107. *Equilibria between* cis- *and* trans-$[(MR_3)_2PtX_2]$ (*where* M = P, As, *and* Sb; X = *Halogen*).

By J. Chatt and R. G. Wilkins.

Equilibrium constants for the isomerisation *cis*-$[(MR_3)_2PtX_2] \rightleftharpoons$ *trans*-$[(MR_3)_2PtX_2]$ (R = hydrocarbon radical, X = halogen) have been estimated. The equilibrium shifts to the *trans*-side when chlorine is replaced by iodine, when phenyl groups are replaced by alkyl groups, when the homologous series is ascended from R = Me to R = Pr^n, and when the atoms, M, are changed in the order Sb, P, and As. The replacement of *n*-propyl by higher *n*-alkyl groups has little effect on the equilibrium.

In 1952 we reported [1] a detailed investigation of equilibria, in benzene solution, between *cis*- and *trans*-$[(MEt_3)_2PtCl_2]$ (M = P, As, and Sb). Attempts to extend this work to other alkyl derivatives proved difficult. The equilibrium for the higher homologues lies so far in favour of the *trans*-isomer that we could not determine its change with temperature sufficiently accurately to evaluate the heats and entropies of isomerisation; the trimethyl homologues were too insoluble. However, the position of equilibrium in benzene at 25° could be evaluated with fair accuracy, and here we shall record how the position of equilibrium changes as the hydrocarbon radical and halogens are changed.

The equilibria studied were of the type *cis*-$[(MR_3)_2PtX_2] \rightleftharpoons$ *trans*-$[(MR_3)_2PtX_2]$.

Lability of Simple Platinous Complexes $[(MR_3)_2PtCl_2]$.—The tri-*n*-alkylphosphine complexes, $[(PR_3)_2PtCl_2]$, are stable in solution at room temperature at least up to the tri-*n*-butyl derivative. The corresponding arsine complexes are labile, isomerising very slowly at room temperature; the qualitatively observed rate of isomerisation decreases slightly from R = Me to R = Pr^n, then increases again with R = Bu^n. The isomerisation can be prevented for long periods by the addition of a trace of a bridged complex $[(MR_3)_2Pt_2Cl_4]$ (M = P or As). The corresponding stibine complexes are much more labile and isomerisation cannot be prevented by addition of a bridged complex, although its rate is diminished considerably; so only the less soluble *cis*-isomers can be isolated in the stibine series.[2] In all cases equilibration of the complexes $[(MR_3)_2PtCl_2]$ was facilitated in the presence of a trace of the free ligand, MR_3, and the equilibrium constants were determined by using solutions containing a trace of MR_3.

Triphenyl compounds $[(MPh_3)_2PtCl_2]$ are too insoluble in benzene at 25° for the position of equilibrium to be measured. Only one isomer of each (M = P, As,* and Sb) was isolated and its colour and insolubility indicated that it was a *cis*-isomer. The effect of the phenyl group on the equilibrium was determined by studying the complexes of $AsBu_2Ph$. The iodo-platinous complexes are much more labile than their chloro-analogues.

Table 1. *Equilibrium constants* (*K*) *of the isomerisation* cis-$[L_2PtX_2] \rightleftharpoons$ trans-$[L_2PtX_2]$ *in benzene at* 25°.

L	PEt_3 *	PPr^n_3	PBu^n_3	PPe_3 †	PPr^n_3	$AsMe_2Et$	$AsEt_3$ *
X	Cl	Cl	Cl	Cl	I	Cl	Cl
cis-Isomer in equilm. (%)	7·52	3·28	3·77	3·40	~0·55	1·8	0·57
K	12·3	29·5	25·5	28·4	~180	55	175
L	$AsPr^n_3$	$AsBu^n_3$	$AsBu^n_2Ph$	$SbEt_3$ *	$SbPr^n_3$	$SbBu^n_3$	$SbEt_3$
X	Cl	Cl	Cl	Cl	Cl	Cl	I
cis-Isomer in equilm. (%)	~0·15	~0·29	9·4	34·4	20	21	~1
K	~650	~340	9·6	1·9	4·0	3·75	~90

* The values for the triethyl series are taken from refs. 1 and 3 for comparison. † Pe = *n*-pentyl.

Influence of the Ligands on the Isomerisation Equilibrium.—The positions of equilibria were determined in benzene solution by measuring the dielectric constants of the solutions as described previously.[3] They are recorded in Table 1, and an estimate of the entropies

---

* *trans*-$[(AsPh_3)_2PtCl_2]$ is known (Jensen, *Z. anorg. Chem.*, 1936, **229**, 237.

[1] Chatt and Wilkins, *J.*, 1952, 4300.

[2] *Idem, J.*, 1953, 70.

[3] *Idem, J.*, 1952, 273.

and heats of isomerisation in the tri-*n*-propyl series of complexes is given in Table 2. These show the same pattern as the triethyl series.[1] In our first paper on this subject,[3] we suggested that the large entropy of isomerisation was due to unequal solvation of the two isomers, caused by their great difference in dipole moments. The equilibrium constant should therefore be very dependent on the polarisability of the solvent. A single experiment with carbon tetrachloride as solvent and *cis*-$[(SbPr^n_3)_2PtCl_2]$ as solute indicates that this is so. The value of K found was 14 as compared with 4 in benzene.

TABLE 2. *Free energies, heats, and entropies of isomerisation* cis- ⟶ trans-$[(MPr^n_3)_2PtCl_2]$ *in benzene at 25°.*

Substance	$-\Delta G$	ΔH	ΔS	Substance	$-\Delta G$	ΔH	ΔS	Substance	$-\Delta G$	ΔH	ΔS
$[(PPr^n_3)_2PtCl_2]$	2005	1975	13·3	$[(AsPr^n_3)_2PtCl_2]$	~3840	—	—	$[SbPr^n_3)_2PtCl_2]$	818	2200	10·1

The ligands, L, are all of the type, MR_2R', and we shall consider in turn the effect of changing M, the hydrocarbon radicals, and X on the position of equilibrium.

Influence of M *on the Equilibrium.*—The percentage of *cis*-isomer in the equilibrium mixtures of *cis*- and *trans*-$[(MR_3)_2PtCl_2]$ increases in the order $M = As < P < Sb$. The difference between the arsenic and phosphorus series is largely due to a change in the heat of isomerisation, but that between the phosphorus and antimony series to a change in the entropy of isomerisation. The possible causes and significance of these changes have been discussed in the light of a detailed analysis of equilibria in the triethyl series of complexes.[1]

Influence of Hydrocarbon Radicals R *and* R′ *on the Equilibrium.*—The equilibrium lies increasingly in favour of the *trans*-isomer as the homologous series is ascended from $R = R' = Me$ to $R = R' = Pr^n$, but the equilibrium constant changes only slightly from $R = R' = Pr^n$ to $R = R' = n$-pentyl. For reasons to be discussed later it is difficult to assess the reliability of the values in Table 2, but comparison with the corresponding data for the ethyl series indicates that the shift in equilibrium with change in alkyl radical is due very largely to a change in the heat of isomerisation. The stabilisation of the *trans*- relative to the *cis*-isomer is probably mainly steric in origin, because it is known that the difference between the electronic effects of the alkyl groups in such complexes is small.[4] The recession in the values of the equilibrium constant at $R = R' = Bu^n$ is probably significant since it was found in the phosphine, arsine, and stibine series. The replacement of a butyl group by a phenyl group shifts the equilibrium markedly to the *cis*-side (cf. the $AsBu^n_3$ and $AsBu^n_2Ph$ complexes). This shift may be partly steric in origin since the rigid phenyl group occupies less space in the immediate neighbourhood of the atom, M, than an alkyl group, but it may also be caused by electronic effects. The greater electronegativity of the phenyl group as compared with an alkyl group should increase the strength of the π-type bond between the atom, M, and the platinum atom, and hence the stability of the *cis*-isomer relative to the *trans*-isomer.[5]

Influence of the Halogen on the Equilibrium.—The replacement of chlorine by iodine causes a large shift of the equilibrium towards the *trans*-side. The stabilisation of the *cis*-isomers in the chloro-series of complexes has been attributed to the rather high double-bonding tendencies of the atom, M, as compared with chlorine.[1, 3] It seems probable from its position in the *trans*-effect series that iodine has a much greater tendency than chlorine to form double bonds to platinum.[6] The shift of the equilibrium towards the *trans*-side, when chlorine is replaced by iodine, is probably caused, therefore, by the closer double-bonding tendencies of iodine and the atoms, M.

No *trans*-isomers of the type $[(SbR_3)_2PtX_2]$ are known in the solid state. Since the equilibrium between *cis*- and *trans*-$[(SbEt_3)_2PtI_2]$ lies much further to the *trans*-side than any other equilibrium in the stibine series, it was of interest to see whether we could isolate *trans*-$[(SbEt_3)_2PtI_2]$. As normally prepared, $[(SbEt_3)_2PtI_2]$ is a yellow solid which melts to a red liquid and gives red solutions in organic solvents. The red benzene solution we now know (Table 1) contains about 99% of the complex as its *trans*-isomer, and so we conclude

---

[4] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.
[5] Chatt and Williams, *J.*, 1951, 3061.
[6] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456, and previous references quoted therein.

that the yellow solid is the *cis*-isomer. These colours are to be expected from our general knowledge of the colours of platinous complexes. When the benzene solution, containing a trace of a bridged complex to suppress so far as possible the lability of the equilibrium, was evaporated at 15 mm. a red oil remained. This changed into a red solid, presumably

TABLE 3. *Experimental quantities measured to determine the equilibrium constants, K, in benzene solution at 25°.*

Temp. (°K)	k_c	k_t	W (mg.)	W_L (mg.)	ΔC-k_L, W_L ($\mu\mu$F)	W_c (mg.)	W_t (mg.)	K
Isomerisation of *trans*-$(PPr_3)_2PtCl_2$								
292·86	22·8	0·261	980·3	3·0	1·027	34·2	946·1	27·65
			1359·6	4·0	1·430	47·7	1311·9	27·5
			595·9	3·0	0·578	19·5	576·4	29·55
298·15	22·1	0·254	802·5	3·0	0·772	25·9	776·6	29·9
			802·6	3·0	0·785	26·5	776·1	29·3
			1391·9	4·0	1·356	45·6	1346·3	29·55
			749·4	3·0	0·699	23·5	725·9	30·85
303·15	21·8	0·258	1006·2	3·0	0·940	31·6	974·6	30·8
			1205·0	3·0	1·126	37·8	1167·2	30·85
			402·4	2·0	0·353	11·7	390·7	33·4
308·15	20·3	0·297	604·0	2·0	0·541	18·1	585·9	32·4
			804·8	2·0	0·720	24·0	780·8	32·5
			1615·4	3·0	1·450	48·4	1567·0	32·4
Isomerisation of *cis*-$(PBu_3)_2PtCl_2$								
298·25	19·8	0·234	789·7	5·0	0·782	30·5	759·2	24·9
			994·6	5·0	0·983	38·3	956·3	25·0
Isomerisation of *trans*-$(PBu_3)_2PtCl_2$								
298·25	19·8	0·234	796·6	5·0	0·762	29·4	767·2	26·1
			959·7	5·0	0·931	36·1	923·6	25·6
Isomerisation of *cis*-$(PPe_3)_2PtCl_2$								
298·27	17·4	0·21 *	990·9	5·0	0·788	33·7	957·2	28·4
Isomerisation of *cis*-$(PPr_3)_2PtI_2$								
298·18	18·8	0·278	606·8	2·0	0·234	3·51	603·3	172
			755·4	2·0	0·330	6·48	748·9	116
Isomerisation of *trans*-$(PPr_3)_2PtI_2$								
298·15	18·8	0·278	607·0	2·0	0·225	3·02	604·0	200
			902·0	2·0	0·327	4·10	897·9	219
Isomerisation of *cis*-$(AsMe_2Et)_2PtCl_2$								
298·25	25·0 *	0·442	900·6	2·0 †	0·832	17·7	882·9	49·9
Isomerisation of *trans*-$(AsMe_2Et)_2PtCl_2$								
298·25	25·0 *	0·442	708·2	2·0	0·600	11·7	696·5	59·5
			796·8	2·0	0·690	13·8	783·0	56·8
			899·3	2·0	0·815	16·8	882·5	52·5
Isomerisation of *cis*-$(AsPr_3)_2PtCl_2$								
288·85	20·0	0·293	913·0	3·0	0·313	2·28	910·7	399
298·22	19·6	0·290	979·6	3·0	0·350	3·42	976·2	286
			1730·7	3·0	0·571	3·58	1727·1	482
			2005·9	3·0	0·742	8·29	1997·6	241
Isomerisation of *trans*-$(AsPr_3)_2PtCl_2$								
288·85	20·0	0·293	1501·1	3·0	0·485	2·28	1498·8	658
			1783·7	3·0	0·578	2·79	1780·9	638
			1993·9	3·0	0·633	2·49	1991·4	800
298·22	19·6	0·290	993·2	3·0	0·330	2·18	991·0	455
			1502·5	3·0	0·468	1·66	1500·8	904
Isomerisation of *trans*-$(AsBu_3)_2PtCl_2$								
298·15	17·4 *	0·248	1596·1	4·5	0·478	4·78	1591·3	333
			1996·9	4·5	0·591	5·60	1991·3	355
Isomerisation of *cis*-$(AsBu_2Ph)_2PtCl_2$								
298·35	17·4	0·25 *	493·6	7·0 ‡	0·950	48·3	445·3	9·2

TABLE 3. (*Continued.*)

Temp. (°K)	k_c	k_t	W (mg.)	W_L (mg.)	ΔC-k_L, W_L ($\mu\mu$F)	W_c (mg.)	W_t (mg.)	K
Isomerisation of *trans*-$(AsBu_2Ph)_2PtCl_2$								
298·35	17·4	0·25 *	342·2	7·0 ‡	0·634	32·0	320·2	10·0
Isomerisation of *cis*-$(SbPr_3)_2PtCl_2$								
292·56	16·9	0·33 *	189·4	1·0	0·730	40·3	149·1	3·70
			199·1	2·0	0·769	42·4	156·7	3·70
			288·5	1·0	1·126	62·1	226·4	3·65
			368·3	2·0	1·416	78·0	290·3	3·72
298·01	16·75	0·33 *	212·1	2·0	0·769	41·2	170·9	4·15
			397·1	2·0	1·449	80·3	316·8	3·94
			514·2	2·0	1·874	103·7	410·5	3·96
			600·6	4·0	2·235	123·9	476·7	3·85
303·13	16·8	0·33 *	292·5	2·0	1·007	55·1	237·4	4·30
			392·0	3·0	1·352	74·2	317·8	4·28
			500·0	3·0	1·726	94·7	405·3	4·28
308·15	16·7	0·33 *	211·5	2·0	0·703	38·6	172·9	4·48
			303·3	2·0	1·003	55·1	248·2	4·51
298·35 §	16·45	0·33 *	399·7	1·0	0·561	26·6	373·1	14·0
Isomerisation of *cis*-$(SbBu_3)_2PtCl_2$								
298·36	15·15	0·27 *	193·2	1·0	0·660	40·8	152·4	3·74
			200·1	1·0	0·683	42·3	157·8	3·73
			249·4	—	0·858	53·2	196·2	3·69
			255·9	1·0	0·858	53·0	202·9	3·83
Isomerisation of *cis*-$(SbEt_3)_2PtI_2$								
298·33	15·0	0·27 *	346·2	‖	0·148	~3·7	~342·5	~92·5

* Estimated by extrapolation of *k* along the homologous or eutropic series. † With $AsEt_3$ as the catalyst, L. ‡ With $AsBu^n_3$ as the catalyst, L. § Carried out in carbon tetrachloride. ‖ Spontaneous isomerisation.

trans-$[(SbEt_3)_2PtI_2]$, but the solid reverted to the original yellow *cis*-$[(SbEt_3)_2PtI_2]$ during about 15 min.

Throughout these investigations, the equilibrium mixture obtained from the isomerisation of the *cis*-isomers was not exactly the same as that obtained by isomerising the *trans*-isomers. The difference was negligible in the isomerisation of the triethyl complexes and most marked in the tri-*n*-propylphosphine complexes. We were not able to discover its exact cause, which appears to be associated only with the *cis*-isomer. Isomerisation of different preparations of *trans*-$[(PPr^n_3)_2PtCl_2]$ always gave the same equilibrium constant, $K = 29{\cdot}5 \pm 0{\cdot}2$ at 25°, but isomerisation of different preparations of the *cis*-isomer gave values ranging from 15 to 28. The equilibrium " constants " obtained by isomerising any particular preparation of *cis*-$[(PPr^n_3)_2PtCl_2]$ were consistent within experimental error (about $\pm 0{\cdot}2$) and usually had a value of about 20 at 25°, but when that preparation was recrystallised the " constant " would apparently change. The various preparations had correct melting points and analyses. The apparent change in equilibrium " constant " with repeated recrystallisation was not consistent : sometimes it would rise and at other times fall. The observed " constant " did not approach a definite value on repeated recrystallisation of the *cis*-$[(PPr^n_3)_2PtCl_2]$ or any other purification procedure which we tried. The " constant " did not depend on the quantity of tri-*n*-propylphosphine used to labilise the equilibrium. Since the isomerisation of *trans*-$[(PPr^n_3)_2PtCl_2]$ gave a definite value for the equilibrium constant we accepted it as most likely to be correct and the values given in Table 2 are based on that assumption.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney, of these laboratories.

Most of the platinous complexes in this investigation were prepared as precipitates by shaking a suspension of the organic ligand (*e.g.*, triethylphosphine) in an aqueous solution of potassium chloroplatinite until reaction was complete. Except for those detailed below they are described by Jensen.[7]

cis-*Bistri*-n-*pentylphosphinedichloroplatinum*.—An ethanolic solution of sodium chloroplatinate and the phosphine (3 mols.) was boiled under reflux until the orange solution had become pale yellow (45 min.). This solution on cooling deposited white crystals of the *complex* which, recrystallised from ethanol, had m. p. 124—125° (Found: C, 47·9; H, 9·0. $C_{30}H_{66}Cl_2P_2Pt$ requires C, 47·7; H, 8·8%).

cis- *and* trans-*Bisethyldimethylarsinedichloroplatinum*.—A di-*n*-butyl ether solution of the arsine, shaken with aqueous potassium chloroplatinite, gave a brown precipitate of $[(AsMe_2Et)_4Pt][PtCl_4]$. This was removed, dried, and then decomposed by boiling its ethanol suspension until it had dissolved. When the solution was cooled, the very pale yellow cis-*isomer* separated and was recrystallised from ethanol; it had m. p. 177—178° (Found : C, 18·1; H, 4·1. $C_8H_{22}Cl_2As_2Pt$ requires C, 18·0; H, 4·1%). A portion of the product was converted into the yellow trans-*isomer* as described for its tri-*n*-propyl analogue,[8] and recrystallised from ether-acetone by cooling to −70°, then having m. p. 173—174° (Found : C, 18·1; H, 4·1%).

cis- and *trans*-Bisdibutylphenylarsinedichloroplatinum were prepared by the general method. The white cis-*isomer*, recrystallised from methanol, had m. p. 120—121° (Found : C, 41·9; H, 5·9. $C_{28}H_{46}Cl_2As_2Pt$ requires C, 42·0; H, 6·0%). The very soluble yellow *trans*-isomer, recrystallised from methanol by cooling to −70°, had m. p. 40—41°. This material still retained a trace of its *cis*-isomer as was evident from the slightly high dielectric constant of its benzene solutions. It was sufficiently pure for the isomerisation experiments.

trans-*Bistri*-n-*propylphosphinedi-iodoplatinum* was obtained by shaking the phosphine with aqueous potassium chloroplatinite (½ mol.) to which had been added potassium iodide (1½ mol.). Recrystallised from ethanol, it was obtained in chrome yellow crystals, m. p. 118—119° (Found : C, 28·3; H, 5·6. $C_{18}H_{42}I_2P_2Pt$ requires C, 28·1; H, 5·5%). The *cis*-isomer was obtained by mixing cold solutions of *cis*-$[(PPr^n_3)_2PtCl_2]$ in acetone (50 c.c.) and of potassium iodide in acetone-ethanol (100 c.c. of 1 : 1). The solution immediately changed from colourless to yellow and potassium chloride separated. The mixture was evaporated to dryness at 15 mm., and the residue extracted with water, then recrystallised from ethanol. The product was a mixture of *cis*- and *trans*-isomers which were separated by extracting the latter with light petroleum (b. p. 60—80°), leaving the cis-*isomer* (2·2 g.). It was converted into its *trans*-isomer on heating, and melted sharply in the range 119—125° (Found : C, 28·1; H, 5·5%).

Bistriethylstibinedi-iodoplatinum, prepared as described by Jensen,[7] is a yellow solid, m. p. 69° (Found : C, 16·6; H, 3·6. Calc. for $C_{12}H_{30}I_2PtSb$: C, 16·6; H, 3·4%). This material, on evaporation of its benzene solution as described on p. 527, gave a red solid which reverted to the yellow form in 15—20 min.

Determination of Equilibrium Constants.—The method whereby the constants were determined, and the meanings of the symbols used in Table 3, are as described by Chatt and Wilkins,[1, 3] except that W_L = the weight of phosphine or arsine used to catalyse the isomerisation, and replaces the symbols W_p and W_a which were used in the previous publications.

The authors thank Miss J. H. Norwood, Mr. M. L. Searle, and Mr. D. J. Odds for experimental assistance.

Imperial Chemical Industries Limited, Akers Research Laboratories,
The Frythe, Welwyn, Herts.

[*Received*, *August* 26*th*, 1955.]

---

[7] Jensen, *Z. anorg. Chem.*, 1936, **229**, 237.

[8] Chatt and Wilkins, *J.*, 1951, 2532.