10. *The Nature of the Co-ordinate Link. Part VII.* Palladous Complexes of Stable* cis-*Configuration.*

By J. CHATT and R. G. WILKINS.

The *cis–trans* equilibria in benzene solutions of palladous complexes of the type $(MR_3)_2PdCl_2$ (M = P, As, and Sb; R = *n*-alkyl) and of $(SbPh_3)_2PdCl_2$ have been examined by measuring the dielectric constants of their solutions at 25°. The quantities of *cis*-isomers in the solutions of the phosphine and arsine complexes are too small for detection by this method; the solutions of the stibine complexes contain 3·5—40% of the *cis*-isomers in labile equilibrium with their *trans*-isomers, the quantities depending on the group R. The quantities of *cis*-isomers in the equilibria are much smaller than in the analogous platinous series (see Table 1). Only the crystalline *cis*-isomers separate from solutions of $(SbR_3)_2PdCl_2$ because their solubilities are so much smaller than those of their *trans*-isomers. The crystalline complexes $(SbR_3)_2PdCl_2$ provide the first example of a series of palladous complexes which are not chelated yet have stable *cis*-configurations.

THE complex chemistry of platinum(II) is very similar to that of palladium(II). Both metals have the same atomic radius, they form only " inner orbital " complexes (Taube, *Chem. Reviews*, 1952, **50**, 69), and their covalently bound ligands occupy a square configuration about the metal atoms. Their complex compounds show much less tendency to dissociate than do those of most bivalent metals, but complexes of palladium are less stable and stereochemically rigid than those of platinum. Thus platinous complexes, L_2PtX_2 (L = neutral ligand, X = univalent acid radical), with few exceptions can be isolated in *cis*- and *trans*-forms but their palladous analogues exist only in one form. *cis*-$(NH_3)_2PdCl_2$ (Grunberg and Shulman, *Compt. rend. Acad. Sci., U.R.S.S.*, 1933, 215) and *cis*-$(NH_3)_2Pd(NO_2)_2$ (Mann, Crowfoot, Gattiker, and Wooster, *J.*, 1935, 1642) and their *trans*-isomers are the only known exceptions. The formation of these *cis*-palladous diamines has been investigated recently by Jonassen and Cull (*J. Amer. Chem. Soc.*, 1951, **73**, 274). There is also some evidence that $(AsMe_3)_2PdCl_2$ may exist in the crystal as the *cis*-isomer (Mann and Purdie, *J.*, 1935, 1549). All the remaining complexes of the type L_2PdX_2, whether L is an amine, trialkylphosphine, trialkylarsine, dialkyl sulphide, or dialkyl selenide, appear to have *trans*-configurations both in solution and in the solid state (Drew and Wyatt, *J.*, 1934, 56; Cox, Saenger, and Wardlaw, *J.*, 1934, 182; Mann and Purdie, *loc. cit.*). Their physical properties are similar to those of their *trans*-platinous analogues, but chemically they behave as a labile equilibrium mixture of *cis*- and *trans*-forms in which the *trans*-form predominates (*e.g.*, see Mann *et al.*, *J.*, 1935, 1642).

Our study of equilibria in the series of complexes $(MR_3)_2PtCl_2$ (M = P, As, or Sb, R = *n*-alkyl) in benzene solution (Part V, *J.*, 1952, 273; Part VI *) shows that the *cis*-configuration is increasingly favoured as M is replaced in the order $As < P \ll Sb$. The

---

* Part VI, *J.*, 1952, 4300.

very much greater equilibrium concentration of *cis*-isomers in the stibine platinous series of complexes is due to the much smaller entropy differences between the isomers in this series than between isomers in the corresponding phosphorus and arsenic series. This is an effect we might expect when any similar series of stibine complexes is compared with the phosphorus and arsenic analogues. We have, therefore, investigated the palladous complexes, $(MR_3)_2PdCl_2$, and find that all the lower alkyl stibine complexes give benzene solutions containing a measurable quantity of the *cis*-isomer in labile equilibrium with its *trans*-isomer.

cis-Isomers are most easily distinguished from their *trans*-isomers by the exceptionally large dielectric constants of their solutions, a consequence of their high electric dipole moments. Thus in the platinous series, $(MR_3)_2PtCl_2$ (M = P, or As), the *cis*-isomers have dipole moments of about 10 D (Jensen, *Z. anorg. Chem.*, 1936, **229**, 225). The *trans*-isomers must have zero moments, but when they are measured and computed in the usual manner a value of about 1 D is found in both the platinous and the palladous series. This apparent moment is due to the exceptionally large atom polarisation of compounds such as those under consideration, which have highly dipolar bonds (Sutton *et al.*, *J.*, 1938, 1254, 1269; Charles and Freiser, *J. Amer. Chem. Soc.*, 1951, **73**, 5223). Jensen found it necessary to assume an atom polarisation of about 20% of the electron polarisation (instead of the usual 0—5%) in order that a number of symmetrical *trans*-platinous complexes should have zero moment. If a similar assumption is made regarding the palladous complexes, then the moments of $(PEt_3)_2PdCl_2$ and $(AsEt_3)_2PdCl_2$, computed to be 1·05 and 1·04 D, respectively (Mann and Purdie, *loc. cit.*), are in fact zero. The quantity of *cis*-isomer in solutions of these palladous complexes is thus too small to have any significant effect on the apparent dipole moment.

It is not possible to obtain accurate dipole moments of co-ordination compounds with small moments from solution measurements. Therefore, we have compared the increment ($\Delta\varepsilon$) in dielectric constant produced by dissolving various quantities of the complex in 43·36 g. of benzene at 25°. The quotient $\Delta\varepsilon/f$, where f is the mol.-fraction of solute, is constant to within our limits of accuracy in the dilute solutions we used.

All the platinous complexes of type $(MR_3)_2PtCl_2$ (where R = Et or Pr^n, and M = P, As, or Sb) of *trans*-configuration give values of $\Delta\varepsilon/f$ lying between 1·8 and 2·8 (Table 3). Those of *cis*-configuration give values in the range 150—170 (Table 4). The values of $\Delta\varepsilon/f$ for a number of palladium complexes are listed for comparison in Table 1. None of these complexes has a purely *cis*-configuration. The solutions of the phosphine and arsine complexes, which we know contain such a small amount of *cis*-isomer that it cannot be detected by this method, have values of $\Delta\varepsilon/f$ in the region 2—3; on the other hand, the stibine complexes in solution give values ranging from 8·5 to 70. Obviously, the benzene solutions of the stibine palladous complexes must contain an appreciable quantity of the *cis*-isomer in equilibrium with its *trans*-isomer.

TABLE 1. *$\Delta\varepsilon/f$ of the palladous complexes,* $(MR_3)_2PdCl_2$, *and percentages of* cis-$(SbR_3)_2PdCl_2$ *and of* cis-$(SbR_3)_2PtCl_2$ *in equilibrium with their* trans-*isomers in benzene solution at* 25°.

	R =				
M	Me	Et	Pr^n	Bu^n	Ph
P	—	2·7 †	2·6	2·2	—
As	—	2·9 † 3·0	2·9	2·6	—
Sb	60—70 *	12·2	8·7	8·6	25·6
% of *cis*-$(SbR_3)_2PdCl_2$	~40 *	6·0	3·8	3·7	14·6
% of *cis*-$(SbR_3)_2PtCl_2$ ...	~80 *	34·4	20·0	20·7	— *

* Accurate values are not possible because these complexes are too insoluble in benzene at 25°.
† Calc. from Mann and Purdie's measurements, *loc. cit.*

If we assume that solutions of pure *cis*-$(SbR_3)_2PdCl_2$ would have a value of $\Delta\varepsilon/f$ of the order of 160 as in the platinous series, we can estimate roughly the percentages of *cis*-isomers in the equilibria. These are tabulated in Table 1 together with the corresponding values in the platinous series. They are found to vary with the size of alkyl group in the same way as they do in the platinous series, where we know that we are measuring equilibria between *cis*- and *trans*-isomers. This supports the view that the high values of $\Delta\varepsilon/f$ in the stibine palladous series are due to equilibria between *cis*- and *trans*-forms; however, the position of equilibrium in the palladous series is shifted well to the *trans*- side. $(SbPh_3)_2PdCl_2$ contains about 14% of its *cis*-isomer in equilibrium with its *trans*-isomer but its almost insoluble platinum analogue has not been investigated.

In the platinous series of complexes $(MR_3)_2PtCl_2$ (M = P, As, or Sb) we know that the *cis*- is always much less soluble than its *trans*-isomer, especially in non-polar solvents. Thus, when they are in labile equilibrium, the *cis*-isomer separates first on evaporation of benzene or light petroleum solutions. This occurs even when the equilibrium concentration of *cis*-isomer is only 0·2% of that of its *trans*-isomer, as it is in the case of $(AsPr_3)_2PtCl_2$ (Chatt and Wilkins, *J.*, 1951, 2532). We should expect similar solubility relations to exist in the palladous series. Thus only the solid *cis*-isomers $(SbR_3)_2PdCl_2$ should be capable of isolation from solution. It is obvious that this is so when we compare the physical properties of the solid palladous complexes in the series $(MR_3)_2PdCl_2$ with one another and with those of their platinum analogues. The *n*-propyl compounds are compared in Table 2. It shows that solid $(SbPr_3)_2PdCl_2$ is analogous to *cis*-$(SbPr_3)_2PtCl_2$ whereas solid $(PPr_3)_2PdCl_2$ and solid $(AsPr_3)_2PdCl_2$ are analogous to *trans*-$(PPr_3)_2PtCl_2$ and *trans*-$(AsPr_3)_2PtCl_2$, respectively. Generally, in series of complexes of this type, the palladous complexes are more highly coloured and more soluble in all solvents than the corresponding platinous complexes. There can be little doubt that the crystalline tertiary stibine palladous chloride complexes have a *cis*-configuration, but isomerise immediately in benzene solution at room temperature.

TABLE 2.

Substance	M. p.		Colour		Solubility in light petroleum	
cis-$(PPr_3)_2PtCl_2$	149°	↑	White	↓	Insoluble	↓
cis-$(AsPr_3)_2PtCl_2$	127		Very pale yellow		Insoluble	
cis-$(SbPr_3)_2PtCl_2$	80		Pale yellow		Insoluble	
trans-$(PPr_3)_2PtCl_2$	85	↑	Pale yellow	↓	Soluble	↓
trans-$(AsPr_3)_2PtCl_2$	51		Yellow		Very soluble	
$(PPr_3)_2PdCl_2$	96	↑	Yellow	↓	Very soluble	↓
$(AsPr_3)_2PdCl_2$	55		Orange-yellow		Extremely soluble	
$(SbPr_3)_2PdCl_2$	66 *	↓	Yellow	↑	Extremely soluble † to give a red solution	

The arrows indicate the direction of increasing m. p., colour, and solubility, the last relating to organic solvents generally. * Melts with decomp.

† Finely divided $(SbPr_3)_2PdCl_2$ dissolves very much more slowly than either its phosphorus or its arsenic analogue although finally a very concentrated red solution is obtained. Obviously, the yellow solid which has a *cis*-configuration and low solubility dissolves slowly, but because it isomerises in solution to the very soluble red *trans*-isomer, concentrated solutions are produced. *cis*-$(SbPr_3)_2PtCl_2$ behaves similarly on dissolving in benzene but it isomerises sufficiently slowly for the rate to be measured. Eventually it gives an orange-red solution containing 80% of the solute as the *trans*-isomer. All the other complexes dissolve without change of colour.

EXPERIMENTAL

Microanalyses are by Mr. W. Brown, of these laboratories.

Preparation of Compounds.—The palladous chloride complexes were prepared by shaking aqueous ammonium palladochloride with the tertiary phosphine, arsine (Mann and Purdie, *J.*, 1935, 1549), or stibine (Morgan and Yarsley, *J.*, 1925, 184; Jensen, *loc. cit.*). The tertiary stibine complexes, $(SbR_3)_2PdCl_2$, have low stability and their ease of decomposition increases rapidly from R = Me to R = Bu. The compounds used were as follows: Bistrimethylstibinedichloropalladium had decomp. pt. 150—165° (Found: C, 13·7; H, 3·4. Calc. for $C_6H_{18}Cl_2PdSb_2$: C, 14·1; H, 3·6%); bistriethylstibinedichloropalladium had decomp. pt. 90—91° (Jensen, *loc. cit.*, records *ca.* 90°). The compounds decompose without melting.

Bistri-n-*propylstibinedichloropalladium.* Tri-*n*-propylstibine (7·0 g.) was shaken for 5 minutes under nitrogen with ammonium palladochloride (4·0 g.) in water (75 c.c.) at 0°. The yellow product was washed with ice-cold water by decantation and collected on a filter. It was dried, and extracted with ligroin (b.p. 100—120°; 100 c.c.), and the bright red extract filtered and cooled to −70°. The yellow solid which separated was quickly filtered off, the recrystallisation repeated, and the twice-recrystallised *complex* dried at 0·01 mm. It had m. p. 66—68°

(decomp.; efferv.) (Found: C, 31·8; H, 6·2. $C_{18}H_{42}Cl_2PdSb_2$ requires C, 31·8; H, 6·2%). This dry product darkens slowly on storage, the darkening becoming obvious after 3—4 days. The bright yellow *n*-butyl analogue, m. p. 64—65° (decomp.), was prepared similarly but darkened much more rapidly.

The samples of ethyl and propyl platinous compounds used in these experiments were the same as those described in Parts III, V, and VI (*J.*, 1951, 2532; *locc. cit.*). Bistri-*n*-butylstibinedichloroplatinum was prepared as described by Jensen (*loc. cit.*) and had m. p. 63—63·5° (Jensen gives 62—63°).

Bistriphenylstibinedichloropalladium. Triphenylstibine (1·2 g.) in ethanol (20 c.c.) was shaken with ammonium palladochloride (0·5 g.) in water (15 c.c.) for ½ hr. at room temperature. The yellow *complex* was filtered off, dried, and purified by dissolution in warm chloroform, filtration (charcoal), and crystallisation by addition of ether; it decomposed at *ca.* 140° (Found: C, 48·5; H, 3·4. $C_{36}H_{30}Cl_2PdSb_2$ requires C, 48·9; H, 3·4%).

Measurements of Dielectric Constants.—The dielectric constants of the benzene solutions at 25° were determined as described in Part VI (*loc. cit.*) and are recorded in Tables 3—5, where W = weight of substance dissolved in 43·36 g. of benzene, f = mol.-fraction of substance, ΔC = increase in capacity of the electrical condenser containing solution as dielectric over its capacity with benzene as dielectric, ε = dielectric constant of solutions given by $\varepsilon = 1 + 1{\cdot}2727(56{\cdot}43 + \Delta C)(56{\cdot}43)^{-1}$ (2·2727 is the dielectric constant of benzene and 56·43 a constant of our apparatus), and $\Delta\varepsilon = \varepsilon - 2{\cdot}2727$.

TABLE 3. $\Delta\varepsilon/f$ *of* trans-$(MR_3)_2PtCl_2$ *in benzene solutions at* 25°.

Substance	W, mg.	$10^5 f$	ΔC, $\mu\mu$F	ε	$10^2\Delta\varepsilon$	$\Delta\varepsilon/f$
$(PEt_3)_2PtCl_2$	609·0	217·8	0·231	2·2779	0·52	2·39
$(AsEt_3)_2PtCl_2$	998·1	303·7	0·366	2·2810	0·83	2·73
	2525·4	764·8	0·917	2·2934	2·07	2·71
	3024·4	914·5	1·112	2·2978	2·51	2·74
$(PPr_3)_2PtCl_2$	782·0	239·6	0·198	2·2772	0·45	1·88
	1005·0	307·7	0·251	2·2784	0·57	1·85
	1277·4	390·8	0·337	2·2803	0·76	1·94
$(AsPr_3)_2PtCl_2$	1003·6	267·3	0·287	2·2792	0·65	2·43
	3037·2	804·6	0·861	2·2921	1·94	2·41

TABLE 4. $\Delta\varepsilon/f$ *of* cis-$(MR_3)_2PtCl_2$ *in benzene solutions at* 25°.

Substance	W, mg.	$10^5 f$	ΔC, $\mu\mu$F	ε	$10^2\Delta\varepsilon$	$\Delta\varepsilon/f$
$(PEt_3)_2PtCl_2$	41·8	14·98	1·112	2·2978	2·51	168
	42·6	15·27	1·129	2·2982	2·55	167
	52·1	18·67	1·376	2·3037	3·10	166
	54·0	19·35	1·436	2·3051	3·24	167
$(AsEt_3)_2PtCl_2$	36·5	11·14	0·832	2·2915	1·88	169
	37·6	11·47	0·852	2·2919	1·92	167
	43·2	13·18	0·967	2·2945	2·18	165
	59·0	18·00	1·340	2·3029	3·02	168
$(SbEt_3)_2PtCl_2$	89·6	23·59	1·630	2·3095	3·68	156
	96·1	25·30	1·723	2·3116	3·89	154
	99·5	26·20	1·792	2·3131	4·04	154
$(PPr_3)_2PtCl_2$	35·7	10·96	0·789	2·2905	1·78	162
	40·4	12·41	0·898	2·2930	2·02	163
$(AsPr_3)_2PtCl_2$	31·0	82·79	0·597	2·2862	1·35	163
	41·5	11·08	0·805	2·2909	1·82	164
	93·6	24·99	1·832	2·3140	4·13	165
$(SbPr_3)_2PtCl_2$	102·4	24·01	1·723	2·3116	3·89	162
	212·1	49·71	3·578	2·3534	8·07	162
$(SbBu_3)_2PtCl_2$	96·3	20·35	1·462	2·3057	3·30	162
	106·8	22·57	1·620	2·3092	3·65	162

The percentages of *cis*-isomers in the solutions of the stibine palladous complexes, recorded in Table 5, were calculated from $\Delta\varepsilon/f$ by means of the relation $\Delta\varepsilon/f = 160f_c/f + 2{\cdot}9f_t/f$, where f_c = mol.-fraction of *cis*-isomer, f_t = that of *trans*-isomer, and $f = f_c + f_t$; 160 is the probable value of $\Delta\varepsilon/f_c$ of a solution of the pure *cis*-isomer, assumed on the basis of our measurements in the platinous series (Table 4), and 2·9 is the probable value of $\Delta\varepsilon/f_t$ of a solution of the pure *trans*-isomer, assumed on the basis of our measurements in the palladous series of phosphine and arsine complexes (Table 5). We consider the uncertainly in these assumptions to give a possible error of ±20% of their value to the figures in the last column of Table 5.

TABLE 5. *$\Delta\varepsilon/f$ of* $(MR_3)_2PdCl_2$ *and percentage of* cis-*isomer in equilibrium with the* trans-*isomer in benzene solution at 25°.*

Substance	W, mg.	10^5f	ΔC, $\mu\mu$F	ε	$10^2\Delta\varepsilon$	$\Delta\varepsilon/f$	*cis*-isomer, %
$(PEt_3)_2PdCl_2$	—	505·8	—	2·2865	1·38	2·73 *	$\sim$0
$(AsEt_3)_2PdCl_2$	996·4	356·4	0·479	2·2835	1·08	3·03	$\sim$0
	—	542·1	—	2·2882	1·55	2·86 *	
$(PPr_3)_2PdCl_2$	997·6	359·5	0·413	2·2820	0·93	2·59	$\sim$0
$(AsPr_3)_2PdCl_2$	502·8	154·3	0·201	2·2772	0·45	2·92	$\sim$0
	998·1	305·9	0·393	2·2816	0·89	2·91	
$(PBu_3)_2PdCl_2$	833·5	257·2	0·254	2·2784	0·57	2·22	$\sim$0
$(AsBu_3)_2PdCl_2$ ...	990·9	265·7	0·301	2·2795	0·68	2·56	$\sim$0
$(SbMe_3)_2PdCl_2$ ...	3·0	1·057	0·033	2·2734	0·07	66	40
	5·3	1·867	0·053	2·2739	0·12	64	
$(SbEt_3)_2PdCl_2$	194·4	58·78	0·320	2·2799	0·72	12·2	6·0
$(SbPr_3)_2PdCl_2$	499·6	132·2	0·508	2·2842	1·15	8·70	3·8
$(SbBu_3)_2PdCl_2$ ...	997·0	234·6	0·894	2·2929	2·02	8·61	3·7
$(SbPh_3)_2PdCl_2$ ...	195·7	398·8	0·452	2·2829	1·02	25·6	14·6

* Calculated from Mann and Purdie's measurements (*loc. cit.*).

The corresponding equilibrium percentages of *cis*-isomers in the platinous series, shown in Table 1, are known with much greater accuracy, except that of $(SbMe_3)_2PtCl_2$ which is almost insoluble in benzene. The value for $(SbEt_3)_2PtCl_2$ is taken from Part VI (*loc. cit.*); the equilibria in the propyl and butyl platinous series will be examined to find the heat and entropy effects of the isomerisations and will be reported later.

The authors thank Miss J. H. Norwood for experimental assistance.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, BUTTERWICK RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[*Received, September 2nd,* 1952.]