Reactions of Carbonyl Sulphide with Hydrated Ruthenium Trichloride & Its Complexes in Presence & Absence of Triphenylphosphine, Triphenylarsine & Triphenylstibine

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The reactions of COS with some ruthenium(II) and ruthenium(III) complexes, and with RuCl₂ xH₂O in the presence and absence of excess of PPh₃, AsPh₃ and SbPh₃ have been investigated. The products have been characterized by elemental analyses, infrared spectra, conductivity measurements, magnetic moments and molecular weight measurements (wherever possible). In most of the cases COS acts as a carbonylating agent but in some it forms S=PPh₃ or S=AsPh₃ complexes. Some thiocarbonyl and molecular COS complexes are also reported.

In our previous communications¹-³ the reactions of carbonyl sulphide (COS) with Pd, Pt and Rh complexes of triphenyl-phosphine, -arsine and -stibine in various oxidation states have been discussed. It has been shown that depending upon the reaction conditions, COS can act either as a carbonylating or thiocarbonylating agent with the formation of triphenylphosphine, arsine sulphide or oxide or it can act as π-bonding ligand with the formation of molecular COS complexes. In a few cases, insertion reactions have also taken place with the formation of thiocarbonylato complexes. In this paper we wish to report the reactions of COS with the hydrides, PPh₃, AsPh₃ or SbPh₃ complexes of Ru(II) and/or Ru(III).

Materials and Methods

All the reagents used were of chemically pure grade. RuCl₃ (PPh₃)₃ (ref. 4), Ru(CO)Cl₂ (PPh₃)₂ (ref. 5), RuCl₃ (PPh₃)₂ (ref. 6), RuCl₃ (AsPh₃) (ref. 7), RuH₂ (CO) (PPh₃)₃ (ref. 8), Ru₃H₄ (PPh₃)₃ (ref. 8) and saturated solution of COS in methanol were prepared by the standard methods. Only freshly prepared COS solution was used in every reaction.

(A) Reaction of COS with RuCl₃ (PPh₃)₃: (i) In the presence of PPh₃ — RuCl₃ (PPh₃)₂ (0.2 g) and PPh₃ (0.6 g) were dissolved in CH₂Cl₂ (15-20 ml) and COS solution (50 ml) in methanol was added to it. The mixture was heated under reflux for 5 hr and the resulting deep red solution concentrated to near dryness. It was extracted with minimum volume of CH₂Cl₂. To the extract cyclohexane was added whereby a red compound was precipitated out which was filtered and washed with cyclohexane and ether. It was purified by reprecipitating it with CH₂Cl₂ and cyclohexane. The compound was washed with ether and dried in vacuo (yield ~ 50%).

From the filtrate after separation of the pink red complex, OPPh₃ was isolated in pure form, by repeated fractional crystallisation.

(ii) In the absence of PPh₃ — RuCl₃ (PPh₃)₂ (0.2 g) in CH₂Cl₂ (15-20 ml) and COS solution (50 ml) in methanol was refluxed for 3 hr. The greenish black solution on concentration yielded a black compound which was filtered, washed with large amount of methanol, ether and dried in vacuo. It was purified by recrystallisation from CH₂Cl₂ and ether. The yield of this complex was rather on the lower side.

Triphenylphosphine sulphide could be isolated from the filtrate after separation of the black compound.

(B) Reaction of COS with Ru(CO)Cl₂ (PPh₃)₂ — The reaction procedure was as in A (i) above. Finally the greenish grey compound was obtained by addition of excess ether, collected and purified similarly as in (i), yield (35-40%).

Triphenylphosphine oxide, isolated from the reaction mixture after separation of the greenish grey compound, was characterised in the same way as in the earlier case.

(C) Reaction of RuCl₃ (PPh₃)₃ with COS — Reaction procedure was similar as in A (ii); yield was better. Triphenylphosphine sulphide was isolated from the filtrate.

(D) Conversion of [Ru(SPPh₃) (PPh₃)Cl₁₃] to Ru(CO) (CS) (PPh₃)Cl₁₂ — [Ru(SPPh₃) (PPh₃)Cl₁₂] (0.2 g) in CH₂Cl₂ (15 ml) was added to COS solution (30 ml) in methanol containing PPh₃ (0.02 g). The solution was refluxed for 5 hr whereby it turned green. It was concentrated in air at room temperature to yield an greenish grey complex, Ru(CO) (CS) (PPh₃)Cl₁₂, which was purified and characterised by the method similar to that given in (B). The filtrate after drying and repeated fractional crystallisation from pet. ether (60-80°) yielded pure needle shaped crystals of S=PPh₃.

(E) Reaction of [Ru(CO) (SPPPh₃)Cl₁₃] with excess PPh₃ — [Ru(CO) (SPPPh₃)Cl₁₃] (0.2 g) and PPh₃ (0.25 g) were dissolved in a mixture of CH₂Cl₂.
(10 ml) and CH₂OH (15 ml) and the solution refluxed for 5 hr. The resulting solution was concentrated on a water-bath whereby a blackish compound [RuCl₄(PPh₃)₂]n separated out, which was filtered and the filtrate on concentration yielded a whitish mass. This on extraction with hot pet. ether (60-80°C) and repeated fractional crystallisation gave pure S = PPh₃ as one of the components.

(F) Reaction of COS with RuCl₃ (AsPh₃)₂ — RuCl₃ (AsPh₃)₂ (0.2 g) was dissolved in CH₂Cl₂ (20 ml) and COS solution (50 ml) in methanol added to it. The solution was refluxed for 4 hr whereby a steel gray coloured compound, [Ru(CO)₂ (SAsPh₃)Cl]n separated out which was filtered and purified by dissolving it in CH₂Cl₂ and reprecipitating it by adding ether. It was filtered, washed with methanol, ether and dried in vacuo yield ~30%.

The filtrate after separation of the steel grey compound, after evaporation and repeated fractional crystallisation yielded pure S = AsPh₃ as one of the components.

(G) Reaction of [Ru(CO)₆(SAsPh₃)Cl]₃ with excess PPh₃ — The reaction procedure was similar to the one given in (F). The complex obtained from the reaction was [RuCl₄(PPh₃)₂]n. From the filtrate after concentration and fractional crystallisation a white compound, characterised as S = AsPh₃ was obtained.

(H) Insertion of COS in ruthenium hydride bond in RuH₂(CO)(PPh₃)₃ — (i) RuH₂(CO)(PPh₃)₃ (0.2 g) was dissolved in benzene (25 ml) and the solution filtered. To the filtrate COS solution (30 ml) in methanol added and the solution refluxed for 4-5 hr until a brownish-yellow colour persisted. The solution was slowly concentrated to 5-8 ml on a water-bath with occasional stirring. Addition of excess ether to this concentrate gave a reddish brown compound in good yield. This was filtered, washed with ether and dried in vacuo m.p. 170° (d). The compound appeared to be a mixture of Ru(PPh₃)₃(CO)₂(SOCH₃) and its decomposition products.

(ii) The reddish brown complex obtained in H(i) was dissolved in CH₂Cl₂ and allowed to dry in air. The solid extracted with minimum volume of CH₂Cl₂ yielded a yellowish brown compound on the addition of excess of ether. It was filtered, washed with ether, purified by dissolving it in CH₂Cl₂ and precipitating it by adding ether.

(iii) A clear solution of RuH₂(CO) (PPh₃)₃ (0.2 g) in benzene (25 ml) and COS solution (30 ml) in methanol was refluxed for 2 hr, whereby the colour of the solution changed to golden yellow. The solution was allowed to dry in air, the dried mass extracted with CH₂Cl₂ (3-5 ml) followed by the addition of an excess of ether which yielded a golden yellow compound. It was filtered washed with ether and purified by dissolving it in CH₂Cl₂ and re-precipitating it by the addition of ether. The complex was found to be [Ru(SPPPh₃)₃ (CO)S] 1.1 CH₂Cl₂ by elemental analyses, infrared spectra and m.m.p.

(I) Reaction of RuH₂ (PPh₃)₃ with COS in presence of PPh₃ — RuH₂ (PPh₃)₃ (0.2 g) and PPh₃ (0.6 g) was dissolved in CH₂Cl₂ (15 ml) and COS solution (30 ml) in methanol added to it. The mixture was heated under reflux for 1-2 hr and concentrated to a small volume (~ 5 ml) in a flash evaporator at 75°C under reduced pressure. Addition of excess of n-hexane to it yielded a dark grey compound which was purified by recrystallisation from CH₂Cl₂/n-hexane, washed with n-hexane and dried in vacuo.

(J) Reaction of [Ru(SPPPh₃)₃ (CO)S] 1.1 CH₂Cl₂ with excess PPh₃ — Experimental procedure was the same as described in (E) and S = PPh₃ was one of the products isolated.

(K) Reaction of COS with RuCl₃ x H₂O in presence of PPh₃ — RuCl₃ x H₂O (0.02 g) was dissolved in COS solution (50 ml) in methanol and PPh₃ (0.12 g) dissolved in methanol added to it. The mixture was refluxed for 4 hr when the colour of the solution became green. It was filtered and allowed to concentrate in air at room temperature whereby a black precipitate appeared. It was filtered, washed with ether and dried in vacuo. It was purified by dissolving it in CH₂Cl₂ and reprecipitating by adding excess of ether. S = PPh₃ was isolated from the filtrate as one of the components.

(L) Reaction of COS with RuCl₃ x H₂O in presence of AsPh₃ — RuCl₃ x H₂O (0.02 g) was dissolved in COS solution (50 ml) in methanol and AsPh₃ (0.12 g) added to it. The mixture was heated under reflux for 4 hr whereby green crystals of RuCl₃ (AsPh₃)₂ CH₂OH appeared (confirmed by comparison with an authentic sample). The red solution left after the separation of green crystals was again refluxed for 2 hr whereby a brownish red crystalline compound precipitated out. This was centrifuged, washed with ether and dried in vacuo. The filtrate after separation of brownish red compound gave S = AsPh₃ as one of the products.

(M) Reaction of COS with RuCl₃ x H₂O in presence of SbPh₃ — RuCl₃ x H₂O (0.02 g) and SbPh₃ (0.15 g) was dissolved in COS solution (50 ml) in methanol and the solution refluxed for 1 hr. whereby a pink red compound separated out which was purified, washed with methanol, ether and dried in vacuo.

(N) Reaction of [RuCl₃ (SAsPh₃)₂ with excess PPh₃] — The reaction procedure was same as in (E). The products include [RuCl₃ (PPh₃)₂]n and S = AsPh₃.

(O) Reaction of Ru(SbPh₃)₃ (COS) Cl₄ with excess PPh₃ — A mixture of Ru (SbPh₃)₃ (COS) Cl₄ (0.2 g) in CH₂Cl₂ (15 ml) and PPh₃ (0.6 g) in methanol (20 ml) was refluxed for 4 hr when the colour of the solution turned reddish brown. The solution was allowed to concentrate in air at room temperature whereby the colour changed to greenish black and on further concentration a dark grey coloured complex separated out. This was purified by dissolving in CH₂Cl₂ and by reprecipitating with excess diethyl ether. This was identified to be [Ru(CO) (SPPPh₃) Cl₄] by the methods given in A (ii).

All the compounds reported here were purified by recrystallization from suitable solvents. The purity of the complexes was further tested by preparing them repeatedly and analysing them. In each case the
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Table 1—Analytical Data, m.p., mol. wt. and Important Infrared Bands of the Complexes

<table>
<thead>
<tr>
<th>Formula</th>
<th>m.p. °C</th>
<th>Found (%) (calc)</th>
<th>Mol. wt.</th>
<th>IR bands other than PPh₃ AsPh₃ or SbPh₃ in cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>{Ru(SPPh₃)(PPh₃)Cl}₃</td>
<td>157</td>
<td>59.2 (59.5) 4.0 (4.1) 4.9 (4.4) 9.5 (9.7)</td>
<td>1440</td>
<td>vP=S 560</td>
</tr>
<tr>
<td>[Ru(CO)Cl₂(SPPPh₃)]₃</td>
<td>&gt;300</td>
<td>46.0 (46.1) 3.2 (3.0) 6.1 (6.5) 14.5 (14.4)</td>
<td>625</td>
<td>v(CO) 1965 and vP=S 590</td>
</tr>
<tr>
<td>Ru(CO)(CS)Cl(PPh₃)</td>
<td>190</td>
<td>47.2 (47.4) 3.3 (3.0) 6.0 (6.3) 14.2 (14.0)</td>
<td>847</td>
<td>v(CO) 1962 (sh), 1950</td>
</tr>
<tr>
<td>Ru(CO)₂(COSH)₂(PPh₃)₃</td>
<td>170</td>
<td>53.2 (53.9) 3.4 (3.7) 9.8 (11.0) 7.8 (8.9)</td>
<td>850</td>
<td>v(CO) 1990, 1960, v(C=S) 1690, 1610, 930 and 845</td>
</tr>
<tr>
<td>[Ru(CO)₂(SPPPh₃)S] 1.1 CH₂Cl₂</td>
<td>190</td>
<td>53.2 (53.9) 3.4 (3.7) 9.8 (11.0) 7.8 (8.9)</td>
<td>1500</td>
<td>v(CO) 1955</td>
</tr>
<tr>
<td>[Ru(CO)₂(PPh₃)S]₃</td>
<td>172</td>
<td>53.9 (53.2) 3.6 (3.3) 7.5 (7.1)</td>
<td>550</td>
<td>v(CO) 1990, 1960, v(C=S) 1690, 1610, 930 and 845</td>
</tr>
<tr>
<td>[Ru(SAsPh₃)(AsPh₃)Cl]₃</td>
<td>215</td>
<td>53.2 (53.9) 3.7 (3.7) 4.1 (3.9) 9.1 (8.7)</td>
<td>1500</td>
<td>v(CO) 1955</td>
</tr>
<tr>
<td>Ru(COS)Cl₂(SbPh₃)₂</td>
<td>&gt;300</td>
<td>47.5 (47.4) 3.5 (3.2) 3.3 (3.1) 7.7 (7.6)</td>
<td>1500</td>
<td>v(CO) 1955</td>
</tr>
</tbody>
</table>

*Chloride and sulphur were estimated using the standard methods after decomposing the complexes with aqua regia or NaOH and NaN₃ (8:1) mixture.

Experimental and calculated values of the elementary analyses corroborated the purity of the compounds.

Results and Discussion

The characterization data of the compounds obtained are given in Table 1. All the compounds reported are non-conducting in nitrobenzene hence (10⁻⁳ M solution) and are not ionic in nature. The mono-, di-, or polymeric nature of the complexes was determined by determining their molecular weights by cryoscopic method. In some cases the molecular weight could not be determined because of either their less solubility or their erratic behaviour in solution and therefore no values are reported in such cases.

In all the compounds carbonyl or/thiocarbonyl groups have been identified by the positions of ν(C=O) or/and ν(C=S) bands in their IR spectra around 1950 and 1300 cm⁻¹ respectively, coordinated COS group by the presence of four characteristic ν(C=O) bands of medium intensity around 1600, 1650, 800, and 830 cm⁻¹; and S = AsPh₃ and S = PPh₃. 

It is interesting to note that COS reacts with PPh₃ complexes of Ru(II), viz. RuCl₂ (PPh₃)₃ to give carbonyl or triphenylphosphine sulphide complexes of Ru(II). The presence of ruthenium in +2 oxidation state in the final product is indicated by the analytical results of halide ion and the diamagnetic nature of the complexes. In the presence of large excess of PPh₃, the reaction of RuCl₂(PPh₃)₃ and COS gave a red complex [Ru(PPh₃)₂(SPPPh₃)]Cl₂ while in the absence of PPh₃, the reaction yielded the black complex [Ru(CO)(SPPh₃)Cl]₂. The formation of the black complex may easily be explained if one presumes that during the course of the reaction, the parent compound RuCl₂(PPh₃)₃ first undergoes dissociation to RuCl₃(PPh₃)₂, followed by formation of a complex having Ru(H-COS) moiety which in the presence of polar solvents like methanol, forms a cationic species and the latter is then attacked by PPh₃ to form the carbonyl complex (Scheme I).

At low concentration of PPh₃, the triphenylphosphine sulphide thus formed in situ as a result of the reaction of COS with PPh₃, is then able to replace PPh₃ in the resulting final product. In those reactions where excess of PPh₃ is added it appears that excess PPh₃ replaces coordinated carbonyl group in the resulting final product giving the red complex [Ru(SPPPh₃)(PPh₃)Cl]₂₃. 

To understand these reactions an attempt has been made to investigate the reactions of COS with [RuCl₂ (PPh₃)₃]; however, these reactions are extremely difficult owing to very low solubility of the parent...
complex and the nature of the final reaction products is dependent on the reaction conditions used. In the present investigation we have encountered a number of products but for none of these experimental conditions could be standardized. However, it appears that one of the possible products was a complex of ruthenium (II) containing both carbonyl and thiocarbonyl groups along with PPh₃.

The reaction of Ru(CO)Cl₃(PPh₃)₃ with COS appears to occur in an altogether different manner. The final product is a carbonyl-thiocarbonyl complex, Ru(CO)(CS)(PPh₃)Cl₂. In this case, it is quite possible that first a π-complex of type (I) is formed followed by a nucleophilic attack of free PPh₃ molecule at the oxygen atom of COS. This will lead to the formation of triphenylphosphine oxide and the carbonyl-thiocarbonyl complex (Scheme 2).

The presence of thiocarbonyl group in this complex is indicated by the presence of sharp and strong band at 1280 cm⁻¹ in its IR spectrum and by the chemical analyses. The ratio of wave numbers of the bands due to νCO and νCS is close to 1.5, which further substantiates the assignment of thiocarbonyl group in the complex²⁻¹⁵.

The reaction of COS with RuCl₃(PPh₃)₃ proceeds as expected, the final product being [RuCl₃(CO)(SPh₃)]₃. The mechanism of the reaction may be the same as that given in Scheme 1. The excess PPh₃ recovered from the filtrate further corroborates the mechanism proposed.

In the reaction of COS with RuCl₃(AsPh₃)₃ — The reaction product [Ru(CO)₃(AsPh₃)Cl₂]₃ is a dark grey compound. The formation of this compound is independent of the amount of AsPh₃ present in solution. The infrared spectra exhibits two bands for terminal CO at 1950 and 1960 (sh) cm⁻¹. The compound is diamagnetic and covalent in nature. The IR spectrum also exhibits a weak band around 515 cm⁻¹ due to νAs=S. The formation of this complex probably occurs via the formation of an intermediate (h₂-COS) complex which reacts with AsPh₃ to give carbonyl complex and S = AsPh₃, triphenylarsine sulphide replaces the triphenyl-AsPh₃ from the complex to give the required product. The presence of S = AsPh₃ is further corroborated by the fact that after prolonged refluxing with excess PPh₃, free S = AsPh₃ is recovered from the filtrate as one of the reaction products.

The reaction of COS with RuCl₃, x H₂O in the presence of excess SbPh₃ gives a pink red complex, RuCl₃(COS)(SbPh₃)₂ in which COS is bonded to the metal atom via two π-bonds through carbon and sulphur. This is supported by its IR spectrum which exhibits four bands at 1650, 1570, 910 and 850 cm⁻¹ the characteristic infrared frequencies of a bindentate COS group¹³,¹⁴. The presence of COS group is further substantiated by the reaction of the pink red complex with PPh₃ which yields a small amount of black [Ru(CO)(S = PPh₃)]Cl₂ as the reaction product.

The above experimental data indicate that the reaction of COS with RuCl₃, x H₂O in the presence of PPh₃, AsPh₃ or SbPh₃ possibly proceeds with the initial formation of an unstable molecular COS complex which reacts with PPh₃ to give [Ru(CO)(SPh₃)Cl₃]₃. AsPh₃, however, is unable to react with coordinated COS but it simply replaces it; SbPh₃ being the weakest base least reactive neither reacts with coordinated COS group nor is able to replace it. It, gives only the molecular COS complex. Thus, the reactions of RuCl₃, x H₂O with COS in presence of PPh₃, AsPh₃ or SbPh₃ indirectly indicate the formation of a molecular COS complex with RuCl₃, x H₂O in the first stage.

Reactions of COS with ruthenium hydride complexes — It appears that the reaction of COS with ruthenium hydrido complexes occurs through the insertion of COS in the ruthenium hydrogen bond resulting in the formation of thioformato complexes. These complexes are, however, very unstable and decompose under normal experimental conditions, e.g. exposure to atmosphere in solution to sulphide-bridged complexes. A mixture of thioformato complex and its decomposed product was however, separated in the reaction of RuH₃(CO)(PPh₃)₃ and COS. which finally decomposed to give a yellowish-brown sulphide-bridged complex on mere exposure to air in solution for a longer time. This complex in its IR spectrum exhibits one sharp intense band at 2022 and a broad intense band around 1962 with a shoulder at 1975 cm⁻¹. This clearly shows the presence of two terminal CO groups. The appearance of two bands of lower intensity around 585 and 565 cm⁻¹ indicates the presence of two different νP=S vibrations. The structure (II) is proposed for this complex.

The reaction of two monothioformate ligand probably obeys Eq. (1),

\[
\text{O} \quad \text{O}
\]

‖

\[
\text{LₙRu-S-C-H} + \text{H-C-S-RuLₙ} \rightarrow \text{LₙRu-S-RuLₙ} + 2\text{CO} + \text{H}_₂\text{S} \quad (1)
\]

and the H₂S thus formed, reacts with PPh₃ (obtained by dissociation of the parent complex) to give S = PPh₃ which in turn forms complex with ruthenium. The possibility of reaction between two monothioformato groups in the same complex is ruled out because firstly it will lead to a complex which will not fit the observed IR and analytical data.

The reaction of RuH₃(PPh₃)₃ in the presence of excess PPh₃ does not yield any monothioformato complex but affords a dark grey bis(carbonylato) sulphide bridged complex, which possibly results from the decomposition of bis-monothioformato complex formed initially in situ. In the IR spectrum only one strong broad band at 1955 cm⁻¹ is present besides the characteristic bands of PPh₃. Hence, the proposed two carbonyl groups are virtually
equivalent in their nature, thereby supporting structure (III) for this complex.

However, in absence of added PPh₃, the same RuH₂(PPh₃)₉ yields an intractable black mass which shows the presence of bridged carbonyl group in its IR spectrum.

Reaction of Ru₄(CO)₆(SPPh₃)₂S₂·xCH₂Cl₂ with excess PPh₃ gives S = PPh₃ as one of the reaction products. S = PPh₃ being a weaker ligand compared to PPh₃ is replaced by the latter. The replaced S = PPh₃ has been isolated and characterised to prove its existence in the parent molecule.

References