

THE CHEMISTRY OF HETERO-ALLENE AND -ALLYLIC DERIVATIVES WITH RHODIUM

I. THE REACTIONS OF RHODIUM(I)-HETERO-ALLYLIC COMPOUNDS WITH HETERO-ALLENES; B. CARBON DISULFIDE *

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Summary

The rhodium(I) complexes $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$, in which $[\text{X}-\text{C}(\text{Z})-\text{Y}]$ represents an uninegative unsaturated heteroallylic bidentate ligand, coordinating via two of the three hetero atoms (X, Y, Z = P, S or N), react at elevated temperature with an excess of the hetero-allene $\text{S}=\text{C}=\text{S}$ to give the rhodium(I)-thiocarbonyl complexes $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS})(\text{PPh}_3)$. In the initial step a first CS_2 molecule is coordinated side-on by one of the $\text{C}=\text{S}$ double bonds. Subsequent reactions can be blocked at this stage by addition of pyridine, resulting in $\text{RhCl}(\eta^2-\text{CS}_2)(\text{PPh}_3)(\text{py})_2$. The formation of the CS complexes occurs in two ways. Either by direct sulfur abstraction from the $\text{Rh}^{\text{I}}(\eta^2-\text{CS}_2)$ complex by PPh_3 or by a dimerisation of two CS_2 molecules and elimination of a CS moiety, resulting in a Rh^{III} -thiocarbonyl-trithiocarbonato complex, immediately followed by demolition of the trithiocarbonato- CS_3^- fragment by PPh_3 to SPPH_3 and CS_2 .

Complexes containing a CS_3^- fragment, but no CS moiety, can also be identified by IR measurements. These products may be formed in a side-reaction upon elimination of CS.

Introduction

In an earlier article [2] we described the reactions of Rh^{I} complexes with hetero-allene molecules $\text{X}'=\text{C}=\text{Y}'$ (X' , $\text{Y}' = \text{S}$, NR , O , CR_2) in general, and with $\text{RN}=\text{C}=\text{S}$ ($\text{X}' = \text{S}$, $\text{Y}' = \text{NR}$) in particular. The mechanism of the disproportiona-

* See also ref. 1.

TABLE I
ANALYTICAL DATA

Compound	colour	Analyses Found (calcd.) (%)						
		C	H	N	S	Cl	P	
I RhCl(η^2 -CS ₂)(PPh ₃)(py) ₂	yellow	54.8 (54.7)	4.0 (4.0)	4.3 (4.4)	10.3 (10.1)	5.7 (5.6)	5.0 (4.8)	
II D RhCl(CS)(PPh ₃) ₂	orange-brown	63.0 (62.9)	4.4 (4.3)		4.4 (4.5)			
III D Rh[SC(S)NEt ₂](CS)(PPh ₃)	orange-brown	52.0 (51.7)	4.8 (4.6)	2.4 (2.5)	17.7 (17.2)			
IV D Rh[PhNC(S)NMe ₂](CS)(PPh ₃)	orange-brown	56.8 (57.1)	4.6 (4.5)	4.7 (4.8)	11.8 (10.9)		4.5 (5.3)	
V D Rh[Ph ₂ PC(S)NPh](CS)(PPh ₃)	orange-brown	62.5 (62.6)	4.6 (4.2)	1.7 (1.9)				
VI D Rh[Ph ₂ P(O)C(S)NPh](CS)(PPh ₃)	yellow-brown	60.3 (61.2)	4.2 (4.1)	2.1 (1.9)				
VII D Rh[Ph ₂ P(S)C(S)NPh](CS)(PPh ₃)	brown	59.1 (59.9)	3.8 (4.0)	1.7 (1.8)				

tion of isothiocyanates leading to Rh^{III} -isocyanide-dithiocarbonimidato complexes was discussed. In this paper the reaction of the Rh^{I} pseudo-allylic chelate complexes, $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$ with an excess of the hetero-allene $\text{S}=\text{C}=\text{S}$ (X' , $\text{Y}' = \text{S}$) is reported, and the products and intermediates formed in this reaction are discussed.

The chemistry of $\text{S}=\text{C}=\text{S}$ with transition metal complexes has been extensively investigated, and reviewed several times [3–6]. Only a few examples of CS_2 complexes, in which the hetero-cumulene is bonded in an η^1 -coordination mode by the lone pair of one of the sulfur atoms, are reported in the literature [7,8], but η^2 -(side-on) coordination by one of the $\text{C}=\text{S}$ double bonds is found more often [7–11].

However, some results are doubtful. Complexes with CS_2 bridges have also been described [20]. Recently, co-dimerisations of CS_2 with alkyne derivatives are reported [29–31]. Under special conditions a transition metal complex may react with CS_2 to give thiocarbonyl (CS) complexes [7,8,10–15]. The mechanism of this reaction is not well understood. Probable reaction-paths in the CS formation from the CS_2 fixation reaction either via a direct reaction with PPh_3 or via a dimerisation process, in which two CS_2 molecules are involved, are discussed and compared with the mechanism of the disproportionation of isothiocyanates, mentioned above.

Experimental

IR spectra were measured on a Perkin-Elmer 283 spectrophotometer ($4000\text{--}200\text{ cm}^{-1}$). $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Varian-XL-1000 FT spectrometer at 40.5 MHz, using the deuterated solvent as internal lock. C, H and N analyses were carried out at the micro-analytical department of this university, and other analyses by Prof. Dipl.-Ing. Dr. H. Malissa and G. Reuter, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany. Analytical data are given in Table 1.

Reactions were carried out in analytical grade solvents under nitrogen.

$\text{RhCl}(\text{PPh}_3)_3$ [16] and $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$ [17,18] were prepared according to literature procedures.

Solutions for IR measurements were prepared in a glove-box from samples taken from the reaction mixtures at appropriate times. No ($\eta^2\text{-CS}_2$) complexes could be isolated, since both the reverse reaction to regenerate the starting materials and subsequent reactions take place very fast.

$\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{py})_2$ (I)

300 mg $\text{RhCl}(\text{PPh}_3)_3$ was dissolved in 20 ml benzene. A small excess of CS_2 was added and after two minutes an excess of pyridine. The yellow solution was diluted with n-hexane. The precipitate was filtered off, washed with small portions of ethanol and diethylether, and dried in vacuo. Yield: 85%.

$\text{RhCl}(\text{CS})(\text{PPh}_3)_2$ (IID)

An excess of oxygen-free CS_2 was added to a solution of 300 mg $\text{RhCl}(\text{PPh}_3)_3$ in 50 ml benzene. After a few minutes the orange colour of the $\eta^2\text{-CS}_2$ appeared. a) With two additional moles PPh_3 , the mixture was refluxed

during one hour. After cooling n-hexane was added. The precipitate was filtered off, washed with ethanol and diethylether, and dried in vacuo. Yield: 60%. b) Without addition of extra PPh_3 , the mixture was refluxed for two hours. The colour became brownish. After cooling and concentration, the complex was isolated by chromatography on silica gel; after elution with n-hexane-dichloromethane, the complex was precipitated by addition of n-hexane. Yield: 30%.

$\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS})(\text{PPh}_3)$ (IIID–VIID)

300 mg $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$ was dissolved in 50 ml benzene or toluene and an excess of CS_2 was added. a) With two extra moles of PPh_3 , the mixtures were heated at about 80°C for two hours. After cooling and addition of n-hexane, the precipitate was filtered off, washed with ethanol and diethylether and dried in vacuo. Yield: IIID–VD 30–40% VID–VIID 20%. b) Without additional PPh_3 the mixtures were heated for several hours (3 h for IIID and IVD, 4 h for VD–VIID) at about 80°C . After cooling and concentration, chromatography on silica gel, elution with n-hexane-dichloromethane, and addition of n-hexane gave the complexes. Yields: IIID 20%, IVD 10%, VD 20%, VID 5%, VIID 5%.

Note: In each case, most of the complex decomposed during the chromatography on silica gel.

Reactions and products

The starting compounds are $\text{RhCl}(\text{PPh}_3)_3$ and complexes of the type $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$, in which $[\text{X}-\text{C}(\text{Z})-\text{Y}]^-$ represents an uninegative ambidentate hetero-allylic ligand. The ligands used in this paper are shown below. The $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$ complexes were reported previously [1,17–18].

In the reaction of these Rh^{I} complexes with an excess of CS_2 in benzene or toluene the initial colour changes rapidly to orange. The IR spectra of the reaction mixtures, measured after five minutes, show new absorptions in the regions 1247–1281s, 1173–1196wm and 595–611m cm^{-1} , given in Table 2. The values of these absorptions indicate the formation of a four-coordinate $\eta^2\text{-CS}_2$ complex (A). These complexes cannot be isolated. Either the starting compound is recovered, or some product formed from it in a subsequent reaction with PPh_3 or CS_2 . The IR values are in agreement with the values of the vibrations in $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PCy}_3)_2$, 1240s, 1186s and 610s cm^{-1} , respectively [11].

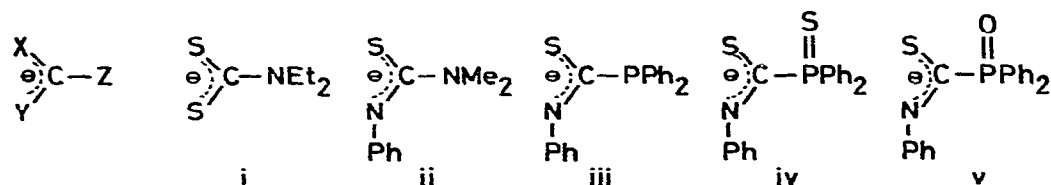


Fig. 1. The ambidentate hetero-allylic chelating ligands $[\text{X}-\text{C}(\text{Z})-\text{Y}]^-$, used in this paper.

TABLE 2

IR ABSORPTIONS OF THE $\text{Rh}(\eta^2\text{-CS}_2)$ COMPLEXES MEASURED IN BENZENE/ CS_2 SOLUTION, FIVE MINUTES AFTER ADDITION OF CS_2

Compound	$\nu(\text{C}=\text{S})$ (cm^{-1})	$2 \nu(\text{M} \begin{smallmatrix} \text{C} \\ \\ \text{S} \end{smallmatrix})^e$ (cm^{-1})	$\nu(\text{M} \begin{smallmatrix} \text{C} \\ \\ \text{S} \end{smallmatrix})$ (cm^{-1})
I $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{py})_2$ ^d	1173s	c	633m
IIA $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)_2$	1251vs	1189w	603m
IIIA $\text{Rh}[\text{SC}(\text{S})\text{NET}_2](\eta^2\text{-CS}_2)(\text{PPh}_3)$	1281 ^a	1180w	595m
IVA $\text{Rh}[\text{PhNC}(\text{S})\text{NMe}_2](\eta^2\text{-CS}_2)(\text{PPh}_3)$	1247s	1173m	604m
VA $\text{Rh}[\text{Ph}_2\text{PC}(\text{S})\text{NPh}](\eta^2\text{-CS}_2)(\text{PPh}_3)$	1254s	1196w	602m
VIA $\text{Rh}[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{S})\text{NPh}](\eta^2\text{-CS}_2)(\text{PPh}_3)$ ^b	1260s	c	611m
VIIA $\text{Rh}[\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPh}](\eta^2\text{-CS}_2)(\text{PPh}_3)$ ^b	1252s	c	c

400–1400 cm^{-1} region. ^a Shoulder of broad absorption. ^b Measured in toluene/ CS_2 . ^c Not observed. ^d Measured in CsI pellets. ^e By Fermi resonance with $\nu(\text{C}=\text{S})$.

In this compound a second CS_2 molecule cannot occupy a coordination site because of steric hindrance caused by the bulky PCy_3 ligands, so that a subsequent reaction is blocked.

However, rapid addition of pyridine to a mixture of $\text{RhCl}(\text{PPh}_3)_3$ and CS_2 in benzene allows isolation of $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{py})_2$ (I). For this product $\nu(\text{C}=\text{S})$ is observed at 1173 cm^{-1} , which is comparable with the values of 1157 cm^{-1} , found for $\text{IrCl}(\text{CO})(\eta^2\text{-CS}_2)(\text{PPh}_3)_2$ and 1152 cm^{-1} for $\text{Pt}(\eta^2\text{-CS}_2)(\text{PPh}_3)_2$ [19]. Van Gaal et al. [11] have concluded that the difference of $\nu(\text{C}=\text{S})$ of an $\eta^2\text{-CS}_2$ moiety between a four coordinate and a three or five coordinate complex amounts to 60–80 cm^{-1} . So we conclude that $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)_2(\text{py})_2$ is a five coordinate Rh species.

The ^{31}P -NMR spectrum of I, measured in CD_2Cl_2 , exhibits a doublet at –27.9 ppm (downfield relative to the reference trimethylphosphate) with a couplings constant $^1J(\text{Rh}-\text{P})$ of 125 Hz, which points to the presence of only one isomer and to an equatorial position for the phosphine ligand. The probable structure of I is given in Fig. 2. The isolation of I is further evidence for the temporary existence of complexes, containing an $\eta^2\text{-CS}_2$ molecule in the reaction between the Rh(I) complexes and an excess of CS_2 .

In contrast, the reaction of a mixture of $\text{RhCl}(\text{PPh}_3)_3$ and $\text{PhN}=\text{C}=\text{S}$ with pyridine gives $\text{RhCl}(\text{PhNC})(\text{PhNCS}_2)(\text{PPh}_3)_2$, and the pyridine has no obvious influence on the course of the reaction.

As mentioned above, the four coordinate intermediate $\text{Rh}^I(\eta^2\text{-CS}_2)$ complexes cannot be isolated. A subsequent reaction, the nature of which depends on the circumstances, occurs. If a large excess of PPh_3 is present or added to

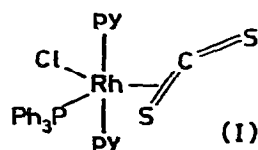


Fig. 2. Probable structure of $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{py})_2$.

TABLE 3
IR ABSORPTIONS OF $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$ AND $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS})(\text{PPh}_3)$ COMPLEXES

Compound	$\nu(\text{C}=\text{S})$ (cm^{-1})	[X-C(Z)-Y] ⁻ chelate absorptions		$\nu(\text{PCS})$ (cm^{-1})	others (cm^{-1})
		$\nu(\text{C}=\text{Z})^a$ (cm^{-1})	$\nu(\text{C}=\text{Z})^a$ (cm^{-1})		
III $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$	1307s				275w
IIID $\text{Rh}[\text{SC}(\text{S})\text{NEt}_2](\text{CS})(\text{PPh}_3)$	b	1488vs ($\nu\text{C}=\text{N}$)			280w
IVD $\text{Rh}[\text{PhNC}(\text{S})\text{NMe}_2](\text{CS})(\text{PPh}_3)$	1284s	1541vs $\nu_{\text{as}}(\text{NCN})$	1111m $\nu_{\text{s}}(\text{NCN})$		
VD $\text{Rh}[\text{Ph}_2\text{PC}(\text{S})\text{NPh}](\text{CS})(\text{PPh}_3)$	1310vs	1546vs ($\nu\text{C}=\text{N}$)		928m	
VII $\text{Rh}[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{S})\text{NPh}](\text{CS})(\text{PPh}_3)$	1311m	1509br ($\nu\text{C}=\text{N}$)		913m	1115vs b
VIIID $\text{Rh}[\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPh}](\text{CS})(\text{PPh}_3)$	1310m	1517br ($\nu\text{C}=\text{N}$)		916m	

Measured in CsI pellets, ^a Z is the exocyclic hetero-atom. ^b Not assigned.

any of the reaction mixtures, direct sulfur abstraction by PPh_3 from the $\eta^2\text{-CS}_2$ fragment takes place, and the excess of CS_2 does not react. The formation of SPPH_3 is confirmed by $^{31}\text{P-NMR}$ spectroscopy. Under these conditions the final metal products D (Fig. 3) are always $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$ and $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS})(\text{PPh}_3)$. These compounds are formed in fairly good yields upon standing at room temperature for about one day or on refluxing for one hour. Treatment of the isolated compound $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PCy}_3)_2$ with extra PCy_3 at room temperature gives the complex $\text{RhCl}(\text{CS})(\text{PCy}_3)_2$ and SPCy_3 [11], which clearly demonstrates that the route to CS formation proceeds via sulfur abstraction from $\eta^2\text{-CS}_2$ by phosphine. In contrast to an earlier report concerning $\text{RhCl}(\text{CS}_2)_2(\text{PPh}_3)_2$ [19], we find that no polar co-solvent is necessary for this sulfur abstraction reaction. The $\text{C}\equiv\text{S}$ absorptions (see Table 3) are observed in the range $1284\text{--}1311\text{ cm}^{-1}$. These values are normal for four-coordinate $\text{Rh}^{\text{I}}(\text{CS})$ complexes [7,10,21,22]. The positions of the $[\text{X}-\text{C}(\text{Z})-\text{Y}]^-$ chelate absorptions do not differ significantly from those of the starting compounds, so that

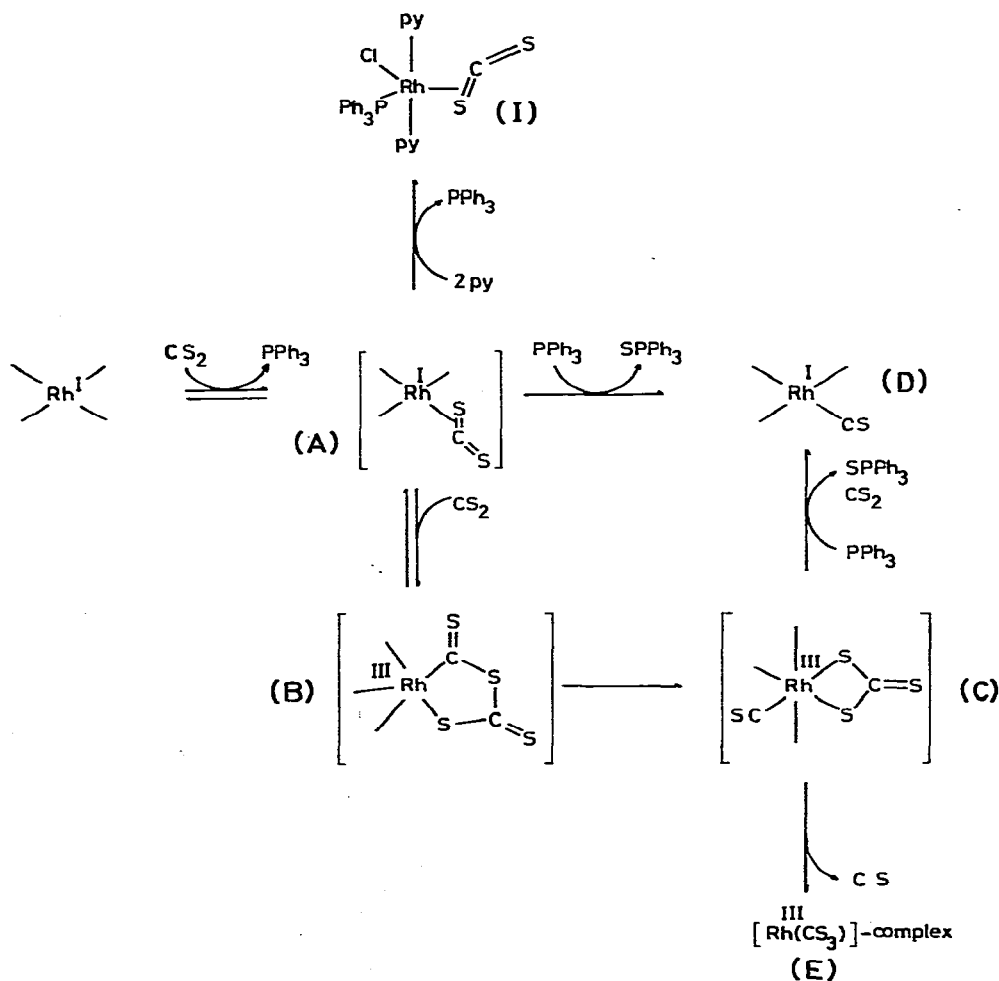


Fig. 3. Survey of reactions between Rh^{I} -phosphine complexes and CS_2 .

the mode of coordination of the ambidentate pseudo-allylic ligands remains unchanged.

If no additional PPh_3 is present, the excess of CS_2 is involved in the reaction. The initial product $\text{RhCl}(\eta^2\text{-CS}_2)(\text{PPh}_3)_2$ (IIA) from the reaction between $\text{RhCl}(\text{PPh}_3)_3$ and CS_2 gives way after fifteen minutes to a second intermediate IIB, which exhibits a strong absorption in the IR spectrum at 1024 cm^{-1} . This absorption persists for not more than one hour, depending on the circumstances such as the CS_2 concentration. A third intermediate IIC must exist, for which we cannot observe any characteristic IR absorption in this solution. After standing for more than 24 hours or after refluxing for several hours, absorptions appear at 1307s , 1043sh , 991s and 841s cm^{-1} . Chromatography on silica gel gives compounds IID and IIE. We tried to isolate IIE from the eluted solutions, but did not succeed, because the IIE decomposes slowly. The IR spectrum of IIE in solution shows peaks at 1043sh , 990s and 841s cm^{-1} , but no absorption in the thiocarbonyl region. These new absorptions are assigned to a trithiocarbonato CS_3^{2-} fragment. The values of C—S vibrations in trithiocarbonato compounds, reported in the literature [24–26,32,33] are comparable with the values observed in this complex.

The reactions of the $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2$ complexes with an excess of CS_2 proceed in a similar way. The initially formed $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\eta^2\text{-CS}_2)(\text{PPh}_3)$ complexes react with another CS_2 molecule. The reaction mixtures from $\text{Rh}[\text{PhNC}(\text{S})\text{NMe}_2](\text{PPh}_3)_2/\text{excess CS}_2$ (IV) and from $\text{Rh}[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{S})\text{NPh}](\text{PPh}_3)_2/\text{excess CS}_2$ (VI) exhibit new absorptions after standing for a longer time or after refluxing for not more than one hour at 1334m , 1040m , 985m , 845m cm^{-1} and at 1358m , 1040m , 990m and 840m cm^{-1} , respectively, (intermediates C). The final solutions (after several hours refluxing) show peaks at 1285s , 1040s , 990s , 850m cm^{-1} and at 1312m , 1040s , 985m and 840m cm^{-1} , respectively. Chromatography of both solutions results in isolation of IVD and VID. In the spectra of the small second fractions, IVE and VIE (compounds which again cannot be isolated) absorptions are observed at 1035s , 980s , 846m cm^{-1} and at 990s and 852m cm^{-1} . Again these absorptions of IVE and VIE are assigned to CS_3^{2-} vibrations. We now attribute the absorptions at 1334 and 1358 cm^{-1} which appear temporarily and then give way to new peaks at 1285 and 1312 cm^{-1} , to intermediate $\text{Rh}^{\text{III}}(\text{CS})$ complexes. The observed values for $\nu(\text{C}\equiv\text{S})$ are in agreement with such an intermediate, since octahedral Rh^{III} complexes show $\nu(\text{C}\equiv\text{S})$ about 50 cm^{-1} higher than square planar Rh^{I} complexes [23]. These C \equiv S vibrations at about 1350 cm^{-1} are present in combination with a set of CS_3^{2-} peaks, which leads us to propose that intermediate C is a six coordinate $\text{Rh}^{\text{III}}(\text{CS})(\text{CS}_3)$ species. The absorptions at 1285 and 1312 cm^{-1} in the spectra of the final solutions demonstrate the formation of the $\text{Rh}^{\text{I}}(\text{CS})$ complexes. The intermediates B are not detected.

No intermediates of types B and C can be observed in the reaction of the other $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{PPh}_3)_2/\text{excess CS}_2$ mixtures. Table 3 gives all relevant IR absorptions of the isolated $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS})(\text{PPh}_3)$ compounds (D), whereas Table 4 shows the important vibrations of the $\text{Rh}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS}_3)_n(\text{PPh}_3)_n$ complexes (E) in solution after the separation of the final solutions on silica gel.

TABLE 4

IR ABSORPTIONS OF THE CS_3^{2-} CONTAINING COMPOUNDS

compound	$\nu(\text{C}_2\text{S}_4)$ (cm^{-1})	$\nu(\text{C}\equiv\text{S})$ (cm^{-1})	$(\text{CS}_3)^{2-}$ absorptions (cm^{-1})		
II B $\text{RhCl}(\text{C}_2\text{S}_4)(\text{PPh}_3)_2$	1024s				
II E $\text{RhCl}(\text{CS}_3)(\text{PPh}_3)_n$			1043(sh)	991s	841s
IV C $\text{Rh}[\text{PhNC}(\text{S})\text{NMe}_2](\text{CS})(\text{CS}_3)(\text{PPh}_3)$		1334m	1040m	985m	845m
IV E $\text{Rh}[\text{PhNC}(\text{S})\text{NMe}_2](\text{CS}_3)(\text{PPh}_3)_m$			1035s	980s	846m
V E $\text{Rh}[\text{Ph}_2\text{PC}(\text{S})\text{NPh}](\text{CS}_3)(\text{PPh}_3)_m$			1040(sh)	983s	842m
VI C $\text{Rh}[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{S})\text{NPh}](\text{CS})(\text{CS}_3)(\text{PPh}_3)$	1358m		a	990m	840m
VI E $\text{Rh}[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{S})\text{NPh}](\text{CS}_3)(\text{PPh}_3)_m$			a	990s	852m

800–1100 cm^{-1} region, measured in C_6H_6 solution. ^a Not assigned.

Discussion

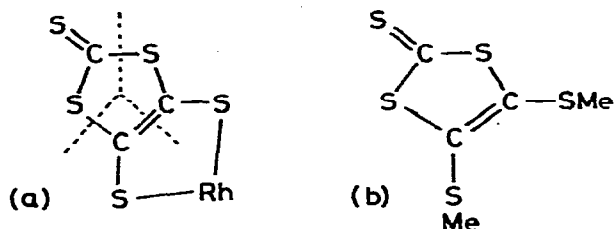
Figure 3 outlines the reaction paths.

The first step, the addition of one CS_2 molecule is definitely reversible. In the formation of B from A, a second CS_2 molecule is coordinated to Rh, probably via an electrophilic attack of its central carbon atom on the endocyclic nucleophilic S atom of the η^2 -coordinated CS_2 to give a dimerised $\text{C}_2\text{S}_4^{2-}$ moiety, coordinated in a bidentate manner to the metal center (B), just as in the dimerisation of isothiocyanates [2]. In the case of $\text{RhCl}(\text{PPh}_3)_2$ - $[\text{SCNC}(\text{O})\text{R}]_2$ this intermediate could be isolated [27,28]. It is plausible that the observed intermediate IIB contains such a C_2S_4 fragment, formed by dimerisation of two CS_2 entities. The absorption at 1024 cm^{-1} was also observed by Baird and Wilkinson [19]. They were able to isolate a complex which analysed for $\text{RhCl}(\text{CS}_2)_2(\text{PPh}_3)_2$, and assumed it to be $\text{RhCl}(\pi\text{-CS}_2)(\sigma\text{-CS}_2)(\text{PPh}_3)_2$. We think that this compound is, in fact, probably $\text{RhCl}(\text{C}_2\text{S}_4)(\text{PPh}_3)_2$. Kubota and Carey have investigated the reaction of $\text{IrCl}(\text{PPh}_3)_3$ with an excess of CS_2 [12]. They postulated compounds containing $\text{Ir}[\text{C}(\text{S})\text{S}-\text{SC}(\text{S})\text{S}]$ and $\text{Ir}[\text{C}(\text{S})\text{S}-\text{S}]$ rings, respectively. On passing CO through a solution of $\text{IrCl}(\text{C}_2\text{S}_5)(\text{PPh}_3)_2$ they have obtained the complex $\text{IrCl}(\text{CO})(\text{C}_2\text{S}_4)(\text{PPh}_3)_2$, the IR spectrum of which shows absorptions at 1042, 990 and 800 cm^{-1} , indicating the formation of trithiocarbonato derivatives.

In the third step a CS moiety is eliminated from the $\text{Rh}[\text{C}(\text{S})\text{SC}(\text{S})\text{S}]$ five membered ring, yielding intermediate C, for which we have evidence in the case of IV and VI. In the disproportionation of isothiocyanates similar species, i.e. $\text{Rh}^{\text{III}}(\text{RNC})(\text{RNCS}_2)$ complexes, are obtained as the final products [2]. Only under vigorous conditions are either RNC or RNCS_2^{2-} removed from these compounds. Also in the case of $\text{Rh}^{\text{III}}(\text{CS})(\text{CS}_3)$ complexes either the CS fragment or the CS_3^{2-} moiety is eliminated. Here, however, the conditions required are considerably milder.

The $\text{C}\equiv\text{S}$ fragment may leave the rhodium to yield the products E, which, however, are unstable and so cannot be isolated. We think that the products E are of the type $\text{Rh}^{\text{III}}\text{Cl}(\text{CS}_3)(\text{PPh}_3)_n$ and $\text{Rh}^{\text{III}}[\text{X}-\text{C}(\text{Z})-\text{Y}](\text{CS}_3)(\text{PPh}_3)_m$, probably with $n = 3$ and $m = 2$. The liberated CS moiety may be involved in a subsequent reaction, e.g. with a $\text{Rh}[\text{C}(\text{S})\text{SC}(\text{S})\text{S}]$ fragment. A new ring system

might be formed by insertion of CS in this metallocycle resulting in a derivative having $(C_3S_5)^{2-}$ coordinated to Rh, as shown below (a). Such a $(C_3S_5)^{2-}$ fragment is formed in the reaction of CS_2 with $Na[Mn(CO)_5]$, and has been identified by methylation to structure (b) [32].



The $(CS_3)^{2-}$ fragment in intermediate C can be destroyed by PPh_3 to yield CS_2 and $SPPH_3$. The presence of $SPPH_3$ is evident from the ^{31}P NMR spectrum of the final solution. Of the complexes, obtained by reaction of CS_2 with Rh^I -phosphine complexes, only the $Rh^I(CS)$ complexes D are indefinitely stable.

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