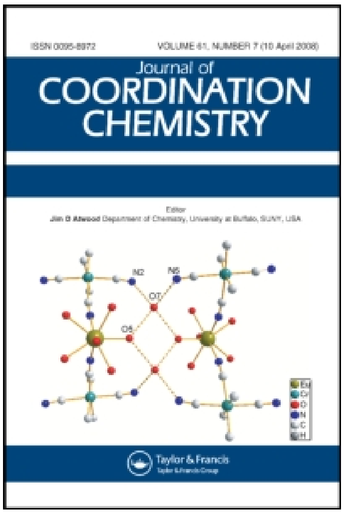

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REACTIONS OF CARBONYLSULPHIDE WITH [$Rh(PPh_3)_3Cl$] AND [$Pt(PPh_3)_3$]

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INTRODUCTION

Activation of small inorganic molecules (H_2, N_2, O_2, CO, NO, CO_2, SO_2, CS_2) by the complexes of transition metal ions like Rh(I), Ir(I), Pt(O) and Ru(II) have gained considerable interest during the last decade.[1–8] Because of the similarity of CO_2 and CS_2 molecules with COS, one would expect COS to form complexes with the transition metal ions analogous to those of CO_2 and CS_2. In addition, COS being susceptible to decomposition into CO and S, could also form carbonyl complexes. Until now, the only reaction of COS that has been successfully carried out is with [$Pt(PPh_3)_3$] which resulted in the formation of [$Pt(COS)(PPh_3)_2$] and [$Pt_2S(CO)(PPh_3)_3$].[8,9] It will, therefore, be interesting to study further the reactions of COS with the complexes of transition metal ions. The results of a preliminary study of such reactions with [$Rh(PPh_3)_3Cl$] and [$Pt(PPh_3)_3$] are reported in this communication.

EXPERIMENTAL

$Rh(PPh_3)_3Cl$ and $Pt(PPh_3)_3$ were prepared according to the methods described in the literature.[10,11]

Reactions of COS with $Pt(PPh_3)_3$

a) To a yellow solution of $Pt(PPh_3)_3$ (0.2 g) in acetone (20 ml), saturated solution of COS in acetone (20 ml) was added and the mixture stirred at room temperature for 20 hr. The resulting solution was concentrated to about 5 ml, at reduced pressure, and methanol (15 ml) was added to it. It was then kept in a refrigerator whereupon light yellow crystals separated out which were filtered, washed with acetone and ether and dried under vacuum (mp 255°d). Anal. Calcd for [$Pt(COS)_2(PPh_3)_2$]: C, 54.35; H, 3.57; S, 7.63; Pt, 23.24. Found: C, 54.42; H, 3.78; S, 7.2; Pt, 23.7.

b) A saturated solution of COS in acetone (20 ml), was added to $Pt(PPh_3)_3$ (0.2 g), and the mixture was refluxed for 10 minutes or stirred for 1 hr at room temperature. A pink compound was obtained which was filtered, washed with acetone and ether, and dried under vacuum. Anal. Calcd for [$Pt(COS)(PPh_3)_2$]: C, 57.0; H, 3.9; S, 4.1; Pt, 25.0. Found: C, 57.23; H, 4.2; S, 4.5; Pt, 25.4.

c) To a boiling solution of $Pt(PPh_3)_3$ (0.2 g) in acetone (25 ml), COS saturated methanol (25 ml) was added, and the solution heated to reflux for 2 hr, and the solution turned yellow. It was concentrated and cooled to give a yellow crystalline compound, which was finally obtained as described above (recrystallized from benzene-methanol mixture, mp 210–12°d). Anal. Calcd for [$Pt_2S(CO)(PPh_3)_3$]: C, 53.4; H, 3.64; S, 2.6; Pt, 31.55. Found: C, 53.6; H, 3.5; S, 2.9; Pt, 30.85.

d) To a solution of $Pt(PPh_3)_3$ (0.3 g) in acetone (50 ml), COS was bubbled for 2 hr, while the solution was refluxed. It was kept overnight at room temperature. The solution was concentrated to about 5 ml under COS atmosphere when a red solution was obtained. It was cooled in a refrigerator to give a greenish-yellow compound, (mp 250°d). Anal. Calcd for [$Pt(COS)_2(PPh_3)_2$]: C, 54.35; H, 3.57; S, 7.63; Pt, 23.24; Found: C, 53.9; H, 3.75; S, 8.1; Pt, 23.0.

Reactions with $Rh(PPh_3)_3Cl$

a) To a suspension of $Rh(PPh_3)_3Cl$ (0.2 g) in a mixture of petroleum ether (bp 40–60°C) (30 ml) and benzene (5 ml), COS was bubbled for 2 hr, and yellow solution was obtained. It was filtered and concentrated to give a yellow compound, which was washed with petroleum ether and dried under vacuum. Anal. Calcd for [$Rh_2Cl_2S(CO)(PPh_3)_3$]: C, 58.77; H, 4.01; Cl, 6.32; S, 2.85. Found: C, 58.7; H, 4.15; Cl, 5.82; S, 3.2.

b) $Rh(PPh_3)_3Cl$ (0.2 g) was dissolved in benzene (25 ml), and COS was bubbled for 3 hr at room temperature. The solution was concentrated to about 5 ml at reduced pressure, when a brown compound separated out. It was filtered off, and from the filtrate, upon cooling in a refrigerator, yellow crystalline compound separated, which was washed with benzene and dried under vacuum (mp 202–5°C). Anal. Calcd for [$RhCl(CO)(PPh_3)_2$]:, C, 63.34; H, 4.34; Cl, 5.14. Found: C, 63.5; H, 4.12; Cl, 4.8.

The carbon and hydrogen analyses in the complexes were carried out by the micro-analytical section of the Indian Institute of Technology, Kanpur. Chloride, sulphur and the metal were estimated using the standard methods.[12] after decomposing the complexes with aqua regia or KOH and KNO_3 mixture. Infrared spectra were recorded with a Perkin Elmer 521, infrared spectrophotometer. NMR spectrum was recorded with a Varian A-60 spectrometer.

RESULTS AND DISCUSSION

A) *Reactions of [$Pt(PPh_3)_3$] with COS*: Baird and Wilkinson[8] have reported the reaction of COS with [$Pt(PPh_3)_3$] with the formation of [$Pt(COS)(PPh_3)_2$] which further rearranges to give [$Pt_2S(CO)(PPh_3)_3$]. Under different set of conditions, a number of different compounds could be formed. Thus, under the conditions described in this communication, a set of four compounds could be isolated. The analytical data of two of the compounds (light-yellow and greenish-yellow in colour) which are not reported in the literature, correspond to the formula [$Pt(COS)_2(PPh_3)_2$] while those of other two compounds to [$Pt(COS)(PPh_3)_2$] and [$Pt_2S(CO)(PPh_3)_3$] reported by Baird and Wilkinson.[8] This has also been confirmed by the mixed melting points and the infrared spectral data of these compounds.

The infrared spectrum of the light yellow [$Pt(COS)_2(PPh_3)_2$], showed two intense and sharp bands at 1700 and 1620 cm^{-1} besides the characteristic bands due to triphenylphosphine. These bands could be due to $\nu_{asy}(CO)$ and $\nu_{sym}(CO)$ respectively of the two COS molecules, linked to platinum in the cis-position. Two more bands at 840 and 860 cm^{-1} of medium to weak intensities were present. These bands have been assigned to $\nu_{asy}(CS)$ and $\nu_{sym}(CS)$ of the coordinated COS molecules in the cis-position. These assignments have been made on the basis of the assignments made by Baird and Wilkinson[8] for the band at 1727 cm^{-1} in the spectrum of their compound [$Pt(COS)(PPh_3)_2$] and the assignments made for the free COS molecule.[13,14] If one assumes the linkage of the COS molecules in [$Pt(COS)_2(PPh_3)_2$] to be in the cis-position, the splitting of the bands due to ν_{CO} and ν_{CS} is expected because of the interaction of two CO or CS groups present in the cis-position. The bands at 1700 cm^{-1} and 1620 cm^{-1} are not due to the coordinated or free solvent (acetone) molecules, which was verified by the nmr spectrum of the compound, where no nmr signal was observed in 7 to 9τ range. The greenish-yellow compound having identical analytical data, may be a different isomer of the light yellow compound. Its infrared spectrum has two intense to medium and sharp bands at 1060 and 975 cm^{-1} besides the bands present in the spectrum of the light-yellow compound. The presence of these bands suggests that possibly one of the two COS molecules in the complex is π-bonded.[7] It is therefore thought that the formula of the complex may be [$Pt(\pi\text{-}COS)(COS)(PPh_3)_2$]. However, this explanation is only tentative.

B) *Reactions of $Rh(PPh_3)_3Cl$ with COS*: The reaction of COS with $Rh(PPh_3)_3Cl$ has been carried out under various experimental conditions, but in no case a complex in which COS molecule is bonded to Rh(I) could be obtained. The only compounds which have been isolated were the carbonyl complexes, [$RhCl(CO)(PPh_3)_2$] and [$Rh_2Cl_2(CO)S(PPh_3)_3$]. The former compound is identical to the trans-[$RhCl(CO)(PPh_3)_2$] already reported in the literature.[15]

The infrared spectrum of [$Rh_2Cl_2(CO)S(PPh_3)_3$] showed all the bands due to triphenylphosphine. Besides, a strong and sharp band appeared at 1980 cm^{-1} assigned to ν_{CO} (terminal) and another sharp band of medium intensity at 580 cm^{-1} assigned to δ_{RhCO}.[16]

It is quite possible that in the reaction, an unstable molecular COS complex was first formed which, under the reaction conditions, decomposed to give either [$RhCl(CO)(PPh_3)_2$] with the precipitation of sulphur or rearranged to give [$Rh_2Cl_2(CO)S(PPh_3)_3$]. The work is in progress to understand the reactions of COS more clearly.

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