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Reactions of COS with Rhodium(I) Complexes and with $RhCl_3 \cdot 3H_2O$ in the Presence of PPh_3, $AsPh_3$ or $SbPh_3$

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The reactions of COS with some rhodium(I) complexes, and with $RhCl_3 \cdot 3H_2O$ in the presence of excess of PPh_3, $AsPh_3$ or $SbPh_3$ have been investigated. The products were characterized by elemental analyses and infrared spectra. In most of the cases COS acts as a carbonylating agent but in some cases it forms, $SPPh_3$ or $SAsPh_3$ complexes. Molecular COS complexes were also obtained.

Introduction

The recent developments in organotransition metal chemistry was largely covered by the activation of small molecules and their subsequent reactions with transition metal ions [1–8]. However, a large number of small molecules have been activated by transition metal ions, but there is little published work concerning COS molecule inspite of its potential for giving various interesting products depending upon the reaction conditions. To date, the literature includes the reaction of COS with $Pt(PPh_3)_3$ [5, 9], $RhCl(PPh_3)_3$ [9], $Pd(PPh_3)_4$ [10], and that with $PdCl_2$ and H_2PtCl_6 in presence of PPh_3 or $AsPh_3$ [10]. In the present communication, we describe a preliminary study of the reactions of COS with a number of rhodium(I) complexes and $RhCl_3 \cdot 3H_2O$ in the presence of PPh_3, $AsPh_3$ or $SbPh_3$ and also direct synthesis of some of those compounds from parent rhodium complex and $SPPh_3$ or $SAsPh_3$.

Experimental

All the reagents used were chemically pure. $RhCl(PPh_3)_3$ [11], $RhCOCl(PPh_3)_2$ [12], $RhCOCl(AsPh_3)_2$ [12], $RhCSCl(PPh_3)_2$ [13], Ph_3PS, Ph_3AsS and a saturated solution of COS in methanol [14] were prepared by the standard methods. A fresh solution of COS was used in every reaction.

Reaction of COS with $RhCl_3 \cdot 3H_2O$ and PPh_3

(a) 50 ml of COS saturated methanol was added to 0.02 g of $RhCl_3 \cdot 3H_2O$ and 0.12 g of PPh_3 dissolved in 20 ml of alcohol The solution was refluxed for one hour whereat a bright yellow crystalline complex separated out. It was filtered, washed with alcohol and ether and dried *in vacuo*, m.p. 199 °C. *Anal.* Calcd for $Rh(CO)Cl(PPh_3)_2$: C, 64.3; H, 4.3; Cl, 5.1. Found: C, 64.5; H, 4.7; Cl, 5.0 (yield 60%). The centrifugate, upon concentration and fractional crystallisation, yielded $S{=}PPh_3$.

(b) 70 ml of an alcoholic solution containing 0.02 g of $RhCl_3 \cdot 3H_2O$, COS, 0.06 g PPh_3 and 20 ml of CH_3OH was refluxed for 7–8 h. Bright yellow crystals of $Rh(CO)Cl(PPh_3)_2(SPPh_3)$ were precipitated in about 35% yield. The crystals were separated by filtration, washed with alcohol and ether and dried *in vacuo*. (m.p. 215 °C). *Anal.* Calcd for $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$; C, 67.0; H, 4.6; S, 3.2; Cl, 3.6. Found: C, 66.5; H, 4.4; S, 2.8; Cl, 4.0. The filtrate upon concentration and repeated fractional crystallisation gave pure $S{=}PPh_3$ which was characterised by m.p., i.r. and analytical data.

Reaction of COS with $Rh(CO)Cl(PPh_3)_2$ in Presence of Large Excess of PPh_3

(a) 0.2 g of $Rh(CO)Cl(PPh_3)_2$ and 1.0 g of PPh_3 were dissolved in 10 ml of $CHCl_3$ and 50 ml of methanol solution of COS was added to this. It was refluxed for 0.5 h whereat a bright yellow crystalline complex was separated out (Yield: 50%). It was filtered, washed thoroughly with methanol and ether and dried *in vacuo* (m.p. 215 °C). *Anal.* Calcd for $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$: C, 67.0; H, 4.6; S, 3.2; Cl, 3.6. Found: C, 66.5; H, 4.4; S, 2.8; Cl, 3.6. The filtrate was again refluxed for 3 h resulting in a brown solution. On concentrating on a water bath a brown compound was separated out (yield 5%). It was filtered, washed thoroughly with excess hot methanol and ether and dried *in vacuo* (m.p. >300 °C). *Anal.* Calcd for $[RhCl(SPPh_3)_2]_2$: C, 59.5; H, 4.2; S, 8.8; Cl, 4.9. Found: C, 59.1; H, 4.5; S, 8.3; Cl, 4.7.

(b) In case the initial amount of added PPh_3 was less than 1.0 g *e.g.*, 0.2 g, the yield of yellow crystalline compound, $[RhCOCl(PPh_3)_2(SPPh_3)]$ (m.p.

215 °C) was low and that of brown compound was relatively high.

Reaction of COS with $Rh(CO)Cl(PPh_3)_2$ in the Absence of PPh_3

0.2 g of $Rh(CO)Cl(PPh_3)_2$ dissolved in 5 ml of $CHCl_3$ was mixed with 30 ml of COS saturated methanol and refluxed for 4 h. The brown compound $[RhCl(SPPh_3)_2]_2$ (m.p. >300 °C) was obtained, which was filtered, washed with large excess of hot methanol, ether and dried *in vacuo* (yield 45%).

Reaction of $RhCl(PPh_3)_3$ with COS

(a) 10 ml solution of $RhCl(PPh_3)_3$ (0.25 g) in CH_2Cl_2 was treated with 30 ml of COS saturated methanol and refluxed for 3 h. A yellow crystalline compound precipitated out which was separated by filtration, washed with alcohol and ether and dried *in vacuo*, m.p. 200 °C. *Anal.* Calcd for $Rh(CO)Cl(PPh_3)_2$: C, 64.3; H, 4.9; Cl, 5.1. Found: C, 64.1; H, 4.4; Cl, 5.4 (yield 10%).

The filtrate was concentrated under reduced pressure at room temperature. A brownish orange complex separated out in about 25% yield which was filtered and washed with ether, and dried in vacuo (m.p. 218 °C). *Anal.* Calcd for $[Rh(CO)Cl(SPPh_3)_2]$: C, 58.8; H, 3.9; S, 8.5; Cl, 4.7. Found: C, 53.3; H, 3.6; S, 8.5; Cl, 4.7.

(b) The same orange brown complex was also isolated as the only product under the following reaction conditions.

By concentrating on a water bath or at room temperature a reaction mixture containing 10 ml solution of $RhCl(PPh_3)_3$ (0.2 g) in CH_2Cl_2 and 50 ml of methanol solution of COS and PPh_3 (0.2 g).

Reaction of $RhCl_3 \cdot 3H_2O$ with $S{=}PPh_3$

0.02 g of $RhCl_3 \cdot 3H_2O$ and 0.2 g of $S{=}PPh_3$ was dissolved in 50 ml of methanol and the mixture was refluxed for about 5 h. On concentrating the resulting brown solution, the brown compound, $[RhCl(SPPH_3)_2]_2$ separated out which was washed with excess hot methanol, ether and dried *in vacuo* (m.p. > 300 °C). It was characterised by i.r. spectral and analytical data.

Reaction of $Rh(CO)Cl(PPh_3)_2$ with $SPPh_3$

A mixture of 0.2 g $Rh(CO)Cl(PPh_3)_2$ and 0.6 g of $S{=}PPh_3$ in 5 ml $CHCl_3$ solution to which 25 ml methanol was added, was refluxed for 30 min and then concentrated under reduced pressure. A bright yellow crystalline compound, $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$ was separated out from a brown solution. The yellow compound was filtered out, washed with methanol and ether and dried *in vacuo* (m.p. 215 °C). *Anal.* Calcd. for $[Rh(CO)Cl(SPPh_3)(PPh_3)_2]$: C, 67.0; H, 4.6; S, 3.2; Cl, 3.6. Found: C, 66.3; H, 4.3; S, 2.9; Cl, 3.8 (yield 50%).

The brown filtrate was concentrated on a water bath whereas a brown compound was separated. It was filtered, washed with excess of hot methanol and ether and dried *in vacuo* (m.p. > 300 °C). *Anal.* Calcd for $[RhCl(SPPh_3)_2]_2$: C, 59.5; H, 4.2; S, 8.8; Cl, 4.9. Found: C, 59.2; H, 3.8; S, 8.4; Cl, 4.6 (yield, 10%).

Conversion of $Rh(CO)Cl(PPh_3)_2(SPPh_3)$ to $[RhCl(SPPh_3)_2]_2$

0.2 g of $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$ and 0.6 g $SPPh_3$ was dissolved in 15 ml $CHCl_3$ and 20 ml methanol was added to it. The mixture was refluxed for about 2 h. The resulting brown solution on concentration $[RhCl(SPPh_3)_2]_2$ was separated almost in pure state. It was filtered, washed with methanol and ether and dried *in vacuo* (m.p. > 300 °C). It was characterised by elemental analyses and the i.r. spectrum.

Conversion of $Rh(CO)Cl(SPPh_3)_2$ to $[RhCl(SPPh_3)_2]_2$

0.2 g of $Rh(CO)Cl(SPPh_3)_2$ was dissolved in *ca.* 10 ml CH_2Cl_2 and 15 ml methanol. The mixture was refluxed for about 1.5 h, whereby a brown solution was obtained. On concentration pure $[RhCl(SPPh_3)_2]_2$ was obtained. It was separated from the solution and characterised by elemental analyses and ir spectrum.

Reaction of $[RhCl(SPPh_3)_2]_2$ with Excess PPh_3

A mixture of 0.2 g of PPh_3 dissolved in 15 ml CH_2Cl_2 and 20 ml methanol was refluxed for 18 h. Reddish crystals of $RhCl(PPh_3)_3$ was obtained on concentration at room temperature. The compound was separated by filtration, washed with alcohol and ether dried *in vacuo.* It was characterised by mixed m.p., ir spectral and analytical data (yield 10%).

The filtrate on concentration followed by repeated fractional crystallisation yielded pure $S{=}PPh_3$ which was identified by m.p., elemental analyses and i.r. spectrum.

Reaction of $[RhCl(SPPh_3)_2]_2$ and $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$ with Pyridine

0.2 g of $[RhCl(SPPh_3)_2]_2$ or $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$ in 5 ml CH_2Cl_2 was treated with 2 ml of pyridine and the mixture was refluxed for one hour, whereat a yellow complex of pyridine with Rh(III) was formed in both cases. The solution, on concentrating, gave some more pyridine complex which was filtered out and purified, characterised by i.r. spectrum, elemental analyses. The filtrate was dried at room temperature and from the solid mass $S{=}PPh_3$ was extracted by repeated fractional crystallisation with petroleum ether. It was characterised by m.p., elemental analyses and i.r. spectra (yield, low).

Reaction of COS with $RhCOCl(AsPh_3)_2$ in Presence of Large Excess of $AsPh_3$

(a) 0.2 g of $Rh(CO)Cl(AsPh_3)_2$ and 1.0 g of $AsPh_3$ dissolved in 10 ml of CH_2Cl_2 and 50 ml of COS solution in methanol was refluxed for one hour whereat yellow needle-shaped crystals were separated out in about 45% yield. The crystals were filtered out, washed with methanol and ether and dried *in vacuo* (m.p., 251 °C). *Anal.* Calcd for $[Rh(CO)Cl(AsPh_3)_2(SAsPh_3)]$: C, 59.1; H, 4.0; S, 2.9; Cl, 3.2. Found: C, 58.5; H, 5.0; S, 2.5; Cl, 3.8.

The brown filtrate was refluxed for about 4 h. On concentration a brown compound was separated out in poor yield (10%). It was filtered, washed thoroughly with excess hot methanol and ether, dried *in vacuo* (m.p. > 300 °C). *Anal.* Calcd for $[Rh(CO)Cl(SAsPh_3)]_2$: C, 45.2; H, 3.0; S, 6.3; Cl, 7.1. Found: C, 44.8; H, 4.0; S, 6.7; Cl, 7.5.

(b) In case the initial amount of added $AsPh_3$ was less than 1.0 g (*e.g.*, 0.2 g), the yield of yellow crystalline compound $[Rh(CO)Cl(AsPh_3)_2(SAsPh_3)]$ (m.p. 251 °C) was low (20%) and that of brown compound was relatively high (50%).

Reaction of COS with $Rh(CO)Cl(AsPh_3)_2$ in the Absence of $AsPh_3$

5 ml solution of $Rh(CO)Cl(AsPh_3)_2$ in CH_2Cl_2 was treated with 30 ml of COS in methanol and refluxed for 4 h. The brown compound $[Rh(CO)Cl(SAsPh_3)]_2$ (m.p. > 300 °C) was obtained (yield 45%). It was filtered, washed with large excess of hot methanol and ether and dried *in vacuo.* The compound was characterised by elemental analyses and ir spectrum.

Reaction of COS with $RhCl_3 \cdot 3H_2O$ in Presence of Excess $AsPh_3$

(a) 0.02 g of $RhCl_3 \cdot 3H_2O$ and 0.12 g of $AsPh_3$ were dissolved in 15 ml of methanol, 50 ml of COS saturated methanol was added to it. The mixture was refluxed for 2 h, whereat a reddish brown compound was separated out (yield 70%). It was filtered, washed with alcohol and ether and dried *in vacuo* (m.p. > 300 °C). *Anal.* Calcd for $RhCl_3(AsPh_3)(SAsPh_3)$: C, 50.6; H, 3.5; S, 3.8; C, 12.5. Found: C, 50.0; H, 3.6; S, 3.9; Cl, 12.7.

(b) The same brown compound was formed when the same reaction mixture was kept at 5 °C for several days or stirred at room temperature for several hours.

Reaction of $Rh(CO)Cl(AsPh_3)_2$ with $S{=}AsPh_3$

(a) A mixture of 0.2 g of $Rh(CO)Cl(AsPh_3)_2$ and 0.6 g of $S{=}AsPh_3$ in 10 ml CH_2Cl_2 and 25 ml of methanol was refluxed for 1 h. A brown solution was resulted. On concentration, a brown compound was separated out. It was filtered, washed with excess hot methanol and ether and dried *in vacuo* (m.p. > 300 °C). *Anal.* Calcd for $[Rh(CO)Cl(SAsPh_3)]_2$: C, 45.2; H, 3.0; S, 6.3; Cl, 7.1. Found: C, 44.6; H, 3.8; S, 6.8; Cl, 7.5, (yield, 15%).

(b) Addition of 0.2 g of $AsPh_3$ and reducing the amount of $S{=}AsPh_3$ to 0.2 g in the above reaction mixture, the yellow needle-shaped crystals were obtained in good yield (40%). The yellow complex was separated and purified in the manner given previously (m.p. 250 °C). *Anal.* Calcd for $[Rh(CO)Cl(AsPh_3)_2(SAsPh_3)]$: C, 59.1; H, 4.0; S, 2.9; Cl, 3.2. Found: C, 58.6; H, 4.6; S, 3.2; Cl, 3.4.

Conversion of $Rh(CO)Cl(AsPh_3)_2(SAsPh_3)$ to $[Rh(CO)Cl(SAsPh_3)]_2$

The reaction procedure was the same as that given previously except that the solvent was CH_2Cl_2. The yield of $[Rh(CO)Cl(SAsPh_3)]_2$ was high and the compound was characterised by elemental analyses and i.r. spectrum.

Reactions of $Rh(CO)Cl(AsPh_3)_2(SAsPh_3)$, $[Rh(CO)Cl(SAsPh_3)]_2$ and $RhCl_3(AsPh_3)(SAsPh_3)$ with Pyridine

The reaction methods were same as with the $SPPh_3$ analogs. The initial yellow complex was also the same in the three cases. After repeated fractional crystallsation in each case pure $S{=}AsPh_3$ was obtained and was characterised by i.r., elemental analyses and m.p. data.

Reaction of COS with $Rh(CS)Cl(PPh_3)_2$ in Presence of PPh_3

0.2 g of $Rh(CS)Cl(PPh_3)_2$ and 0.4 g of PPh_3 were dissolved in 10 ml of CH_2Cl_2 to which 30 ml of COS saturated methanol was added. The mixture was refluxed for one hour, whereat shining yellow crystals were separated out. The product was centrifuged out, washed with methanol and ether and dried *in vacuo* (m.p. 230 °C). *Anal.* Calcd for $Rh(CO)(CS)Cl(PPh_3)_2$: C, 62.1; H, 4.1; S, 4.4; Cl, 4.8. Found: C, 62.6; H, 4.2; S, 4.0; Cl, 4.8 (yield 30%).

The centrifugate was dried at room temperature, and the solid mass was extracted with petroleum ether. Repeated fractional crystallisation from petroleum ether gave pure $SPPh_3$.

Reaction of COS with $RhCl_3 \cdot 3H_2O$ in presence of Excess $SbPh_3$

0.02 g of $RhCl_3 \cdot 3H_2O$ and 0.12 g of $SbPh_3$ were dissolved in 20 ml of methanol. 50 ml of COS saturated methanol was added to it and the reaction mixture was refluxed for 1 h. An orange-brown compound was separated out. It was filtered out, washed with alcohol and ether, dried *in vacuo* (m.p. 198 °C). *Anal.* Calcd for $[Rh(COS)Cl(SbPh_3)]_2$: C, 39.2; H,

TABLE I. Structural Formula, IR Data, Colour and Molecular Weights of the Complexes.

Structural Formula	Colour	Mol. wt.	Major IR spectral bands other than PPh_3 in cm^{-1}
$Rh(CO)Cl(S{=}PPh_3)_2$	Orange-brown		$\nu(CO)$, 1946; $\nu(P{=}S)$; 550
$Rh(CO)Cl(PPh_3)_2$	Yellow	735	$\nu(CO)$, 1960; $\delta(RhCO)$, 575
$Rh(CO)Cl(PPh_3)_2)SPPh_3)$	Yellow	1394	$\nu(CO)$, 1965; $\nu(P{=}S)$, 547; $\delta(RhCO)$, 577
$[RhCl(SPPh_3)_2]_2$	Dark brown	1259	$\nu(P{=}S)$ region is blocked by PPh_3 bands
$Rh(CO)Cl(AsPh_3)_2(SAsPh_3)$	Yellow	1142	$\nu(CO)$, 1965; $\nu(As{=}S)$, 502; $\delta(RhCO)$, 569
$[Rh(CO)Cl(SAs\text{-}Ph_3)]_2$	Dark grey	926	$\nu(CO)$, 1955; $\nu(As{=}S)$, 500
$Rh(CO)(CS)Cl(PPh_3)_2$	Yellow	501	$\nu(CO)$, 1970; $\nu(CS)$, 1305
$RhCl_3(AsPh_3)(SAsPh_3)$	Orange brown	766	$\nu(As{=}S)$, 510
$[Rh(COS)Cl(SbPh_3)]_2$	Orange brown	607	$\nu_{asy}(CO)$, 1650; $\nu_{sym}(CO)$, 1570; $\nu_{asy}(CS)$, 910; $\nu_{sym}(CS)$, 850

2.7; S, 5.8; Cl, 6.4. Found: C, 40.0; H, 3.1; S, 5.2; Cl, 6.1 (yield (50%)).

Reaction of PPh_3 with COS

0.5 g of PPh_3 was dissolved in 100 ml of COS in methanol and the mixture was kept at room temperature for 4 days. After concentration, white needle-shaped crystals of $S{=}PPh_3$ were precipitated out. These were filtered and characterised by m.p., i.r. spectral and analytical data.

Reaction of $AsPh_3$ with COS

Dry COS was bubbled through 15 ml benzene solution of $AsPh_3$ for 2.5 h. The deposition of sulfur occurred and the solution after concentration yielded pure $AsPh_3$.

All the compounds reported here were purified by recrystallisation from suitable solvents. The purity of the complexes were further tested by preparing them a number of times and analysing them. In each case the experimental and calculated value of the analytical results corroborates the purity of the compounds.

The carbon and hydrogen analyses in the compounds were carried out by the Micro-Analytical Laboratory of the Indian Institute of Technology, Kanpur. Chloride and sulphur were estimated using the standard methods [15] after decomposing the complexes with *aqua regia* or NaOH and $NaNO_3$ mixture. The oxidation state of rhodium was determined by the oxidation with ceric ammonium sulphate in presence of platinum catalyst and back titrating the excess ceric ammonium sulphate with ferrous ammonium sulphate using ferroin as indicator [16]. Infrared spectra were recorded with a Perkin Elmer 521, infrared spectrophotometer in KBr pellets. The infrared spectral data (calibrated against polystyrene) for all the complexes with their assignment are given in Table I. Melting points were measured in a Fischer Melting Point apparatus and were uncorrected. Magnetic measurements were carried out in a Gouy type magnetic balance. Molecular weights were determined by cryoscopic method.

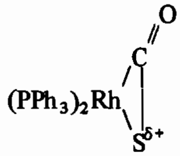
Results and Discussion

The analytical data and oxidation reduction titration results indicate that the rhodium in the complexes is present in +1 oxidation state unless otherwise stated which is also corroborated by their diamagnetic character. Further, because of the highly reducing nature of COS as well as PPh_3 the possibility of oxidation of rhodium from +1 to +3 state is remote. Their mono-, di-, or polymeric nature is established by their molecular weights which were determined cryoscopically. In some cases the complexes behaved erratically in solution, hence their molecular weights are not reported.

In all these compounds carbonyl and/or thiocarbonyl groups were identified by the positions of $\nu(C{\equiv}O)$ or/and $\nu(C{=}S)$ bands in their infrared spectra around 1900 cm^{-1} and 1300 cm^{-1} respectively, COS group, by the presence of four characteristic COS bands of medium intensity around 1600, 1650, 800, 830 cm^{-1} [17, 18] and $S{=}AsPh_3$ and $S{=}PPh_3$, by the presence of sharp to medium intense bands due to $\nu(As{=}S)$ and $\nu(P{=}S)$ at 500 cm^{-1} and 530 cm^{-1} respectively [19, 20]. The position of these bands are given in Table I.

Reactions with Triphenylphosphine Complexes

It is obvious from the formula assigned to various complexes that in most of the reactions COS is acting as a carbonylating agent and the sulphur atom combines with PPh_3 or $AsPh_3$ to form $S{=}PPh_3$ or $S{=}AsPh_3$ [21]. This coordinates with rhodium to form phosphine or arsine sulfide complexes. In these reactions COS possibly first acts as a ligand bound in a three membered ring. In presence of polar solvents, *e.g.*, methanol, a cationic species of rhodium(I) containing (h^2-COS) is formed which in turn is attacked by PPh_3 to form a carbonyl complex of rhodium(I) and triphenylphosphine sulfide which further coordinates or forms adduct with the carbonyl complex. Thus,



$$(PPh_3)_2Rh(COS^{\delta+}) + :PPh_3 \rightarrow (Ph_3P)_2Rh(CO) + Ph_3P{=}S \xrightarrow{Cl^-} Rh(CO)Cl(PPh_3)_2$$

$$Rh(CO)Cl(PPh_3)_2 + SPPh_3 \rightarrow (Ph_3P)_2Rh(CO)Cl(SPPh_3)$$

The formation of $[(PPh_3)_2Rh(CO)Cl(S{=}PPh_3)]$ is shown by the direct reaction of $S{=}PPh_3$ with $Rh(CO)Cl(PPh_3)_2$. The band position of ν(CO) (1965 cm^{-1})is in comformity with those present in rhodium(I) complexes (1960 cm^{-1} for Rh(I) complexes, 2100 cm^{-1} for Rh(III) complexes) [13].

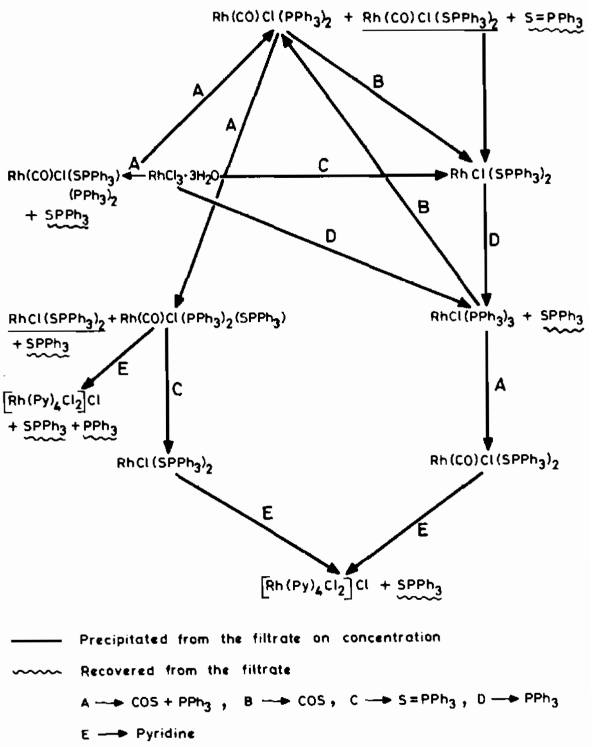
Free phosphine in these reactions was present either as a result of the dissociation of rhodium(I) complex or was added in the system from outside. In all cases the first product obtained was a carbonyl complex with or without the presence of coordinated or adduct $S{=}PPh_3$. But as the refluxing time was prolonged or the solution was concentrated, carbonyl and the phosphine molecules were substituted by triphenylphosphine sulfide with the formation of the final product $[RhCl(SPPh_3)_2]_2$ (Scheme).

Effect of added Phosphine

The percentage yield of yellow compounds seems to be directly related to the amount of added phosphine, possibly in the presence of a large excess of PPh_3 the dissociation of rhodium(I) complex is suppressed which after the formation of carbonyl species competes for PPh_3 and $S{=}PPh_3$. PPh_3 concentration being more in the system gets bonded preferentially over $S{=}PPh_3$ which could not be substituted for CO or PPh_3. In the absence of added PPh_3, all the PPh_3 in the system arising as a result of dissociation of the complex get converted into $S{=}PPh_3$ which combines with the rhodium(I) to form the brown complex. This is substantiated by the fact that $Rh(CO)Cl(PPh_3)_2$ on refluxing with excess $S{=}PPh_3$ gave $[RhCl(SPPh_3)_2]_2$ rather than $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$. It is also evident that the formation of brown compound takes place under stringent conditions while yellow compounds are formed under relatively mild conditions.

Reactions with Triphenylarsine Complexes

It appears that COS reacts with triphenylarsine complexes in the same manner as with triphenylphosphine complexes, except that triphenylarsine sulfide could not replace carbonyl group from the carbonyl complexes of rhodium(I). Though triphenylarsine failed to react with COS like its phosphine analogue, it appears that COS activated by the $Rh(CO)Cl(AsPh_3)_2$ reacts with $AsPh_3$ to give $S{=}AsPh_3$. At this stage it is not possible to conclude if the reaction $COS + AsPh_3 \rightarrow SAsPh_3 + CO$ is activated by the metal ions/complex without further kinetic studies.



However, the relatively longer reaction time for achieving the maximum yield of $[Rh(CO)Cl(MPh_3)_2(S{=}MPh_3)]$ by the reaction

$$Rh(CO)Cl(MPh_3)_2 + COS + MPh_3 \rightarrow [Rh(CO)Cl(MPh_3)_2(S{=}MPh_3)]$$

(M = P and As) suggests that arsine possibly reacts at a slower rate as compared to phosphine.

The reaction of COS with $SbPh_3$ complexes could not give carbonyl complexes even on prolong refluxing. It, however, forms π-COS complex. It appears that $SbPh_3$ being relatively weak base its lone pair of electron is not able to pull out sulfur atom from the COS molecule bonded to rhodium(I) atoms, as π-complex.

It is quite interesting to note that in the reaction of COS with $Rh(CS)Cl(PPh_3)_2$, CS remains intact and is not replaced by either CO or PPh_3 group. The presence of CS and CO was suggested by their i.r.

spectra. The presence of CS group is further corroborated by the ratio ν_{CO}/ν_{CS} (1.5) which is the same as in the ruthenium(II) complex [23].

It should, however, be pointed out here that the mechanism proposed for the formulation of the complexes is one of the very many possible ones which could be easily written. It is not possible to decide one over the other without further kinetic studies.

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