

Insertion Reactions of Carbonyl Sulfide and Carbon Disulfide with $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$)

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Abstract

Monothioformate and dithioformate complexes of $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) have been synthesized as a result of the insertion reactions of $[\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ with carbonyl sulfide and carbon disulfide. The complexes were characterized by microanalytical, infra red, ^1H NMR, ^{13}C NMR spectral data, molecular weight determination along with other studies.

Introduction

Despite the extensive literature on the insertion reactions of small molecules the number of reports on the reactivity of heteroallenes (CXY) ($\text{X}, \text{Y} = \text{O}, \text{S}, \text{Se}$) towards M-H or M-alkyl bonds and especially towards complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{X}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ [**I**], ($\text{X} = \text{H}, \text{alkyl}$; $\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$) remains small. Though recently some papers concerning the formation of dithioformates or formates as a result of transition metal hydride reactions with CS_2 or CO_2 respectively have appeared [1–10], COS reactions with metal hydrides yielding monothioformates are almost missing, when one would expect a parallel behaviour of COS with CO_2 or CS_2 because of its similarity with them. Previous work indicates only one or two such examples [4, 11]. In addition, COS , being susceptible to easy decomposition into CO and S , may also provide a convenient route for metal carbonyl synthesis under ambient conditions [12]. Considering these, the paucity of COS insertion reactions and the versatility of the reactivity of **I** [13–18], we became interested in COS reactions with the latter complexes. This communication reports the results of such a study. Furthermore, since a reaction of CS_2 with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{PPh}_3)_2]$ has already appeared in the literature [19], we also wish to describe herein similar reactions of CS_2 with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E}, \text{E}' = \text{As}, \text{Sb}$) as an extension to the previous work.

Experimental

All the chemicals used were of Analar grade. Solvents were dried before use. The complexes **I** and dry COS gas were prepared by the literature methods [17, 18, 20]. CS_2 was distilled from P_2O_5 prior to use.

The analytical and spectral data of the products were obtained as described elsewhere [18]. Molecular weights were taken on a Kanuer Vapour Pressure Osmometer. The ^{13}C NMR spectra of the compounds were taken on a JEOL FT-90 spectrophotometer. The results are given in Table I.

(a) Reactions of COS with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$)

In a typical experiment, gaseous COS was allowed to pass through a 30 ml stirred methanolic suspension (*ca.* 0.004 M in hydride) for about 2 h whereby the suspension changed into a greenish brown solution. It was centrifuged. Removal of the solvent from the centrifugate under low pressure yielded a greenish yellow coloured complex which was crystallized from CH_2Cl_2 /petroleum ether. The acetone (dried) solution of the crystallized product was allowed to run down a freshly prepared neutral alumina column and eluted with acetone. The eluent was concentrated under low pressure yielding pure microcrystalline product. It was vacuum dried and analyzed. A few PPh_3 containing products decomposed on the alumina column and therefore the solutions of these compounds were not passed through the column. They were analyzed as such.

(b) Reactions of CS_2 with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{EPh}_3)(\text{E}'\text{Ph}_3)]$ ($\text{E} = \text{Sb}, \text{E}' = \text{P}, \text{As}, \text{Sb}$)

Stirring a 30 ml CS_2 solution of the hydride (*ca.* 0.004 M) for about 8 h at room temperature yielded a dark red solution which was worked out by the same procedure as in (a) to give a red-brown microcrystalline product. All the complexes were purified by neutral alumina column chromatography.

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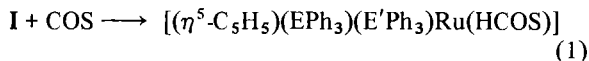
TABLE I. Analytical and Spectral Data of the Complexes

Complex ^a (melting point (°C), colour)	Analyses Found (calc.) (%)			IR data (nujol) (cm ⁻¹)	NMR data		Molecular weight Found (calc.)
	C	H	S		¹ H	¹³ C	
[Ru(OCHS)(PPh ₃) ₂ (η ⁵ -C ₅ H ₅)] (145, GY)	66.7 (67.1)	4.4 (4.8)	5.0 (4.26)	1661(s) ν(C=O) 1095(s) ν(C=S)	11.48(CHS), 1H	82.6, s, C ₅ H ₅ 127.9-137.4, m, Ph 181.8, t, (CHS)	736 (751)
[Ru(OCHS)(AsPh ₃) ₂ (η ⁵ -C ₅ H ₅)] (127-130, YB)	62.2 (60.9)	4.6 (4.3)	4.2 (3.8)	1660(s) ν(C=O) 1100(s) ν(C=S)	11.5(CHS), 1H	82.8, s, C ₅ H ₅ 127.9-137.4, m, Ph 181.64 t, (CHS)	825 (839)
[Ru(OCHS)(SbPh ₃) ₂ (η ⁵ -C ₅ H ₅)] (130, YB)	54.0 (53.1)	3.9 (4.37)	3.4 (4.5)	1658(s) ν(C=O) 1094(s) ν(C=S)	11.5(CHS), 1H	82.6, s, C ₅ H ₅ 127.9-137.4, m, Ph 179.9, t, (CHS)	918 (933)
[Ru(OCHS)(AsPh ₃)(PPh ₃)(η ⁵ -C ₅ H ₅)] (133-135, YB)	63.4 (64.05)	4.5 (4.8)	4.0 (3.5)	1665(s) ν(C=O) 1100(s) ν(C=S)	11.48(CHS), 1H	83.2, s, C ₅ H ₅ 127.9-137.4, m, Ph 180.8, t, (CHS)	800 (795)
[Ru(OCHS)(PPh ₃)(SbPh ₃)(η ⁵ -C ₅ H ₅)] (128, YB)	59.8 (58.9)	4.27 (4.5)	3.8 (4.4)	1660(s) ν(C=O) 1095(s) ν(C=S)	11.54(CHS), 1H	82.6, s, C ₅ H ₅ 127.9-137.4, m, Ph 181.8, t, (CHS)	830 (842)
[Ru(SCHS)(AsPh ₃) ₂ (η ⁵ -C ₅ H ₅)] (115-120, RB)	58.9 (59.5)	4.2 (5.1)	7.4 (8.1)	1020(br) ν(C=S)	11.6(CHS), 1H	83.2, s, C ₅ H ₅ 127.9-137.4, m, Ph 202.02, t, (CHS)	831 (855)
[Ru(SCHS)(SbPh ₃) ₂ (η ⁵ -C ₅ H ₅)] (100-105, RB)	53.0 (54.1)	3.8 (4.9)	6.7 (7.2)	985m(br) ν(C=S)	11.58(CHS), 1H	83.4, s, C ₅ H ₅ 127.9-137.4, m, Ph 202.3, t, (CHS)	932 (949)
[Ru(SCHS)(AsPh ₃)(PPh ₃)(η ⁵ -C ₅ H ₅)] (110-115, RB)	62.1 (62.84)	4.4 (3.7)	7.9 (8.3)	1020(s) ν(C=S)	11.6(CHS), 1H	83.6, s, C ₅ H ₅ 127.9-137.4, m, Ph 20.08, t, (CHS)	792 (811)
[Ru(SCHS)(PPh ₃)(SbPh ₃)(η ⁵ -C ₅ H ₅)] (115-120, RB)	58.9 (60.13)	4.2 (5.05)	7.5 (7.9)	990m(br) ν(C=S)	11.6(CHS), 1H	83.2, s, C ₅ H ₅ 127.9-137.4, m, Ph 202.02, t, (CHS)	843 (858)

^aGY = greenish yellow; YB = yellowish brown; RB = reddish brown; (CHS) = thioformato group.

Results and Discussion

Reactions of COS with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ (E, E' = P, As, Sb) (partially soluble) in CH₃OH produce greenish yellow microcrystalline complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{EPh}_3)(\text{E}'\text{Ph}_3)(\text{HCOS})]$ (eqn. (1))



which were purified by recrystallization from CH₂-Cl₂/petroleum ether followed by column chromatography. The products were characterized by elemental analyses, molecular weights and spectroscopy. The presence of coordinated COS in the form of monothioformate is confirmed by the IR spectra (Fig. 1) in which the characteristic bands arising due to $\nu(\text{C}=\text{S})$ and $\nu(\text{CO})$ of the coordinated $(\text{HCOS})^-$ besides those of the coordinated $(\eta^5\text{-C}_5\text{H}_5)$ and (E or E'Ph₃) are observed at 1100 and 1661 cm⁻¹ respectively. Room temperature ¹H NMR spectra of all the COS reaction complexes (recorded in CDCl₃) are similar. (A representative spectrum is given in Fig. 2.) These spectra support the presence of C₅H₅ ring bonded as $\eta^5\text{-C}_5\text{H}_5$ (δ +4.59, singlet, integrating for 5H) and the hydrogen atom as H-C (δ = 11.48 ppm, singlet, integrating for 1 H). They

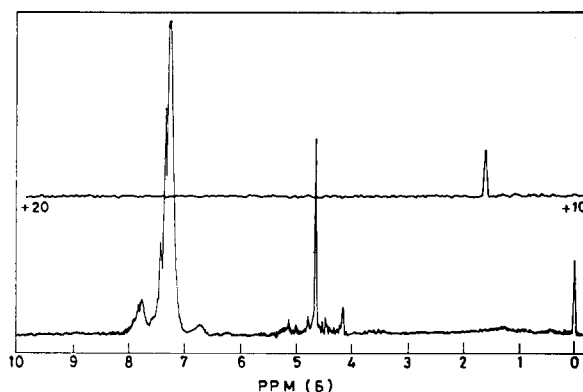


Fig. 2. ¹H NMR spectrum of $[\text{Ru}(\text{HCOS})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$.

also exhibit multiplets associated with PPh₃, AsPh₃ or SbPh₃ protons (*ca.* δ +7–8 ppm, integrating for 30 protons). In the ¹³C NMR spectrum, the thiocarbonyl carbon resonates at δ 181.87 ppm.

These complexes are highly soluble in halogen containing and polar organic solvents, but insoluble or less soluble in hydrogen type solvents.

The reddish brown coloured solids obtained by the reactions of CS₂ with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ (E, E' = P, As, Sb) are formulated as $[\text{Ru}(\text{SCHS})(\eta^5\text{-C}_5\text{H}_5)(\text{E}'\text{Ph}_3)(\text{EPh}_3)]$ on the basis of elemental analysis, spectroscopy and molecular

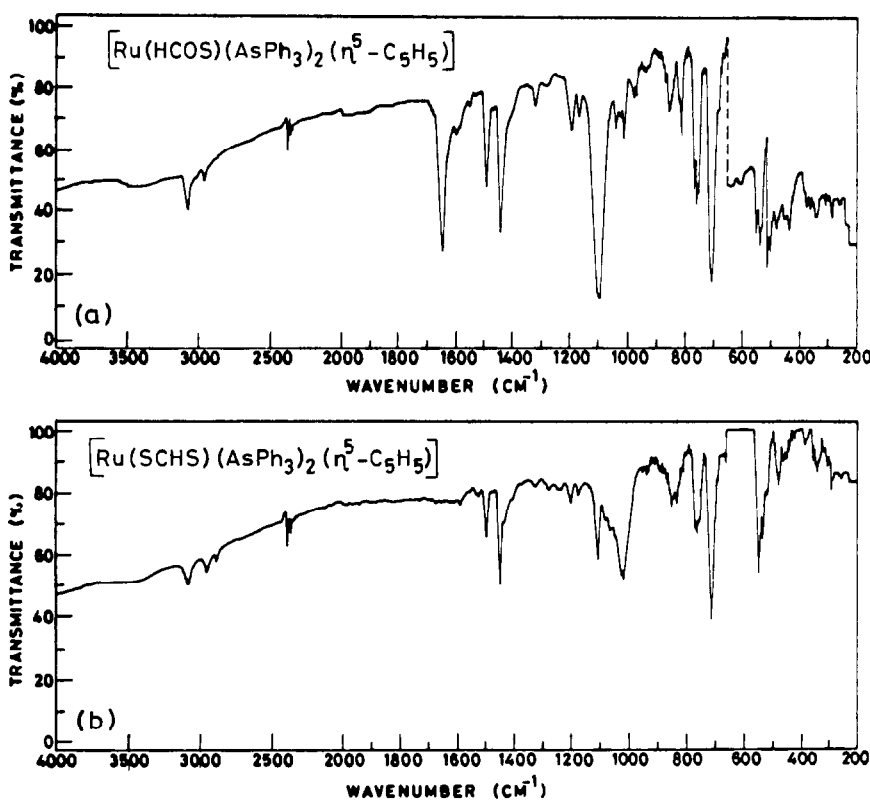
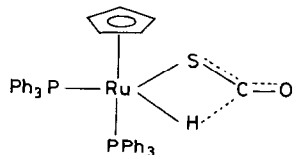


Fig. 1. Infra red spectra of (a) $[\text{Ru}(\text{HCOS})(\text{AsPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$; (b) $[\text{Ru}(\text{SCHS})(\text{AsPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$.

weights. Their IR spectra exhibit, besides the characteristic bands of cyclopentadiene and $E(\text{or } E')\text{Ph}_3$, an intense broad band around 1000 cm^{-1} with a shoulder of medium intensity around 970 cm^{-1} . These have been assigned to $\nu_{\text{asy}}(\text{C}=\text{S})$ and $\nu_{\text{sym}}(\text{C}=\text{S})$ respectively conforming to the earlier data of dithioformate complexes [19]. Their room temperature ^1H NMR spectra (CDCl_3) feature absorbances similar to those observed in the spectra of COS reaction products. In the ^{13}C NMR spectrum, the thiocarbonyl carbon resonates at δ 202.02 ppm. These data imply that the complex contains dithioformate as one of the coordinated ligands. The CS_2 reaction complexes are relatively more stable compared to those of COS reactions which means they can also be further purified chromatographically. (Presumably the stability of these complexes correlates with the basicity of di and monothioformates.) Their solubilities in various solvents are similar to those of the COS reaction products.

The implication of the preceding results is that the structures of these complexes could be explained in terms of (a) bidentacy or (b) monodentacy of di and monothioformates towards one metal ion. Although the spectral data could not unambiguously distinguish between the two alternatives, the interaction of these ligands with the metal ion as bidentate would yield an unlikely twenty electron system with an increased coordination number (five or seven depending upon the Cp behaving as mono or tridentate respectively). Taking into account the instability of a twenty electron system, the monodentacy of these ligands has been assumed in our complexes. Furthermore, the monodentacy of monothioformates requires a choice to be made between sulfur and oxygen as the bonding site. In the absence of X-ray data, the preferential soft sulfur-soft ruthenium(II) interaction is rationalized on the basis of HSAB principles.

In general, the mechanism of insertion reactions of COS or CS_2 into metal hydrogen bonds should presumably be akin to that of other analogous insertion processes [7], in which the reaction occurs via adduct formation, followed by rapid metal-hydrogen bond cleavage with concomitant C-H bond formation.



The present system being coordinatively saturated, formation of a four centred transition state [7] for COS or CS_2 insertion should proceed with initially the loss of one of the EPh_3 molecules, though the possibility of a thermodynamically relatively unstable

activated complex without prior loss of an EPh_3 molecule with the formation of a five coordinated 20 electron system and a concomitant coordination of COS or CS_2 at the metal centre also exists. The lack of kinetic data does not allow us to make a choice between the two alternatives. However in both cases an acid-base interaction of the anionic hydride at the electrophilic carbon centre may occur prior to the formation of a four centred transition state, followed by finally formation of di or monothioformate complexes. An interaction of this type has been observed in a number of cases cited in the literature.

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