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Stable Dimeric Complexes with Sulfur Monoxide Ligand: Formation of $[Ru(SO)X(PPh_3)]_2$ (X = Cl or Br)

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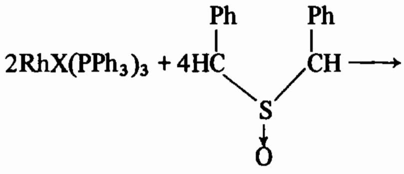
The complexing properties of free sulfur monoxide, because of its very short life (milliseconds) [1] are not yet known in any detail. Schmid and Ritter [2] for the first time have synthesized an iridium complex $[Ir(SO)_2(dppe)_2]Cl$ and recently Laszlo [3] has been able to fix the unstable sulfur monoxide in a cluster $Fe_3(CO)_9(S)(SO)$. Herein we wish to report the syntheses and characterization of sulfur monoxide complexes of rhodium(I).

A solution of stilbene episulfoxide (0.2 g) in CH_2Cl_2 (15 ml) was added to a stirred solution of $RhCl(PPh_3)_3$ (0.1 g) in CH_2Cl_2 (20 ml) at 30 °C under argon atmosphere. The reaction mixture was refluxed for one and a half hours and the resulting solution was concentrated under reduced pressure to about 10 ml. On addition of petroleum ether a light brown complex was precipitated out which was centrifuged out, washed several times with petroleum ether (40–60°) and n-hexane and dried in vacuum. It was recrystallized as a light brown complex $[Rh(SO)Cl(PPh_3)]_2$ (*1*) (m.p. 210 °C) with dichloromethane–petroleum ether (1:3) (yield, 0.029 g, 60%).

Using a similar procedure, a brown complex $[Rh(SO)Br(PPh_3)]_2$ (*2*) was prepared by the reaction of stilbene episulfoxide and $RhBr(PPh_3)_3$. Triphenylphosphine oxide, triphenylphosphine sulphide and stilbene were recovered from the washings.

Total product analyses revealed that in addition to complexes (*1*) and (*2*), the only other major products of the reactions were $OPPh_3$, $SPPh_3$ and $C_6H_5CH=CHC_6H_5$. It is well documented that stilbene episulfoxide in CH_2Cl_2 and other solvents undergoes decomposition to stilbene and SO [4–7], which can react with PPh_3 to give $OPPh_3$ and $SPPh_3$. It is, therefore, presumed that in the reaction medium, after the decomposition of episulfoxide, a part of SO is picked up by rhodium complex and a part combined with PPh_3, which may be present in the reaction medium, as a result of dissociation of the complex. The reactions may, therefore, be represented as:



$$2RhX(PPh_3)_3 + 4\overset{Ph}{\overset{|}{HC}}\diagdown\underset{\underset{O}{\downarrow}}{S}\diagup\overset{Ph}{\overset{|}{CH}} \longrightarrow$$

$$[Rh(SO)X(PPh_3)]_2 + 2OPPh_3 + 2SPPh_3 + \\ + 4PhHC=CHPh$$

where Ph = C_6H_5.

Both complexes (*1*) and (*2*) are air stable, nonelectrolytes in solution, diamagnetic solids, soluble in dichloromethane, chloroform, benzene and acetone and insoluble in ethanol, ether and hexane. The i.r. spectrum of (*1*) showed absorption at 1040 cm^{-1} and 260 cm^{-1} besides the characteristic bands of triphenylphosphine. The bands at 1040 cm^{-1} and 260 cm^{-1} were assigned respectively to ν_{SO} [2, 8] and ν_{Rh-Cl} (Cl *trans* to P or bridged chlorine or both). No band was observed in the range 300 to 400 cm^{-1} which ruled out the possibility of a terminal chlorine atom. The IR spectrum of (*2*) showed an absorption band at 1040 cm^{-1} due to ν_{SO}.

On treatment with excess of triphenylphosphine, the complexes (*1*) and (*2*) decomposed to give $RhX(PPh_3)_3$ (X = Cl, Br), $(C_6H_5)_3P=O$ and $(C_6H_5)_3P=S$, which further substantiated the presence of coordinated SO [2, 8]:

$$[Rh(SO)X(PPh_3)]_2 + 8PPh_3 \longrightarrow 2RhX(PPh_3)_3 + \\ + 2O=PPh_3 + 2S=PPh_3$$

All the products formed during the reactions were characterized by elemental analyses (C, H, S, P, Cl, Br, Rh), infrared spectra, magnetic and conductivity measurements.

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