

Rhodium(I) carbonyl complexes of triphenylphosphine chalcogenides and their catalytic activity

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Abstract

Rhodium(I) carbonyl complexes $[\text{Rh}(\text{CO})_2\text{CIL}]$ where $L = \text{Ph}_3\text{PO}$, Ph_3PS and Ph_3PSe , were synthesized and characterized by elemental analysis, i.r. and by ^1H -, ^{13}C - and ^{31}P -n.m.r. spectroscopy. The $\nu(\text{CO})$ band frequencies in the complexes follow the order: $\text{Ph}_3\text{PO} > \text{Ph}_3\text{PS} > \text{Ph}_3\text{PSe}$, in keeping with the hard/soft nature of the interactions. The complexes undergo oxidative additions with electrophiles such as MeI , PhCH_2Cl and I_2 to give, e.g. $[\text{Rh}(\text{CO})(\text{COMe})\text{CIIL}]$ which react with PPh_3 to give *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$. The catalytic activity of the $[\text{Rh}(\text{CO})_2\text{CIL}]$ complexes in carbonylation of MeOH is higher than that of the well-known $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species.

Introduction

Rhodium(I) carbonyl complexes containing bidentate chelating ligands such as diphenylphosphinomethane-oxide [1] and diphenylphosphinomethanesulfide [2] have aroused considerable interest because of their reactivity and catalytic activity [1–3]. It is therefore of interest to study rhodium(I) carbonyl complexes containing monodentate phosphine chalcogenides since such complexes are uncommon. A literature survey reveals that only one, $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Cy}_3\text{PO})]$ where $\text{Cy} = \text{C}_6\text{H}_{11}$, has so far been reported [4]. In the prevailing scenario for the carbonylation of methanol to generate ethanoic acid, the $[\text{RhI}_2(\text{CO})_2]^-$ species is still the preferred commercial catalyst [5]. Research activities continue to modify the catalyst for enhancement of its activity by incorporating different ligands in the metal complex [1, 2]. In this paper we describe the synthesis of $[\text{Rh}(\text{CO})_2\text{CIL}]$ complexes and their oxidative additions with different electrophiles. The catalytic activity of these complexes in the carbonylation of MeOH has been evaluated.

Experimental

All the solvents used were distilled under N_2 prior to use. Elemental analyses were made on a Perkin-Elmer 2400 elemental analyzer. I.r. spectra (4000 – 400) cm^{-1} were recorded using a Specord 75 spectrophotometer in KBr discs. N.m.r. data were recorded on a Bruker DPX 300 MHz spectrometer and the ^1H -, ^{13}C - and ^{31}P -chemical shifts are quoted relative to SiMe_4 , CDCl_3 and 85% H_3PO_4 respectively in CDCl_3 . The carbonylation

of MeOH was carried out in a 150 cm^3 teflon coated pressure reactor fitted with a pressure gauge (M/S Berghof Type-Heizung 75–150, Germany). $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from M/S Arrora Matthey Ltd., Calcutta. Analytically pure PPh_3 , S powder, Se, MeI , I_2 and PhCH_2Cl were purchased and used without further purification. The ligands ($L = \text{Ph}_3\text{PO}$, Ph_3PS and Ph_3PSe) were prepared from PPh_3 by literature methods [6–8]. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared by passing CO gas over $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ powder at 100°C [9].

Synthesis of complexes

$[\text{Rh}(\text{CO})_2\text{CIL}]$, $L = \text{Ph}_3\text{PO}$, Ph_3PS and Ph_3PSe
 $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (100 mg) was dissolved in CHCl_3 (40 cm^3) and, to this solution, a stoichiometric quantity ($\text{Rh}:\text{L} = 1:2$) of the respective ligand was added. The reaction mixture was then stirred for 10 min at room temperature and the solvent was evaporated under vacuum. The solid compound thus obtained was washed with petroleum ether and stored over silica gel in a desiccator.

$[\text{Rh}(\text{CO})(\text{COMe})\text{CIIL}]$, $L = \text{Ph}_3\text{PO}$, Ph_3PS
and Ph_3PSe

$[\text{Rh}(\text{CO})_2\text{CIL}]$ (100 mg) was dissolved in CHCl_3 (40 cm^3) and MeI (6 cm^3) was added. The reaction mixture was then stirred for 6 h and the solid product was separated and purified by following the above procedure.

$[\text{Rh}(\text{CO})(\text{COCH}_2\text{Ph})\text{Cl}_2\text{L}]$, $L = \text{Ph}_3\text{PO}$, Ph_3PS
and Ph_3PSe

$[\text{Rh}(\text{CO})_2\text{CIL}]$ (100 mg) was dissolved in CHCl_3 (40 cm^3). To these solutions PhCH_2Cl (2 cm^3) was added

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and the reaction mixture was then stirred for 6 h. The solid compound was separated and purified as above.

[*Rh(CO)ClI₂L*], *L* = *Ph₃PO*, *Ph₃PS* and *Ph₃PSe*
[*Rh(CO)₂CIL*] (100 mg) was dissolved in *CHCl₃* (40 cm³) and to these solutions *I₂* (50 mg) was added and the reaction mixture was then stirred at room temperature for 12 h. The solid compound was separated and purified as above.

Carbonylation of MeOH using [*Rh(CO)₂CIL*] as catalyst

MeOH (0.708 mol, 3.16 cm³), MeI (0.006 mol, 1 cm³), H₂O (0.055 mol, 1 cm³), [*Rh(CO)₂Cl*]₂ (0.025 mmol, 10 mg), ligand (0.1 mmol) were placed in the reactor and then pressurized with CO gas up to 6 bar (0.036 mol) at *ca.* 30 °C. The reactions were carried out at 130 °C (15 bar) and at 160 °C (20 bar) for 30 and 90 min respectively. The reaction products were collected and analyzed by GC.

Result and discussion

Synthesis and characterization of [*Rh(CO)₂CIL*]

The [*Rh(CO)₂Cl*]₂ dimer is split by a stoichiometric quantity of triphenylphosphine chalcogenide (*L*) to give *cis*-dicarbonyl compounds of the type [*Rh(CO)₂CIL*]. The i.r. spectra of the complexes (Table 1) show two equally intense $\nu(\text{CO})$ bands in the 1980–2080 cm⁻¹ range, attributable to the *cis* disposition of the two carbonyl groups. The positions of the $\nu(\text{CO})$ bands follow the order: *Ph₃PO* > *Ph₃PS* > *Ph₃PSe*, which may be explained in terms of ‘hard-soft’ interactions between the metal and the chalcogen donor. In [*Rh(CO)₂Cl(Ph₃PS)*] and [*Rh(CO)₂Cl(Ph₃PSe)*] complexes, the sulfur and selenium donors are ‘soft’ and interact strongly with ‘soft’ rhodium(I), in contrast to the ‘hard’ oxygen in the [*Rh(CO)₂Cl(Ph₃PO)*] complex. Such interactions increases the electron density on the

central metal atom which may donate more d_{π} -electrons to the antibonding π^* -orbital of the CO and consequently lead to a decrease in the C–O bond order, which in turn reduces the $\nu(\text{CO})$ frequency. In [*Rh(CO)₂CIL*], the $\nu(\text{PO})$, $\nu(\text{PS})$ and $\nu(\text{PSe})$ bands occur at 1160, 593 and 538 cm⁻¹ which are *ca.* 40, 40 and 20 cm⁻¹ lower than their corresponding free ligand stretching values [10, 11] and agreed with data on the reported complexes [12, 13]. The ¹H-n.m.r. spectra of the complexes show a set of multiplets in the δ 6.8–7.8 p.p.m. range assigned to the phenyl groups of triphenylphosphine chalcogenides. No significant change is observed between coordinated and free ligand proton environment as the protons are remote from the coordinating atom. The ³¹P-n.m.r. values in the [*Rh(CO)₂CIL*] (*L* = *Ph₃PO*, *Ph₃PS* and *Ph₃PSe*) complexes (Table 2) are at δ 37.38, 46.71 and 32.21 p.p.m. respectively, while their corresponding free ligand values occur at δ 30.37, 44.54 and 36.53 p.p.m. Thus the magnitude of shift is small (2.5–7.0 p.p.m.) as is to be expected for phosphorus which is remote from the coordinating chalcogen donors in the ligands. The shifts are in agreement with reported data [14]. In [*Rh(CO)₂Cl(Ph₃PS)*] and [*Rh(CO)₂Cl(Ph₃PSe)*] complexes a downfield shift, and in [*Rh(CO)₂Cl(Ph₃PO)*] complex an upfield shift, are observed. The ¹³C-n.m.r. spectra of the carbonyl carbon resonance in [*Rh(CO)₂Cl*]₂ occurs at 178 p.p.m. which represents a downfield shift of *ca.* 3–6 p.p.m. (Table 2) on complexation with chalcogenide ligands. This shift is due to the higher electron density donation towards carbonyl carbon from the electron rich central metal atom in the complex.

Reactivity of the [*Rh(CO)₂CIL*] complexes

The chalcogenides in the rhodium(I) complexes may be easily replaced by other stronger donor ligands because the rhodium–chalcogenide bonds are weak. The [*Rh(CO)₂CIL*] complex reacts with *PPh₃* to yield [*Rh(CO)Cl(PPh₃)₂*], confirmed by its $\nu(\text{CO})$ frequency

Table 1. Analytical data and i.r. bands of rhodium carbonyl complexes

Complexes	Colour	Found (Calcd.) (%)		I.r. spectra (cm ⁻¹) $\nu(\text{CO})$	$\nu(\text{PX}^*)$ (X = O, S, Se)
		C	H		
[<i>Rh(CO)₂Cl(Ph₃PO)</i>]	deep brown	51.3 (50.8)	3.1 (3.2)	2080, 2005	1160
[<i>Rh(CO)₂Cl(Ph₃PS)</i>]	red-brown	51.5 (49.2)	3.7 (3.1)	2068, 2001	593
[<i>Rh(CO)₂Cl(Ph₃PSe)</i>]	dark red	44.5 (44.9)	3.3 (2.8)	2058, 1985	538
[<i>Rh(CO)(COMe)ClI(Ph₃PO)</i>]	red-brown	40.2 (41.0)	2.6 (2.9)	2067, 1719	1175
[<i>Rh(CO)(COMe)ClI(Ph₃PS)</i>]	dark red	39.0 (40.0)	2.8 (2.9)	2069, 1721	581
[<i>Rh(CO)(COMe)ClI(Ph₃PSe)</i>]	deep red	36.9 (37.2)	2.7 (2.7)	2065, 1720	541
[<i>Rh(CO)(COCH₂Ph)Cl₂(Ph₃PO)</i>]	red-brown	54.0 (54.2)	3.1 (3.7)	2075, 1840	1150
[<i>Rh(CO)(COCH₂Ph)Cl₂(Ph₃PS)</i>]	red-brown	52.9 (52.8)	3.1 (3.6)	2085, 1720	594
[<i>Rh(CO)(COCH₂Ph)Cl₂(Ph₃PSe)</i>]	red-brown	50.9 (49.0)	3.1 (3.3)	2080, 1725	542
[<i>Rh(CO)ClI₂(Ph₃PO)</i>]	dark brown	32.6 (32.7)	2.4 (2.1)	2075	1174
[<i>Rh(CO)ClI₂(Ph₃PS)</i>]	dark brown	30.0 (31.9)	1.9 (2.1)	2082	587
[<i>Rh(CO)ClI₂(Ph₃PSe)</i>]	dark brown	29.1 (30.0)	1.7 (2.0)	2072	537

* Free *Ph₃PO* – 1200 cm⁻¹; *Ph₃PS* – 633 cm⁻¹ and *Ph₃PSe* – 558 cm⁻¹.

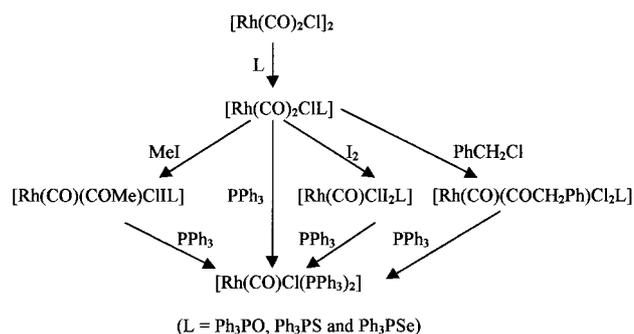
Table 2. ^1H -, ^{13}C - and ^{31}P -n.m.r. data of selected rhodium complexes

Complexes	^1H -n.m.r.		^{31}P -n.m.r.*	^{13}C -n.m.r.		
	C_6H_5	CH_3		CO	C_6H_5	CH_3
$[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PO})]$	7.49–4.74m	–	37.38	181	132.43–128.63m	–
$[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PS})]$	7.84–7.50m	–	46.71	180	133.15–129.15m	–
$[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PSe})]$	7.26–7.76m	–	32.21	183	134.64–128.74m	–
$[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PO})]$	7.49–7.63m	2.06	32.76	163, 206	132.64–129.36m	23.16
$[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PS})]$	7.44–7.92m	2.09	44.51	167, 209	134.74–128.84m	22.53
$[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PSe})]$	7.52–7.65m	2.16	32.28	172, 202	133.13–128.29m	22.05

* Free Ph_3PO – 30.37, Ph_3PS – 44.54 and Ph_3Pse – 36.53 p.p.m.

at 1962 cm^{-1} [15, 16] and by elemental analysis. Rhodium(I) complex $[\text{Rh}(\text{CO})_2\text{ClL}]$, are coordinatively unsaturated [17] and therefore may undergo oxidative addition (OA) with various electrophiles such as MeI , PhCH_2Cl , I_2 etc. The OA reactions with MeI yield five-coordinate rhodium acyl species, $[\text{Rh}(\text{CO})(\text{COMe})\text{ClL}]$ which are probably formed through an unstable six-coordinate intermediate $[\text{Rh}(\text{CO})_2\text{ClIMEI}]$ [18]. The oxidized products show $\nu(\text{CO})$ bands at *ca.* 2070 cm^{-1} and 1720 cm^{-1} , attributed to terminal and acyl $\nu(\text{CO})$ frequencies respectively. The ^1H -n.m.r. spectra of the $[\text{Rh}(\text{CO})(\text{COMe})\text{ClL}]$ complexes, show a singlet at *ca.* δ 2 p.p.m. due to the acyl group methyl proton, along with a set of multiplets, in the δ 6.9–8.01 p.p.m. range, due to phenyl group of the triphenylphosphine chalcogenides. The ^{31}P -n.m.r. spectra of $[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PO})]$ and $[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PS})]$ complexes show a downfield shift of *ca.* δ 2 p.p.m., while the $[\text{Rh}(\text{CO})(\text{COMe})\text{Cl}(\text{Ph}_3\text{PSe})]$ complex shows an upfield shift of *ca.* δ 4 p.p.m. compared to their free ligands (Table 2). The ^{13}C -n.m.r. spectra of $[\text{Rh}(\text{CO})(\text{COMe})\text{ClL}]$ complexes exhibit four different types of resonances, at δ 205, 180, 128–134 (m) and 25 p.p.m., attributable to acetyl carbonyl, terminal carbonyl, phenylic and methyl carbon resonance respectively and thus substantiate the formation of penta-coordinate acylrhodium(III) carbonyl complexes. Similarly, the $[\text{Rh}(\text{CO})_2\text{ClL}]$ complexes undergo oxidative addition with PhCH_2Cl to give five-coordinate $[\text{Rh}(\text{CO})(\text{COCH}_2\text{Ph})\text{Cl}_2\text{L}]$ species which might be formed through a six-coordinate unstable intermediate $[\text{Rh}(\text{CO})_2(\text{CH}_2\text{Ph})\text{Cl}_2\text{L}]$. The oxidized products show $\nu(\text{CO})$ bands at *ca.* 2080 and 1720 cm^{-1} , attributable to terminal and acyl carbonyl group respectively. $[\text{Rh}(\text{CO})_2\text{ClL}]$ reacts with I_2 to yield $[\text{Rh}(\text{CO})\text{I}_2\text{ClL}]$, exhibiting one $\nu(\text{CO})$ band at *ca.* 2080 cm^{-1} , which is obviously due to oxidized rhodium(III) complexes [17, 18]. The oxidized products $[\text{Rh}(\text{CO})(\text{COMe})\text{ClL}]$, $[\text{Rh}(\text{CO})(\text{COCH}_2\text{Ph})\text{Cl}_2\text{L}]$ and $[\text{Rh}(\text{CO})\text{Cl}_2\text{L}]$, upon treatment with an excess of PPh_3 , form *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$, characterized by its i.r. spectrum and elemental analysis. The different reactions involved in this study are shown in Scheme 1.

The $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PS})]$ and $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PSe})]$ complexes are very stable in the solid state and in solution because of the stronger interaction between soft-sulphur or selenium and soft-rhodium(I), but the



Scheme 1.

$[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PO})]$ complex decomposes within a few hours of its formation, maybe due to weaker interactions between the soft-rhodium(I) and hard-oxygen of PPh_3O . On the other hand, the oxidized products containing Ph_3PO are more stable than those of Ph_3PS and Ph_3PSe because of stronger interactions between hard-oxygen and hard-rhodium(III).

Carbonylation of MeOH in the presence of $[\text{Rh}(\text{CO})_2\text{ClL}]$ complexes

The results of carbonylation of MeOH carried out at different temperatures, pressures and time periods are presented in Table 3. G.C. analyses of the products reveal that *ca.* 12% MeCO_2Me along with a trace of MeCO_2H acid was formed, when the reaction was carried out in the presence of the well-known catalyst precursor $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ for *ca.* 30 min at $130\text{ }^\circ\text{C}$ and at 15 bar. Under the same experimental conditions, the use of catalyst precursor $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PO})]$, $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PS})]$ and $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PSe})]$ resulted in much higher conversions: *i.e.* 23, 36 and 25% respectively. On increasing temperature, pressure and reaction time (Table 3) the catalyst precursor $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ showed a *ca.* 64% conversion, while the catalyst precursors $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PO})]$, $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PS})]$ and $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Ph}_3\text{PSe})]$ gave considerably higher yields: *i.e.* 73, 75, and 72% respectively. The results thus clearly indicate that the catalyst precursors containing chalcogenide ligands show higher yields than that exhibited by the $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ species. Again, among the three

Table 3. Conditions for carbonylation and yields

Catalyst	Temp. (°C)	Pressure (bar)	Time (h)	AcOH (%)	AcOMe (%)	Total conversion (%)
[Rh(CO) ₂ Cl] ₂	130	15	0.5	Trace	11.58	12
	150	20	1.5	11.76	51.74	64
[Rh(CO) ₂ Cl(Ph ₃ PO)]	130	15	0.5	Trace	22.33	23
	150	20	1.5	19.39	53.88	73
[Rh(CO) ₂ Cl(Ph ₃ PS)]	130	15	0.5	Trace	35.46	36
	150	20	1.5	18.15	56.86	75
[Rh(CO) ₂ Cl(Ph ₃ PSe)]	130	15	0.5	Trace	27.42	28
	150	20	1.5	20.27	51.33	72

chalcogenide-containing catalyst precursors, [Rh(CO)₂-Cl(Ph₃PS)] shows the highest yield. The factor responsible for such high efficacy has yet to be ascertained. A similar observation was also reported [19] for bis-alkoxycarbonylation of olefins using palladium(II)-chalcogenides complexes as catalysts.

Conclusions

The [Rh(CO)₂ClL] complexes where L = Ph₃PO, Ph₃PS and Ph₃PSe, were synthesized and characterized. 'Hard-soft' interactions between the metal and the chalcogen donors were found to be operative. Such complexes undergo oxidative additions with different types of electrophiles. The catalytic activity of the complexes in carbonylation of MeOH is higher than that of the well-known [Rh(CO)₂I₂]⁻ species.

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