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HYDROCARBON METAL SULPHIDE COMPLEXES
III*. THE STEREOCHEMISTRY OF SOME RHODIUM DERIVATIVES

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SUMMARY

The preparations of $[RSRh(CO)_2]_2$ ($R=CH_3$, C_6H_5, p-FC_6H_4, C_6F_5) are reported, and their stereochemistry investigated. Rapid cleavage of the thio bridge by triphenylphosphine leads to complexes of the type *cis*-$RSRh(CO)(PPh_3)_2$. The slow isomerisation of these to the *trans*-isomer can be followed spectrometrically.

Continuing interest in this laboratory on the stereochemistry of metal carbonyl sulphur complexes[2] prompted this investigation of sulphur derivatives of the cobalt group of metals.

Several papers[3-6] have been published on the reactions of cobalt carbonyl with thiols and a wide range of products have been described. Due to the uncertainty of the composition of many of these products and the polynuclear nature of others, it was concluded that cobalt would be unsuitable for study. Hieber[7] has briefly mentioned some mercaptides of rhodium carbonyl, and the work described in this paper develops from these complexes.

EXPERIMENTAL

For general experimental comments see Part I[2]. In addition some qualitative IR spectra were obtained on a Perkin–Elmer 237 grating instrument. ^{19}F and ^{1}H NMR spectra were obtained on a Perkin–Elmer R10 instrument. Molecular weights were determined osmometrically; in suitable cases mass-spectrometric values were obtained using an A.E.I. MS-9 instrument.

Bis-μ-(phenylthio)bis(dicarbonylrhodium) (I, $R=C_6H_5$)

$[ClRh(CO)_2]_2$ (0.8 g, 0.002 mole)[8] and thiophenol (0.55 g, 0.002 mole) were stirred together in THF (30 ml) in the presence of excess triethylamine. After 15 min the mixture was evaporated and chromatographed on silica gel. Elution with ether/petrol (1/1) gave (I, $R=C_6H_5$) (0.46 g, 34%) as dark red crystals, m.p. 187° (dec.) after recrystallisation from methylene chloride/pentane.

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* For Part II see ref. 1.

** Abstracted in part from the Ph.D. thesis of R.H., June, 1967.

Bis-μ-[(pentafluorophenyl)thio]bis(dicarbonylrhodium) (*I*, $R = C_6F_5$)

To a stirred suspension of sodium hydride (0.144 g, 0.006 mole) in THF (50 ml), cooled by an ice bath, pentafluorothiophenol (1.2 g, 0.006 mole) was added dropwise; this gave a white suspension of sodium pentafluorothiophenoxide. A solution of $[ClRh(CO)_2]_2$ (1.11 g, 0.003 mole) in THF (20 ml) was added dropwise to this suspension and the mixture was stirred at room temperature for 15 h. The mixture was evaporated and chromatographed on silica gel. Elution with ether/petrol (1/1) gave (I, $R = C_6F_5$) (0.84 g, 64%) as pale orange crystals, m.p. 187° (dec.) after recrystallisation from ether.

TABLE 1

ANALYTICAL DATA

Compound	Analyses: found (calcd.) (%)				
	C	H	O	S	Mol.wt.
(I) C_6H_5	35.92	1.98		11.23	530^a
	(35.85)	(1.88)		(11.96)	(536)
C_6F_5	26.57			8.24	736^a
	(26.84)			(8.96)	(716)
p-FC_6H_4	33.45	1.43		11.09	
	(33.50)	(1.41)		(11.20)	
CH_3	12.48	1.26	15.95	16.15	412^b
	(12.38)	(1.56)	(16.49)	(16.52)	(412)
(II) C_6H_5	67.21	4.21		4.08	707^a
	(67.60)	(4.61)		(4.22)	(764)
C_6F_5	60.42	3.58		3.37	
	(60.47)	(3.54)		(3.74)	

[a] Osmometric mol. wt. in C_6H_6. [b] Mass spectrometric value.

Bis-μ-[(p-fluorophenyl)thio]bis(dicarbonylrhodium) (*I*, $R = p$-FC_6H_4)

A solution of *p*-fluorothiophenol (1.28 g, 0.01 mole) and $[ClRh(CO)_2]_2$ (1.6 g, 0.004 mole) in THF (60 ml) was stirred at room temperature for 1 h. The mixture was filtered, evaporated, and chromatographed on silica gel using petrol. Approximately 2 g of complex (I, $R = p$-FC_6H_4) were obtained as dark red crystals, m.p. 170° (with decomposition commencing ~125°) after recrystallisation from methylene chloride/petrol.

Bis-μ-(methylthio)bis(dicarbonylrhodium) (*I*, $R = CH_3$)

Methanethiol (2 ml) was added to a solution of $[ClRh(CO)_2]_2$ (0.8 g, 0.002 mole) in THF (10 ml) at 0°, and the mixture stirred for 1 h as it attained room temperature. Evaporation of solvent followed by chromatography on "Florisil" using petrol as eluant yielded a red band, from which the methylthio derivative (I, $R = CH_3$) (0.6 g, 73%) was isolated. Recrystallisation from ether/petrol (1/1) produced dark red crystals, m.p. 87.5°. The sample showed a parent ion in the mass spectrometer at *m/e* 412, and the characteristic stepwise loss of 4 CO groups.

(Phenylthio)carbonylbis(triphenylphosphine)rhodium (*II*, $R=C_6H_5$)

A solution of bis-μ-(phenylthio)bis(dicarbonylrhodium) (1.1 g, 0.0022 mole) in THF (25 ml) was added dropwise to a slurry of Ph_3P (1.31 g, 0.005 mole) and the mixture was stirred at room temperature for 15 h. The mixture immediately became yellow, and the progress of the subsequent reaction was followed by IR spectroscopy (see *Discussion*). The product was isolated by chromatography on silica gel of the residue after evaporation. Elution with petrol/ether (1/1) gave a trace of Ph_3P followed by (II, $R=C_6H_5$) (0.5 g, 16%) as yellow crystals, m.p. 240° (dec.) after recrystallisation from ether.

[(Pentafluorophenyl)thio]carbonylbis(triphenylphosphine)rhodium (*II*, $R=C_6F_5$)

(*a*). A solution of (I, $R=C_6F_5$) (0.2 g, 0.00035 mole) in THF (25 ml) was added to a slurry of excess Ph_3P in THF causing an immediate change in colour to yellow. The initial stages of the reaction were followed by IR spectroscopy. After 15 h the mixture was evaporated and chromatographed on silica gel. Elution with ether/petrol (1/1) gave some Ph_3P followed by (II, $R=C_6F_5$) (0.16 g, 54%), isolated as yellow crystals, m.p. 177° after recrystallisation from ether.

(*b*). Pentafluorothiophenol (0.4 g, 0.002 mole) and excess triethylamine were added to a solution of chlorocarbonylbis(triphenylphosphine)rhodium (1.32 g, 0.002 mole) inTHF (25 ml). After 15 h the solution was evaporated and the residue chromatographed on silica gel. Elution with ether/petrol (1/1) gave (II, $R=C_6F_5$) (1.4 g, 87%) identified by comparison (m.p. and IR) with the sample from (*a*).

If excess C_6F_5SH is used in this reaction, the product is contaminated by a brown-red carbonyl-free solid which cannot be separated from (II, $R=C_6F_5$).

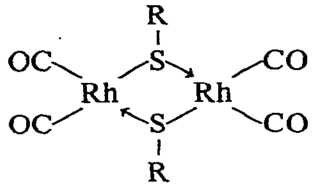
(Methylthio)carbonylbis(triphenylphosphine)rhodium (*II*, $R=CH_3$)

Bis-μ-(methylthio)bis(dicarbonylrhodium) (50 mg, 12 mmoles) in THF (50 ml) was added to a solution of Ph_3P (126 mg, 48 mmoles) in THF (50 ml). The progress of the reaction was followed by IR spectroscopy, and after 1 h the mixture was evaporated. Attempted chromatography of the residue on alumina, silica gel, or "Florisil" caused decomposition. However by extracting the reaction residue repeatedly with cold petrol, evaporating the extracts and chilling the concentrate, bright yellow crystals of (II, $R=CH_3$) were obtained. The brown crystalline residue after extraction did not contain metal carbonyl and was not identified. The complex (II, $R=CH_3$) could not be obtained analytically pure due to instability factors, but several samples each contained P/S in the ratio 2/1. An ^1H NMR spectrum of the crystallised complex in CD_3CN showed a singlet at τ 7.80 (and aromatic proton signals). Infrared spectra of the crystallised complex in CH_3CN, THF, C_6H_6 and CS_2 were identical to those of the final reaction mixture. These spectroscopic results indicated that the final product of the reaction had not changed during isolation (see *Discussion*).

DISCUSSION

A wide variety of bridging mercaptide type complexes has been reported[13]. The possibility of these complexes exhibiting stereoisomerism is of particular interest and isomers have been detected for binuclear mercaptides of Fe[2,9], Cr[10], Mo[11,12] and Ni[10].

Treatment of $[ClRh(CO)_2]_2$ with mercaptide anion (*cf.* ref. 7 where base was omitted) gives complexes $[Rh(CO)_2SR]_2$ (I, R=CH_3, C_6H_5, C_6F_5, *p*-FC_6H_4). By drawing a structural analogy with $[Fe(CO)_3SR]_2$[13], and more especially with $[ClRh(CO)_2]_2$[14], it is probable that the Rh–S ring in (I) is non planar. On this assumption



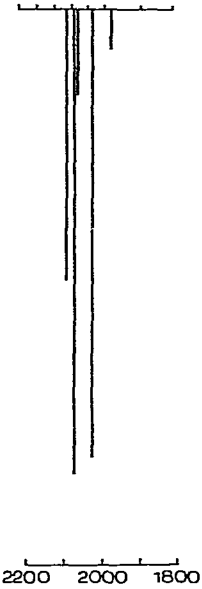
(I)

three isomers can be envisaged for (I) based upon different configurations of the SR group (Ia, Ib and Ic). Using a combination of IR and NMR spectroscopy, some structural assignments can be made.

Infrared spectra

The three deep red complexes (I, R=CH_3, C_6H_5, *p*-FC_6H_4) gave similar spectra for the fundamental metal carbonyl vibrations. This type of spectrum is shown in Fig. 1. The four peaks show the expected shifts due to different R groups, but apart from solvent shifts do not alter significantly in CS_2, THF, CCl_4 and C_6H_{12}. This suggests that the three complexes may have similar gross geometries, and these do not change with solvent.

The geometry of the orange pentafluoro complex (I, R=C_6F_5)* is probably



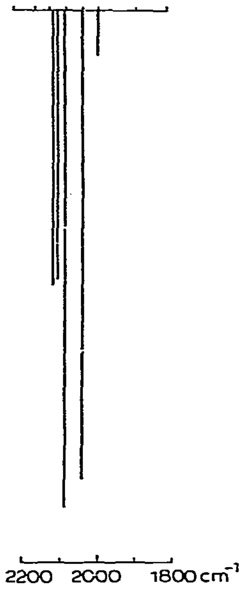


Fig. 1. Metal carbonyl peaks for $[RSRh(CO)_2]_2$ (R=CH_3, C_6H_5, *p*-FC_6H_4).

Fig. 2. Metal carbonyl peaks for $[C_6F_5SRh(CO)_2]_2$.

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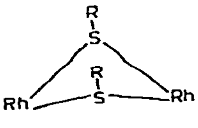
* The preparation of this material has been described very recently[24] but without structural assignment.

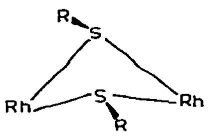
different from that of the other three compounds since the IR carbonyl vibrations of the former exhibit a different pattern (Fig. 2). This pattern is also unaffected by solvent*.

NMR spectra

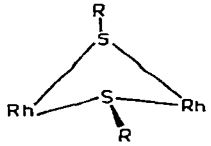
In several solvents the methyl derivative (I, $R=CH_3$) showed a simple ^1H NMR spectrum. The finely resolved 1/2/1 triplet ($J=1.7$ Hz) centred at τ 7.29 is consistent with Rh–H coupling [^{103}Rh (100%): $I=\frac{1}{2}$] through the $Rh_2SC–H$ system. The ^1H NMR spectra of the derivatives (I, $R=C_6H_5$, p-FC_6H_4) could not be analysed unambiguously. However the ^{19}F NMR position of a p-fluoro group is extremely sensitive to its environment. Isomers ($R=p$-FC_6H_4) of geometry (Ia) and (Ib) would be expected to show a single ^{19}F signal, but (Ic) should show two signals.



(Ia)



(Ib)



(Ic)

In fact one signal was obtained at +117.8 ppm from $CFCl_3$ (CH_2Cl_2 solution). Accumulated spectra** (128 scans) revealed additional fine structure in this signal due to ^{19}F–^1H coupling, but the two most intense peaks of the symmetrical multiplet were separated by less than 0.08 ppm. Structure (Ic) would be expected to show a larger difference in chemical shifts for two different fluorine nuclei, and, taken with the IR evidence, this geometry can be discounted. On the basis of the evidence available it is not possible to differentiate between (Ia) and (Ib). However considering the similarity of the IR spectra, and the NMR data, it is clear that the derivatives (I, $R=CH_3$, C_6H_5, p-FC_6H_4) have the same gross geometry.

The ^{19}F NMR spectrum of (I, $R=C_6F_5$) in $CHCl_3$ showed the characteristic three multiplet pattern: δ(o-F) +128.3 ppm; δ(p-F) +152.5 ppm; and δ(m-F) +160.7 ppm relative to $CFCl_3$. The fine structure of each symmetrical multiplet was obtained by accumulating** 500 scans, and showed only one type of C_6F_5 group was present, except in the event of accidental co-incidence of chemical shift of o-, m-, and p-fluorine atoms for each ring. It thus appears unlikely that this C_6F_5 derivative has the asymmetric geometry (Ic). Since the IR spectrum of this material is different from that of the others ($R=CH_3$, etc.), it is tentatively suggested that of the pair of structures (Ia) and (Ib), the C_6F_5 derivative possesses one configuration and the derivatives (I, $R=CH_3$, C_6H_5, p-FC_6H_4) the other configuration. There is no evidence for inversion at sulphur in any of the complexes described herein, but this point is being investigated.

Phosphine cleavage of dimeric rhodium complexes

It was reported[7] that treatment of (I, $R=C_6H_5$) with PPh_3 produced $RSRh(CO)(PPh_3)_2$ (II, $R=C_6H_5$). The structure of this terminal mercaptide complex has

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* Acetonitrile reacts with these compounds (I).

** These ^{19}F spectra were obtained through the courtesy of M. J. Green of Perkin-Elmer Ltd. on an R10 instrument (56.458 MHz), using a CAT because of low sample solubility. Resolution was >0.05 ppm.

been confirmed, and, contrary to an earlier report[15], (II, R = C_2H_5, C_6H_5)[7] appear to have been the first terminal-mercaptide–metal carbonyl complexes reported. For comparison of chemical reactivity of (I, R = C_6F_5) with it's phenyl analogue, the C_6F_5 complex[24] (II, R = C_6F_5) has also been prepared. In an attempt to determine the mechanism of this cleavage [(I)→(II)] the reaction of the methyl analogue has been investigated. Each of the complexes (II) show a single IR fundamental carbonyl frequency (Table 2), the differences in location being appropriate to the group R.

TABLE 2

INFRARED SPECTRA (ABSORPTIONS (cm^{-1}) IN CCl_4)

R	(I)					(II)
C_6H_5[a]	1982	2016	2050[c]	2061	2078	1975
C_6F_5[b]	1995	2025	2073	2087	2090	1980
p-FC_6H_4[a]	1985	2022	2059[c]	2068	2083	
CH_3[a]	1972	2008	2047[c]	2055	2074	1969[d]

[a] See Fig. 1. [b] See Fig. 2. [c] Ill-resolved shoulder. [d] CH_3CN soln.

Additional proof of the structure of (II, R = C_6F_5) follows from its preparation from *trans*-$ClRh(CO)(PPh_3)_2$ and pentafluorothiophenol in triethylamine. Irrespective of their initial stereochemistry, two routes can be visualised for the conversion of (I) to (II). One of these proceeds via a terminal mercaptide intermediate (III) and the other through a bridging mercaptide intermediate (IV) (Fig. 3).

It is assumed that, by analogy to other similar types of bis(triphenylphosphine)-rhodium complexes, the final product has a *trans* configuration.

There are several complexes of the type (III) known[16,17,18] *i.e.* tetracoordinate dicarbonylrhodium complexes. In all cases these complexes exhibit two CO stretching frequencies, one around 2000 cm^{-1} and the other above 2500 cm^{-1}. Complexes of the type (IV) however, are unknown. Due to the fact that there is only one CO ligand attached to the metal in (IV) and that the other three ligands have relatively poorer acceptor properties, there should be a relatively high degree of back-donation from the metal to the CO ligand. This would result in the two CO stretching frequencies expected for (IV) being much lower than those of (III). Hence it should be possible to differentiate between (III) and (IV) by following the progress of the reaction by infrared spectrometry in the metal carbonyl region.

The reaction of (I, R = C_6F_5) with triphenylphosphine in THF was carried out in an infrared solution cell and spectra of the metal carbonyl region were run continuously for 2½ h. The first spectrum showed an absorption at 1995 cm^{-1} with a shoulder at 1980 cm^{-1}. Spectra over the two hours showed the absorption at 1995 cm^{-1} diminishing and the one at 1980 cm^{-1} intensifying. The final spectrum, which remained constant, showed a single sharp absorption at 1980 cm^{-1} corresponding to (II, R = C_6F_5).

The first spectrum run after mixing showed no trace of starting material (I, R = C_6F_5) and indicates that the initial reaction with triphenylphosphine is a very fast one. This is also suggested by the immediate change in colour from orange to yellow. The subsequent spectra indicated that only one intermediate exists for a

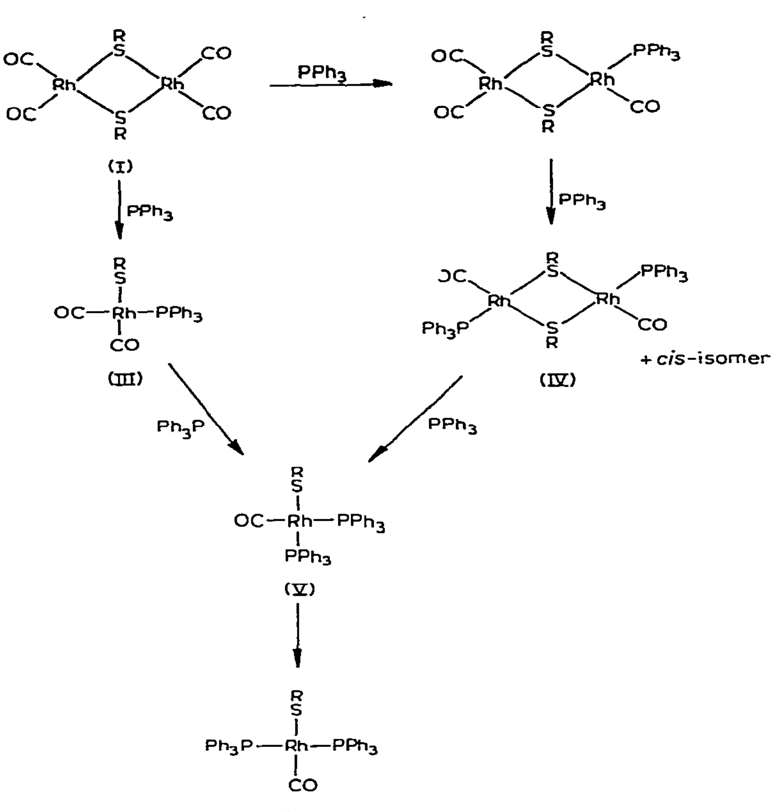

Fig. 3.

detectable length of time and, therefore, only one stage in the conversion of (I) to (II) is observable. The simplicity of the spectra and the proximity of the absorptions suggests a change occurring between two similar species. The spectra do not correspond to those expected for (III) and (IV). Isomerisation of (V) to (II) would account for the spectra observed however, although the source of (V) cannot be stated with certainty since this conversion is common to both routes shown in Fig. 3.

Substitution reactions with bridged binuclear metal carbonyls have been shown[19] to usually break the bridge rather than replace a carbonyl ligand at the metal. This fact, and the larger number of steps required via intermediate (IV) suggests that this route is an unlikely one.

The route through intermediate (III) is the shortest and most attractive. The second phosphine substitution would probably take place *trans* to the SC_6F_5 group since the *trans* effect would weaken the Rh–CO bond *trans* to the thio group. This second substitution would then give *cis*-$Rh(PPh_3)_2(CO)SC_6F_5$.

There are a large number of complexes of the type $ML_2(CO)X$ known[20,21,22]. With a single exception[23], only one isomer of these complexes has been isolated and, on the basis of dipole moment measurements[21], the *trans* configuration has been assigned to all of them. Recently, however, it has been reported[23] that $Rh(PPh_3)_2(CO)Cl$ can exist as a mixture of *cis* and *trans* isomers with the *cis* isomer having a higher CO stretching frequency (1978 cm^{-1}) than the *trans* isomer (1965 cm^{-1}).

On the basis of this evidence, we believe we are following only the last transformation in the reaction (I, R$=C_6F_5$) with triphenylphosphine. This is the slow isomerisation of *cis*-$Rh(PPh_3)_2(CO)SC_6F_5$ to *trans*-$Rh(PPh_3)_2(CO)SC_6F_5$. Similar behaviour was observed with the phenyl complex (I, R$=C_6H_5$) and with the methyl complex (I, R$=CH_3$), although acetonitrile proved to be a more convenient solvent for the reaction of the latter.

As an additional probe into the mechanism of the transformation of (I) to (II), the reaction between (I, R$=CH_3$) and Ph_3P in CD_3CN was followed by ^1H NMR spectroscopy, parallel to the IR monitoring. With a Rh/P ratio of 2/1, methyl signals due to (I) (τ 7.29, triplet) and (II) (τ 7.81, singlet*) were visible as well as a diffuse multiplet (two doublets?) centred at τ 8.62. The latter multiplet decreased in intensity with time, as the singlet at τ 7.81 increased. Similar behaviour was observed at intermediate ratios Rh/P up to 1/2, when immediately upon mixing (I) and Ph_3P, only the peaks at τ 8.62 and 7.81 were observed. The final reaction product showed only the singlet at τ 7.81. These observations are consistent with the evidence from IR spectroscopy that the observable transformation is (V) to (II).

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* Width of peak at half height $\simeq$1.8 Hz.