231. *cis-trans* Isomerization of bis(Dialkylsulfide)Dihaloplatinum(II) Complexes in Solution[1])

by **Raymond Roulet** and **Claude Barbey**

Institute of inorganic and analytical chemistry, University of Lausanne

(18. VII. 73)

Summary. The equilibrium energetics and the kinetics of *cis-trans* isomerization of some bis(dialkylsulfide)dihaloplatinum(II) complexes have been examined by ^{1}H-NMR. spectroscopy. The isomers are stable in chloroform but each form isomerizes to an equilibrium mixture when free dialkylsulfide is added. The *cis* to *trans* process is endothermic and the position of the equilibrium is markedly dependent on the nature of the donor atoms and of the solvent. The rate of isomerization of $Pt(Me_2S)_2Cl_2$ is first order in complex and in Me_2S. The isomerization proceeds by a double displacement mechanism as it is shown that the tris(dimethylsulfide)chloroplatinum(II) cation is an isolable intermediate of the reaction. When free Me_2S is added to *trans*-$Pd(Me_2S)_2Cl_2$, isomerization does not occur and one observes instead a fast ligand exchange. Its mechanism is the usual associative one for substitutions in square planar d^8-complexes.

1. Introduction. – Although many square planar platinum(II) complexes have been isolated in their *cis* and *trans* forms, only a few of them exhibit an observable isomerization in solution. This process occurs for the bis (trialkylphosphine) platinum complexes. *Chatt et al.* [1] studied the thermodynamics of this process in 1952 and *Haake* [2] has studied the mechanism of isomerization. The process is catalyzed by free phosphine and *Haake* postulated that the isomerization takes place through the pseudorotation of the phosphine groups in a 5-coordinated intermediate (or transition state). This year, an extensive study of these platinum-phosphine complexes has appeared by *Powell & Cooper* [3]. These authors gave conclusive experimental evidence for the mechanism first suggested by *Basolo & Pearson* [4] which requires two consecutive substitutions to effect the *cis-trans* isomerization. *Cattalini* [5] found the same mechanism to be operative in the case of the dichlorodiaminepalladium(II) complexes.

In 1930 *Angell & Drew* [6] isolated some isomers of the square planar bis(dialkylsulfide)dihaloplatinum(II) complexes and they observed qualitatively that a *trans-cis* isomerization takes place in alcohol. In 1971 *Allen et al.* [7] noted a *trans-cis* rearrangement in the solid phase for the corresponding pentamethylenesulfide complexes.

2. Equilibrium energetics of the *cis-trans* isomerization. – A convenient way of studying the isomerization of the dialkylsulfideplatinum complexes is by ^{1}H-NMR.-spectroscopy. Each isomer is also identified by its IR.-spectrum (two bands for the ν(Pt-Cl) of the *cis* isomer which has C_{3v} symmetry and one for the D_{2h} *trans*-isomer), and in one case by dipole moment measurements (Table 4).

Fig. 1a shows for example the ^{1}H-NMR.-spectrum of the two bis(dimethylsulfide) dichloroplatinum(II) isomers; the 1:4:1 triplet is due to the coupling with the platinum 195 isotope ($I = {}^1/_2$). For all the dialkylsulfide complexes examined, the plati-

[1]) Presented at the XVth ICCC in Moscow, June 1973. Proceedings, p. 507.

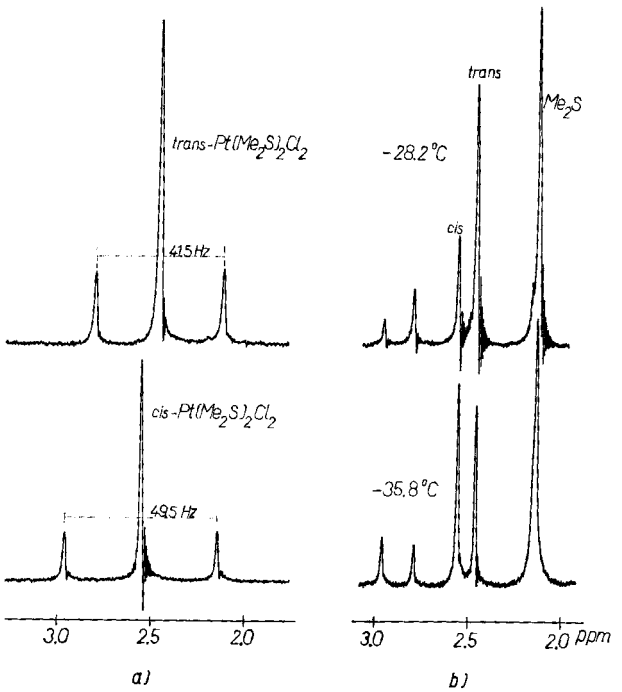


Fig. 1. *^{1}H-NMR. spectra of a)* cis-*and* trans-*$Pt(Me_2S)_2Cl_2$ in CH_2Cl_2 at 20°, b) equilibrium mixture of both isomers in presence of free Me_2S*

num-proton coupling constant is greater for the *cis* than for the *trans* form (Table 4). The complexes are stable in chloroform but each form isomerizes to an equilibrium mixture when free dialkylsulfide is added, even in catalytic amounts (Fig. 1b). One has a true equilibrium because the results are the same when starting with the pure *cis* or the pure *trans* form and when performing several cooling-heating cycles between measurements. The sum of the concentrations of both isomers is constant with time and independent from the amount of free ligand present. As there is no exchange between free and coordinated dialkylsulfide at the NMR. time scale up to the boiling point of the solvent, one has a direct measure of the equilibrium constant $K = [trans]/[cis]$ by integrating the respective signals of the two isomers. The NMR.-spectrum of the *cis*-dibenzylsulfide-platinum complexes is more complicated (Table 4) but the calculation remains straightforward as the 1:4:1 triplet of the *trans* form becomes discernible when adding a trace of free ligand and working at 90 MHz.

On plotting the logarithm of the equilibrium constant *versus* the inverse of temperature (Fig. 2), one sees that the percentage of the *trans* form is always greater at higher temperature for all the systems examined.

The enthalpy of formation of the *trans* isomer is always positive, thus the *cis* to *trans* process is endothermic. The two major contributions to the enthalpy term are the ΔH for internal bond strength changes and the ΔH of solvation. For the first contribution, the isomer with the more efficient π bonding will have the greater total bond strength. As sulfide ligands have a larger *trans* effect than chloro groups, the

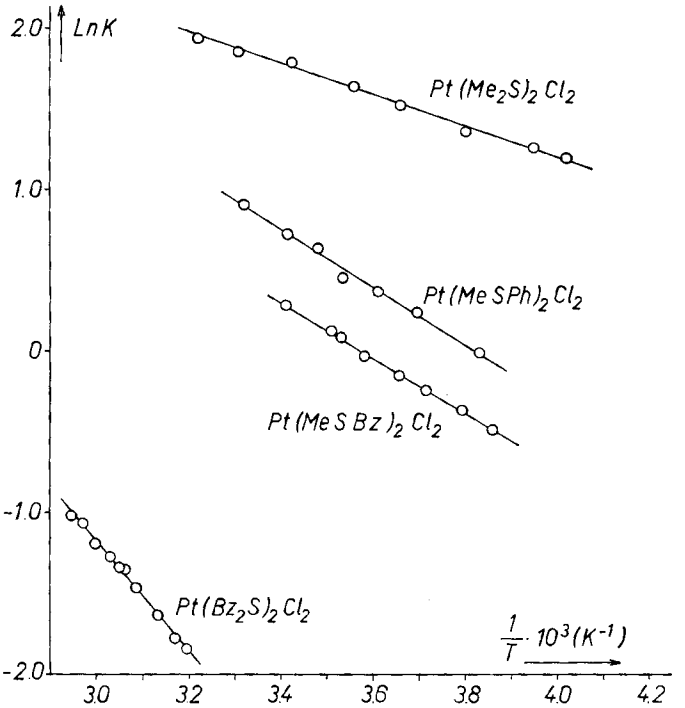


Fig. 2. *Effect of temperature and of the nature of R on the* cis-trans *equilibrium constant of various* $Pt(R_2S)_2Cl_2$ *complexes*

Table 1. Cis-trans *equilibria of* $Pt(R_2S)_2X_2$ *complexes*

in chloroform	T (°K)	K [a]	ΔG (kcal/mol)	ΔH (kcal/mol) [b]	ΔS (e.u.)
Me_2S/Cl	302	6.4 ± 0,1	−1.1 ± 0.1	1.9 ± 0.2	10 ± 1
MeSBz/Cl	293	1.32 ± 0.03	−0.16 ± 0.01	3.4 ± 0.2	12 ± 1
Bz_2S/Cl	313	0.16 ± 0.01	+1.15 ± 0.02	6.7 ± 0.4	18 ± 1
Bz_2S/Br	309	0.48 ± 0.05	+0.45 ± 0.05	4.8 ± 0.2	14 ± 1
Bz_2S/I	306	3.4 ± 0.1	−0.74 ± 0.03	2.0 ± 0.1	9 ± 1
MeSPh/Cl	301	2.5 ± 0.1	−0.54 ± 0.03	3.6 ± 0.4	14 ± 2
in dichloromethane					
Me_2S/Cl	301	1.88 ± 0.04	−0.38 ± 0.01	2.3 ± 0.1	9 ± 1
MeSBz/Cl	294	0.39 ± 0.03	+0.55 ± 0.04	3.2 ± 0.2	9 ± 1
Me_2Sc/Cl	313	> 20 in $CHCl_3$			
Me_2Se/Cl	276	4.0 ± 0.1	in $CHCl_3$ + 30 v% $PhNO_2$		

[a] Means of 5–9 measurements [b] Range of temperatures: 30–60°

isomer which allows the greater amount of platinum-sulfur π back donation will have the larger overall bond strength. This would be the *cis* isomer in which the sulfides are *trans* to the chloro groups. The second contribution favors also the *cis* isomer since the dipole-dipole interactions between the complex and the solvent are greater in the more polar *cis* isomer than in the less polar *trans* isomer.

The major contribution to the entropy term is probably the ΔS of solvation. This should favor the *trans* isomer since the *cis* complex will have more associated solvent molecules than the less polar *trans* form; this gives positive ΔS for the *cis* to *trans* processes. Contrary to the platinum-phosphine case [1], the process is not entropy controlled as the magnitude of $T\Delta S$ is not always greater than the enthalpy term. Going from dimethyl- to dibenzylsulfide (Table 1), the basicity of the ligands decreases and their ability to accept electrons by π back donation increases. The two factors favor the *cis* isomer in accordance with the decrease of K and the increase of ΔG and ΔH. For the same sulfide, on going from the chloro- to the iodocomplex, the *trans* effect of the halide group increases. Therefore there is a smaller difference in total bond energy between the two iodo isomers than between the two corresponding chloro isomers. This contributes in making the *cis* to *trans* process less and less endothermic. As expected, on going from chloroform to the more polar dichloromethane, the equilibrium is shifted in favor of the more polar *cis* form. The stable form of the bis (dimethylselenide)dichloroplatinum(II) complex in chloroform is the *trans* isomer and the *cis* isomer was identified only in much more polar solvent mixtures.

3. Kinetics of the *cis-trans* isomerization. – The isomerization of *trans*-bis-(dimethylsulfide) dichloroplatinum (II) in presence of free dimethylsulfide is slow

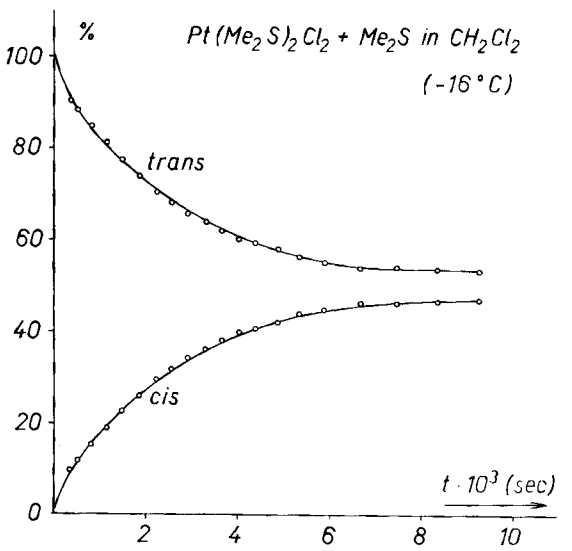


Fig. 3. *Reaction between* trans-$Pt(Me_2S)_2Cl_2$ *and* Me_2S *in* CH_2Cl_2 *at* $-16.4°$

Table 2. *Rate constants of* cis- $\underset{k_2'}{\overset{k_2}{\rightleftarrows}}$ trans- $Pt(Me_2S)_2Cl_2$ *at* $-16.4°$ *in* CH_2Cl_2

[*trans*] M	0.10	0.09	0.11	0.15	0.14
$[Me_2S]$ M	0.10	0.09	0.05	0.03	0.004
$10^4(k_2+k_{-2})s^{-1}$*	3.9	3.5	2.0	1.5	0.3

$k_2 = (1.9 \pm 0.3)10^{-3}\ M^{-1} \cdot s^{-1}$; $k_{-2} = (2.0 \pm 0.2)10^{-3}\ M^{-1} \cdot s^{-1}$

* 90–95% of reaction followed for the first 4 figures, 41% for the 5th.

enough to follow by ^{1}H-NMR. the disappearance of one isomer and the appearance of the other. The same is true for the reverse process (Fig. 3).

The rate constants are obtained from the function $-\ln([trans] - [trans]_{eq}) = (k_2 + k_{-2})t - \ln([trans]_o - [trans]_{eq})$ and the value of K.

The observed rate law for the isomerization is first order in both complex and free ligand. This suggests an associative mechanism. The ^{1}H-NMR.-spectra show only the presence of the two isomers and of free dimethylsulfide but the intermediate of the isomerization process may be identified by the following experiments.

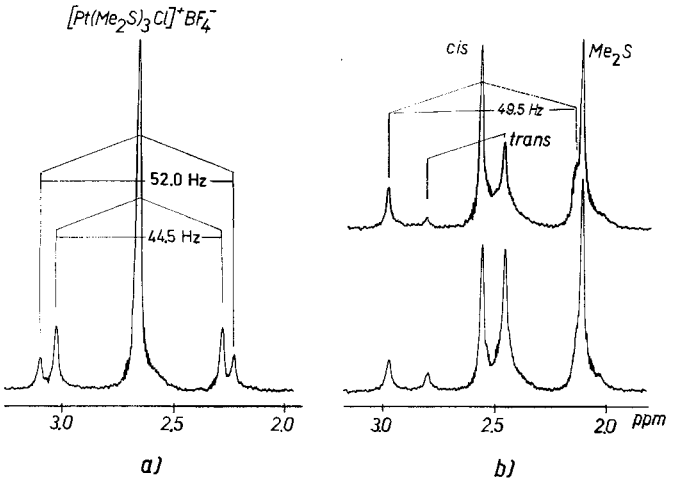


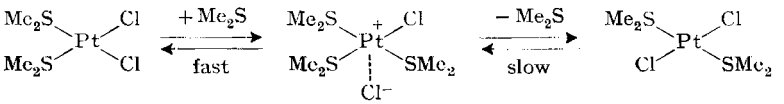
Fig. 4. ^{1}*H-NMR. spectra of a)* $[Pt(Me_2S)_3Cl]BF_4$ *in* CH_2Cl_2 *at 20°, b) after addition of* Ph_4AsCl *(1:1) (upper spectrum after 3 min., lower one after 30 min.)*

The tris(dimethylsulfide)chloroplatinum(II)tetrafluoroborate has been isolated in the solid state [8]. It is stable in solution as long as there are no halide anions present (Fig. 4a). In the NMR.-spectrum, the main peaks of the two nonequivalent sulfides have practically the same chemical shift but the integration of the satellites have a ratio of one to two. This is in accordance with the fact that the tris complex has one sulfide trans to chloride and two sulfides trans to each other. When tetraphenylphosphonium chloride is added to the tris complex in dichloromethane, a fast substitution of sulfide by chloride takes place, giving the *cis* complex as dimethylsulfide has a greater *trans* effect than chloride. As the fast formation of the *cis* isomer is accompanied by the liberation of dimethylsulfide, one observes also the slower *cis-trans* isomerization (Fig. 4b).

If the tris complex is an intermediate of the *cis-trans* isomerization, the rate determining step of the *trans* to *cis* process should be its formation by a slow substitution of one chloride by a sulfide, followed by the fast substitution of one of the two sulfides *trans* to each other by a chloride. To measure the rate of this determining step, one should avoid the reaction of chloride with the tris complex. We thus added an excess of silver perchlorate to the *trans* complex in dichloromethane and the reaction was initiated by adding the free dimethylsulfide. The ^{1}H-NMR. spectra taken at various

intervals of time showed the disappearance of the *trans* and the appearance of the tris complex (there was no evidence of any $Pt(Me_2S)_4^{2+}$ formed). The rate law was first order in *trans* complex and in dimethylsulfide and the measured second order rate constant (at –16°C) was the *same* as the one of the *trans-cis* isomerization itself. As expected the reverse process, *i.e.* the reaction between the *cis* complex and dimethylsulfide in presence of $AgClO_4$ was rapid ($k_2 > 10^{-1}$ l · mol^{-1} · s^{-1}), and the rate of substitution in the tris complex of one sulfide *trans* to sulfide by chloride was much faster than the substitution of one sulfide *trans* to chloride. Unfortunately this last fact has precluded the determination of the rate constant of the tris → *trans* process.

We propose that the *cis-trans* isomerization of bis(dialkylsulfide)-platinum(II) complexes proceeds by the *double displacement* mechanism:



4. The corresponding dimethylsulfide-palladium(II) complexes. – The *trans*-$Pd(Me_2S)_2Cl_2$ is the only isomer present in a chloroform solution of the complex. We did not find any evidence of *cis-trans* interconversion, even by adding a trace of

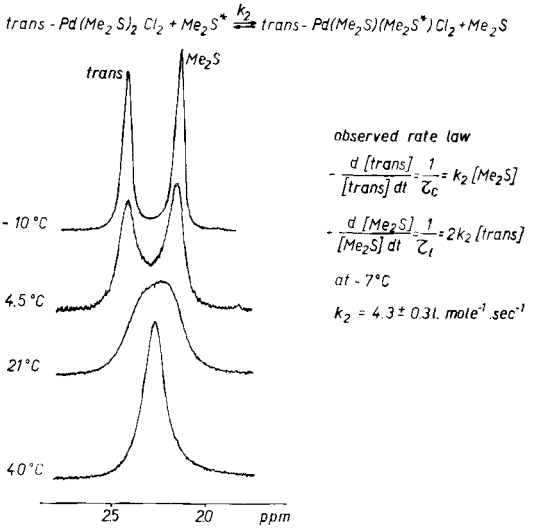


Fig. 5. *Dimethylsulfide exchange of* trans-$Pd(Me_2S)_2Cl_2$ *in* $CDCl_3$

Table 3. *Rate constant of ligand exchange in* $CDCl_3$ *at* $-7°$.

Trans-$Pd(Me_2S)_2Cl_2 + Me_2S^* \overset{k_2}{\rightleftarrows}$ *trans*-$Pd(Me_2S)(Me_2S)^*Cl_2 + Me_2S$ [*trans*] = 0.18 M

$[Me_2S]$ M	$1/\tau_c$(s^{-1})	$1/\tau_1$(s^{-1})	$1/\tau_c[Me_2S]$	$^1/_2\ \tau_1$ [*trans*]
0.33	1.4 ± 0.2	1.2 ± 0.3	4.2	3.4
0.49	2.2 ± 0.2	1.6 ± 0.2	4.5	4.4
0.82	3.4 ± 0.2	1.5 ± 0.2	4.1	4.2

dimethylsulfide and cooling down the solution. Instead, a fast ligand exchange was observed by ^{1}H-NMR. (Fig. 5).

The measurements of the residence times τ were made under the conditions of "slow exchange". The observed rate law is first order in both complex and ligand. Thus the mechanism is probably the usual associative one for substitution in square planar d^8-complexes.

Table 4. *Characterization of the various PtL_2X_2 complexes*

Complex	% metal		% Cl		IR. spectrum	^{1}H-NMR. spectrum[e]	
	calc.	found	calc.	found	ν (Pt-Cl) cm^{-1}	δ (ppm)	J_{Pt-H}(Hz)
cis-$Pt(Me_2S)_2Cl_2$	50.0	49.6	18.2	18.2	305, 320[c]	2.55	49.5
trans-$Pt(Me_2S)_2Cl_2$	50.0	50.4	18.2	18.1	344[c]	2.45	41.5
cis-$Pt(MeSPh)_2Cl_2$[a]	37.9	37.8	13.8	13.9	310, 330	2.74	47.0
trans-$Pt(MeSPh)_2Cl_2$[a]	37.9	38.1	13.8	13.7	340	2.63	44.0
cis-$Pt(MeSBz)_2Cl_2$	36.0	35.9	13.1	13.0	306, 316	2.36; 2.20	50.0
trans-$Pt(MeSBz)_2Cl_2$	36.0	36.2	1.11[b]	1.14	356	2.28	42.0
cis-$Pt(Bz_2S)_2Cl_2$	28.1	28.0	10.2	11.3	315, 325	[f]	[f]
cis-$Pt(Bz_2S)_2Br_2$	24.9	25.0	1.03[b]	0.99		[f]	[f]
trans-$Pt(Bz_2S)_2I_2$	22.2	22.4	0.92[b]	0.94		4.34	37.0
trans-$Pd(Me_2S)_2Cl_2$	35.2	35.4	23.4	23.5	360[d]	2.42	–
trans-$Pt(Me_2Se)_2Cl_2$	40.3	40.2	14.7	14.8	336[d]	2.35	37.0
cis-$Pt(Me_2Se)_2Cl_2$					294, 308	2.52	42.0

[a] Dipole moment in $CHCl_3$ at 25°: $\mu = 10.3 \pm 0.1$ D (*cis*), 3.6 ± 0.2 D (*trans*) in $CHCl_3$. [b] These figures are the % H. [c] Ref. [8], *cis*: 305, 319; *trans*: 344 cm^{-1}. [d] Ref. [9]: 361 and 340 cm^{-1}. [e] In $CHCl_3$; δ (ppm) of free ligands are for Me_2S: 2.13, MeSPh: 3.42 (methyl), MeSBz: 2.01 (Methyl), Bz_2S: 3.58 (–CH_2–). [f] The methylene protons spectrum is a superposition of an ABX (34%) onto an AB pattern (66%) with $J_{AX} > J_{BX}$ (X = Pt-195) [13]. For the *trans* chloro isomer: δ (–CH_2–) = 4.10 ppm, J_{Pt-H} = 34.5 Hz; for the *trans* bromo isomer: δ = 4.21 ppm, J_{Pt-H} = 35.0 Hz.

5. Experimental part. – *5.1. Solvent and compounds.* All solvents and liquids were purified, dried by standard methods [11] and degassed with nitrogen before use. The following compounds have been prepared by published methods: *cis*- and *trans*-$Pt(Me_2S)_2Cl_2$ [12], *cis*-$Pt(MeSBz)_2Cl_2$ [13], *cis*-$Pt(Bz_2S)_2Cl_2$ [10], $[Pt(Me_2S)_3Cl]BF_4$ [8] and *trans*-$Pt(Me_2Se)_2Cl_2$ [9]. *Preparation of* cis- *and* trans-*$Pt(MeSPh)_2Cl_2$*: an ethanolic solution of thioanisol (5.7 mmol) was added to an aqueous solution of K_2PtCl_4 (2,4 mmol) and the mixture stirred for 6 h. A yellow precipitate formed containing 60% of *cis* isomer. The product was washed with hexane and vacuum dried. The two isomers were separated by their different solubilities in water and benzene and recrystallized from ethanol (total yield: 40%). Trans-*$Pt(MeSBz)_2Cl_2$*: 0.5 mmol *cis*-$Pt(MeSBz)_2Cl_2$ and 0.8 mmol MeSBz were dissolved in $CHCl_3$ and refluxed for 4 h. After evaporation of the solvent, the crystalline product was washed with hexane and the *trans* isomer extracted with benzene (yield: 40%). Trans-*$Pt(Bz_2S)_2I_2$*: an ethanolic solution of Bz_2S (2.5 mmol) was added to a solution prepared by adding KI (4 mmol) to K_2PtCl_4 (1 mmol) dissolved in water. The precipitate was filtered after 10 h. and recrystallized from ethanol (orange needles, yield: 64%). Cis-*$Pt(Me_2Se)_2Cl_2$*: Me_2Se was added to a saturated solution of the *trans* isomer in CH_2Cl_2 + 30 v% nitrobenzene at – 20°. After 2 h. the solvent was evaporated at the same temperature. The precipitate was washed with hexane and benzene to eliminate respectively Me_2Se and the unreacted *trans* isomer which may be recycled. The *cis* complex was recrystallized from ethanol (yellow needles, yield 25%). Trans-*$Pd(Me_2S)_2Cl_2$*: a mixture of 3.1 mmol K_2PdCl_4 and 6.8 mmol Me_2S in water was stirred for 1 h. The precipitate was filtered and recrystallized from ethanol (orange needles, yield: 62%).

5.2. ^{1}H-NMR. Spectra were recorded with *Varian* A-60A, A-60D and *Bruker* HX-90 spectrometers. Temperatures were measured with the V-943346-05 and 06 tubes and calibrating

curves. Integrations were obtained electronically and by planimetry. *IR.* spectra were recorded on *Perkin Elmer* 521 and *Beckman* IR 20A instruments.

5.3. Dipole moment measurements. The dielectric constants were measured with the *Sargeant* oscillometer and the refractive indices with the *Abbé* refractometer. *Guggenheim*'s equation was used [14] to obtain the dipole moments. We thank Mr. *C. Enciso* for these measurements.

We would like to express our thanks to the *Swiss National Foundation for Scientific Research* for financial support, the Organic Chemistry Institute (Dir: Prof. *H. Dahn*) and *Nestlé SA* for the use of the *Varian* spectrometers.

BIBLIOGRAPHY

[1] *J. Chatt & R. G. Wilkins*, J. chem. Soc. *1952*, 273, 4300; *1956*, 525.
[2] *P. Haake & R. M. Pfeiffer*, Chem. Commun. 1969, 1330; J. Amer. chem. Soc. *92*, 4996 (1970).
[3] *D. G. Cooper & J. Powell*, J. Amer. chem. Soc. *95*, 1102 (1973).
[4] *F. Basolo & R. G. Pearson*, 'Mechanisms of Inorganic Reactions', p. 426, Ed. John Wiley & Sons 1967.
[5] *L. Cattalini & M. Martelli*, J. Amer. chem. Soc. *91*, 312 (1969).
[6] *F. G. Angell, H. D. K. Drew & W. Wardlaw*, J. chem. Soc. *1930*, 349.
[7] *E. A. Allen, N. P. Johnson, D. T. Roseveav & W. Wilkinson*, Chem. Commun. *1971*, 171.
[8] *P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. S. Smith & K. M. Thomas*, J. chem. Soc. Dalton *1972*, 1904.
[9] *J. R. Allkins & P. J. Hendra*, J. chem. Soc. *1967*, 1325.
[10] *P. Haake & P. C. Turley*, J. Amer. chem. Soc. *89*, 4611 (1967).
[11] *D. D. Perrin, W. F. L. Armarego & D. R. Perrin*, 'Purification of Laboratory Chemicals', Pergamon Press 1966.
[12] *E. G. Cox, H. Saenger & W. Wardlaw*, J. chem. Soc. *1934*, 182.
[13] *P. C. Turley & P. Haake*, J. Amer. chem. Soc. *89*, 4617 (1967).
[14] *G. J. Moody, J. D. R. Thomas*, 'Dipole moments in inorganic chemistry', p. 26, University Press, London 1971.

232. Arbeiten über Phosphorsäure- und Thiophosphorsäureester mit einem heterocyclischen Substituenten

7. Mitteilung[1])

Thio- und Dithiophosphorsäureester von der Art des GS 13005 mit einem analogen oder homologen heterocyclischen Ring

von **Kurt Rüfenacht**

Forschung Agrarchemikalien, R-1038.4.13, *Ciba-Geigy AG.*, CH-4002 Basel

(6. VIII. 73)

Summary. To complete results presented in this and in previous papers of this series as well as published in patents of other authors a review is given on known and new variations of the heterocyclic moiety in GS 13005 type thio- and dithiophosphoric acid esters (**1**, **2**) by modification of the 1,3,4-thiadiazol-2(3*H*)-one ring **5** and by its replacement by analogue five- and homologue six-membered rings.

Among new esters of this type some containing the pyrazolinone ring **3** or a 2-alkoxy-4*H*,6*H*-1,3,4-thiadiazin-5-one ring **10** (homologue of the original 5-methoxy-1,3,4-thiadiazol-2(3*H*)-one ring in GS 13005) show no remarkable pesticidal activity, some others containing a pyrazole

[1]) 6. Mitteilung s. [1].