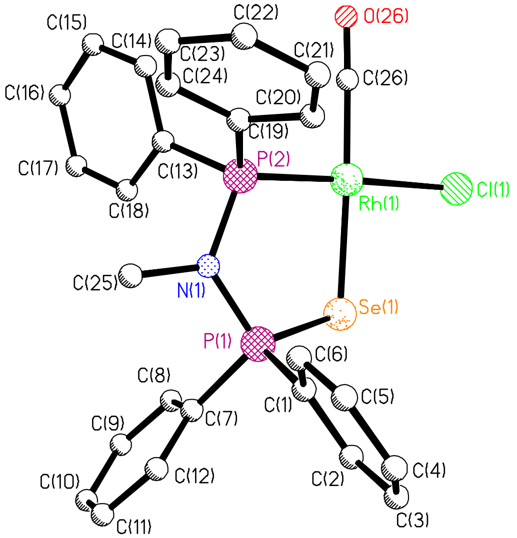


Fig. 1. Molecular structure of **2** showing atomic labeling.

Table 2
Crystal data and structure refinement details for **2**

Empirical formula	$C_{26}H_{23}ClNOP_2RhSe$
Formula weight	644.71
Temperature (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	17.5618(19)
b (Å)	15.8421(17)
c (Å)	18.906(2)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5260.0(10)
Z	8
Crystal size (mm^3)	.1 × .1 × .1
Reflections collected	33 751
Independent reflections [R_{int}]	4734 [0.1302]
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0440$, $wR_2 = 0.0897$

Table 3
Selected bond lengths (Å) and angles (°) for **2**

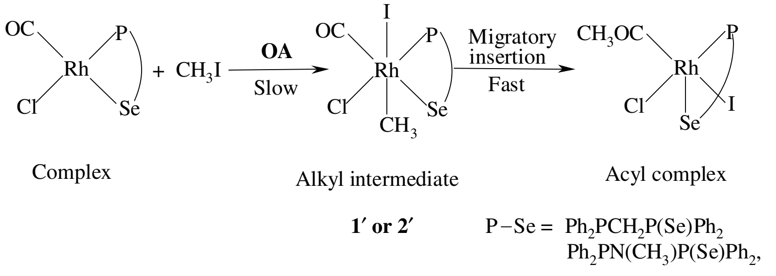
Rh(1)–C(26)	1.810(5)	Rh(1)–P(2)	2.201(12)
Rh(1)–Se(1)	2.464(6)	Rh(1)–Cl(1)	2.381(11)
C(26)–O(26)	1.158(6)	Se(1)–P(1)	2.153(13)
P(1)–N(1)	1.654(4)	P(1)–C(1)	1.784(5)
P(1)–C(7)	1.789(5)	N(1)–C(25)	1.495(5)
N(1)–P(2)	1.717(4)	P(2)–C(13)	1.807(5)
P(2)–C(19)	1.818(5)		
C(26)–Rh(1)–P(2)	90.55(15)	C(26)–Rh(1)–Cl(1)	91.83(15)
P(2)–Rh(1)–Cl(1)	177.14(5)	C(26)–Rh(1)–Se(1)	170.14(15)
P(2)–Rh(1)–Se(1)	92.44(3)	Cl(1)–Rh(1)–Se(1)	85.46(3)
O(26)–C(26)–Rh(1)	175.5(4)	P(1)–Se(1)–Rh(1)	98.64(4)
N(1)–P(1)–C(1)	110.7(2)	N(1)–P(1)–C(7)	106.7(2)
C(1)–P(1)–C(7)	107.2(2)	N(1)–P(1)–Se(1)	109.71(14)
C(25)–N(1)–P(1)	118.4(3)	C(25)–N(1)–P(2)	119.5(3)
P(1)–N(1)–P(2)	122.1(2)	N(1)–P(2)–C(13)	102.1(2)
N(1)–P(2)–Rh(1)	112.89(13)	C(13)–P(2)–Rh(1)	114.75(16)
C(19)–P(2)–Rh(1)	116.52(15)	C(13)–P(2)–C(19)	106.2(2)

formed by the P, Se, C (of CO) and Cl atom. The ligand forms a chelate (bite angle P–Rh–Se 92.44°) through phosphorous and selenium donors and maintains a five-membered less strained ring structure. The longer bond length in Rh–Se (2.46 Å) than in Rh–P (2.20 Å) may indicate a weaker interaction in the former and is likely to cleave easily during catalytic reaction.

2.3. OA reaction and their kinetics

The OA reactions of **1** and **2** with CH_3I yield complexes $[Rh(COCH_3)ClI(Ph_2PCH_2P(Se)Ph_2)]$ (**3**) and $[Rh(COCH_3)ClI(Ph_2PN(CH_3)P(Se)Ph_2)]$ (**4**), respectively, through their corresponding unisolable rhodium(III) alkyl intermediates (Scheme 1). The $^{31}P\text{–}\{^1H\}$NMR spectrum of **3** shows a doublet of doublet centered at $\delta = 50.2$ and a doublet at $\delta = 33.3$ ppm. Similarly, **4** shows a doublet of doublet centered at $\delta = 117.0$ ppm along with a doublet at $\delta = 68.4$ ppm, these reveal that, like in **1** and **2**, in the oxidized products the ligands also remain in metal–Se chelating mode. The ^1H NMR spectra of **3** and **4** show a new singlet at $\delta = 2.18$ and $\delta = 2.81$ ppm, respectively, along with the other characteristic resonances for the ligands, which are in consistent with the formation of the acyl group ($-COCH_3$).

Kinetic studies for the OA reaction of CH_3I with **1** and **2** were carried out in order to understand the effect of ligand backbone. Fig. 2a shows a plot of absorbance against time for the disappearance of the terminal ν(CO) band of **1** (1977 cm^{-1}) and formation of a new terminal ν(CO) band at higher energy 2063 cm^{-1} which is a characteristic band [35,36] for Rh(III) alkyl intermediate ($[Rh(CO)(CH_3)ICl(Ph_2PCH_2P(Se)Ph_2)]$ (**1′**)) (Scheme 1) along with the formation of acyl ν(CO) band at around 1700 cm^{-1}. The decay of the terminal ν(CO) band of **1** indicates that the course of the reaction proceeds in an exponential manner while the initial formation and then decay of the terminal ν(CO) band of **1′** indicates that at a reaction time of about 5 min the concentration of the intermediate reaches a maximum after which it follows a similar kinetics to that of **1**. Similar type of plot (Fig. 2b) was also obtained for **2** in which the decay of the terminal ν(CO) band at 1981 cm^{-1} accompanies with the growth and decay of another new terminal ν(CO) band at around 2060 cm^{-1} which is due to formation of a hexacoordinated Rh(III) alkyl intermediate ($[Rh(CO)(CH_3)ICl(Ph_2PN(CH_3)P(Se)Ph_2)]$ (**2′**)). From Fig. 2b, it is clear that the concentration of the intermediate increases up to a period of about 15 min and then starts decreasing in a manner similar to that of the decaying curve of **2**. The rate of decay of the terminal ν(CO) band of **2** was slower than **1** and the course of the reaction proceeds exponentially. The growth of the acyl ν(CO)



Scheme 1. OA and migratory insertion reactions of **1** and **2** with CH_3I.

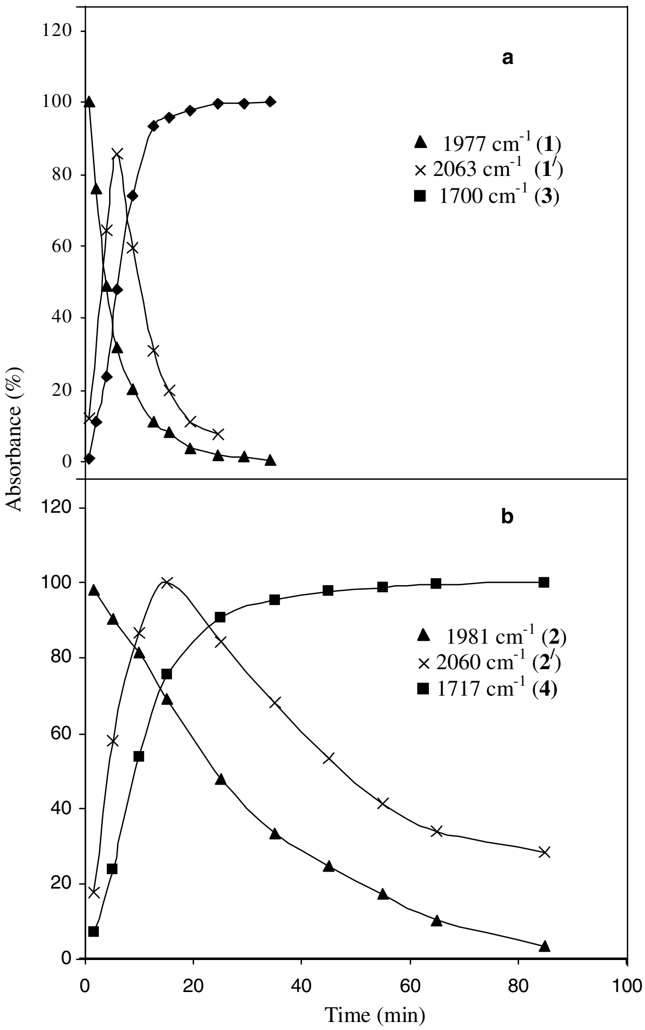


Fig. 2. Absorbance of ν(CO) against time for different carbonyl species: decay (▲) of terminal ν(CO) band (a) for the complexes **1** and (b) for **2**; variation (×) of terminal ν(CO) band (a) for intermediate (**1′**) and (b) for (**2′**); and the growth (■) of the acyl ν(CO) band (a) for the complex **3** and (b) for **4** during the course of OA reactions with CH_3I.

bands at 1700 and 1717 cm^{-1} for **3** and **4** were also found to follow a similar type of kinetics as that of decay of terminal ν(CO) bands for **1** and **2**. Kinetics measurements were done by applying pseudo-first-order conditions, i.e., at high concentration of CH_3I. A linear fit of pseudo-first-order was observed for the entire course of the OA reactions of CH_3I with **1** and **2** 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. From the slope of the plot, the rate constants for both the reactions were calculated and found to be 24.67×10^{-4} and 5.47×10^{-4} s^{-1} for **1** and **2**, respectively. The values of the rate constants clearly indicate that the OA reaction of **1** is almost 4.5 times faster than that of **2**. This can be substantiated by higher electron density, i.e., higher nucleophilicity of **1** over **2** as indicated from the ν(CO) stretching values of the complexes (Table 1).

Table 4
Results of carbonylation of methanol

Catalyst precursor	Acetic acid[a] (%)	Methyl acetate[a] (%)	Total conversion (%)	TON[b]
$[Rh(CO)_2I_2]^{-1c}$	3.34	30.74	34.08	648
1	9.6	29.2	38.8	870
1[d]	9.1	27.8	36.9	827
2	7.2	35.2	42.4	901
2[d]	6.8	33.8	40.6	863

[a] Yields 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 the catalytic condition.

[d] Recycled.

2.4. Catalytic activity of 1 and 2 for carbonylation of methanol

The results of batch carbonylation of methanol to acetic acid and its ester in the presence of **1**, **2**, and $[Rh(CO)_2Cl]_2$ as catalyst precursors are shown in Table 4. GC analyses of the products reveal that **2** exhibits a maximum conversion of 42.4% with the highest turn over number (TON) 901 compared to the other complexes. Under the same experimental condition, the well-known catalyst precursor $[Rh(CO)_2I_2]^-$ generated in situ [37,38] from $[Rh(CO)_2Cl]_2$ shows 34.08% conversion with a TON 648 while **1** exhibits 38.8% conversion with TON 870. Data from Table 4, in general, reveal an order of efficiency of the catalytic activity of the precursors as **2** > **1** > $[Rh(CO)_2I_2]^-$. It is well known that OA step plays a key role in enhancing the catalytic efficacy of such reaction. As expected from higher OA reaction rate of **1** over **2**, the former should act more efficiently over the latter in the carbonylation reaction. But in practice, the reverse situation was observed. To explain this, one must consider the fact that higher electron donating ligands make the metal center more nucleophilic and may lead to the formation of stronger Rh–C (acyl) bond [36b] which may cause retardation of the rate of the reductive elimination reaction required for completion of the catalytic cycle. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reactions, the ν(CO) bands compared well with the ν(CO) values of a solution containing a mixture of the parent rhodium(I) carbonyl complexes and the rhodium(III) acyl complexes. Thus, it may be inferred that the ligands remained bound to the metal centre during the entire course of the catalytic reactions. It is worth to mention that the catalysts showed almost the same efficacy for their recycled experiments (Table 4), indicating adequate stability of the catalysts.

3. Experimental

3.1. General procedure

The reagents were procured from M/s Aldrich Chemicals, USA and M/s Lancaster, UK. All solvents were distilled under N_2 prior to use. All operations were carried out under oxygen-free nitrogen atmosphere using standard Schlenk technique. Microanalyses were performed by St. Andrews University service (Chemistry Department). FT-IR spectra (4000–400 cm^{-1}) were recorded using a Perkin–Elmer 2000 spectrometer in $CHCl_3$ and as KBr discs. The ^1H NMR (270 MHz), ^{13}C (67.94 MHz) and $^{31}P\{^1H\}$NMR (109.36 MHz) spectra were recorded in $CDCl_3$ solution on a Jeol Delta 270 MHz Spectrometer. The chemical shifts for ^1H and ^{13}C NMR are quoted relative to $SiMe_4$ as internal standard and for ^{31}P relative to 85% H_3PO_4 as external standard. The carbonylation reactions of alcohol were carried out in a 100 cm^3 teflon coated high pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). The ligands $(C_6H_5)_2PCH_2P(Se)(C_6H_5)_2$ and $(C_6H_5)_2PN(CH_3)P(Se)(C_6H_5)_2$ were prepared by the literature methods [39,40]. The starting complex $[Rh(CO)_2Cl]_2$ was prepared by known method [41].

3.2. Synthesis of $[\overline{Rh(CO)Cl(Ph_2PCH_2P(Se})Ph_2]$ (**1**)

$[Rh(CO)_2Cl]_2$ (0.100 g, 0.257 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and was added dropwise to the solution of ligand ($Ph_2PCH_2P(Se)Ph_2$) (0.238 g, 0.514 mmol in 10 cm^3 CH_2Cl_2) with constant stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about 1 h and the solvent was evaporated under reduced pressure in a rotavapor to obtain a yellow solid. The compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield: 0.31 g. IR data (KBr) $\nu(CO) = 1977\ cm^{-1}$; $\nu(P–Se) = 513\ cm^{-1}$. ^1H NMR: $\delta = 4.32$ (t, $J_{PH} = 10$ Hz, 2H, –CH_2–), 7.19–7.43 (m, 10 H, Ph), 7.60–7.69 (m, 10 H, Ph) ppm. ^{31}P NMR: $\delta = 51.1$(dd, $J_{PP} = 56$ Hz, $J_{RhP} = 164$ Hz), 35.2 (d, $J_{PP} = 56$ Hz, $J_{PSe} = 561$ Hz) ppm. ^{13}C NMR: $\delta = 44.84$ (dd, $^1J_{CP} = 17$, 50 Hz), 133.15 ($^1J_{CP} = 12$ Hz), 132.97 ($^1J_{CP} = 3$ Hz), 132.25 ($^1J_{CP} = 10$ Hz), 130.98 ($^1J_{CP} = 2$ Hz), 129.15 ($^1J_{CP} = 12$ Hz), 128.56 ($^1J_{CP} = 10$ Hz), 126.35 ($^1J_{CP} = 5$), 125.28 ($^1J_{CP} = 5$), 183.06 (s, CO) ppm. Free ligand: IR: $\nu(P–Se) = 527\ cm^{-1}$; ^{31}P NMR: $\delta = -26.4$d, 31.3d ($J_{PSe} = 725$ Hz, $J_{PP} =$ 85Hz) ppm, ^1H NMR: $\delta = 3.49$ (d, 2H, $^2J_{HP}(Se) =$ 13 Hz, –CH_2–) ppm. ^{13}C NMR: $\delta = 34.98$ (dd, $^1J_{CP(Se)} =$ 47.4, $^1J_{CP} = 31$ Hz, –CH_2–), 128.42–133.21 (m, Ph) ppm. $C_{26}H_{22}ClOP_2RhSe$: found C 49.12, H 3.42; calc. C 49.60, H 3.49%.

3.3. Synthesis of $[\overline{Rh(CO)Cl(Ph_2PN(CH_3)P(Se})Ph_2]$ (**2**)

$[Rh(CO)_2Cl]_2$ (0.154 g, 0.396 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and was added dropwise to the solution of ligand ($Ph_2PN(CH_3)P(Se)Ph_2$) (0.380 g, 0.792 mmol in 15 cm^3 CH_2Cl_2) with constant stirring under nitrogen atmosphere. Reaction took place immediately with effervescence and color changes from pale yellow to deep red. The reaction mixture was stirred at room temperature for about 1 h and the solvent was evaporated under reduced pressure in a rotavapor to obtain a light brown solid. The compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.49 g. IR data (KBr) $\nu(CO) = 1981\ cm^{-1}$, $\nu(P–Se) = 543\ cm^{-1}$. ^1H NMR: $\delta = 2.48$(d, $J_{HH} = 6$, 10 Hz, 3H, –CH_3), 7.24–7.60 (m, 20H, Ph) ppm. ^{31}P NMR $\delta = 119.14$ (dd, $J_{PP} = 72$, $J_{RhP} = 169.50$ Hz), 66.42 (d, $J_{PP} = 72.17$, $J_{PSe} =$ 481.18 Hz) ppm. ^{13}C NMR: $\delta = 35.63$ (s, –CH_3), 128.60–134.08 (m, Ph), 181.42 (s, CO) ppm. Free ligand: IR: $\nu(P–Se) = 551\ cm^{-1}$. ^{31}P NMR: $\delta = 55.73$ (d), 76.08 (d, $J_{PSe} =$ 760.03, $J_{PP} = 96.23$ Hz) ppm. ^1H NMR: $\delta = 2.65$ (d, 3H, –CH_3–), 7.41–7.90 (m, Ph) ppm. ^{13}C NMR: δ(ppm) 33.02 (t, –CH_3), 127.87–133.90 (m, Ph) ppm. $C_{26}H_{23}ClNOP_2RhSe$: found C 48.23, H, 3.50, N 2.07; calc. C 48.45, H 3.57, N 2.17%.

3.4. Synthesis of $[\overline{Rh(CH_3CO)ClI(Ph_2PCH_2P(Se})Ph_2]$ (**3**)

The complex **1** (0.115 g, 0.182 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and to this CH_3I (6 cm^3) was added. The reaction mixture was then stirred at room temperature under nitrogen atmosphere for about 3 h and the solvent was evaporated under vacuum. Yellow-reddish colored compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.12 g. IR data (KBr): $\nu(CO)_{acyl} = 1700\ cm^{-1}$. ^1H NMR: $\delta = 4.42$ (t, 2H, –CH_2–), 7.26–7.81 (m, 20H, Ph), 2.18 (s, 3H, –CH_3) ppm. ^{31}P NMR: $\delta = 50.2$ (dd, $J_{PP} = 43$ Hz, $J_{RhP} =$ 145 Hz), 33.3 (d, $J_{PP} = 43$ Hz) ppm. $C_{27}H_{25}ClIOP_2RhSe$: calc. C 42.03, H 3.24; found C 41.88, H 3.20%.

3.5. Synthesis of $[\overline{Rh(CH_3CO)ClI(Ph_2PN(CH_3)P(Se})Ph_2]$ (**4**)

The complex **2** (0.106 g, 0.164 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and to this CH_3I (6 cm^3) was added. The reaction mixture was then stirred at room temperature under nitrogen atmosphere for about 5 h and the solvent was evaporated under vacuum. Yellow-reddish colored compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.11 g. IR (KBr): $\nu(CO)_{acyl} = 1717\ cm^{-1}$. ^1H NMR: $\delta = 2.52$ (d, 3H, –CH_3), 7.11–7.87 (m, 20H, Ph), 2.81 (s, 3H, –CO-CH_3) ppm. ^{31}P NMR: $\delta = 117.0$ (dd, $J_{PP} = 41$, $J_{RhP} =$ 169 Hz), 68.4 (d, $J_{PP} = 41$ Hz) ppm. $C_{27}H_{26}ClINOP_2RhSe$: calc. C 41.23, H 3.31, N 1.78; found C 41.01, H 3.30, N 1.73%.

3.6. Reaction kinetics

The OA reactions of **1** and **2** with CH_3I were monitored by using IR spectroscopy in a solution cell (1.0 mm path length). The complexes **1** and **2** (10 mg) were added to neat CH_3I (1 cm^3) at room temperature. An aliquot (0.5 ml) of the reaction mixture was transferred by syringe into the IR cell. Then the kinetic measurement was made by monitoring the simultaneous decay of the terminal ν(CO) of **1** and**2** in the range 1976–1984 cm^{-1}, growth of the acyl ν(CO) of **3** and **4** in the range 1700–1720 cm^{-1} and also the terminal ν(CO) of the intermediate Rh(III)-complexes. A series of spectra were taken at regular intervals. The OA reactions of CH_3I with **1** and **2** were found to be concentration dependent on the complexes as well as on CH_3I. Therefore, in order to provide a pseudo-first-order condition, the reaction was carried out in a large excess of CH_3I.

*3.7. Carbonylation of methanol using **1** and **2** 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 **1** or **2** (0.054 mmol) were taken and then pressurized with CO gas (18 bar at room temperature, 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) with variation of reaction time. The products were collected and analyzed by GC. The recycle experiments were done by maintaining the same experimental conditions as described above with the dark brown solid mass as catalyst obtained by evaporating the carbonylation reaction mixture under reduced pressure.

3.8. X-ray Crystallography

The X-ray crystallography data were collected at room temperature using Mo Kα radiation with a SMART system and the structure refinements were done by full-matrix least-square on F^2 using SHELXTL 97 computer program [42]. Supplementary data are available from the CCDC, 12 Union Road, Cambrigde, CB2 1EZ, UK on request. CCDC deposit number 258976. See http://www.ccdc.cam.ac.uk.

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