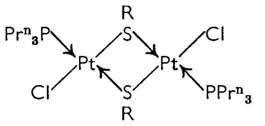
568. *Isomerism and Isomerisation of Thio-bridged Complexes of Platinum*(II).

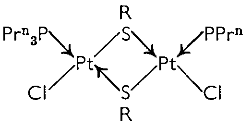
By J. Chatt and F. A. Hart.

Thio-bridged complexes of platinum(II) have been prepared from several thiols R·SH, and it is shown that with one bridging sulphur atom and one bridging chlorine atom the *cis*-isomers (III) are obtained. With two sulphur atoms in the bridges both *cis*- and *trans*-isomers (I and II) are obtained, and the *cis*-isomer is the more stable when R is aliphatic, the *trans*- when it is aromatic. A novel type of isomerism (VII and VIII) depending on the relative positions of two different bridging thio-groups has been discovered, and also a covalent compound (VII; R = p-$C_6H_4·NO_2$) of dipole moment 14·8 D. The sulphur atoms in the bridge have a pyramidal configuration.

In 1952 we isolated the isomeric thio-bridged complexes (I and II; R = Et),[1] and were surprised that the *trans*-isomer (I; R = Et) isomerised to the *cis*-isomer (II; R = Et), despite the large amount of electrical energy associated with the latter configuration (dipole moment 10·3 D). Similarly, the palladium analogue of (II; R = Et) was isolated, but the corresponding *trans*-compound could not be obtained.

(I)

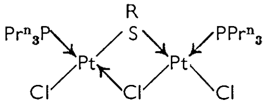


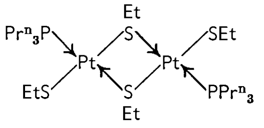


(II)

In an attempt to find out why the form (II) is favoured, we have now prepared four more pairs of complexes (I) and (II), with R = C_6H_{11}, C_6H_5, p-$C_6H_4·NO_2$, and p-$C_6H_4·OMe$, and have determined the equilibrium position between the isomers of each pair in benzene solution. We have also investigated the corresponding monothio-complexes, which were obtained only as *cis*-isomers of type (III), and also two isomeric tetrathio-complexes, (IV) and (V).

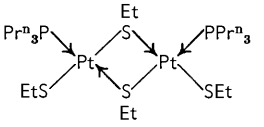
(III)

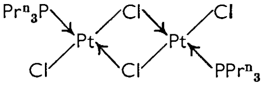




(IV)

(V)





(VI)

The configurations of the isomers were established by their electric dipole moments [1] (Table 1), and the equilibria in benzene between the isomers were determined by measuring the dielectric constants of their solutions at equilibrium [method (*a*)]. This method was used in similar studies of mononuclear platinous complexes.[2] Most of the bridged isomers are stable in benzene at room temperature and their isomerisation was catalysed by a trace of dibutylphenylphosphine, but in three cases (I and II; R = Ph, p-$C_6H_4·NO_2$, and p-$C_6H_4·OMe$), equilibrium was also reached by heating the solutions free from catalyst at 60° for 2—5 days [method (*b*)]. The equilibrium percentages of isomers obtained by both methods are probably accurate to within 5% and are listed in Table 2.

Preparation of Complexes.—The monothio-bridged complexes (III; R = C_6H_{11}, Ph, p-$C_6H_4·NO_2$, and p-$C_6H_4·OMe$) and their *trans*-dithio-analogues (I) were obtained by

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[1] Chatt and Hart, *Nature*, 1952, 673; *J.*, 1953, 2363.
[2] Chatt and Wilkins, *J.*, 1952, 273.

TABLE 1. *Dipole moments of thio-bridged complexes of platinum*(II).*

$10^3\omega$	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-10^2\Delta v$	$_{T}P$	$_{E}P$	$_{O}P$	μ
trans-[$Pt_2(SEt)_4(PPr^n_3)_2$] (IV), pale yellow, m. p. 144°.							
5·667	2·196						
7·363	2·924						
51·41		3·482					
14·80			0·783	245·9	227·9	−4	*ca.* 0
cis-[$Pt_2(SEt)_4(PPr^n_3)_2$] (V), pale yellow, m. p. 119°.							
2·724	19·01						
3·866	26·88						
58·77		3·722					
43·61			2·74	1399	196·5	1183	7·61
trans-[$Pt_2Cl_2(S{\cdot}C_6H_{11})_2(PPr^n_3)_2$] (I; R = C_6H_{11}), pale yellow, m. p. 181—187° (resolidifies, remelts at 217°).							
3·323	1·552						
3·450	1·590						
25·09		1·48					
37·32		2·30					
44·36		2·71		268	211	37	1·35
trans-[$Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}OMe)_2(PPr^n_3)_2$] (I; R = p-$C_6H_4{\cdot}OMe$), pale yellow, m. p. 170°.							
22·83	20·97						
16·67	15·32						
18·19	16·78						
20·47	19·00						
37·02		3·043					
19·40			1·10	366·5	254	86·9	2·06
trans-[$Pt_2Cl_2(S{\cdot}C_6H_5)_2(PPr^n_3)_2$] (I; R = Ph), pale yellow, m. p. 165°.							
23·40	13·23						
26·40	14·92						
22·36	12·58						
18·64	10·50						
63·63		5·434					
49·06			2·80	277	241·5	11·6	0·75
trans-[$Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)_2(PPr^n_3)_2$] (I; R = p-$C_6H_4{\cdot}NO_2$), yellow, m. p. 181°.							
20·31	55·71						
20·69	56·52						
16·39	44·87						
61·02		5·813					
46·77			2·75	742	267	449	4·68
cis-[$Pt_2Cl_2(S{\cdot}C_6H_{11})_2(PPr^n_3)_2$] (II; R = C_6H_{11}), pale yellow, m. p. 217°.							
1·520	18·392						
1·667	19·921					2292	10·6
cis-[$Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}OMe)_2(PPr^n_3)_2$] (II; R = p-$C_6H_4{\cdot}OMe$), pale yellow, m. p. 154°.							
1·930	25·22					2607	11·3
cis-[$Pt_2Cl_2(S{\cdot}C_6H_5)_2(PPr^n_3)_2$] (II; R = Ph), pale yellow, m. p. 136° (resolidifies, remelts *ca.* 164°).							
1·705	22·76						
3·424	46·53						
3·934	53·79					2547	11·2
cis-[$Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)_2(PPr^n_3)_2$] (II; R = p-$C_6H_4{\cdot}NO_2$), yellow, m. p. 129—131°.							
1·409	23·60						
1·000	16·76					3436	13·0
cis-P(SPh)P-*cis*-[$Pt_2Cl_2(SEt)(S{\cdot}C_6H_5)(PPr^n_3)_2$] (VIII; R = C_6H_5), pale yellow, m. p. 101—104°.							
2·959	41·19					2495	11·05
cis-P(SEt)P-*cis*-[$Pt_2Cl_2(SEt)(S{\cdot}C_6H_5)(PPr^n_3)_2$] (VII; R = C_6H_5), cream, m. p. 159°.							
2·293	32·24						
1·907	26·46					2502	11·1
cis-P(SEt)P-cis-[$Pt_2Cl_2(SEt)(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)(PPr^n_3)_2$] (VII; R = p-$C_6H_4{\cdot}NO_2$), pale yellow, m. p. 199°.							
3·000	24·140						
4·761	24·106						
20·62		7·35					
36·55		7·52					
				4692	201	4471	14·8

TABLE 1. (*Continued.*)

$10^3\omega$	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-10^2\Delta v$	${}_{T}P$	${}_{E}P$	${}_{O}P$	μ
† *cis*-$[Pt_2Cl_3(p\text{-}S{\cdot}C_6H_4{\cdot}OMe)(PPr^n_3)_2]$ (III; R = p-$S{\cdot}C_6H_4{\cdot}OMe$), pale yellow, m. p. 249°.							
0·358	6·70					3367	12·8
cis-$[Pt_2Cl_3(S{\cdot}C_6H_5)(PPr^n_3)_2]$ (III; R = C_6H_5), pale yellow, m. p. 182°.							
3·787	80·29						
6·097	132·81						
2·543	53·20					3707	13·5
† *cis*-$[Pt_2Cl_3(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)(PPr^n_3)_2]$ (III; R = p-$C_6H_4{\cdot}NO_2$), pale yellow, m. p. 184°.							
0·328	5·47						
0·339	5·93					3121	12·4

* ω is the weight fraction of solute, $\Delta\epsilon = \epsilon_S - \epsilon_B$ where ϵ_S = dielectric constant of solution, ϵ_B = that of benzene; similarly for Δn, where n = refractive index; and for Δv where v = specific volume. ${}_{T}P$ = molar total polarisation (c.c.), ${}_{O}P$ = molar orientation polarisation.

† Approx. value (low solubility).

TABLE 2. *Equilibria between* cis- *and* trans-*isomers of thio-bridged complexes of platinum*(II).

	$\Delta\varepsilon/\omega$ *cis*	$\Delta\varepsilon/\omega$ *trans*	$\Delta\varepsilon/\omega$ at equil., reached from . *cis*	*trans*	*cis*-Isomer (%) at equil. reached from *cis*	*trans*	Method
$[Pt_2(SEt)_4(PPr^n_3)_2]$	6·97	0·392	4·76	4·89	67·5	69·4	*a*
$[Pt_2Cl_2(SEt)_2(PPr^n_3)_2]$	13·22	0·467	11·69	11·55	87·1	86·0	*a*
$[Pt_2Cl_2(SPh)_2(PPr^n_3)_2]$	13·53	0·564	1·34 1·35	0·746 0·759	6·1	1·5	*a*
			0·965	0·854	3·1	2·2	*b* (132 hr.)
$[Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}OMe)_2(PPr^n_3)_2]$	13·70	0·922		1·16		1·9	*a*
				1·38		3·6	*b* (120 hr.)
$[Pt_2Cl_2(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)_2(PPr^n_3)_2]$	16·75	2·74		3·12 3·10		2·6	*a*
			3·07 2·96	3·33 3·33	1·9	4·2	*b* (45 hr.)
$[Pt_2Cl_3(SPh)(PPr^n_3)_2]$	21·27	0·5 *	20·2 19·5		~93		*a*
$[Pt_2Cl_3(p\text{-}S{\cdot}C_6H_4{\cdot}NO_2)(PPr^n_3)_2]$	17·08		17·2 15·4		~90—100 †		*a*
$[Pt_2Cl_2(S{\cdot}C_6H_{11})_2(PPr^n_3)_2]$	12·03	0·464	11·08 11·06	10·36 10·79	91·7	87·4	*a*

* Estimated value. † Approx. value (low solubility).

treating an alcoholic solution of the tetrachloro-compound (VI) with one and with two molar proportions respectively of the thiol or its sodium salt.

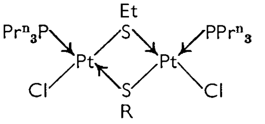
Because of these reactions it is surprising that the *cis*-dithio-bridged complexes (II; R = Ph, p-$C_6H_4{\cdot}NO_2$, and p-$C_6H_4{\cdot}OMe$) were prepared from the corresponding monothio-bridged complexes (III) by reaction with one equivalent of the thiol.

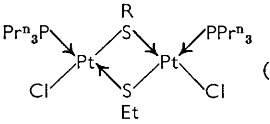
The tetraethylthio-isomers (IV) and (V) were prepared by treating compound (I; R = Et) with the sodium salt of ethanethiol at 5°. At room temperature this reaction gave only a very small proportion of the *cis*-isomer.

The above bridged complexes, except the monothio-complexes, are easily soluble in organic solvents and corresponding *cis*- and *trans*-isomers have very similar solubilities. This property contrasts markedly with that of the mononuclear platinum(II) complexes, *e.g.*, $[(PPr^n_3)_2PtCl_2]$, where the *cis*- is always very much less soluble than the *trans*-isomer in organic solvents.

Mixed Dithio-bridges: a New Type of Isomerism.—A novel type of isomerism arises within the class of *cis*-dithio-complexes (II) if the two bridging thio-groups are different. The compound (VII; R = Ph) is produced by the action of thiophenol on the monoethylthio-compound (III; R = Et), while the isomer (VIII; R = Ph) is given by the action of ethanethiol on the monophenylthio-compound (III; R = Ph). The strict preservation of configuration during the introduction of the second thio-bridging group is proved by the isolation of compound (VII; R = p-$C_6H_4NO_2$), having a dipole moment of 14·8 D, when the monothio-compound (III; R = Et) is treated with p-nitrothiophenol. If the positions of the bridging groups had been reversed, the isomer (VIII; R = p-C_6H_4·NO_2) with a

(VII)





(VIII)

dipole moment of about 8 D would have resulted. 14·8 D appears to be the highest dipole moment observed for a purely covalent molecule and is of the order of those found in salts, *e.g.*, tetra-n-butylammonium acetate, 11·2 D (picrate, 17·8 D).[3]

Equilibria in Benzene Solution.—(a) *The monothio-bridged complexes, type* (III). We could not estimate accurately the equilibrium positions in the monothio-series of complexes because only *cis*-isomers were available; also they had rather poor solubility in organic solvents. Indeed, compound (III; R = p-C_6H_4·OMe) was too insoluble in benzene for any measurements.

The dielectric constants of solutions of the substances (III; R = Ph and p-C_6H_4·NO_2) changed only a little on addition of dibutylphenylphosphine, which normally isomerises tertiary phosphine complexes of platinum(II). If this small change was caused by isomerisation it indicated that the equilibrium mixtures of (III; R = Ph and p-C_6H_4·NO_2) contain over 90% of the *cis*-isomers.

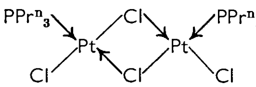
(b) *The dithio-bridged complexes, types* (I) *and* (II). There is a marked distinction between the aliphatic and alicyclic members of this class (I, II; R = Et and C_6H_{11}) and the aromatic members (I, II; R = Ph, p-C_6H_4·NO_2, and p-C_6H_4·OMe). The former give an equilibrium mixture containing about 90% of *cis*-isomers, but the latter give only 2—3% of *cis*-isomers. Previously [1] we incorrectly stated that compounds (I and II; R = Et) gave an equilibrium mixture containing >99% of the *cis*-isomer: the correct value is 86—87%.

Although there must be some steric interaction between the groups R and the tripropylphosphine ligands, steric effects cannot be responsible for the difference between the aliphatic and the aromatic members, because the bulky cyclohexylthio- and the ethylthio-complexes gave similar equilibrium mixtures. We therefore conclude that the preference for the *trans*-configuration in the aromatic dithio-bridged complexes is due to electronic and not to steric effects. It is remarkable, therefore, that the powerful electron-attracting and -repelling groups p-NO_2 and p-MeO in (I, II) have no detectable influence on the equilibrium position.

(c) *The tetrathio-complexes, types* (IV) *and* (V). Compounds (IV) and (V) gave an equilibrium mixture containing about 68% of the *cis*-isomer (V).

DISCUSSION

Our experiments have uncovered some interesting facts but do not explain them. The tetrachloro-bridged complex $(PPr^n_3)_2Pt_2Cl_4$ exists in the solid in the *trans*-form (VI),[4] and its solution appears to contain about 2% of the *cis*-isomer (IX).[1] The introduction of only one bridging thio-group, whether aromatic or aliphatic, gives compounds which exist in the solid as *cis*-isomers (III) only; the equilibrium mixture contains only a few percent of *trans*-isomer. It might be thought that this result could be correlated with the *trans*-effects of the ligands about the platinum atoms. Groups of high *trans*-effect in *trans*-positions to each other introduce configurational instability into the molecule.[5]



(IX)

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[3] Geddes and Kraus, *Trans. Faraday Soc.*, 1936, **32**, 583.

[4] Chatt, *J.*, 1951, 652.

[5] Chatt and Williams, *J.*, 1951, 3061; Chatt and Wilkins, *J.*, 1952, 4300.

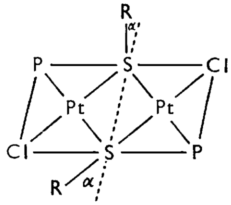
In the *trans*-isomer of compound (III), sulphur and phosphorus, both groups of moderate to high *trans*-effects, would be in *trans*-positions to each other. In the *cis*-isomer (III), however, only the chlorine atoms of relatively low *trans*-effect are in *trans*-positions to sulphur and to phosphorus, and so we might expect it to be the stable isomer. This effect may contribute, but we doubt whether it provides sufficient explanation of the stability of the *cis*-isomer of type (III). Neither phosphorus nor sulphur appears to have sufficiently high *trans*-effects to do this, because *trans*-$[(PPr^n_3)_2PtCl_2]$ and *trans*-$[(Pr^n_2S)_2PtCl_2]$, where a similar consideration would apply, both predominate to over 95% in equilibrium with their *cis*-isomers.[6] Also this does not explain the stabilisation of *cis*-isomers when there are two ethylthio-groups in the bridge.

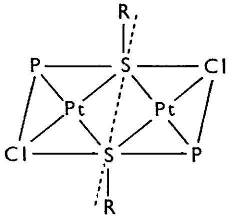
The bridged dithio-complexes present a further enigma. Why should the aliphatic thiols give stable *cis*-isomers of type (II) and the aromatic thiols stable *trans*-isomers of type (I), although the presence of p-NO_2 and p-OMe groups scarcely affects the equilibrium in the aromatic series? Even when all four acid radicals are ethylthio-groups the *cis*-isomer still predominates at equilibrium.

There is some property of the aliphatic thio-bridge which causes the *cis*-isomer to be preferred, and this is to some extent destroyed in the aromatic thio-bridges. The PtS_2Pt ring is probably an " inorganic aromatic ring " with a d_π–d_π-system covering both platinum and sulphur atoms. It is not clear how this could stabilise the *cis*-isomers, but, if it did and if the filled p-orbital on the sulphur atoms took any part in it, then the effect of the aromatic radicals might be explained as due to interaction of the p-orbital with the aromatic π-orbitals, so reducing their availability for the PtS_2Pt ring system. The aromatic thiols might thus behave more like bridging halogen atoms, where the p-electrons are more firmly held to the halogen by its greater electronegativity. Even then we should expect that the availability of the p-electrons, and so the position of equilibrium, would depend very much on the nature of substituents in the aromatic ring; and that the aromatic monothio-complexes would have a *trans*-configuration. Neither was observed.

If the p-electrons on the sulphur atoms were strongly delocalised into either the aromatic systems or the PtS_2Pt ring, we should also expect to find something approaching a planar arrangement of groups around the sulphur atoms. However, the *trans*-isomers of type (I) have definite dipole moments and any completely planar structure is ruled out. A non-planar co-ordination about the sulphur atoms allows either a *cis*- or a *trans*-arrangement of groups R about the PtS_2Pt rings (X) or (XI) respectively, but the observed moments eliminate the non-dipolar form (XI). If in (X), the angle α is assumed to be half the tetrahedral angle, then compound (X; R = Ph) should have a moment of about 2·1 D and (X; $R = p\text{-}C_6H_4{\cdot}NO_2$) a moment of about 8·3 D. The observed moments are 0·75 D and 4·7 D, respectively, indicating either that α is less than 30° or, much more probably, that the groups R oscillate so that the true state is a dynamic equilibrium of (X) and (XI) with α greater than 30°.

(X)





(XI)

EXPERIMENTAL

The preparation of the mono- and di-ethylthio-complexes has been described. Of the new compounds described below the monothio-complexes are stable, but the dithio- and tetrathio-complexes, especially (II; $R = p\text{-}C_6H_4{\cdot}NO_2$) and (IV), are somewhat labile in hot solvents and

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[6] Chatt and Wilkins, *J.*, 1956, 525; also unpublished work.

care is needed in their recrystallisation. Purification to constant molar polarisation was used to establish the purity of compounds whenever lability of isomers made the m. p.s unreliable. This procedure is indicated by an asterisk. The colours and m. p.s of the pure compounds are given in Table 1.

cis-PSP-cis-sym-μ-*Chloro-μ′-phenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (III; R = Ph). The tetrachloro-compound (VI) (1 g.) in ethanol (50 c.c.) was treated at 15° with a solution of thiophenol (0·129 g., 1 mol.) in ethanol (5 c.c.). The solvent was removed at 12 mm. after 1 hr., and the residue recrystallised thrice from alcohol, giving the pure *complex* (0·40 g.) (Found: C, 31·2; H, 5·1%; *M*, ebullioscopically in 1·70% chloroform solution, 902. $C_{24}H_{47}Cl_3SP_2Pt_2$ requires C, 31·1; H, 5·1%; *M*, 926).

cis-PSP-cis-sym-μ-*Chloro-μ′*-o-*nitrophenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (III; R = p-C_6H_4·NO_2) was prepared similarly in 40% yield (Found: C, 29·8; H, 4·8. $C_{24}H_{46}O_2NSCl_3P_2Pt_2$ requires C, 29·65; H, 4·8%).

cis-PSP-cis-sym-μ-*Chloro-μ′*-p-*methoxyphenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (III; R = p-C_6H_4·OMe). The tetrachloro-compound (VI) (2·0 g.) in ethanol (100 c.c.) was treated at 15° with a solution of *p*-methoxythiophenol (0·328 g., 1 mol.) in ethanol (7 c.c.). The *monothio-compound* (1·37 g.) which had separated after 2 hr. was thrice recrystallised from ethyl methyl ketone (yield, 0·30 g.) (Found: C, 31·6; H, 5·2. $C_{25}H_{49}OSCl_3P_2Pt_2$ requires C, 31·4; H, 5·2%).

cis-PSP-cis-sym-μ-*Chloro-μ′-cyclohexylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (III; R = C_6H_{11}) was prepared similarly, though the reaction was slower (80% yield; m. p. 237°) (Found: C, 31·1; H, 5·7. $C_{24}H_{53}SCl_3P_2Pt_2$ requires C, 30·9; H, 5·7%).

cis-sym-*Di-μ-phenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (II; R = Ph). The monothio-compound (III; R = Ph) (1·5 g.) in chloroform (20 c.c.) was treated with thiophenol (0·164 c.c., 1 mol.) in alcohol. After 24 hr. at 5° the solvent was removed at 12 mm. and the residue, which sinters at 133° and then resolidifies, was quickly recrystallised four times from ethanol to give the pure cis-*isomer* * (0·48 g.) (Found: C, 36·0; H, 5·2%; *M*, ebullioscopically in 1·04% benzene solution, 972. $C_{30}H_{52}Cl_2S_2P_2Pt_2$ requires C, 36·0; H, 5·2%; *M*, 1000).

cis-sym-*Di-μ*-p-*nitrophenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (II; R = p-C_6H_4·NO_2). The monothio-compound (III; R = p-C_6H_4·NO_2) (1 g.) in chloroform (10 c.c.) was treated with a solution of *p*-nitrothiophenol (0·160 g., 1 mol.) in chloroform (3 c.c.), and after 3 hr. at 5° the solvent was removed at 12 mm. The residue, thrice crystallised from chloroform (2·5 c.c.) by careful addition of ether (5 c.c.), and twice more by adding benzene (6 c.c.), afforded the pure *product* * (0·31 g.) (Found: C, 33·1; H, 4·7. $C_{30}H_{50}Cl_2O_4S_2N_2P_2Pt_2$ requires C, 33·05; H, 4·6%).

cis-sym-*Di-μ*-p-*methoxyphenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (II; R = p-C_6H_4·OMe). The monothio-compound (III; R = p-C_6H_4·OMe) (0·60 g.) in chloroform (7 c.c.) was treated at 20° with *p*-methoxythiophenol (0·940 g., 1 mol.) in alcohol (1·88 c.c.). After 24 hr. at 5° the solvent was removed, and the residue, a mixture of *cis*- and *trans*-isomers, was twice crystallised from chloroform (1 c.c.) by carefully adding ether (5 c.c.). This gave clusters of pale yellow needles of the product (III; R = p-C_6H_4·OMe) together with a few yellow prisms of its *trans*-isomer. Quick treatment with chloroform (1 c.c.) dissolved the needles, leaving the more bulky crystals of the *trans*-isomer. The product was crystallised from the chloroform solution by addition of ether, and two more similar crystallisations gave the pure cis-*isomer* * (0·05 g.) (Found: C, 36·0; H, 5·25. $C_{32}H_{56}O_2S_2Cl_2P_2Pt_2$ requires C, 36·25; H, 5·3%).

cis-sym-*Di-μ-cyclohexylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (II; R = C_6H_{11}). The *trans*-dithio-compound (I; R = C_6H_{11}) (0·30 g.) was heated at 190° until the melt had completely resolidified (5 min.), and the resultant solid twice recrystallised from ethanol, giving the pure cis-*isomer* (0·13 g.) (Found: C, 35·8; H, 6·4%; *M*, in 0·72% benzene solution, 1018; in 0·91% solution, 970. $C_{30}H_{64}Cl_2S_2P_2Pt_2$ requires C, 35·6; H, 6·4%; *M*, 1012).

trans-*Di-μ-phenylthio-dichlorobis*(*tri-n-propylphosphine*)*diplatinum* (I; R = Ph). The tetrachloro-compound (VI) (2 g.) in alcohol (100 c.c.) was treated with a solution of sodium (0·108 g., 2 atom-equiv.) and thiophenol (0·516 g., 2 mol.) in alcohol (15 c.c.). After 19 hr. at 20°, the mixture was evaporated to 30 c.c., and the product (2·1 g.; m. p. 164°) filtered off. It was washed with water, and recrystallised four times from ethyl methyl ketone, giving lemon-yellow crystals of the pure trans-*isomer* (0·37 g.) (Found: C, 35·9; H, 5·35; S, 6·35%; *M*, ebullioscopically in 1·2% benzene solution, 1075; in 2·4% solution, 1054. $C_{30}H_{52}Cl_2S_2P_2Pt_2$ requires C, 36·0; H, 5·2; S, 6·4%; *M*, 1000).

trans-*Di*-μ-p-*methoxyphenylthio-dichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (I; R = *p*-C_6H_4·OMe) was prepared similarly, but without the use of sodium (yield 30%) (Found: C, 36·4; H, 5·3%; *M*, ebullioscopically in 1·1% benzene solution, 1072; in 2·6% solution, 1058. $C_{32}H_{56}O_2S_2Cl_2P_2Pt_2$ requires C, 36·25; H, 5·3%; *M*, 1060).

trans-*Di*-μ-p-*nitrophenylthiodichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (I; R = *p*-C_6H_4·NO_2). The tetrachloro-compound (VI) (1·25 g.) in alcohol (50 c.c.) was treated with a solution of *p*-nitrothiophenol (0·454 g., 2 mol.) in alcohol (25 c.c.), and a sticky yellow precipitate, which became granular after the reaction mixture had been shaken for 90 min., separated. This was collected (1·02 g.; m. p. 173—176°) and recrystallised from alcohol to give the pure *compound* (0·55 g.) (Found: C, 33·1; H, 4·7; N, 2·7%; *M*, ebullioscopically in 1·6% benzene solution, 1082; in 2·4% solution, 1061. $C_{30}H_{50}O_4N_2Cl_2S_2P_2Pt_2$ requires C, 33·05; H, 4·6; N, 2·6%; *M*, 1090).

trans-*Di*-μ-*cyclohexylthio-dichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (I; R = C_6H_{11}). The tetrachloro-compound (VI) (1·10 g.) in acetone (30 c.c.) was treated with cyclohexanethiol (0·60 g., 4 mol.). After 16 hr., the solvent was removed at 12 mm., and the residue recrystallised four times from methanol, to give the pure trans-*isomer* (0·20 g.) (Found: C, 35·8; H, 6·3; S, 5·7. $C_{30}H_{64}Cl_2S_2P_2Pt_2$ requires C, 35·6; H, 6·4; S, 6·05%).

cis-P(SEt)P-cis-sym-μ-*Ethylthio*-μ′-*phenylthio-dichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (VII; R = Ph). The monothio-compound (III; R = Et) (2·0 g.) in chloroform (50 c.c.) was treated with a solution of thiophenol (0·250 g., 1 mol.) in ethanol (5 c.c.). After 24 hr. at 20°, the solvent was removed at 12 mm., and the residue recrystallised twice from ethyl methyl ketone, to give the pure *dithio-compound* (0·44 g.) (Found: C, 32·8; H, 5·5%; *M*, in 1·11% benzene solution, 938; in 1·07% solution, 901. $C_{26}H_{52}S_2Cl_2P_2Pt_2$ requires C, 32·8; H, 5·5%; *M*, 952).

cis-P(SEt)P-cis-sym-μ-*Ethylthio*-μ′-p-*nitrophenylthio-dichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (VII; R = *p*-C_6H_4·NO_2) was prepared similarly in 53% yield (Found: C, 31·5; H, 5·2%; *M*, in 0·68% benzene solution, 960; in 0·54% solution, 975. $C_{26}H_{51}O_2NS_2Cl_2P_2Pt_2$ requires C, 31·3; H, 5·2%; *M*, 997).

cis-P(SPh)P-cis-sym-μ-*Ethylthio*-μ′-*phenylthio-dichlorobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (VIII; R = Ph) was prepared similarly from (III; R = Ph) and ethanethiol (yield 20%) and recrystallised from methanol (Found: C, 32·9; H, 5·4. $C_{26}H_{52}S_2Cl_2P_2Pt_2$ requires C, 32·8; H, 5·5%).

cis-sym-*Di*-μ-*ethylthio-diethylthiobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (V). The *cis*-dithio-compound (II; R = Et) (2·5 g.) in ether (250 c.c.) was treated at −10° with a solution of sodium (0·127 g., 2 atom-equiv.) and ethanethiol (0·408 c.c., 2 mol.) in alcohol (10 c.c.). After 44 hr. at 5°, the mixture had deposited a lemon-yellow mixture, m. p. *ca.* 145°, of the two isomers. This was dissolved in light petroleum (b. p. 60—80°; 40 c.c.) and filtered; on slow spontaneous evaporation, the *product* separated as yellow plates (2·38 g.) which were recrystallised eleven times from methanol (yield, 0·24 g.) (Found: C, 32·75; H, 6·6%; *M*, ebullioscopically in 2·3% benzene solution, 883; in 4·7% solution, 937. $C_{26}H_{62}S_4P_2Pt_2$ requires C, 32·7; H, 6·5%; *M*, 955).

trans-sym-*Di*-μ-(*ethylthio*)-*diethylthiobis*(*tri*-*n*-*propylphosphine*)*diplatinum* (IV). The *trans*-dithio-compound (I; R = Et) (1·5 g.) in alcohol (300 c.c.) was treated at 15° with a solution of sodium (0·0763 g., 2 atom-equiv.) and ethanethiol (0·206 g., 2 mol.) in alcohol (10 c.c.) and kept for 66 hr. The mixture was then evaporated at 12 mm. to 50 c.c., and the *product* obtained as prisms (0·95 g.) which were washed with water and twice recrystallised from ethanol (Found: C, 33·0; H, 6·6%; *M*, ebullioscopically in 3·1% benzene solution, 927; in 4·5% solution, 902. $C_{26}H_{62}S_4P_2Pt_2$ requires C, 32·7; H, 6·5%; *M*, 955).

Dipole Moments.—These were measured and calculated as in previous work,[1] but a platinum-plated glass cell was used with a liquid capacity of about 8 c.c. An allowance of 10% of the electron polarisation, ${}_{\mathrm{E}}P$, was made for the atom polarisation. All measurements refer to benzene solutions at 25°.

Determinations of Equilibrium between cis- *and* trans-*Isomers*.—*Method* (*a*). A known weight (*ca.* 30 mg.) of a pure isomer was dissolved in a weighed amount (8—9 g.) of carefully dried benzene and isomerised by addition of about 0·3 mg. of dibutylphenylphosphine. After the isomers had come to equilibrium at 25°, the dielectric constant of the solution was determined. The percentage of *cis*- and *trans*-isomers present was then calculated from dielectric constants of similar solutions of the pure *cis*- and *trans*-isomers, as described by Chatt and Wilkins.

Method (*b*). A known weight (*ca.* 30 mg.) of the compound, dissolved in a weighed amount (9—10 c.c.) of carefully dried pure benzene, was heated at 60° until equilibrium between the isomers was attained (the period required was determined by trial experiments). The dielectric constant of the solution was then found, and the equilibrium position calculated as above.

To show that the reaction studied was isomerisation, and not, *e.g.*, disproportionation, equilibrium solutions were evaporated to dryness at 12 mm. after the measurements (and after adding a trace of $[Pt_2Cl_4(Pr^n{}_3P)_2]$ to remove the $PBu^n{}_2Ph$ from those solutions containing it). The residue, when it consisted almost entirely of one isomer, was identified by mixed m. p. and, when it was a mixture, from its infrared spectrum. It was not possible to confirm the identity of the minor component of the mixture except in the case of $[Pt_2Cl_2(S{\cdot}C_6H_{11})_2(PPr^n{}_3)_2]$.

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