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The Oxidative Addition of Unsaturated Cyclic Five-membered Disulphides to $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$

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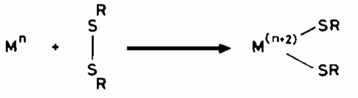
The reaction of $RhCl(PPh_3)_3$ with the cyclic disulfides hexachloronaphthalene-1,8-disulfide ($S_2C_{10}Cl_6$), 4-phenyl-1,2-dithiolium chloride ($[HC(\overline{S)C(Ph)C(S})H]Cl$) and 3,5-bis(dimethylamino-1,2,4-dithiazolium chloride ($[Me_2NC(\overline{S)NC(S})NMe_2]Cl$) results, via oxidative addition of the S–S bond, in the complexes $RhCl(S_2C_{10}Cl_6)(PPh_3)_2$, $RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2$ and $RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$, respectively.

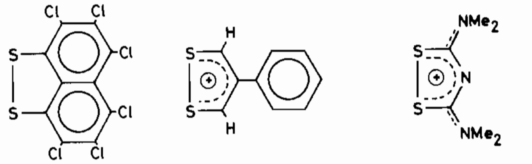
Upon reaction of $Pt(PPh_3)_4$ with $[HC(\overline{S)C(Ph)C(S})H]Cl$ cis-*$PtCl_2(PPh_3)_2$ is formed and no (β-dithioketonato)Pt(II) complex. The reaction of $Pt(PPh_3)_4$ with $[Me_2NC(\overline{S)NC(S})NMe_2]Cl$ is solvent dependent: in chloroform $Pt\{[Me_2NC(S)NC(S)NMe_2](PPh_3)_2\}Cl$ and in benzene $Pt[Me_2NC(S)NC(S)NMe_2]Cl(PPh_3)$ is formed.*

Introduction



$$M^{n} + \begin{matrix}R\\S\\|\\S\\R\end{matrix} \longrightarrow M^{(n+2)}\begin{matrix}SR\\SR\end{matrix}$$

In the past, various bis(alkyl- or arylsulfido)phosphine complexes of group VIII metals have been prepared via oxidative addition of the disulfide linkage in RS–SR (R = alkyl or aryl) to the corresponding d^8 (Rh^I, Ir^I) and d^{10} (Ni^0, Pt^0, Pd^0) metal phosphine complexes. In the Ni-triad $[Ph_2P(CH_2)_2PPh_2]Ni(SPh)_2$ [1], $[(Ph_3P)Pd(SPh)(\mu\text{-}SPh)]_2$ and $(Ph_3P)_2Pt(SPh)_2$ [2] have been prepared by oxidative addition of PhS–SPh to $[Ph_2P(CH_2)_2PPh_2]Ni(CO)_2$, $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$, respectively. In the Co triad the reaction of PhS-SPh with $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PMePh_2)_2$ has been reported to give $[IrCl(\mu\text{-}SPh)(SPh)(CO)(PPh_3)]_2$ [3] and $IrCl(SPh)_2(CO)(PMePh_2)_2$ [4], respectively. A related disulfide bond breaking occurred in the reaction of $Et_2NC(S)$–S–S–C(S)NEt_2 with $[MCl(C_8H_{14})_2]_2$ (M = Rh, Ir), to give $[MCl(SC(S)NEt_2)_2]_2$ [5].



(1) (2) (3)

Figure 1. Structures of the unsaturated cyclic five-membered disulfides. *1* = hexachloronaphthalene-1,8-disulfide; *2* = 4-phenyl-1,2-dithiolium chloride (*2*-Cl) or bromide (*2*-Br); *3* = 3,5-bis(dimethylamino)-1,2,4-dithiazolium chloride (*3*-Cl) or bromide (*3*-Br).

Oxidative addition of cyclic disulfides to low valent group VIII metal phosphine complexes has been less well investigated: $(Ph_3P)_2M[F_3CC(S):C(S)CF_3]$ (M = Ni, Pd, Pt) resulted from oxidative addition of bis-(trifluoromethyl)-1,2-dithiethene ($F_3CC(\overline{S):C(S})CF_3$) to $(Ph_3P)_2Ni(CO)_2$ and $M(PPh_3)_4$ (M = Pd, Pt), respectively [6]. Recently, the oxidative addition of two S–S bonds in tetrathionaphthalene to two $Pt(PPh_3)_4$ molecules has been reported [7].

In this paper the oxidative addition of the –S–S– bond in a number of five-membered cyclic disulfides to $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ is described. The disulfides used are shown in Figure 1. The disulfides *2* and *3* are positive ions. In *2* and *3* stabilization of the positive charge occurs by strong π-delocalization, as indicated by the planar structure of the five-membered ring [8, 9].

The reaction of *1* with zerovalent metal complexes of the Ni triad has already been reported: oxidative addition of the S–S band in *1* to $Ni(C_8H_{12})_2$ in the presence of PPh_3 gave the trinuclear $[Ni(S_2C_{10}Cl_6)(PPh_3)]_3$ and the reaction of *1* with $M(PPh_3)_4$ (M = Pd, Pt) gave $(PPh_3)_2M(S_2C_{10}Cl_6)$ (M = Pd, Pt) [10].

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TABLE I. Analytical Values and Molecular Weights.

Code	Compound[a]	Colour	%C	%H	%Br	%Cl	%N	%S	Mol. Weight[b]
I	*trans*-$RhCl(S_2C_{10}Cl_6)(PPh_3)_2$	orange	53.5	3.0		23.3		6.2	1046[c]
			(52.1)	(2.8)		(23.4)		(6.0)	(1060)
I-Br	*trans*-$RhBr(S_2C_{10}Cl_6)(PPh_3)_2$	brown	50.0	2.8	7.1	19.1			1090[d]
			(50.0)	(2.7)	(7.2)	(19.3)			(1104)
II	*trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2 \cdot C_6H_6$	purple	64.2	4.6		7.5		6.7	965[e]
			(64.1)	(4.5)		(7.4)		(6.7)	(956)
III	*trans*-$RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$	orange	56.7	4.7		8.0	4.7	7.1	873[c]
			(56.8)	(4.8)		(8.0)	(4.7)	(7.2)	(889)
IVA	$[Pt\{Me_2NC(S)NC(S)NMe_2\}(PPh_3)_2]Cl \cdot 2CHCl_3$	white	44.3	3.7		18.1	3.2	4.8	
			(44.6)	(3.7)		(21.0)	(3.5)	(5.4)	
IVB	$PtCl[Me_2NC(S)NC(S)NMe_2](PPh_3)$	green-yellow	42.2	4.1			6.4		
			(42.2)	(4.0)			(6.1)		
V	$RhBr_2[SC(S)NMe_2](PPh_3)_2 \cdot 2CDCl_3$[f]	red	43.2	3.1			1.2		
			(42.9)	(3.3)			(1.2)		

[a] *cis* and *trans* denote relative position of the PPh_3 groups. [b] Osmometric. [c] In chloroform. [d] In toluene. [e] In benzene.
[f] Probably a mixture of *cis*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$ (VA) and *trans*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$ (VB).

Experimental

All reactions starting with $RhX(PPh_3)_3$ (X = Cl, Br) or $Pt(PPh_3)_4$ were performed under nitrogen, using Schlenk apparatus. I.R. spectra were obtained with Perkin-Elmer 257 and 283 spectrophotometers. H-N.M.R. spectra were recorded on a Varian T-60 and Bruker WH-90-FT and $^{31}P(^1H)$-N.M.R. spectra on a Varian XL-100-FT spectrometer at 40.5 MHz using the deuterated solvent as an internal lock. C, H and N analyses were performed at the micro-analytical department of this university. Br, Cl and S analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany. The analytical results are given in Table I.

Starting Materials

The starting complexes $RhX(PPh_3)_3$ (X = Cl, Br) [11] and $Pt(PPh_3)_4$ [12] and the disulfides $C_{10}Cl_6S_2$ [13], $[HC(S)C(Ph)C(S)H]X$ ($X = Cl^-, Br^-$) [14], and $[Me_2NC(S)NC(S)NMe_2]X$ ($X = Cl^-, Br^-$) [15] were prepared according to literature procedures.

Reaction of $RhCl(PPh_3)_3$ with the Disulfides 1–3

trans*-*$RhCl(S_2C_{10}Cl_6)(PPh_3)_2$ (I)*

0.3 mmol $RhCl(PPh_3)_3$ and 0.3 mmol $S_2C_{10}Cl_6$ (*1*) were stirred in 10 ml of toluene for 4 hours. I precipitated spontaneously as an orange precipitate, which was filtered off, washed with n-hexane and dried *in vacuo*. If the reaction is performed at lower concentrations, a brown precipitate is obtained after addition of n-hexane. The orange and the brown precipitate showed no differences in their I.R. and ^{31}P N.M.R. spectrum.

trans-*$RhBr(S_2C_{10}Cl_6)(PPh_3)_2$ (I-Br)*

The complex was prepared in a procedure analogous to that for I, using $RhBr(PPh_3)_3$ and was obtained as a brown precipitate by addition of n-hexane.

trans-*$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2$* (II)

0.2 mmol $[HC(S)C(Ph)C(S)H]Cl$ (*2*-Cl) was dissolved with stirring in a solution of 0.2 mmol $RhCl(PPh_3)_3$ in 15 ml of chloroform. The colour of the solution changed from dark-red to brown-red, after which the purple *trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2 \cdot CHCl_3$ precipitated. When dichloromethane was used, *trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2 \cdot CH_2Cl_2$ precipitated upon addition of n-hexane. Recrystallization of the products from benzene–n-hexane yielded *trans*-$RhCl_2[HC(S)C(Ph)C(S)H] \cdot C_6H_6$. The presence of the solvent molecules in the adducts was confirmed by the I.R. and ^1H N.M.R. spectrum.

trans-*$RhBr_2[HC(S)C(Ph)C(S)H](PPh_3)_2$ (II-Br)*

The complex was prepared by reaction of $RhBr(PPh_3)_3$ and *2*-Br, in a procedure analogous to that for II.

trans-*$RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$ (III)*

0.2 mmol $[Me_2NC(S)NC(S)NMe_2]Cl$ (*3*-Cl) was dissolved with stirring in a solution of 0.2 mmol $RhCl(PPh_3)_3$ in 15 ml of chloroform. The colour of the solution changed from dark-red to orange, after which the orange *trans*-$RhCl_2[Me_2NC(S)NC(S)$-

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**trans* denotes relative position of the PPh_3 groups.

$NMe_2](PPh_3)_2 \cdot 2CHCl_3$ precipitated. When dichloromethane was used, *trans*-$RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$ precipitated upon addition of n-hexane. The presence of $CHCl_3$ in the solvent adduct was confirmed by the I.R. spectrum.

trans-*$RhBr_2[Me_2NC(S)NC(S)NME_2](PPh_3)_2$ (III-Br)*

The complex was prepared by reaction of $RhBr(PPh_3)_3$ and *3*-Br in a procedure analogous to that for III.

Reaction of $Pt(PPh_3)_4$ with the Disulfides 2 *and* 3

Formation of cis-*$PtCl_2(PPh_3)_2$ from $Pt(PPh_3)_4$ and $[HC(S)C(Ph)C(S)H]Cl$ (2-Cl)*

a) Reaction of 0.2 mmol *2*-Cl and 0.2 mmol $Pt(PPh_3)_4$ in 10 ml of benzene for 12 hours gave a red precipitate in which the presence of *cis*-$PtCl_2(PPh_3)_2$ was indicated by its ν(M–Cl) absorptions. The nature of the products other than *cis*-$PtCl_2(PPh_3)_2$ could not be identified.

b) 0.4 mmol *2*-Cl and 0.2 mmol $Pt(PPh_3)_4$ were stirred in 10 ml of benzene for 72 hours. After that period a white precipitate had formed, which was identified as *cis*-$PtCl_2(PPh_3)_2$ by its I.R. spectrum (ν(M–Cl) = 320 cm^{-1} (s), 295 cm^{-1} (s)) and its elemental analysis.

$[Pt\{Me_2NC(S)NC(S)NMe_2\}(PPh_3)_2]^+Cl^-$ (IVA)

0.2 mmol $Pt(PPh_3)_4$ and 0.2 mmol $[Me_2NC(S)NC(S)NMe_2]Cl$ (*3*-Cl) were stirred in 10 ml of chloroform for 12 hours. Upon addition of n-hexane to the pale-yellow solution a white precipitate of $[Pt\{Me_2NC(S)NC(S)NMe_2\}(PPh_3)_2]Cl \cdot 2CHCl_3$ was formed. The presence of $CHCl_3$ was confirmed by the I.R. spectrum. IVA is a conductor in $CHCl_2$: Λ_o = 65 ohm^{-1} cm^2 mol^{-1} at 25 °C.

$PtCl[Me_2NC(S)NC(S)NMe_2](PPh_3)$ (IVB)

0.2 mmol $Pt(PPh_3)_4$ and 0.2 mmol $[Me_2NC(S)NC(S)NMe_2]Cl$ (*3*-Cl) were stirred in 10 ml of benzene for 12 hours. The spontaneously formed green-yellow precipitate of IVB was filtered off and recrystallized from $CHCl_3$–n-hexane.

cis *and* trans-*$RhBr_2$*$[SC(S)NMe_2]$*$(PPh_3)_2$ (VA and VB) as Reference Compound for ^{31}P N.M.R.*

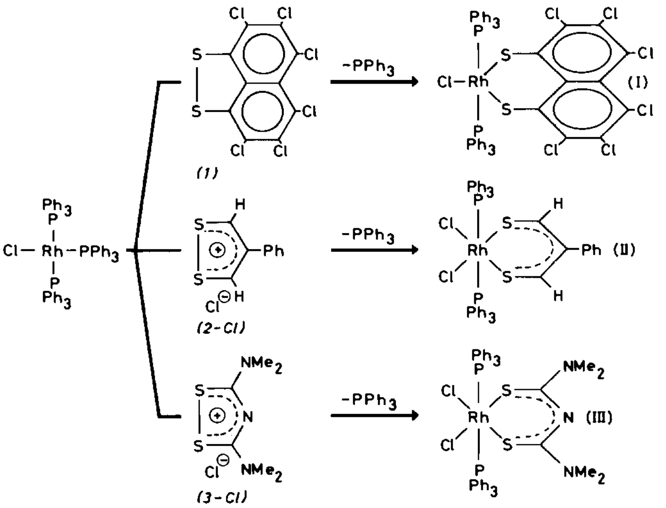
0.4 mmol $RhCl(PPh_3)_3$ and 0.4 mmol $NaS_2SNMe_2 \cdot 2H_2O$ were stirred in 80 ml of acetone for 25 minutes. The precipitate of NaCl was filtered off. 0.4 mmol Br_2 (in benzene) was added and the colour of the solution changed from orange to yellow. After a few minutes a yellow precipitate of $RhBr_2[SC(S)NMe_2](PPh_3)_2 \cdot CH_3C(O)CH_3$ was obtained. ^1H N.M.R. and ^{31}P N.M.R. spectra in $CDCl_3$ indicated the precipitate to contain a mixture of VA and VB. The presence of about one mol of acetone was indicated by the ^1H N.M.R. spectrum. Upon prolonged standing, $RhBr_2[SC(S)NMe_2](PPh_3)_2 \cdot 2CDCl_3$ slowly precipitated from the $CDCl_3$ solution as red crystals.

Results and Discussion

Reaction of $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ with the Disulfides $S_2C_{10}Cl_6$ (1) $[HC(S)C(Ph)C(S)H]^+$ (2) and $[Me_2NC(S)NC(S)NMe_2]^+$ (3)

Synthesis

The observed reactions of the disulfides *1*, *2*-Cl and *3*-Cl (see Figure 1) with $RhCl(PPh_3)_3$ and the



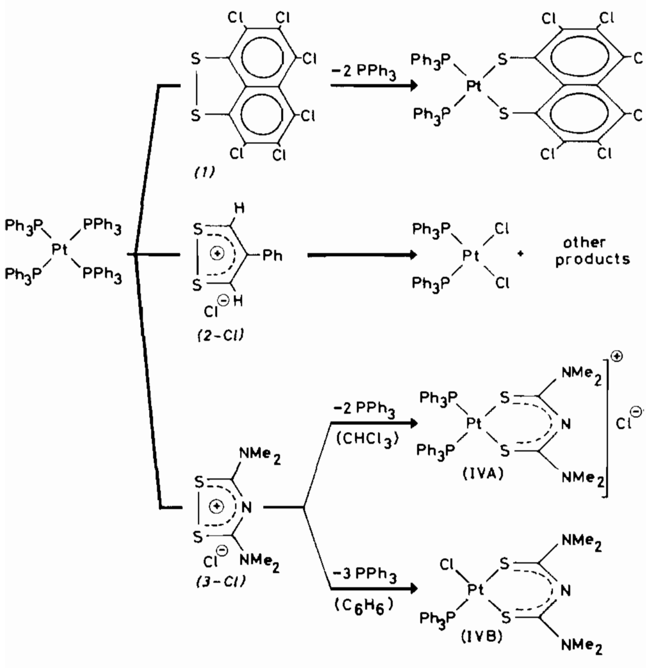
Scheme 1. Formation of the complexes I, II and III from the disulfides *1*, *2*-Cl and *3*-Cl.

structures of the complexes formed are shown in Scheme 1. In all three cases insertion of Rh into the S–S bond of the ring compound occurs and a six-membered ring containing Rh(III) and the S–S-coordinated chelates hexachloronaphthalene-1,8-dithiolate (dinegative), dithiodiformylphenylmethanate (mononegative) or N,N,N′,N′-tetramethyldithiobiuretate (mononegative) is formed. Apart from the dithiobiuretato complexes $A(Ph_3P)Rh[Me_2NC(S)NC(S)NMe_2]$ (A = Ph_3P, CO) and $RhO_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$ [16, 17] no Rh complexes of these S,S-coordinating chelates had been reported before.

$RhCl(CO)(PPh_3)_2$ was observed to be unreactive to the disulfides at room temperature. $[RhCl(CO)_2]_2$ reacted with *3*-Cl in methanol to $[Me_2NC(S)NC(S)NMe_2]^+[RhCl_2(CO)_2]^-$, as was inferred from the I.R. spectrum which showed absorptions due to $[RhCl_2(CO)_2]^-$ [18] and *3* (Table III). In the ^1H N.M.R. spectrum the N-Me resonances of *3* were the same as observed in the corresponding Cl^- salt (*3*-Cl).

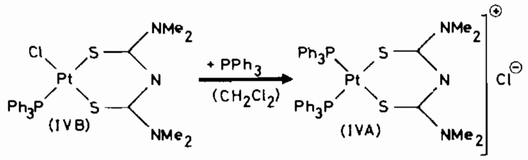
$$[Me_2NC(\overgroup{S)NC(S})NMe_2]^+Cl^- + \tfrac{1}{2}[RhCl(CO)_2]_2 \rightarrow [Me_2NC(\overgroup{S)NC(S})NMe_2]^+[RhCl_2(CO)_2]^- \quad (1)$$

Scheme 2 gives the reactions of $Pt(PPh_3)_4$ with the disulfides *2* and *3*.



Scheme 2. Reaction of $Pt(PPh_3)_4$ with the disulfides, *1*, *2* and *3* (the formation of $Pt(S_2C_{10}Cl_6)(PPh_3)_2$ has been reported by others [10]; a suggested structure is given).

A probable structure for $Pt(S_2C_{10}Cl_6)(PPh_3)_2$, formation of which from $Pt(PPh_3)_4$ and *1* already has been reported [10], has been included for the sake of completeness. In the reaction of $Pt(PPh_3)_4$ with *2*-Cl no formation of a (β-dithioketonato)Pt(II) complex was observed, but instead *cis*-$PtCl_2(PPh_3)_2$ was isolated. Although other products are formed in this reaction, they could not be identified. *Cis*-$PtCl_2(PPh_3)_2$ could have been formed by oxidative addition of the S–S bond in *2* and subsequent displacement of the dithiodiformylphenyl methanato ligand by Cl^-, its further reactions being unknown. The reaction of *3*-Cl with $Pt(PPh_3)_4$ showed a solvent dependence: in chloroform the ionic $[Pt(Me_2NC(S)NC(S)NMe_2)(PPh_3)_2]Cl$ (IVA) is formed, but in benzene displacement of PPh_3 by Cl^- occurred to give $Pt[Me_2NC(S)NC(S)NMe_2]Cl(PPh_3)$ (IVB). Upon addition of PPh_3 to a solution of IVB in CD_2Cl_2 immediate formation of IVA is observed in the ^{31}P N.M.R. spectrum (Table II):



Spectral parameters and structures

The equivalence of the PPh_3 groups in the ^{31}P N.M.R. spectra of I, II and III (scheme 1) and the values of $^1J(Rh\text{-}P)$ indicate a *trans* position of the PPh_3 groups (Table II). The values of $^1J(Rh\text{-}P)$ in II and III are comparable to that for the *trans*-PPh_3 groups in *trans*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$ (VB: $^1J(Rh\text{-}P) = 88$ Hz.)

This compound and *cis*-$RhBr_2(PPh_3)_2[SC(S)CNMe_2]$ were prepared as reference compounds. If the PPh_3 groups in II and III were in *cis* position and both *trans* to the S atoms of the chelate $^1J(Rh\text{-}P)$ would be expected to be 130 hz, like in *cis*-$RhBr_2[S(C)CNMe_2](PPh_3)_2$ (VA: $^1J(Rh\text{-}P) = 126$ Hz, Table II). The larger value of $^1J(Rh\text{-}P)$ of I compared to II and III is in accordance with the expected decrease in s-character of the Rh hybrid orbitals to 5/6, on going from the five-coordinated complex I to the six-coordinated complexes II and III.

Comparison of the values of $^1J(Pt\text{-}P)$ in the complexes IVA and IVB with that in $Pt[Me_2NC(S)NC(S)NMe_2]H(PPh_3)$ prepared before [16] (Table II) indicates the following order of increasing *cis*-influence (= decreasing $^1J(Pt\text{-}P)$) on $^1J(Pt\text{-}P)$: H < Cl < PPh_3. The *cis*-influence order, Cl < P, has been observed before in other square planar Pt(II) complexes [19].

For the complexes I, II and III, absorptions due to ν(M–Cl) could be assigned by comparison of the corresponding chlorine and bromine complexes

TABLE II. ^1H N.M.R. and $^{31}P\{^1H\}$ N.M.R. Parameters.

Code	Compound[f]	^{31}P N.M.R.[a]				^1H N.M.R.[b]		
		Solvent	δ (p.p.m.)	^1J(M-P) (Hz)	Atom or Group *trans* to PPh_3	Solvent	τ(NMe_2) in p.p.m.	τ of Other Protons
I	*trans*-$RhCl(S_2C_{10}Cl_6)(PPh_3)_2$	$CDCl_3$	−16.3	102	PPh_3			
I-Br	*trans*-$RhBr(S_2C_{10}Cl_6)(PPh_3)_2$	$C_6D_5CD_3$	−16.8	101	PPh_3			
II	*trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2$	CD_2Cl_2	−15.4	85	PPh_3	CD_2Cl_2		2.41(2)d(^3J(Rh-S-C-H = 4Hz) (>C–H)
III	*trans*-$RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$	CD_2Cl_2	−13.3	89	PPh_3	CD_2Cl_2	7.33(12)[c]	
VB	*trans*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$	$CDCl_3$	−17.2	88	PPh_3	$CDCl_3$	7.66(6)	
VA	*cis*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$	$CDCl_3$	−35.7	126	PPh_3	$CDCl_3$	6.92(6)	
	$Pt[Me_2NC(S)NC(S)NMe_2]H(PPh_3)$	CD_2Cl_2	−21.8	3658	S	CD_2Cl_2	6.68(6)br, 6.84(6)	20.7(Pt-H) (^1J(Pt-H) = 1081Hz) (^2J(P-H)$_{cis}$ = 19Hz)
IVB	$Pt[Me_2NC(S)NC(S)NMe_2]Cl(PPh_3)$	CD_2Cl_2	−17.4	3300	S	CD_2Cl_2	6.61(3)br, 6.85(3)br, 7.01(6)br	
IVA	$[Pt(Me_2NC(S)NC(S)NMe_2)(PPh_3)_2]Cl$	CD_2Cl_2	−16.3	3112	S	CD_2Cl_2	6.82(6)br, 7.01(6)br[d]	
2	$[HC(S)C(Ph)C(S)H]Cl$					D_2O		−1.30(2) (>C–H)[e]
3	$[Me_2NC(S)NC(S)NMe_2]Cl$					$CDCl_3$	6.18(6), 6.28(6)	

[a] δ rel. to TMP (O=P(OMe)$_3$). [b] τ rel. to TMS; d = doublet; br = broadened singlet. [c] Coalescence temperature −5 °C. [d] Coalescence temperature +53 °C. [e] τ rel. to HMDS. [f] *cis* and *trans* denote relative position of the PPh_3 groups.

TABLE III. I.R. Parameters of the Complexes (cm^{-1}; CsJ disks, unless otherwise stated).

Code	Compound[a]	Absorptions of S,S-coordinating Chelate		ν(M–Cl)
		ν(C⋯NMe$_2$)	Other Absorptions	
I	*trans*-$RhCl(S_2C_{10}Cl_6)(PPh_3)_2$	–	1515(m), 1413(m), 1275(s), 1243(s), 951(m), 832(m)	305(m), 292(m)
II	*trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2 \cdot CH_2Cl_2$	–	1598(m), 1500(m), 1370(s), 1322(m), 941(s), 902(m), 872(w)	299(m), 284(w)
III	*trans*-$RhCl_2[Me_2NC(S)NC(S)NMe_2](PPh_3)_2$	1515(vs)	1400(w), 1360(s), 1323(s), 1130(s), 905(m)	305(m), 288(m)
IVA	$[Pt\{Me_2NC(S)NC(S)NMe_2\}(PPh_3)_2]Cl \cdot 2CHCl_3$	1523(vs) 1526(vs), CH_2Cl_2	1400(sh), 1377(s), 1314(s), 1126(s), 910(w, br)	
IVB	$Pt[Me_2NC(S)NC(S)NMe_2]Cl(PPh_3)$	1503(vs) 1510(vs), CH_2Cl_2	1397 (w), 1364(s), 1327(s), 1127(s), 909(w)	308(m)
3-Cl	$[Me_2NC(S)NC(S)NMe_2]Cl$	1577(vs) 1572(vs), CH_2Cl_2		
	$[Me_2NC(S)NC(S)NMe_2]^+RhCl_2(CO)_2]^-$	1581(vs)	2060, 1986 (ν(CO))	
VA VB	$RhBr_2[SC(S)NMe_2](PPh_3)_2 \cdot$acetone[b]	1530(vs)	1396(s), 1253(m), 1157(s), 985(w)	
VIII	$[Pt(SC(S)NMe_2)(PPh_3)_2]Br$	1570(vs)	1402(s), 1234(w), 1161(m), 960(w)	

[a] *cis* and *trans* denote relative position of the PPh_3 groups. [b] Mixture of *cis*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$ (VA) and *trans*-$RhBr_2[SC(S)NMe_2](PPh_3)_2$ (VB).

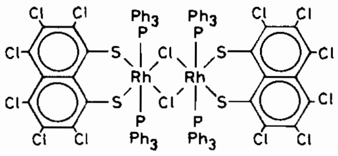
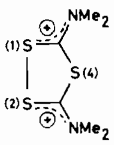


Figure 2. Suggested structure for $RhCl(S_2C_{10}Cl_6)(PPh_3)_2$ in the solid state.



(4)

Figure 3. Structure of 4-Br = 3,5-bis-(dimethyliminium)-1,2,4-trithiolanedibromide ($(Me_4bitt)Br_2$).

(Table III). Although the monomeric molecular weight (Table I) indicates I to be monomeric in solution, the presence of two ν(M–Cl) absorptions in the solid state suggests a dimeric structure involving chlorine bridges (Figure 2). ν(Pt–Cl) in IVB has been assigned by comparison of IVA and IVB.

The absorptions assigned to the S,S-coordinating chelates are given in Table III. The assigned I.R. absorptions due to the dithiobiuretate in III, IVA and IVB are close to the values assigned in other Rh and Pt complexes before [16].

^{1}H N.M.R. spectral parameters of the complexes are given in Table II. In *trans*-$RhCl_2[HC(S)C(Ph)C(S)H](PPh_3)_2$ a doublet is observed for both methyne protons of the six-membered chelate ring. This is ascribed to a ^3J(Rh-S-C-H) coupling (4 H). The methyne proton resonance has shifted 3.7 p.p.m. upfield from its resonance position in the starting disulfide [HC(S)C(Ph)C(S)H] Cl (Table II), indicating an increase in electron density in accordance with the formal two electron reduction of the ligand system upon insertion of the Rh into the five-membered ring. In the dithiobiuretato complexes *trans*-$RhCl_2[Me_2NC(S)NC(S)NMe_2(PPh_3)_2$ (III) and $[Pt(Me_2NC(S)NC(S)NMe_2)(PPh_3)_2(PPh_3)_2]Cl$ (IVA) both NMe_2 groups are observed to be equivalent in accordance with the suggested structures. The NMe_2 resonances in both complexes have shifted upfield compared to the NMe_2 resonance of 3-Cl (+1.1 p.p.m. for II and +0.7 p.p.m. for IVA). Together with the observed decrease in $\nu(\mathrm{C{\cdots}NMe_2})$ of *ca.* 60 cm^{-1}, this parallels the formal reduction of the ring upon breaking of the S–S bond. The two N-Me resonances in the ^{1}H N.M.R. spectrum of IVA at room temperature (coalescence temperature = +53 °C) and of III at lower temperature (coalescence temperature = –5 °C) indicate hindered rotation around the C-NMe$_2$ bonds.

Reaction of $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ with $[Me_2NC(S)SC(S)NMe_2]Br_2$ (4-Br)

Preliminary investigations on the five membered disulphide 4, related to 3, reveal that in the latter case not only S–S but also C–S(4) breaking (see Figure 3) occurs on reacting with $Rh(Cl(PPh_3)_3$ and $Pt(PPh_3)_4$.

By I.R., ^{1}H-, and ^{31}P N.M.R. spectroscopy we found that the reaction of 4-Br with $RhCl(PPh_3)_3$ results in the formation of *cis*- and *trans*-$RhXY(PPh_3)_2[SC(S)NMe_2]$, *trans*-$RhXY(PPh_3)_2[\eta^2\text{-}SCNMe_2]$ (X = Br, Y = Cl, Br), $Me_2NC(S)Cl$ and $SPPh_3$, while in the reaction of $Pt(PPh_3)_4$ with 4 $[Pt(PPh_3)_2(SC(S)NMe_2)]Br$ is formed. This reactivity of 4 is in accord with the following observations. The non-planar structure of 4 and the relatively long C–S(4) bond ($[\mathrm{C–S(4)}]_{av}$ = 1.74(3); $[\mathrm{C–S(2)}]_{av}$ = 1.68(3) [20]) suggest a less extensive π delocalization, compared to 3, as indicated in Figure 3. In $Me_2NC(S)SC(S)NMe_2$ (thiurammonosulphide), which is the reduced form of 4, oxidative addition of the C–S bond to $RhCl(PPh_3)_3$ [21] and $Pt(PPh_3)_4$ [22] has been observed.

A remarkably analogous reaction has been reported in the literature [23]. $IrCl(CO(PPh_3)_2$ and $Pt(PPh_3)_4$ react with a mixture of $(F_3C)_2CC(S)SC(S)C(CF_3)_2$ and $(F_3C)_2CC(S)S_2C(S)C(CF_3)_2$ to give the complexes $IrCl(CO)[\eta^2\text{-}SCC(CF_3)_2](PPh_3)_2$, $Ir(CO)Cl[\eta\text{-}SCC(CF_3)_2](PPh_3)_2$, $Ir(CO)Cl[SC(S)C(CF_3)_2](PPh_3)_2$, $Pt[\eta^2\text{-}SCC(CF_3)_2](PPh_3)_2$ and $Pt[SC(S)C(CF_3)_2](PPh_3)_2$.

In earlier oxidations of $M(II)[SC(S)NR_2]_2$ (M = Ni, Pd, Pt) and Au(I) $[SC(S)NR_2]$ by R_4bitt^{2+} only indirect evidence of supply of $SC(S)NR_2$ by R_4bitt^{2+} had been obtained and no $SCNMe_2$ complexes had been isolated [24, 25].

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