Co-ordination Chemistry of Sulphines. Part 5.[1] σ-S and η^3-SCS Co-ordination of Sulphines to Rhodium(I). Fluxional Behaviour of [$Rh^ICl(PR_3)$(XYCSO)] (R = alkyl; X, Y = aryl, *S*-aryl, *S*-alkyl, or Cl) Complexes and Influence of Sulphine Geometry on the Formation of [$Rh^ICl(PR_3)_2$(XYCSO)]

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Sulphines react with [{Rh^ICl(cyclo-C_8H_{14})$_2$}$_2$] and PR_3 (R = C_6H_{11} or Pr^i) to afford complexes of the type [$Rh^ICl(PR_3)_n$(sulphine)] (*n* = 1 or 2), in which the number of phosphines depends on the nature of the sulphine side bonds. If no reactive (C–S,C–Cl) side bonds are present, the sulphine co-ordinates *via* σ-S to Rh^I with two phosphines in *trans* positions. If one or two C–S side bonds are present the sulphine co-ordinates η^3-SCS to a rhodium(I) centre, which is bonded to only one phosphine. None of these complexes undergoes a C–S oxidative-addition reaction. For the η^3-SCS co-ordinated complexes [$Rh^ICl(PR_3)$\{(*E*)-(MeS)(*p*-MeC_6H_4)CSO\}] and [$Rh^ICl(PR_3)$\{(*E*)-(R'S)$_2$CSO\}] (R = C_6H_{11} or Pr^i, R' = C_6H_4Me-*p* or Ph) a fluxional process is found (^{31}P and ^1H n.m.r.), which can be described either as an (*E*)–(*Z*) isomerization of the MeS, *p*-MeC_6H_4S, or PhS group of the co-ordinated side bonds or as an intramolecular PR_3–Cl interchange. For the corresponding (*Z*) stereoisomers this process could not be detected. The complex [Rh^ICl\{$P(C_6H_{11})_3$\}\{(*E*)-(MeS)(*p*-MeC_6H_4)CSO\}],(*E*)–(2b), and $P(C_6H_{11})_3$ form an equilibrium mixture with *trans*-[Rh^ICl\{$P(C_6H_{11})_3$\}$_2$\{(*E*)-(MeS)(*p*-MeC_6H_4)CSO\}],(*E*)-(4b), in which the sulphine is σ-S co-ordinated. On the other hand, the corresponding (*Z*) stereoisomer, (*Z*)-(2b), is in equilibrium with $P(C_6H_{11})_3$ and *cis*-[Rh^ICl\{$P(C_6H_{11})_3$\}$_2$\{(*Z*)-(MeS)(*p*-MeC_6H_4)CSO\}],(*Z*)-(6b), a five-co-ordinate rhodium(I) complex with an η^3-SCS co-ordinated sulphine. This difference between the (*E*) and (*Z*) stereoisomers can be understood in terms of the geometric arrangement of the pseudo-allylic co-ordination.

SULPHINES, XYC=S=O (X, Y = aryl, *S*-aryl, *S*-alkyl, or Cl), co-ordinate in an η^2-CS mode to $Pt^0(PR_3)_2$ with retention of configuration.[1,2] The structure of one representative, *i.e.* [$Pt^0(PPh_3)_2(C_{12}H_8CSO)$]·$\frac{1}{2}C_6H_6$ ($C_{12}H_8CSO$ = fluorene-9-ylidenesulphine), has been established by an *X*-ray crystal-structure analysis.[3] In solution, such sulphine complexes containing a C–S side bond undergo intramolecular C–S oxidative addition to $Pt^0(PR_3)_2$ if R = Ph but are stable if R = C_6H_{11}.[1,3-6] These reactions are accompanied by (*E*)–(*Z*) isomerization of the sulphine skeleton.[1,3-6] The thermodynamic stability of the η^2-CS co-ordination complexes with respect to their oxidative-addition products depends on the sulphine configuration. They are unstable when a C–S side bond is situated *syn* to the S=O bond, whereas in the *anti* configuration their thermodynamic stability is similar to that of the oxidative-addition products,[3-6] for which the structure of one representative, *i.e. cis*-(*E*)-[Pt^{II}(PhS)(PhSCSO)$(PPh_3)_2$]·C_6H_6 has been established by an *X*-ray crystal-structure analysis.[4,5]

On changing the co-ligands in the η^2-CS co-ordination compounds from PPh_3 to the bulkier $P(C_6H_{11})_3$, the barrier to intramolecular C–S oxidative addition is increased to such an extent that this reaction ceases to occur and only intramolecular (*E*)–(*Z*) isomerization of the sulphine skeleton is detected.[1] An overall mechanism has been proposed on the basis of which the intramolecular C–S oxidative addition and reductive coupling, and the intramolecular (*E*)–(*Z*) isomerization of both the η^2-CS co-ordination compounds and the Pt-substituted sulphines, could be explained.[1] A key intermediate in these reactions is a bis(phosphine)platinum species with an η^3-SCS co-ordinated sulphine molecule.

In order to test the validity of this mechanism for other metals, we have studied the reactivity of sulphines towards Rh^I, Ir^I, and Pd^0. Rhodium(I) complexes undergo oxidative-addition reactions with a variety of bonds, such as N–H,[7] C–S,[8,9] C–N,[8,9] C–Cl,[10] and S–S.[11] Furthermore, rhodium(I) centres have proved to be good sites for complexation of heterocumulenes, such as X=C=Y (X, Y = *N*-aryl, *N*-alkyl, S, or Cl) [12] and aryl–N=S=O.[13] It is shown that rhodium(I)–sulphine chemistry is surprisingly different from that found for platinum, as evidenced by the η^3-SCS co-ordination of R'S–C(X)=S=O (X = R' or SR'; R' = *p*-MeC_6H_4 or Ph) to $Rh^ICl(PR_3)$ and the absence of oxidative-addition reactions.

EXPERIMENTAL

Apparatus.—Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer, ^1H n.m.r. spectra on Varian-T60A, -HA100, and Bruker-WM250 instruments, and ^{31}P-\{^1H\} n.m.r. spectra on Varian-XL100 and Bruker-WM250 spectrometers. Elemental analyses were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht. Molecular weights were determined with a Hewlett–Packard (model 320B) vapour-pressure osmometer.

Preparation of the Compounds.—The sulphines, $C_{12}H_8C$=S=O (1a),[14] (*E*)- and (*Z*)-(MeS)(*p*-MeC_6H_4)C=S=O (*E*)- and (*Z*)-(1b), (*p*-$MeC_6H_4S)_2$C=S=O (1c), and $(PhS)_2$C=S=O (1c'),[15] and the starting complex [{$Rh^ICl(C_8H_{14})_2$}$_2$] (C_8H_{14} = cyclo-octene) [16] were prepared according to literature procedures.

The σ-S complexes *trans*-[$Rh^ICl(PR_3)_2(C_{12}H_8CSO)$], (4a) and (5a), and the η^3-SCS complexes [$Rh^ICl(PR_3)$\{(R'S)-(X)CSO\}], (*E*)- and (*Z*)-(2b), -(3b), -(2c), -(2c'), and -(3c) (R = C_6H_{11} or Pr^i; R' = *p*-MeC_6H_4 or Ph; X = R' or R'S), were prepared according to the following general procedure.

A mixture of $[\{Rh^{I}Cl(C_8H_{14})_2\}_2]$ (0.5 mmol) and PR_3 (2.0 mmol; R = C_6H_{11} or Pr^i) was stirred in n-pentane (*ca.* 15 cm^3) under a nitrogen atmosphere for *ca.* 30 min. In the case of R = C_6H_{11}, a lilac precipitate was formed, probably $[Rh^{I}Cl\{P(C_6H_{11})_3\}_2]$,[12] while for R = Pr^i a solution was obtained containing very small amounts of solid, which were removed by filtration. An oxygen-free solution of either one of the sulphines (1a), (*E*)- or (*Z*)-(1b), (1c), or (1c') (1.0 mmol) in toluene (*ca.* 2 cm^3) was then added to either the suspension (R = C_6H_{11}) or the clear dark red solution (R = Pr^i) of the reaction mixture. The rhodium–sulphine complexes slowly precipitated; they are either brown in the case of *trans*-$[Rh^{I}Cl(PR_3)_2(C_{12}H_8CSO)]$ or orange to red in the case of $[Rh^{I}Cl(PR_3)\{(R'S)(X)CSO\}]$. For analytical data see Table 1. The solid complexes are stable in air and decompose only very slowly in solution, when exposed to air.

TABLE 1

Analytical data of $[Rh^{I}Cl(PR_3)_n(XYCSO)]$

	Compound	Analysis [a]/% C	H	P	S	Cl	M [a]
(4a)	*trans*-$[Rh^{I}Cl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)]$	63.9	8.40	6.00	3.40	4.10	823 [b]
		(64.55)	(8.20)	(6.80)	(3.50)	(3.90)	(912)
(5a)	*trans*-$[Rh^{I}Cl(PPr^i_3)_2(C_{12}H_8CSO)]$	50.6	6.70	9.10	4.60	5.20	656 [b]
		(55.55)	(7.55)	(9.25)	(4.80)	(5.15)	(671)
(*E*)-(2b)	$[Rh^{I}Cl\{P(C_6H_{11})_3\}\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$	53.0	7.40	5.10	8.30	5.20	653 [b,c]
		(52.65)	(7.05)	(5.05)	(10.4)	(5.60)	(617)
(*Z*)-(2b)	$[Rh^{I}Cl\{P(C_6H_{11})_3\}\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$	53.2	7.40	4.80	8.40	5.10	653 [b,c]
		(52.65)	(7.05)	(5.05)	(10.4)	(5.60)	(617)
(*E*)-(3b)	$[Rh^{I}Cl(PPr^i_3)\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$	44.3	6.50	6.20	12.1	6.80	481 [b,c]
		(43.6)	(6.30)	(6.25)	(12.95)	(6.95)	(497)
(*Z*)-(3b)	$[Rh^{I}Cl(PPr^i_3)\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$	43.6	6.50	6.10	11.8	6.90	481 [b,c]
		(43.6)	(6.30)	(6.25)	(12.95)	(6.95)	(497)
(2c)	$[Rh^{I}Cl\{P(C_6H_{11})_3\}\{(p\text{-}MeC_6H_4S)_2CSO\}]$ [d]	55.1	6.80	4.30	12.5	4.60	712 [b]
		(54.7)	(6.55)	(4.30)	(13.3)	(4.75)	(725)
(3c)	$[Rh^{I}Cl(PPr^i_3)\{(p\text{-}MeC_6H_4S)_2CSO\}]$ [d]	46.9	6.10	5.80	14.9	6.10	649 [b]
		(47.7)	(5.85)	(5.15)	(15.9)	(5.70)	(605)
(2c')	$[Rh^{I}Cl\{P(C_6H_{11})_3\}\{(PhS)_2CSO\}]$ [d]	54.4	6.40	4.50	12.8	4.70	658 [e]
		(53.45)	(6.25)	(4.45)	(13.8)	(4.95)	(697)

[a] Calculated values are given in parentheses. [b] By osmometry in $CHCl_3$. [c] Measured for a mixture of (*E*) and (*Z*) stereoisomers. [d] Mixture of (*E*) and (*Z*) stereoisomers. [e] By osmometry in C_6H_6.

RESULTS

Synthesis and Structure of σ-S *Co-ordinated Sulphine Complexes trans*-$[Rh^{I}Cl(PR_3)_2(C_{12}H_8CSO)]$.—The reaction of $[\{Rh^{I}Cl(C_8H_{14})_2\}_2]$ with PR_3 (R = C_6H_{11} or Pr^i) and $C_{12}H_8C{=}S{=}O$ (1a) in a 1 : 4 : 2 molar ratio yielded *trans*-$[Rh^{I}Cl(PR_3)_2(C_{12}H_8CSO)]$ (4a; R = C_6H_{11}) and (5a; R = Pr^i). The structure of these rhodium complexes has been elucidated by i.r. and n.m.r. spectroscopy (see Table 2). The three ν(CSO) absorptions in the i.r. spectrum of (4a), which are very similar to those of the free sulphine (1a),[2] indicate that in the solid the sulphine is not co-ordinated *via* the π bonds of the C=S=O moiety. The same absorptions were found for (5a), but in that case a ν(CSO) absorption was also present at 1 058 cm^{-1}. The ^1H n.m.r. spectra showed both for (4a) and (5a) one *ortho* proton at *ca.* 10.3 p.p.m. and one at *ca.* 8.6 p.p.m. This indicates that the sulphine ligand is σ-S co-ordinated, because in this molecular configuration one *ortho* proton resides above the rhodium co-ordination plane and close to the metal in the deshielding zone.[17–20] The other *ortho* proton (8.6 p.p.m.) is situated *syn* to the S=O bond. In the case of the free ligand (1a) this proton is found at 8.55 p.p.m.[2]

The equivalence of the P atoms and the ^1J(Rh–P) value of *ca.* 112 Hz found in the ^{31}P n.m.r. spectra of (4a) and (5a) indicate that these atoms are in *trans* positions. The ^1J(Rh–P) of *trans*-$[Rh^{I}Cl(PR_3)_2(R'NSO)]$ (R' = aryl) have similar values of *ca.* 109 Hz.[13] The ^1H n.m.r. spectra of (5a) showed that the Me groups within each PPr^i_3 group have differing chemical shifts [δ(H) = 1.34 and 1.20 p.p.m., each with ^3J(P–H) = ^5J(P–H) = ^3J(H–H) = 7.7 Hz] as a result of the dissymmetry at the Rh centre. The combined spectroscopic data indicated that the sulphines in (4a) and (5a) are σ-S co-ordinated (see Figure 1). Only for *trans*-$[Rh^{I}Cl(PPr^i_3)_2(C_{12}H_8CSO)]$ may the observation of one ν(CSO) absorption at 1 058 cm^{-1} suggest that in the solid state an isomer, containing an η^2-CS sulphine, is present.

For *trans*-$[Rh^{I}Cl(PR_3)_2(R'NSO)]$, an equilibrium between σ-S and η^2-NS co-ordination has been found in solution.[13] The absence of η^2-CS isomers of (4a) and (5a) in $CDCl_3$ is most probably due to the steric hindrance between the neighbouring bulky PR_3 (R = C_6H_{11} or Pr^i) ligands and the $C_{12}H_8$ group. In the case of σ-S co-ordination, steric interaction of this planar $C_{12}H_8$ with the *cis* ligands is minimal.

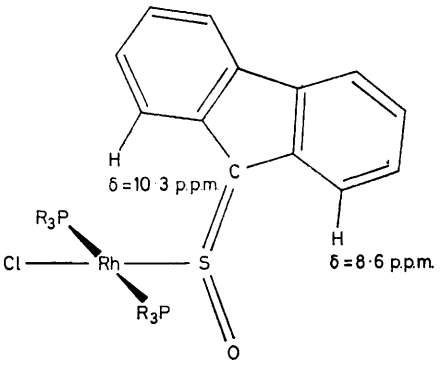


FIGURE 1 Structure of *trans*-$[Rh^{I}Cl(PR_3)_2(C_{12}H_8CSO)]$ (R = C_6H_{11} or Pr^i) (4a) and (5a)

Synthesis and Structures of the η^3-SCS *Co-ordinated Sulphine Complexes* $[Rh^{I}Cl(PR_3)\{(R'S)(X)CSO\}]$.—(*a*) *Rhodium*(I) *complexes of* (*E*)- *and* (*Z*)-(MeS)(*p*-MeC_6H_4)C=S=O. The reactions of $[\{Rh^{I}Cl(C_8H_{14})_2\}_2]$ and PR_3 (R = C_6H_{11} or

TABLE 2

Spectroscopic data of [RhICl(PR$_3$)$_n$(XYCSO)]

Compound	Isomer	Infrared [a]/cm^{-1} ν(CSO)	Infrared [a]/cm^{-1} ν(Rh–Cl)	^{31}P N.m.r. in CDCl$_3$ ^1J(Rh–P)/Hz	^{31}P N.m.r. in CDCl$_3$ δ(P) [d]/p.p.m.	^{31}P N.m.r. in CDCl$_3$ θ_c/°C e	^{31}P N.m.r. in CDCl$_3$ θ_c/°C f	^{31}P N.m.r. in other solvents [b] ^1J(Rh–P)/Hz	δ(P) [d]/p.p.m.	θ_c/°C e	Solvent	^{1}H N.m.r. in CDCl$_3$ [c] δ(H$_o$) [g,h]/p.p.m.	δ(H$_m$) [g,i]/p.p.m.	^3J(H$_o$–H$_m$) [h,i]/Hz	δ(H$_s$) [g,j]/p.p.m.	^3J(Rh–H$_s$) [j]/Hz	δ(H$_t$) [g,k]/p.p.m.	θ_c [e]/°C
[RhICl{P(C$_6$H$_{11}$)$_3$}$_2$(C$_{12}$H$_8$CSO)]	(4a)	1 119, 1 087, 1 018	*l*	113	28.9	25						10.28 [m] 8.63 [n]	7.68	8.2				25
[RhICl(PPri$_3$)$_2$(C$_{12}$H$_8$CSO)]	(5a)	1 118, 1 091, 1 058, 1 022	*l*	112	37.7	25						10.29 [m] 8.58 [n]	7.67	7.7				25
[RhICl{P(C$_6$H$_{11}$)$_3$}{(MeS)(R′)CSO}] [o]	(*E*)-(2b)	1 056	*l*	178	49.9	49	−4 [p] −12 [q]	181	54.9	53.5	4 [p] −2 [q]	7.69	7.21	8.5	2.27	4.0	2.30	25
	(*E*$_1$)-(2b)			178	49.7	−22		182	54.9	−46.5	C$_7$D$_8$							
	(*E*$_2$)-(2b)			171	49.5	−22		174	54.2	−46.5	C$_7$D$_8$							
	(*Z*)-(2b)	1 045	307	185	50.8	28						7.61	7.16	8.0	2.42	3.5	2.30	25
[RhICl(PPri$_3$){(MeS)(R′)CSO}] [o]	(*E*)-(3b)	1 064, 1 053	*l*	179	60.2	22	3 [p] 3 [q]					7.71	7.24	8.5	2.28	3.9	2.33	25
	(*E*$_1$)-(3b)			178	58.7	−52.5						7.61	7.20	7.6	2.31	4.1	2.34	−20
	(*E*$_2$)-(3b)			172	60.1	−52.5						7.83	7.25	7.3	2.15	4.1	2.23	−20
	(*Z*)-(3b)	1 036	301, 288	187	61.0	22						7.60	7.13	7.7	2.40	3.8	2.32	21
[RhICl{P(C$_6$H$_{11}$)$_3$}{(R′S)$_2$CSO}] [o]	(*E*)-(2c)	1 074, 1 056	297	174	53.7	45.5	10 [p] 16 [q]	176	58.5	45	23 [p] (19.5) [p] 27 [q] (12.5) [q]	*l*	*l*	*l*			*l*	25
								(174)	(53.8)	(35.5)	C$_7$D$_8$ (CD$_2$Cl$_2$)							
	(*E*$_1$)-(2c)			170	53.9	35.5		177	58.4	−37.5	C$_7$D$_8$							
								(174)	(54.0)	(−12)	(CD$_2$Cl$_2$)							
	(*E*$_2$)-(2c)			173	53.8	−35.5		173	59.0	−37.5	C$_7$D$_8$							
								(171)	(53.8)	(−12)	(CD$_2$Cl$_2$)							
	(*Z*)-(2c)			183	53.9	45.5		187	58.5	45	C$_7$D$_8$	*l*					2.40 2.32	25
								(183)	(54.6)	(35.5)	(CD$_2$Cl$_2$)							
[RhICl(PPri$_3$){(R′S)$_2$CSO}] [o]	(*E*)-(3c)	1 051	294	176	64.8	49	15 [p] 23 [q]					*l*	*l*					
	(*E*$_1$)-(3c)			175	64.5	−26												
	(*E*$_2$)-(3c)			162	64.7	−26												
	(*Z*)-(3c)			185	65.7	49						*l*	*l*				2.40 2.32	25
[RhICl{P(C$_6$H$_{11}$)$_3$}{(PhS)$_2$CSO}]	(*E*)-(2c′)	1 055	303					174	54.3	37	21 [p] 11 [q]	CD$_2$Cl$_2$						
	(*E*$_1$)-(2c′)							174	54.5	−20	CD$_2$Cl$_2$							
	(*E*$_2$)-(2c′)							171	54.3	−20	CD$_2$Cl$_2$							
	(*Z*)-(2c′)							183	55.2	37	CD$_2$Cl$_2$							

[a] KBr mull. [b] Measured at 40.5 MHz. [c] Measured at 250 MHz. [d] Relative to H_3PO_4 (85%); downfield is positive. [e] Probe temperature. [f] Coalescence temperature. [g] Relative to $SiMe_4$. [h] H_o = *ortho* protons [i] H_m = *meta* protons. [j] H_s = protons of MeS. [k] H_t = protons of Me group of *p*-MeC_6H_4. [l] Could not be assigned. [m] *ortho* proton *syn* to RhI. [n] *ortho* proton *syn* to S=O. [o] R′ = *p*-MeC_6H_4. [p] For low-field signal of rhodium doublet. [q] For high-field signal of rhodium doublet.

Pr^i) with either pure (*E*)- or pure (*Z*)-(MeS)(*p*-MeC$_6$H$_4$)C=S=O, (*E*)- and (*Z*)-(1b), are summarized in equations (1) and (2). Retention of the sulphine configuration (*E* or *Z*) was found in all products. Elemental analyses pointed to the presence of one phosphine per rhodium atom, while molecular-weight determinations showed these complexes to be monomeric in $CHCl_3$ (see Experimental section). The structures of these complexes could be derived from ^{31}P, ^1H n.m.r., and i.r. data, elemental analyses, and molecular-weight determinations.

$$\tfrac{1}{2}[\{Rh^ICl(C_8H_{14})_2\}_2] + PR_3 + \underset{(E)\text{-(1b)}}{(E)\text{-(MeS)(}p\text{-MeC}_6H_4)C{=}S{=}O} \xrightarrow{\text{n-pentane}} [Rh^ICl(PR_3)\{\underset{(E)\text{-(2b) or -(3b)}}{(E)\text{-(MeS)(}p\text{-MeC}_6H_4)CSO\}] + 2C_8H_{14} \quad (1)$$

$$\tfrac{1}{2}[\{Rh^ICl(C_8H_{14})_2\}_2] + PR_3 + \underset{(Z)\text{-(1b)}}{(Z)\text{-(MeS)(}p\text{-MeC}_6H_4)C{=}S{=}O} \xrightarrow{\text{n-pentane}} [Rh^ICl(PR_3)\{\underset{(Z)\text{-(2b) or -(3b)}}{(Z)\text{-(MeS)(}p\text{-MeC}_6H_4)CSO\}] + 2C_8H_{14} \quad (2)$$

The ^1H n.m.r. spectra of (*Z*)-(2b) and -(3b) in $CDCl_3$ showed no *ortho*-hydrogen atoms to low field of 8 p.p.m., indicating that isomers containing σ-S co-ordinated sulphines are absent. Two further possibilities can then be envisaged for the structures of the rhodium complexes: (*i*) the intact sulphine is co-ordinated as such and (*ii*) C–S oxidative addition has occurred. The i.r. spectra (KBr mulls) of (*Z*)-(2b) and -(3b) showed one ν(CSO) absorption at *ca.* 1 040 cm^{-1}, (*E*)-(2b) likewise one, and (*E*)-(3b) two ν(CSO) absorptions at *ca.* 1 058 cm^{-1} (see Table 2).* The absorptions of η^2-CS and η^2-NS co-ordinated cumulenes in the region 1 000—1 070 cm^{-1} for $[Pt^0(PPh_3)_2(XYCSO)]$,[1-3] $[Fe(CO)_3\{H_2C(H)C(H)CSO\}]$,[21] $[Pt^0(PPh_3)_2(R'NSO)]$ (R′ = aryl),[13] and *trans*-$[Rh^ICl(PR_3)_2(R'NSO)]$ (R = C_6H_{11} or Pr^i) [13] are assigned mainly to ν(SO). The ν(CSO) absorptions of the present rhodium–sulphine complexes can likewise be assigned to ν(SO). Because no other ν(CSO) absorptions could be found, the C=S π bond of the cumulene fragment in each case must be involved in co-ordination to the Rh atom. For the complexes $[Pt^0(PR_3)_2(XYCSO)]$ (R = Ph or C_6H_{11}) [1,2] we also found no absorptions assignable to ν(C=S) of the co-ordinated C=S bond. The i.r. data, furthermore, indicate that the sulphine skeleton is retained upon attachment to the rhodium centre. The possibility that C–S oxidative addition had occurred could be ruled out on the basis of the ^{31}P n.m.r. data, recorded on $CDCl_3$ solutions of (*E*)- and (*Z*)-(2b) and -(3b) at room temperature (see Table 2). The ^1J(Rh–P) values of *ca.* 180 Hz are too high for rhodium(III) complexes containing only one phosphine per rhodium,[9] and thus point to a rhodium(I) centre.[7,22] The monomeric molecular weights confirm that the Cl atom is co-ordinated to the Rh^I. In most of the i.r. spectra a ν(Rh–Cl) could indeed be assigned. This would mean that, in the case of η^2-CS co-ordination, analogous to that found for Pt^0, we would be dealing with three-co-ordinate Rh^I. Three-co-ordination at Rh^I has been found in the case of two co-ordinated bulky phosphines.[22] In these cases the fourth co-ordination position is effectively protected from further reaction. The present rhodium–sulphine complexes are stable in $CHCl_3$ at room temperature and stable towards oxidation by air in solution for at least 24 h. It therefore seems plausible to assume that the rhodium(I) centre is four- rather than three-co-ordinate. This situation is possible when the sulphines in these complexes act as four-electron donors, *i.e.* when the sulphine is bonded as a bidentate ligand.

The ^1H n.m.r. spectra showed ^3J(Rh–H) coupling of *ca.* 4 Hz on the protons of the MeS group (see Table 2), indicating that the S atom of the MeS group is co-ordinated to the rhodium(I) centre. This was inferred by comparison of these data with those obtained for $[Pt^0(PR_3)_2\{(E)\text{-(MeS)(}p\text{-MeC}_6H_4)CSO\}]$ and $[Pt^0(PR_3)_2\{(Z)\text{-(MeS)(}p\text{-MeC}_6H_4)CSO\}]$ (R = Ph or C_6H_{11}), which did not show ^4J(Pt–H) on the MeS protons [1-3] in contrast to *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(MeS)(p\text{-MeC}_6H_4CSO)(PPh_3)_2]$ which exhibited ^3J(Pt–H) = 52 Hz and contained a direct Pt–SMe bond.[3] The sulphines in the rhodium(I) complexes are then co-ordinated either *via* both the C=S π bond and one lone pair of the MeS group (π,σ) or in a pseudo-allylic fashion, which likewise involves participation of both the π-C=S and σ-S electron density. In the first case, the formal hybridization at the S atom of the C–S side bond is sp^3 while in the second case it is sp^2. The second co-ordination mode would imply that the present rhodium complexes are isostructural and isoelectronic with the allylic complexes $[Pd^{II}Cl(PPh_3)\{H_2CC(H)CH_2\}]$.[23] However, the real rhodium(I)–sulphine interaction could be a mixture of the (π,σ) and pseudo-allylic interactions. Taking into account the *syn–anti* and *syn, syn–anti, anti* stereoisomerism observed for $[Pd^{II}Cl(PR_3)\{H_2CC(H)CH_2\}]$,[23] four structures for the (*E*) and (*Z*) sulphine complexes can be anticipated (see Figure 2).

(*b*) *Rhodium*(I) *complexes of* (R′S)$_2$C=S=O (R′ = *p*-MeC$_6$H$_4$ *or* Ph). Starting from the sulphines (*p*-MeC$_6$H$_4$S)$_2$C=S=O (1c) and (PhS)$_2$C=S=O (1c′), the complexes $[Rh^ICl(PR_3)\{(E)\text{-}(R'S)_2CSO\}]$ and $[Rh^ICl(PR_3)\{(Z)\text{-}(R'S)_2CSO\}]$ (*E*)- and (*Z*)-(2c; R = C_6H_{11}, R′ = *p*-MeC$_6$H$_4$), (*E*)- and (*Z*)-(2c′; R = C_6H_{11}, R′ = Ph), (*E*)- and (*Z*)-(3c; R = Pr^i, R′ = *p*-MeC$_6$H$_4$) could be synthesized. The reactions are summarized in equation (3).

$$3[\{Rh^ICl(C_8H_{14})_2\}_2] + 6PR_3 + \underset{(1c),\ (1c')}{6(R'S)_2C{=}S{=}O} \xrightarrow{\text{n-pentane}} 2[Rh^ICl(PR_3)\{\underset{(E)\text{-}}{(E)\text{-}(R'S)_2CSO}\}] + 4[Rh^ICl(PR_3)\{\underset{(Z)\text{-(2c), -(3c), and -(2c')}}{(Z)\text{-}(R'S)_2CSO}\}] + 12C_8H_{14} \quad (3)$$

The ^{31}P n.m.r. spectra recorded on $CDCl_3$ solutions of the reaction products at room temperature always showed one doublet with ^1J(Rh–P) *ca.* 184 Hz and a low-intensity doublet with ^1J(Rh–P) *ca.* 175 Hz. On the basis of these values, the species could not be oxidative-addition products. Because the free sulphines (R′S)$_2$C=S=O do not show (*E*)–(*Z*) isomerization, the formation of two complexes from each sulphine implies the co-ordination of the S atom of one of the C–S side bonds to Rh^I. The other possibility, *i.e.* the existence of different P, Cl co-ordination isomers, seems unlikely, because then it should be expected that (*E*)-(MeS)(*p*-MeC$_6$H$_4$)C=S=O would also give rise to two complexes, which is not the case [see part (*a*)]. Co-ordination of the C–S side bond *syn* to the S=O bond to the rhodium(I)

* The splitting of the ν(CSO) absorption of (*E*)-(3b) and -(2c) could be caused by the existence, for each complex in the solid state, of two (*E*) stereoisomers. See Figure 2.

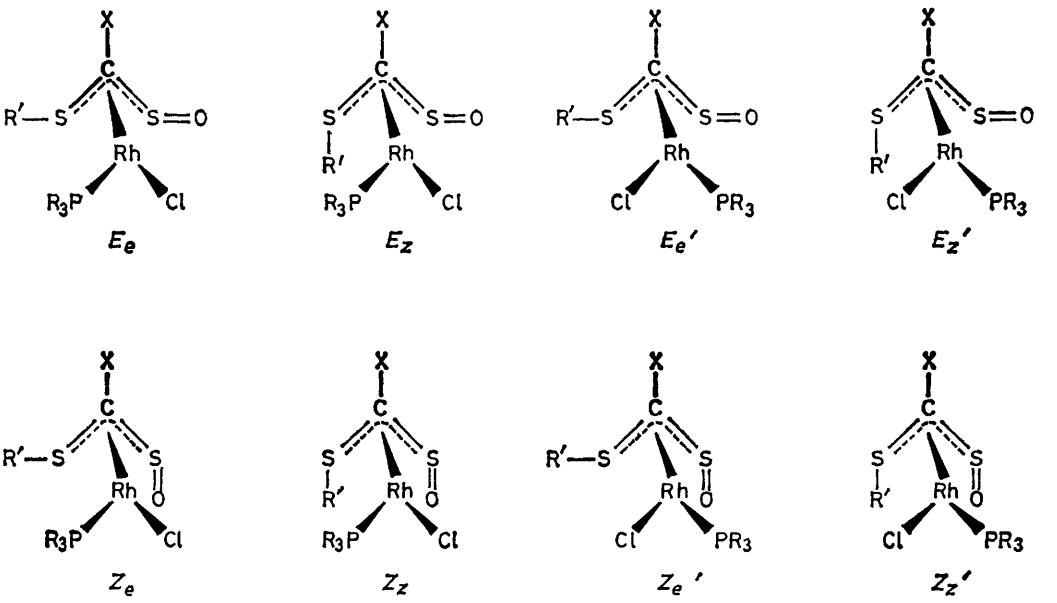


FIGURE 2 Four possible structures for [$Rh^ICl(PR_3)\{(E)$-(MeS)(p-MeC_6H_4)CSO}] and [$Rh^ICl(PR_3)\{(Z)$-(MeS)(p-MeC_6H_4)CSO}] (E)- and (Z)-(2b; R = C_6H_{11}), -(3b; R = Pr^i) and [$Rh^ICl(PR_3)\{(E)$-(R'S)$_2$CSO}] and [$Rh^ICl(PR_3)\{(Z)$-(R'S)$_2$CSO}] (E)- and (Z)-(2c; R = C_6H_{11}, R' = p-MeC_6H_4), -(2c'; R = C_6H_{11}, R' = Ph), -(3c; R = Pr^i, R' = p-MeC_6H_4)

atom gives [$Rh^ICl(PR_3)\{(Z)$-(R'S)$_2$CSO}], while of the other C–S side bond yields [$Rh^ICl(PR_3)\{(E)$-(R'S)$_2$CSO}]. The assignment of the higher ^1J(Rh–P) to the (Z) and the lower to the (E) stereoisomer could be derived from comparison of these complexes with the (E) and (Z) stereoisomers of [$Rh^ICl(PR_3)\{$(MeS)(p-MeC_6H_4)CSO}] (see Table 2). The sulphines (R'S)$_2$C=S=O co-ordinate to Rh^I in the same way as (E)- and (Z)-(MeS)(p-MeC_6H_4)C=S=O, *i.e.* η^3-SCS. For the complexes (E)- and (Z)-(2c) and -(3c) four structures are also possible (see Figure 2).

Fluxional Behaviour of [$Rh^ICl(PR_3)\{(E)$-(MeS)(p-MeC_6H_4)CSO}] (R = C_6H_{11}, *or* Pr^i) *and* [$Rh^ICl(PR_3)\{(E)$-(R'S)$_2$CSO}] (R = C_6H_{11} *or* Pr^i, R' = p-MeC_6H_4 *or* Ph) *in Solution*.—The ^{31}P n.m.r. resonance patterns of [$Rh^ICl(PR_3)\{(E)$-(MeS)(p-MeC_6H_4)CSO}] (E)-(2b; R = C_6H_{11}), and (E)-(3b; R = Pr^i), [$Rh^ICl(PR_3)\{(E)$-(R'S)$_2$CSO}] (E)-(2c; R = C_6H_{11}, R' = p-MeC_6H_4), (E)-(2c'; R = C_6H_{11}, R = Ph), and (E)-(3c; R = Pr^i, R' = p-MeC_6H_4) consist of two doublets with different values of ^1J(Rh–P). In the case of (E)-(2b) and -(3b) the doublets have different intensities at temperatures lower than −15 °C, while at higher temperatures these two doublets coalesce into one doublet at *ca.* 40 °C. The ^1J(Rh–P) values, chemical-shift positions, and coalescence temperatures in several solvents are given in Table 2.

The ^{1}H n.m.r. spectra recorded on $CDCl_3$ solutions of the isopropyl complex (E)-(3b) at 60 and 250 MHz showed at −20 °C two resonance patterns each consisting of an AB pattern for the aryl protons, a singlet for the alkyl protons of p-MeC_6H_4, and a doublet [^3J(Rh–H)] for the protons of the MeS group. Furthermore, two sets of four lines of equal intensity for the Pr^i groups were observed. Within each Pr^i group the methyls are inequivalent due to dissymmetry at the rhodium centre and their protons couple with the CH proton and the phosphorus atom [^3J(H–H) = 7.1, ^3J(P–H) = 14.8 Hz]. At 60 MHz the two resonance patterns at −20 °C coalesce on increasing the temperature and finally at room temperature one resonance pattern is found (see Table 2).

The combined data indicate that the complexes (E)-(2b), -(3b), -(2c), -(2c'), and -(3c) undergo a dynamic process, which at temperatures below −20 °C is in the slow-exchange and at room temperature in the fast-exchange limit. Because ^1J(Rh–P) and ^3J(Rh–H) remain present at room temperature the phosphine and the MeS group remain attached to the Rh atom in the fast-exchange limit. Two exchange processes can be considered to explain the fluxional behaviour of the complexes. First, (E)–(Z) isomerization of the co-ordinated C–S side bond (*anti* with respect to the S=O bond). The (E) and (Z) configurations of the MeS, p-MeC_6H_4S, and PhS groups are indicated by subscripts *e* and *z* respectively (see Figure 2). Secondly, an interchange of PR_3 and Cl. If the PR_3 group is co-ordinated *trans* to the C–S side bond this is indicated by a prime (see Figure 2). The present data do not indicate which of the two mechanisms is actually operative. If the first mechanism occurs then three situations are possible: (*a*) PR_3 fixed *trans* to C=S=O, (*b*) PR_3 fixed *trans* to C–SR', and (*c*) PR_3 and Cl are in fast exchange over the whole temperature range. The first mechanism is analogous to the *syn–anti* exchange found in allyl–palladium chemistry.[23] If the second mechanism occurs, then again three situations are possible: (*a*), the R'S group is fixed in the (E) configuration, (*b*) the R'S group is fixed in the (Z) configuration, and (*c*) the R'S group is in fast exchange between the (E) and (Z) configurations over the whole temperature range. The second mechanism is analogous to the *syn*, *syn–anti*, *anti* exchange found in allyl–palladium chemistry.[23] The two possible mechanisms, each with its three variations, are summarized in the Scheme (see also Figure 3).

The most likely co-ordination site for the PR_3 group is *trans* to the C=S=O frame because herein the C=S bond has more double-bond character than in the C–S side bond. It has already been found that in [$Pd^{II}Cl(PPh_3)\{H_2CC$-(H)CH_2}] the C • • • C bond *trans* to the PPh_3 group has more double-bond character than the C • • • C bond *trans* to

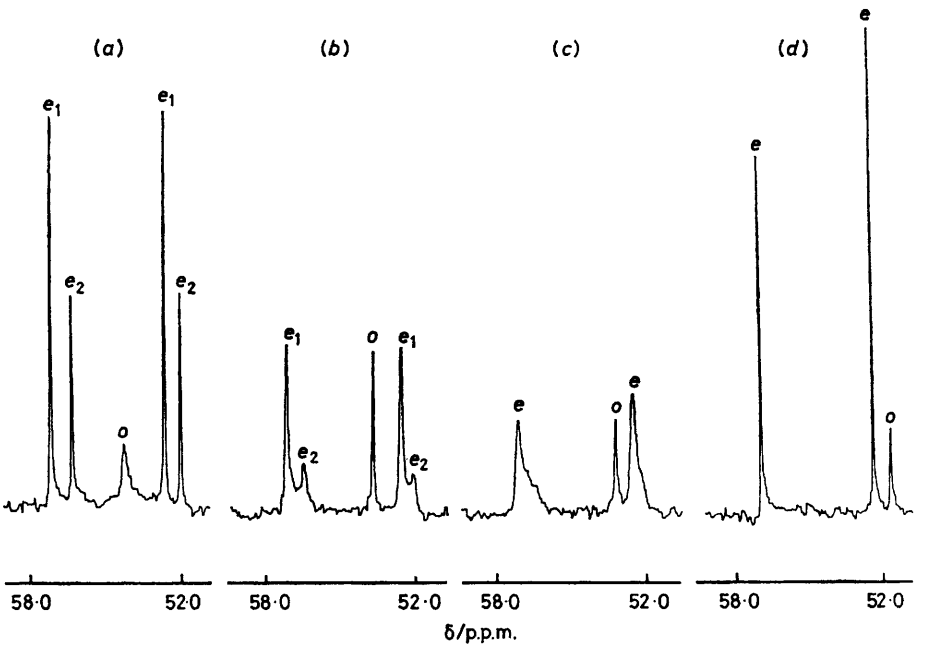
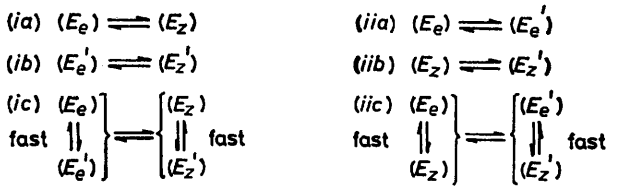


FIGURE 3 Phosphorus-31 n.m.r. spectra recorded on a $C_6D_5CD_3$ solution of $[Rh^ICl\{P(C_6H_{11})_3\}\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*E*)-(2b) at −46.5 (*a*), −6.5 (*b*), 3.5 (*c*), and 48.0 °C (*d*); e_1 and e_2 refer to (*E*)-(2b) in slow exchange, *e* to (*E*)-(2b) in fast exchange, and *o* to $P(C_6H_{11})_3O$

the Cl atom. This means that if the first mechanism is operative, process (*ia*) is most likely.

Most remarkable is the observation that the (*Z*) stereoisomers do not undergo this fluxional behaviour. The complexes $[Rh^ICl(PR_3)\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*Z*)-



SCHEME The possible fluxional processes

(2b; R = C_6H_{11}) and (*Z*)-(3b; R = Pr^i) do not show any temperature dependence in the ^{31}P and ^1H n.m.r. spectra over the temperature range −50 to 40 °C. This means that if one of the possible exchange mechanisms (see the Scheme) deduced for the (*E*) stereoisomers is also present for the (*Z*) stereoisomers, this process either remains in the fast-exchange limit or the (*Z*) stereoisomers are rigid. Within this temperature range, the ^{31}P n.m.r. spectra of $[Rh^ICl\{P(C_6H_{11})_3\}\{(Z)\text{-}(R'S)_2CSO\}]$ (*Z*)-(2c; R′ = p-MeC_6H_4) and (*Z*)-(2c′; R′ = Ph) are temperature independent. On further lowering the temperature the doublets for the (*Z*) stereoisomers broaden and disappear. In CD_2Cl_2 at −120 °C a new broad resonance pattern for (*Z*)-(2c′) is present, which, however, could not be interpreted.

The Reaction of $[Rh^ICl\{P(C_6H_{11})_3\}\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ *and* $[Rh^ICl\{P(C_6H_{11})_3\}\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ *with* $P(C_6H_{11})_3$ *in* $CDCl_3$.—In order to investigate the possible influence of free $P(C_6H_{11})_3$ on the fluxional processes, ^{31}P n.m.r. spectra were recorded at various temperatures on mixtures of $P(C_6H_{11})_3$ with both $[Rh^ICl\{P(C_6H_{11})_3\}\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*Z*)-(2b) and $[Rh^ICl\{P(C_6H_{11})_3\}\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*E*)-(2b) in $CDCl_3$ under an N_2 atmosphere.

Experiments with the (Z) *stereoisomers*. At room temperature the ^{31}P n.m.r. spectrum of (*Z*)-(2b) and $P(C_6H_{11})_3$ (*ca.* 1 : 1 molar ratio) in $CDCl_3$ showed the corresponding doublet and singlet signals as well as a low-intensity doublet for (*E*)-(2b) and a singlet for $P(C_6H_{11})_3O$. At −38 °C the signals for (*Z*)-(2b) and $P(C_6H_{11})_3$ were considerably broadened although the other signals were sharp again. At this latter temperature a new doublet is found. At −72 °C an eight-line pattern was detected, and the signals for (*Z*)-(2b) and $P(C_6H_{11})_3$ are sharp again. On raising the temperature the eight-line pattern and the signals of (*Z*)-(2b) and $P(C_6H_{11})_3$ broaden and to our knowledge the processes being observed were fully reversible (see Figure 4).

These results may be explained in the following way. The eight-line resonance pattern is assigned to *cis*-(*Z*)-$[Rh^ICl\{P(C_6H_{11})_3\}_2\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*Z*)-(6b), being a five-co-ordinate rhodium(I) complex with an η^3-SCS co-ordinated sulphine, in which one phosphine is co-ordinated *trans* to the sulphine molecule [^1J(Rh–P) = 153 Hz, δ(P) = 47.9 p.p.m. ^2J(P–P) = 20 Hz] and the other phosphine is co-ordinated to the unique fifth co-ordination site [^1J(Rh–P) = 123 Hz, δ(P) = 16.4 p.p.m., ^2J(P–P) = 20 Hz]. Intermolecular exchange between this five-co-ordinate species, the original four-co-ordinate (*Z*)-(2b), and free $P(C_6H_{11})_3$ (see Figure 5) is slow at temperatures below *ca.* −40 °C but fast at room temperature. Because in four-co-ordinate (*Z*)-(2b) ^1J(Rh–P) is detected in the slow- and the fast-exchange limits, the incoming $P(C_6H_{11})_3$ group must be the same as the outgoing $P(C_6H_{11})_3$ ligand. Thus, the $P(C_6H_{11})_3$ ligand initially present in the complex remains bonded to the rhodium centre. Accordingly, intramolecular exchange of the $P(C_6H_{11})_3$ groups in five-co-ordinate (*Z*)-(6b) must remain slow over the whole temperature range.

Experiments with the (E) *stereoisomers*. The ^{31}P n.m.r.

spectra recorded on the $CDCl_3$ solution of a mixture of (*E*)-(2b) and $P(C_6H_{11})_3$ (*ca.* 1 : 1 molar ratio) at room temperature showed a doublet for (*E*)-(2b), singlets for $P(C_6H_{11})_3$ and $P(C_6H_{11})_3O$, and a minor doublet for (*Z*)-(2b). The resonance patterns of (*Z*)-(2b) and $P(C_6H_{11})_3$ showed the

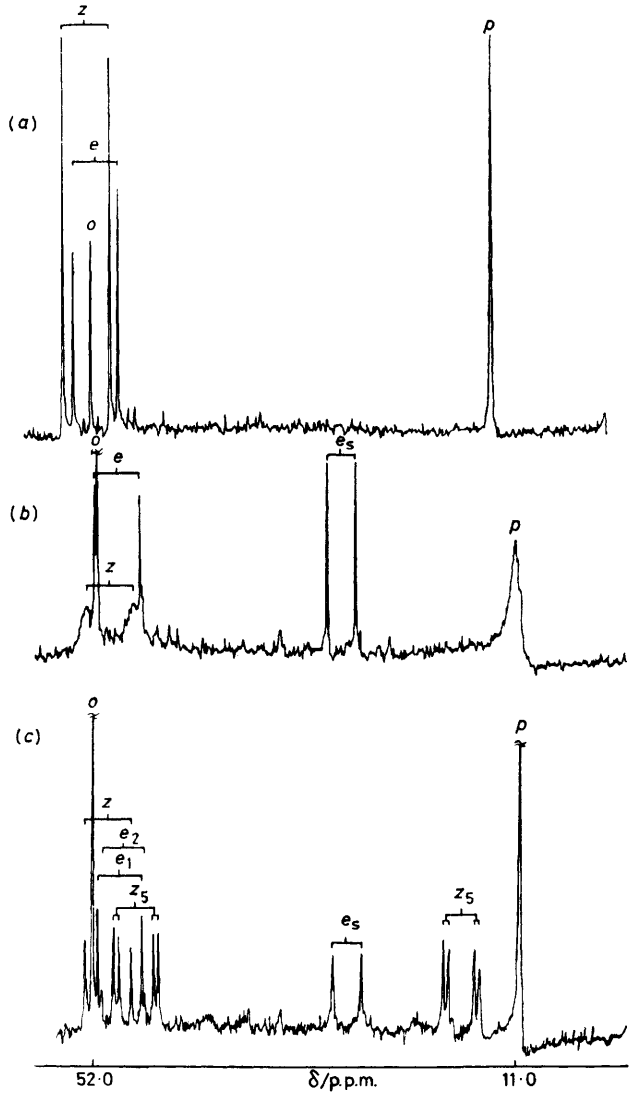


FIGURE 4 Phosphorus-31 n.m.r. spectra recorded on a $CDCl_3$ solution of a mixture of (*E*)- and (*Z*)-(2b) and $P(C_6H_{11})_3$ at 21.5 (*a*), −39.0 (*b*), and −72.0 °C (*c*); *z* refers to (*Z*)-(2b), *e* to (*E*)-(2b) in fast exchange, e_1 and e_2 to (*E*)-(2b) in slow exchange, *p* to $P(C_6H_{11})_3$, *o* to $P(C_6H_{11})_3O$, z_5 to (*Z*)-(6b), and e_s to (*E*)-(4b)

same temperature behaviour as found above. The concentration of (*Z*)-(2b) was too low to detect the eight-line pattern below −38 °C of the five-co-ordinate (*Z*)-(6b). On lowering the temperature from 30 to −40 °C a new doublet arises and steadily increases in intensity without changing its linewidth. The ^{31}P n.m.r. data of this unknown complex [^1J(Rh–P) = 113 Hz, δ(P) = 28.1 p.p.m.] are very similar to those of the σ-S co-ordinated rhodium–sulphine complex *trans*-[$Rh^ICl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)$] (4a) and therefore it seems plausible to assign this new doublet to *trans*-[$Rh^ICl\{P(C_6H_{11})_3\}_2\{(E)$-(MeS)(*p*-$MeC_6H_4$)CSO}] (*E*)-(4b), in which the sulphine is σ-S co-ordinated. The constant linewidth of (*E*)-(4b) from −40 to 30 °C indicates that the formation of (*E*)-(4b) and reformation of (*E*)-(2b) proceeds slowly on the n.m.r. time scale. An intermediate in this process could be *cis*-[$Rh^ICl\{P(C_6H_{11})_3\}_2\{(E)$-(MeS)(*p*-$MeC_6H_4$)CSO}] (*E*)-(6b), with a structure similar to (*Z*)-(6b) (see Discussion section and Figure 6). The extra minor doublet found in the mixture of (*Z*)-(2b) and $P(C_6H_{11})_3$ must be logically assigned to (*E*)-(4b), since (*E*)-(2b) is also present.

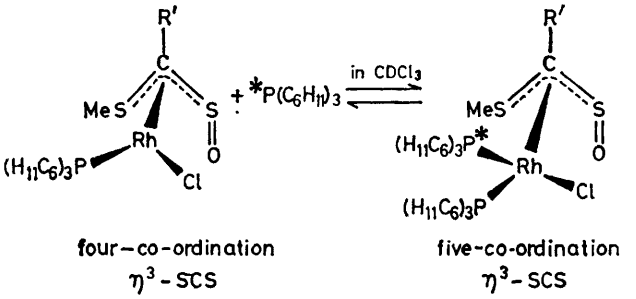


FIGURE 5 The equilibrium between (*Z*)-(2b) and (*Z*)-(6b)

The coalescence temperatures of both (*E*)-(2b) stereoisomers in the presence of free $P(C_6H_{11})_3$ are *ca.* −4 and −20 °C (low- and high-field signals respectively). This implies a very slight increase of the exchange rate by the presence of free $P(C_6H_{11})_3$ as compared with the coalescence temperatures in the absence of free $P(C_6H_{11})_3$ which are −4 and −12 °C respectively.

A detailed report concerning the reaction of [$Rh^ICl(PPr^i_3)\{(MeS)(p\text{-}MeC_6H_4)CSO\}$] and [$Rh^ICl\{P(C_6H_{11})_3\}\{(MeS)(p\text{-}MeC_6H_4)CSO\}$] with $P(C_6H_{11})_3$ and PPh_3, which lead to intramolecular scrambling, is deposited as Supplementary Publication No. SUP 23168 (7 pp.).*

Substitution of XYCSO *in* [$Rh^ICl(PR_3)_n$(XYCSO)] *by* CO.—The σ-S co-ordination of the sulphine in *trans*-[$Rh^ICl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)$] (4a) was ascribed to steric hindrance, between the phosphines and the $C_{12}H_8$ group, which prevents η^2-CS co-ordination (see first part of Results section). In order to study whether η^2-CS co-ordination of $C_{12}H_8C{=}S{=}O$ could be stabilized by substitution of one phosphine by the smaller CO, the reaction between (4a) and CO was investigated by ^{31}P and ^1H n.m.r. spectroscopy. The ^{31}P n.m.r. spectra recorded directly after bubbling CO through a $CDCl_3$ solution of (4a), as well as through the reaction mixture of [$\{Rh^ICl(C_8H_{14})_2\}_2$] and $P(C_6H_{11})_3$ (in a 1 : 4 molar ratio) in $CDCl_3$, showed one doublet with ^1J(Rh–P) = 118 Hz and δ(P) = 37.1 p.p.m., assigned to *trans*-[$Rh^ICl(CO)\{P(C_6H_{11})_3\}_2$],[24-26] indicating that CO substitutes the sulphine instead of one of the phosphines.

The reaction of [$Rh^ICl\{P(C_6H_{11})_3\}\{(E)$-(MeS)(*p*-$MeC_6H_4$)CSO}] and [$Rh^ICl\{P(C_6H_{11})_3\}\{(Z)$-(MeS)(*p*-$MeC_6H_4$)CSO}] (*E*)- and (*Z*)-(2b), and mixtures of [$Rh^ICl\{P(C_6H_{11})_3\}\{(E)$-(*p*-$MeC_6H_4S)_2$CSO}] and [$Rh^ICl\{P(C_6H_{11})_3\}\{(Z)$-(*p*-$MeC_6H_4S)_2$CSO}] (*E*)- and (*Z*)-(2c), each containing an η^3-SCS co-ordinated sulphine, with CO in $CDCl_3$ gave, as well as *trans*-[$Rh^ICl(CO)\{P(C_6H_{11})_3\}_2$], two other CO complexes, which were identified with the help of ^{31}P n.m.r. as *cis*-[$Rh^ICl(CO)_2\{P(C_6H_{11})_3\}$][24-26] [$^1J$(Rh–P) = 120 Hz, δ(P) = 39.1 p.p.m.] and *cis*-[$(Rh^ICl(CO)\{P(C_6H_{11})_3\})_2$][24-26] [$^1J$(Rh–

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

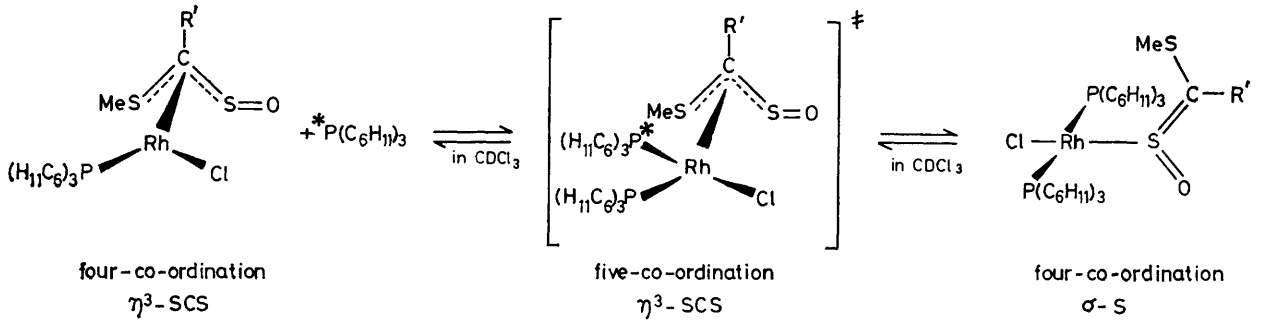


FIGURE 6 The equilibrium between (*E*)-(2b) and (*E*)-(4b) with (*E*)-(6b) as intermediate

P) = 171 Hz, δ(P) = 62.4 p.p.m.]. Moreover, the presence of the corresponding free sulphines was established by ^{1}H n.m.r. These rhodium–carbonyl complexes were also formed after bubbling CO through a $CDCl_3$ solution of $[\{Rh^ICl(C_8H_{14})_2\}_2]$ and $P(C_6H_{11})_3$ (in a 1 : 2 molar ratio). We conclude that the η^3-SCS co-ordinated sulphines were displaced by CO instead of changing the co-ordination mode to η^2-CS or σ-S.

DISCUSSION

Stable η^3-SCS *Co-ordinated Sulphines.*—For $[Pt^0(PR_3)_2\{(R'S)XCSO\}]$ (R = C_6H_{11} or Ph; η^2-CS co-ordination) the $Pt^0(PR_3)_2$ group can glide to the C–S side bond and give C–S oxidative addition in the case of R = Ph. When R = C_6H_{11} only backgliding is observed. In the intermediate η^3-SCS co-ordinated complex, (*E*)–(*Z*) isomerization takes place.[1-6]

The reaction of $[\{Rh^ICl(C_8H_{14})_2\}_2]$ with a C–S side bond containing sulphines (R'S)XC=S=O in the presence of PR_3 (R = C_6H_{11} or Pr^i) gave complexes of the type $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$. An intermediate in this reaction could be $[Rh^ICl(PR_3)L\{(R'S)(X)CSO\}]$ (L = PR_3 or C_8H_{14}), in which the sulphine is η^2-CS or σ-S co-ordinated. During the gliding movement of the $Rh^ICl(PR_3)L$ unit along the S–C=S frame, L dissociates and the stable η^3-SCS co-ordinated complex $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$ is formed. The fact that this complex does not undergo C–S oxidative addition forming $[Rh^{III}Cl(R'S)(XCSO)(PR_3)]$ is probably caused by the much greater thermodynamic stability of the η^3-SCS complex with respect to the η^2-CS and σ-S complexes, and in contrast to the instability of the η^3-SCS platinum(0) complex, $[Pt^0(PR_3)_2\{(R'S)(X)CSO\}]$, with respect to the η^2-CS platinum(0) complex. The η^3-SCS platinum(0) complex either undergoes C–S oxidative addition forming $[Pt^{II}(R'S)(XCSO)(PR_3)_2]$ or backgliding, forming the η^2-CS complex $[Pt^0(PR_3)_2\{(R'S)(X)CSO\}]$.

Even addition of PR''_3 to $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$ (R, R'' = C_6H_{11} or Pr^i) does not give rise to C–S oxidative addition. Instead an equilibrium mixture is formed consisting of the η^3-SCS complexes $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$, $[Rh^ICl(PR''_3)\{(R'S)(X)CSO\}]$, *cis*-$[Rh^ICl(PR_3)_2\{(R'S)(X)CSO\}]$, *cis*-$[Rh^ICl(PR''_3)_2\{(R'S)(X)CSO\}]$, and *cis*-$[Rh^ICl(PR_3)(PR''_3)\{(R'S)(X)CSO\}]$, the σ-S complexes *trans*-$[Rh^ICl(PR_3)_2\{(R'S)(X)CSO\}]$, *trans*-$Rh^ICl(PR''_3)_2\{(R'S)(X)CSO\}]$, and *trans*-$[Rh^ICl(PR_3)(PR''_3)\{(R'S)(X)CSO\}]$, and the free phosphines PR_3 and PR''_3. Even in the case of sulphines containing the more reactive C–Cl side bond the reaction with $[\{Rh^ICl(C_8H_{14})_2\}_2]$ and PR_3 (R = C_6H_{11}, Pr^i, or Ph) gave no identifiable oxidative-addition products.

The present complexes $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$ undergo (*E*)–(*Z*) isomerization, as was expected, because the η^3-SCS complexes $[Pt^0(PR_3)_2\{(R'S)(X)CSO\}]$ (R = C_6H_{11} or Ph) were postulated to be intermediates in the corresponding isomerization of the η^2-CS complexes $[Pt^0(PR_3)_2\{(R'S)(X)CSO\}]$ and the metallosulphines $[Pt^{II}(R'S)(XCSO)(PR_3)_2]$.[1] The considerably lower isomerization rate for the rhodium(I) complexes (several days for completion if no excess of PR_3 is present) as compared with the platinum(0) complexes (within a few minutes to 24 h) can be ascribed to the greater thermodynamic stability of the rhodium(I) complexes.

In addition to the canonical structures, $-S-\dot{\underset{|}{C}}=S=O$ and $-S-\dot{\underset{|}{C}}=S^+-O^-$, usually applied for free sulphines, η^3-SCS co-ordination also stabilizes the other canonical structures, $-\overset{+}{S}=\dot{\underset{|}{C}}-\bar{S}=O$ and $-\overset{+}{S}=\dot{\underset{|}{C}}-S-O^-$. This will diminish the C=S double-bond character in the C=S=O moiety relative to the free sulphines and sulphines which are σ-S co-ordinated, and accordingly will lower the barrier to the (*E*)–(*Z*) isomerization in the η^3-SCS complexes $[Rh^ICl(PR_3)\{(R'S)(X)CSO\}]$ (R = C_6H_{11} or Pr^i) and $[Pt^0(PR_3)_2\{(R'S)(X)CSO\}]$‡ (R = C_6H_{11} or Ph). A possible pathway for this process could be a σ–π mechanism which was previously found for $[Pd^{II}Cl\{H_2CC(H)CH_2\}(PPh_3)]$.[23]

Influence of the Sulphine Geometry on the Course of the Addition of Phosphine to $[Rh^ICl(PR_3)\{(MeS)(p\text{-}MeC_6H_4)CSO\}]$.—The complexes $[Rh^ICl\{P(C_6H_{11})_3\}\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ and $[Rh^ICl\{P(C_6H_{11})_3\}\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$, (*E*)- and (*Z*)-(2b), form equilibrium mixtures with $P(C_6H_{11})_3$ and the five-co-ordinate complexes *cis*-$[Rh^ICl\{P(C_6H_{11})_3\}_2\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ and *cis*-$[Rh^ICl\{P(C_6H_{11})_3\}_2\{(Z)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*E*)- and (*Z*)-(6b). The (*E*) stereoisomer of this five-co-ordinate complex could not be detected because it reacts further to give the σ-S, four-co-ordinate *trans*-$[Rh^ICl\{P(C_6H_{11})_3\}_2\{(E)\text{-}(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (*E*)-(4b).

Although no *X*-ray crystal-structure data of η^3-SCS

rhodium complexes are available at present, the dihedral angle between the –S–C=S=O and P–Rh–Cl planes is assumed to be comparable to that between the allyl and $PdCl_2$ plane in $[\{Pd^{II}(allyl)Cl\}_2]$.[23] This brings the lone pair of the S atom of the C=S=O moiety closer to the Rh atom in the (*E*) than in the (*Z*) stereoisomers. Consequently, a change of co-ordination mode from η^3-SCS to σ-S proceeds more easily in the case of the (*E*) than in that of the (*Z*) stereoisomers.

The net result of the reaction between $[Rh^ICl(PPr^i_3)\{(E)$-(MeS)(*p*-MeC_6H_4)CSO}] and $[Rh^ICl(PPr^i_3)\{(Z)$-(MeS)(*p*-MeC_6H_4)CSO}], (*E*)- and (*Z*)-(3b), with $P(C_6H_{11})_3$ is a scrambling of the phosphines. When the complexes (*Z*)-(2b) and -(3b) are in fast exchange with $P(C_6H_{11})_3$ and PPr^i_3 their ^1J(Rh–P) could still be observed. This implies that the scrambling of the phosphines must proceed *via* a mechanism which is slow on the n.m.r. time scale over the whole investigated temperature range. Thus even when the addition and dissociation of the second phosphine are fast on the n.m.r. time scale, the interchange of the two phosphines on the metal remains slow. Unfortunately, the precise scrambling mechanism could not be elucidated from the present ^{31}P n.m.r. measurements, but for the (*E*) stereoisomers the mixed σ-S complex *trans*-$[Rh^ICl\{P(C_6H_{11})_3\}(PPr^i_3)\{(E)$-(MeS)(*p*-$MeC_6H_4$)CSO}] (*E*)-(8b) possibly is the origin of the phosphine scrambling.

Conclusions.—In rhodium–sulphine chemistry, two novel co-ordination modes of sulphines have been found, *i.e.* σ-S and η^3-SCS. Particularly, the η^3-SCS co-ordination of the sulphines (*E*)- and (*Z*)-(MeS)(*p*-MeC_6H_4)C=S=O (*E*)- and (*Z*)-(1b) and $(R'S)_2C$=S=O (1c; R′ = *p*-MeC_6H_4) and (1c′; R′ = Ph), all containing one or two C–S side bonds, to Rh^I is very important. This type of co-ordination had already been postulated in the rearrangements of sulphines in the co-ordination sphere of Pt, but has now been established as a stable co-ordination mode in rhodium chemistry. The reason why $C_{12}H_8C$=S=O (1a) co-ordinates in a σ-S mode to $Rh^ICl(PR_3)_2$ (R = C_6H_{11} or Pr^i) is obvious since η^2-CS co-ordination would give rise to steric hindrance between the $C_{12}H_8$ group and the *trans* positioned phosphines. However, it has not been possible to explain why the thermodynamic stability of η^3-SCS co-ordination to Rh^I is such that C–S oxidative addition and η^2-CS co-ordination were not found.

The geometry of the sulphine skeleton determines the course of addition of phosphines to $[Rh^ICl(PR_3)\{(MeS)(p\text{-}MeC_6H_4)CSO\}]$ (R = C_6H_{11} or Pr^i) (*E*)- and (*Z*)-(2b) and -(3b). Furthermore, a fluxional behaviour was found for the (*E*) complexes $[Rh^ICl(PR_3)\{(E)$-(MeS)(*p*-MeC_6H_4)CSO}] (2b; R = C_6H_{11}) and (3b; R = Pr^i), $[Rh^ICl(PR_3)\{(E)$-$(R'S)_2CSO\}]$ (2c; R = C_6H_{11}, R′ = *p*-MeC_6H_4) (2c′; R = C_6H_{11}, R′ = Ph), and (3c; R = Pr^i, R′ = *p*-MeC_6H_4), but not for the corresponding (*Z*) complexes. This illustrates the difference in chemical behaviour of sulphine complexes caused by the geometry of the sulphine skeleton (C–S side bond *anti* or *syn* to the S=O bond). Although (*E*)- and (*Z*)-(MeS)(*p*-MeC_6H_4)C=S=O are stereoisomers they act as completely different ligands.

The process which is responsible for the dynamic behaviour found for (*E*)-(2b), -(3b), -(2c), -(3c), and -(2c′) could not be deduced, despite an extensive n.m.r. investigation. Therefore, a detailed mechanistic description of the two remaining possibilities, *i.e.* (*E*)–(*Z*) isomerization of the C–S side bond and PR_3–Cl interchange, is not as yet possible.

The sulphines are ligands with a very subtle and fascinating co-ordination behaviour. Important factors are the presence of C–S and C–Cl side bonds, the nature of the metal atom, the bulkiness of the phosphine co-ligands, and the geometry of the sulphine skeleton. The developments in the understanding of these factors has already led to a successful new synthesis of the already known and stable sulphines (R′S)(RS)C=S=O (R,R′ = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$),[27] using platinum complexes. With these synthetic routes we are currently involved in the preparation of new and possibly unstable sulphines in the co-ordination sphere of Pt.

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