824. *The Nature of the Co-ordinate Link. Part VI.* A Comparison of Equilibria between* cis- *and* trans-$(MEt_3)_2PtCl_2$, *where* M = P, As, *and* Sb.

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The isomerisations of *cis*-$(AsEt_3)_2PtCl_2$ and *cis*-$(SbEt_3)_2PtCl_2$ in benzene solutions are endothermic reactions; $\Delta H_{As} = 1{\cdot}2$ kcal. mol.$^{-1}$, $\Delta S_{As} = 14{\cdot}2$ cal. mol.$^{-1}$ deg.$^{-1}$; $\Delta H_{Sb} = 2{\cdot}4$, $\Delta S_{Sb} = 9{\cdot}4$ at 25° (in the same units). The equilibrium mixture of *cis*- and *trans*-arsine complexes at 25° contains only 0·57% of *cis*-isomer, but the stibine equilibrium mixture contains 34·4% as compared with 7·5% for the corresponding equilibrium in the phosphine series. The phosphine and stibine complexes differ in their entropies of isomerisation; the phosphine and arsine complexes in their heats of isomerisation. The total bond strengths of the *cis*-isomers are very approximately 10 kcal. higher than those of their *trans*-isomers. If this difference is due to π-bonding between *d*-orbitals of the platinum and the donor (M) atoms then the strength of the π-component of the M–Pt bond must stay almost constant throughout the series M = P to M = Sb. On the other hand, the strength of the σ-component of the bond must fall from M = P to M = Sb to account for the qualitatively observed weakening of the M–Pt bond. Steric effects would have a negligible effect on these equilibria. Possible causes of the great stability of the tertiary phosphine, arsine, and stibine platinous complexes relative to their trialkylamine analogues are discussed.

This study was undertaken to see what further evidence it would reveal for or against the suggestion that electron pairs from *d*-orbitals contribute by π-bonding (partial double-bonding) to the strength of the bond between metals with filled *d*-orbitals, and donor atoms with vacant *d*-orbitals in complex compounds such as $(MR_3)_2PtCl_2$ (Chatt, *J.*, 1949, 3340, and earlier references quoted therein; *Nature*, 1950, **165**, 637, 859; Part I, *J.*, 1950, 2301; Part II, *J.*, 1951, 652; *Research*, 1951, **4**, 180; Wilkins, *Nature*, 1951, **167**, 434; Coates, *J.* 1951, 2003; Part III, Chatt and Wilkins, *J.*, 1951, 2532; Part IV, Chatt and Williams,

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* Part V, *J.*, 1952, 273.

J., 1951, 3061; Kabesh and Nyholm, *J.*, 1951, 3245; Part V, *loc. cit.*; Chatt, "The General Chemistry of Olefin Complexes with Metallic Salts," in "Cationic Polymerisation and Related Complexes," Ed. P. H. Plesch, Heffer, Cambridge, 1952).

In Part V, we showed that the total bond energy of *cis*-$(PEt_3)_2PtCl_2$ is about 10 kcal. greater than that of its *trans*-isomer. This we consider to be evidence that *d*-orbitals contribute to a greater (although it could be smaller) extent in the binding of phosphorus than in the binding of chlorine to platinum. This contribution is probably by π-bonding between the *d*-orbitals of the phosphorus and platinum atoms. However, the platinum atom is much larger than the phosphorus atom and, other factors being equal, we should expect π-bonding to be greatest when the atom M is approximately the same size, and uses the same type of *d*-orbital, as the platinum atom, because the π-bond will then be most symmetrical. The tetrahedral covalent radii of the relevant atoms are P = 1·10, As = 1·18, Sb = 1·36, and Pt = 1·31 Å, and the *d*-orbitals used are P = 3*d*, As = 4*d*, Sb = 5*d*, and Pt = 5*d*. On this basis, π-bonding between antimony and platinum should be particularly favoured and it should increase in the order P<As<Sb. On the other hand, the attraction of M for the electrons from *d*-orbitals of the platinum atom will increase as M becomes more electronegative, so on this basis π-bonding should decrease in the order P>As>Sb. We have therefore examined, by the method described in Part V, the equilibrium between *cis*- and *trans*-$(AsEt_3)_2PtCl_2$ and -$(SbEt_3)_2PtCl_2$, and compared the data obtained with those previously published for the triethylphosphine complexes. This work, which we describe below, indicates that the *d*-orbital contribution to the M–Pt bond remains approximately constant throughout the series. It does not prove that the *d*-orbital contribution is by π-bonding since it may be by greater *d*-character of the σ-bonds. However, if it is by π-bonding, which we consider probable in the light of the experiments recorded in Part IV, then the effects of increasing size and decreasing electronegativity of M, operating against each other as the series is ascended from M = P to M = Sb, are almost balanced.

Initially, we chose to investigate equilibria in the tri-*n*-propyl series of complexes, $(MPr_3)_2PtCl_2$, because the solubilities of its members in benzene are more suitable than those of other members of the homologous series (see Wilkins, Report on Co-ordination Chemistry Conference, *Nature*, 1951, **167**, 434). However, it proved unsuitable for our present purpose. The equilibrium between the arsine complexes lay so far to the *trans*-side that its shift with temperature could not be measured sufficiently accurately to determine the heat and entropy of isomerisation. This is also true of the tri-*n*-butyl and presumably of higher homologues. The trimethyl series of complexes could not be used because its members of *cis*-configuration are almost insoluble in benzene. The triethyl series provided the only compromise in the tri-*n*-alkyl series between insufficient solubility of the *cis*-isomers and unfavourable position of equilibrium between the arsine complexes. The equilibrium mixtures of *cis*- and *trans*-$(AsEt_3)_2PtCl_2$ contains only 0·57% of the *cis*-isomer, but measurements of the shift of equlibrium with temperature, sufficiently accurate to determine ΔH, were just possible with our apparatus.

Using the technique described in Part V, we determined the thermodynamic functions listed in Table 1. The triethylarsine complexes were examined between 15° and 70° and the triethylstibine complex over the range 15—35°.

TABLE 1. *Data relating to the isomerisation* cis ⟶ trans-$(MEt_3)_2PtCl_2$ *in benzene at* 25°.

	cis-Isomer	$\log K = A - BT^{-1}$			$-\Delta G$,†	ΔH, †	
Substance	in equilm., %	A	B	K †	15°-cal.	15°-cal.	ΔS † ‡
$(PEt_3)_2PtCl_2$ *	7·5	2·901	540	12·3 ± 0·2	1480 ± 12	2470 ± 210	13·3 ± 0·7
$(AsEt_3)_2PtCl_2$...	0·57	3·108	258	175 ± 10	3060 ± 45	1180 ± 200	14·2 ± 0·8
$(SbEt_3)_2PtCl_2$...	34·4	2·049	527	1·91 ± 0·02	383 ± 8	2410 ± 350	9·4 ± 1·0

* Taken from Part V for comparison. ‡ In 15°-cal. mol.$^{-1}$ degree^{-1}.

† P, As, and Sb will be used as suffixes with these and other symbols to indicate that they refer to the triethyl-phosphine, -arsine, and -stibine complexes and their isomerisation reactions.

Equilibrium Positions and ΔG.—The three equilibrium constants fall in an irregular sequence K_P being intermediate between K_{As} and K_{Sb}. The high equilibrium concentration of the *cis*-isomer in the stibine equilibrium is caused by the relatively low entropy change of the isomerisation reaction and not by exceptionally strong π-bonding between the antimony and platinum atoms, which would have been reflected in a relatively large value of ΔH_{Sb}. This observation again illustrates the importance of entropy changes in equilibria involving highly dipolar molecules such as co-ordination compounds, even of very closely similar types. The very low concentration of *cis*-isomer in the arsine series is caused by the exceptionally low heat of isomerisation, the entropy change ΔS_{As} being comparable with that in the phosphine series.

Entropy Change.—ΔS_{P} and ΔS_{As} are not significantly different but ΔS_{Sb} is lower than the other two. In Part V we attributed the high value of ΔS_{P} to greater solvation of the highly dipolar *cis*-$(PEt_3)_2PtCl_2$ compared with its non-polar *trans*-isomer. Jensen (*Z. anorg. Chem.*, 1936, **229**, 250) found the dipole moments of *cis*-$(MEt_3)_2PtCl_2$, where M = P, As, and Sb, in benzene solution to be 10·7, 10·5, and 9·2 D., respectively. He also stated that no correction was made for the spontaneous isomerisation of the complexes in the time which elapsed between making up his solutions and measuring their dielectric constants. By the addition of a trace of the bridged complex, $(AsEt_3)_2Pt_2Cl_4$, to the benzene solutions we were able to depress spontaneous isomerisation, so that its slight effect could be accurately estimated (cf. Part III, *loc. cit.*). Using Jensen's method and formula, we find the moments (μ) of the *cis*-complexes to be $\mu_{\text{P}} = 10{\cdot}9$, $\mu_{\text{As}} = 10{\cdot}9$, and $\mu_{\text{Sb}} = 10{\cdot}5$ D. These moments are so similar that the decrease in solvation, due to the slightly smaller dipole moment of the stibine complex as compared with those of the other two, could scarcely account for the fairly large differences $\Delta S_{\text{P}} - \Delta S_{\text{Sb}}$ and $\Delta S_{\text{As}} - \Delta S_{\text{Sb}}$. It may be that decreasing dipole moment and increasing molecular size in their effect on solvation are mainly responsible for the observed differences in ΔS, but we should have expected ΔS_{As} to lie a little nearer to the mean of ΔS_{P} and ΔS_{Sb} if these were the only factors involved.

Heat of Isomerisation, ΔH.—The irregularity in the values of ΔH as the series is ascended is very marked; ΔH_{As} has about half the value of ΔH_{P} and ΔH_{Sb}. In Part V, we split ΔH_{P} into three important components: (1) the energy change due to the rearrangement of electric charges which takes place on isomerisation; (2) the difference in heat of solvation of the two isomers from an infinitely dilute gas phase into benzene solution at 25°; (3) the change in bond energy which occurs during isomerisation. Assuming that all the positive charge resides at the centres of the atoms M and the negative charge at the centres of the chlorine atoms so that the platinum atom has zero charge, we have calculated from the dipole moments approximations to (1) (Table 2) (see Part V). The maximum value of (2) is equal to $T\Delta S$, so, using $T\Delta S$ as the real value of (2), we obtain approximations to (3) as shown below. The signs of these heat effects are positive when they represent heat absorption in the isomerisation reaction *cis* ⟶ *trans*; $\Delta H = (1) + (2) + (3)$. All are in kcal./mole.

TABLE 2.

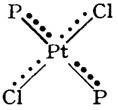
Substance	Charge on M and Cl	(1)	(2) = $T\Delta S$	ΔH	(3)
$(PEt_3)_2PtCl_2$	0·341*e*	−13·7	4·0	2·5	12·2
$(AsEt_3)_2PtCl_2$	0·334*e*	−12·7	4·2	1·2	9·7
$(SbEt_3)_2PtCl_2$	0·310*e*	−10·6	2·8	2·4	10·2

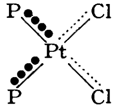
The differences in total bond energy (3) between the *cis*- and *trans*-isomers are of course only first approximations. Although (1) may be appreciably in error the true values will fall in regular sequence as do those we give. Thus the observed irregularities in ΔH must be due to irregularities in (3), modified by those in (2). The values of (2) are maximum values, but because ΔS_{P} and ΔS_{As} are equal, the values of (3) for the phosphine isomers and arsine isomers are comparable. The corresponding value of (3) for the stibine isomers is less certain, because ΔS_{Sb} is much smaller than ΔS_{P} and ΔS_{As}, and the error in estimating the heat effect associated with ΔS will increase in importance as ΔS increases.

The figures (3) represent approximately the increase in total bond energy when the two MEt_3 groups and Cl atoms are moved from *trans*- to *cis*-positions. We suppose that this increase is due to stronger π-bonding in the M–Pt bond when the M atoms occupy *cis*-positions. Both phosphorus and chlorine have vacant *d*-orbitals so that both the P–Pt and the Cl–Pt bonds could have partial double-bond character. It is assumed that the P–Pt bond has greater double-bond character than has the Cl–Pt bond because phosphorus is higher than chlorine in the *trans*-influence series (see Part IV).

In (I) and (II), we represent by dotted lines, the π, or other bond components in which electron pairs from filled *d*-orbitals of the metal atom contribute in some manner to the strength of the M–Pt and Cl–Pt bonds. The strengths of these components are represented by the size of the dots. In the *trans*-complex (I) both P–Pt bonds must use the same *d*-orbitals in the π-component : hence the π-components are weaker than in the *cis*-complex where each P–Pt bond has available a different *d*-orbital. On the other hand, the chlorine atoms in the *cis*-complex (II) are now competing with the phosphorus atoms for electrons from *d*-orbitals of the platinum atom, so will get a smaller share than they had in the *trans*-complex. The values (3) thus represent the gain in energy due to the greater double-bond character of the P–Pt bonds when they are in *cis*-relationship, less the loss in energy due to smaller double-bond character of the Pt–Cl bonds. The greater the tendency of electron pairs from *d*-orbitals of the platinum atom to contribute to the P–Pt bond, the greater would be this difference. The values (3) are thus an arbitrary measure of the strength of the π, or other component of the M–Pt bond to which the *d*-orbitals make special contribution. They indicate that the strength of this component stays almost constant as the series is ascended from M = P to M = Sb. This is the only certain information about the M–Pt bond provided by this study.

(I)





(II)

However, it appears from the values of (3) in Table 2 that the *d*-orbitals contribute more in binding platinum to phosphorus than to arsenic or to antimony. Thus we expect that triethylphosphine will stand higher in the *trans*-influence series than triethylarsine. It is harder to predict the exact position of triethylstibine in the series because ΔS_{Sb} is unexpectedly small compared with ΔS_{P} and ΔS_{As} and we cannot calculate exactly the heat associated with these entropy effects.

The fact that the dipole moments of *cis*-$(\mathrm{MEt_3})_2\mathrm{PtCl_2}$ fall from M = P to M = Sb in spite of increased bond length requires some explanation. Our results indicate that it is not due to greater drift of electrons from the *d*-orbitals of the platinum atom into the *d*-orbitals of the atom M, *i.e.*, stronger π-bonding, so it must be due to weakening of the σ-bond. The classical co-ordinate link should have a bond moment of 4·80 *l* (*l* is the bond length in Å) but the observed value is usually some fraction *x* of this. In the complexes of aluminium and boron, where double bonding cannot occur, *x* is usually less than 0·6 and it appears that as *x* falls the co-ordinate link becomes weaker (Phillips, Hunter, and Sutton, *J.*, 1945, 155). The decrease in dipole moments in spite of greater bond length, *i.e.*, the decreasing *x* in the series of bonds P–Pt, As–Pt, and Sb–Pt, is probably to be associated with the marked parallel weakening of the bonds, for which there is ample qualitative evidence (*e.g.*, see Chatt, *J.*, 1951, 652). This is an effect which need not be associated with double bonding. Our evidence indicates that electron pairs from *d*-orbitals, other than those involved in the symmetrical dsp^2 hybrids, contribute more than 5 kcal. to the strength of the M–Pt bonds; nevertheless, the high dipole moments of the order 10 D., observed for the *cis*-complexes $(\mathrm{MEt_3})_2\mathrm{PtCl_2}$, emphasise that the M–Pt bond is in the main a single co-ordinate bond.

Steric Effects.—The platinum atom is so large that steric effects in both *cis*- and *trans*-isomers of the series of complexes $(\mathrm{MEt_3})_2\mathrm{PtCl_2}$ (M = P, As, and Sb) are negligible, and can scarcely affect the equilibrium. On the other hand, the nitrogen atom in tertiary amine complexes is sufficiently small to cause considerable strain between the attached hydrocarbon radicals and the adjacent groups on the platinum atom (cf. triethylamine–trimethylborine complexes, Brown *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1332; 1948, **70**, 2878). There would be more steric strain in the *cis*- than in the *trans*-complexes, but only *trans*-$(\mathrm{NMe_3})_2\mathrm{PtCl_2}$ would be reasonably free from steric effects. This steric effect would be an important factor in lowering the stability of $(\mathrm{Et_3N})_2\mathrm{PtCl_2}$ and its higher homologues relatively to that of the trimethyl analogue. It cannot be the general explanation of the much lower stability of tertiary amine platinous complexes relatively to their phosphorus analogues, because even *trans*-$(NMe_3)_2PtCl_2$, where the steric effect is negligible, is unknown.

Instability of Tertiary Amine Complexes.—We consider that two factors are responsible for the very much greater stability of trialkyl-phosphine, -arsine, and -stibine platinous and similar complexes than of their nitrogen analogues: (1) The enhanced strength of the M–Pt bond due to π-bonding between the *d*-orbitals of the atom M and the platinum atom; such bonding is impossible in the N–Pt bond because there are no 2*d*-orbitals. (2) The greater covalent character of the M–Pt than of the N–Pt bond.

The M–Pt bond is in the main a classical co-ordinate bond and it is not likely that the first factor alone will be sufficiently strong to account for the great difference in stability. The second factor is probably important because platinum forms only "inner orbital" complexes (Taube, *Chem. Reviews*, 1952, **50**, 69), in which the ligands are bound by strong covalent bonds. The electronegativities of phosphorus, arsenic, antimony, and platinum are about equal to 2 but that of nitrogen is 3. The much greater electronegativity of nitrogen means that the N–Pt co-ordinate bond will have about 25% ionic character on the basis of Hannay and Smyth's formula (*J. Amer. Chem. Soc.*, 1946, **68**, 171). We should thus have greater dissociation of the N–Pt bond especially in the presence of water, and this would lead to general decomposition of the platinous complex. If, however, the aliphatic tertiary nitrogen atom is part of a multidentate ligand, *e.g.*, $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$,* which for dimensional reasons fits closely around the metal atom, then the tertiary nitrogen atom is held so that its dissociation from the platinum atom is impossible. In these circumstances, a stable complex with a co-ordinate bond from the tertiary nitrogen to the metal results (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **109**, 444; *J.*, 1926, 482). Monoamines form stable complexes with platinum and similar metals only when the electronegativity of the nitrogen atoms can be reduced. This can occur by neutralisation of the positive charges which develop on complex formation. It takes place either by transmission of the positive charge to hydrogen atoms as in the ammines (Pauling, *J.*, 1948, 1461) or by polarisation of an aromatic system as in pyridine complexes. No mechanism is available to remove the positive charge from the nitrogen atoms of the tertiary alkylamine complexes, and that may be the fundamental cause of their instability. There is no necessity to neutralise the positive charges which develop during the co-ordination of the much less electronegative atoms M, but in fact the first factor above will cause some neutralisation.

EXPERIMENTAL

The triethyl-arsine and -stibine complexes were prepared by the method described in Part III (*loc. cit.*) for the tri-*n*-propyl complexes. They have a greater tendency than their propyl analogues to isomerise spontaneously, so are more difficult to purify. Sharp m. p.s are not good criteria of purity because softening causes isomerisation and immediate melting. The compounds were therefore purified until their *k* values (essentially the same as dielectric constants, see p. 4305) were not altered by further recrystallisation. Five or six rapid recrystallisations from ethanol containing a trace of the bridged $(AsEt_3)_2Pt_2Cl_4$ in the case of the *trans*-isomer, followed by rapid drying at 0·1 mm. after recrystallisation, were sufficient. Our compounds were as follows: *trans*-$(AsEt_3)_2PtCl_2$, m. p. 120—121°; Jensen (*loc. cit.*) reports 120—121°, Nyholm (*J.*, 1950, 843) reports 119°. *cis*-$(AsEt_3)_2PtCl_2$, m. p. 154—155°; Jensen reports 142—142·5°, Nyholm, 142° (Found: C, 24·6; H, 5·1. Calc. for $C_{12}H_{30}As_2Cl_2Pt$: C, 24·4; H, 5·1%); the purification of this compound is best effected by growing large crystals from ethanol solution. *cis*-$(SbEt_3)_2PtCl_2$, m. p. 102·5—103°; Jensen reports 104—104·5°. *trans*-$(SbEt_3)_2PtCl_2$ could not be isolated (compare the propyl analogue, Part III).

The equilibrium concentrations of isomers in benzene were determined by measuring the changes in dielectric constants of benzene solutions of each pure isomer when they were isomerised in the presence of a trace of triethylarsine as catalyst. Isomerisations at temperatures up to 35° were done in the electrical condenser or cell. Those above 35° were carried out in a separate vessel, and the equilibria quenched by the addition of a trace of $(AsEt_3)_2Pt_2Cl_4$ at the higher temperature. The quenched equilibrium mixtures were cooled rapidly, poured into the cell,

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* The authors are grateful to the referees for reminding them of this type of exception to the general observation that tertiary alkylamines form only unstable co-ordination compounds with the transition metals.

and their dielectric constants measured at 25°. Triethylarsine and $(AsEt_3)_2Pt_2Cl_4$ were used to catalyse and quench both arsine and stibine equilibria.

The quantities of benzene used in these experiments were those delivered from a particular 50-c.c. graduated flask at the temperature of the dielectric-constant determination; these were, at 15°, 43·81 g.; 20°, 43·58 g.; 25°, 43·36 g.; 30°, 43·14 g.; and 35°, 42·94 g. The increase in electrical capacity of the cell (ΔC) containing mixed solutions of the concentrations we used, over its capacity with pure benzene as dielectric, is given by the equation: $\Delta C = k_cW_c + k_tW_t + k_aW_a$, where W_c = weight of *cis*-isomer, W_t = weight of *trans*-isomer, and W_a = weight of tertiary arsine added to catalyse the isomerisation. The k values are constants for any given substance at any given temperature and were determined by using pure solutions of each component.

cis-$(AsEt_3)_2,PtCl_2$ and *cis*-$(SbEt_3)_2PtCl_2$ isomerise spontaneously in benzene solution at room temperature; hence to measure k_c for these substances, a trace (*ca.* 0·2 mg.) of bridged $(AsEt_3)_2Pt_2Cl_4$ was added to their pure solutions. It completely arrested the isomerisation of the arsine complex for sufficient time to allow measurements to be made, and slowed down the isomerisation of the stibine complex sufficiently to permit accurate extrapolation to zero time. The results are recorded in Table 3. W is the total weight of complex used in the experiments, *i.e.*, $W = W_c + W_t$.

The dipole moments of the *cis*-compounds were redetermined at 25° in benzene, the values of ΔC obtained during the determination of the various k_c's being used. This was necessary because Jensen, who required the moments only to determine configuration, made no allowance for spontaneous isomerisation which affects the result appreciably in the case of the stibine complex. The dielectric constant (ε_s) of a solution containing W_c g. of *cis*-complex, of molecular weight M, in 49·33 c.c. of benzene is given by the equation $\varepsilon_s = 1 + 1{\cdot}273(56{\cdot}43 + \Delta C)(56{\cdot}43)^{-}$

TABLE 3

Temp., °K	$10^4/T$	k_c	k_t	W, mg.	W_a, mg.	$\Delta C - k_aW_a$, μμF	W_c, mg.	W_t, mg.	K	log K
Isomerisation of *trans*-$(AsEt_3)_2PtCl_2$										
290·26	34·45	23·05	0·375	1505·1	2·4	0·762	8·7	1496·4	172	2·236
				1858·0	2·4	0·954	11·3	1846·7	164	2·215
				2178·2	2·4	1·109	12·9	2165·3	168	2·225
298·21	33·53	22·63	0·367	2520·3	2·4	1·241	14·2	2506·1	176	2·246
				3018·3	2·4	1·488	17·1	3001·2	176	2·246
308·16	32·45	22·27	0·382	2410·5	2·4	1·208	13·1	2397·4	183	2·262
				2855·9	2·4	1·439	15·9	2840·0	179	2·253
340·4 *	29·38	—	—	3045·5	0·9	1·422	13·7	3031·8	221	2·344
340·7 *	29·35	—	—	2014·0	0·9	0·937	8·9	2005·1	225	2·352
341·5 *	29·28	—	—	2008·6	0·9	0·927	8·5	2000·1	235	2·371
Isomerisation of *cis*-$(AsEt_3)_2PtCl_2$										
298·21	33·53	22·63	0·367	1008·6	5·6	0·495	5·6	1003·0	179	2·253
				1380·8	5·6	0·677	7·6	1373·2	180	2·255
				1503·4	5·6	0·729	8·0	1495·4	187	2·272
341·65 *	29·27	—	—	1000·8	2·8	0·462	4·2	996·6	234	2·369
				1483·4	2·8	0·696	6·8	1476·6	216	2·334
Isomerisation of *cis*-$(SbEt_3)_2PtCl_2$										
290·88	34·38	18·74	0·355 †	196·4	0·3	1·380	71·2	125·2	1·758	0·245
				258·0	0·3	1·822	94·1	163·9	1·742	0·241
298·38	33·51	18·05	0·355 †	254·4	Nil	1·634	87·2	167·2	1·917	0·283
				293·7	Nil	1·898	101·4	192·3	1·896	0·278
				295·0	0·3	1·914	102·3	192·7	1·884	0·275
303·33	32·97	17·63	0·355 †	196·9	0·3	1·168	63·6	133·3	2·096	0·321
				202·5	0·3	1·208	65·8	136·7	2·078	0·318

* In these determinations isomerisation was quenched by addition of a trace of bridged compound (3 mg. or 9 mg.), and the mixture analysed at 25°.

† The values of k_t for the triethylstibine complexes were estimated by extrapolation of the k values for the triethyl-phosphine and -arsine complexes.

where the dielectric constant of benzene is assumed to be 2·273 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 683) and 56·43 is a cell constant. The dipole moment can then be calculated by using Jensen's approximate formula (*loc. cit.*) which gives the sum of the orientation and atom polarisations (${}_{O}P$ and ${}_{A}P$):

$${}_{O}P + {}_{A}P \simeq \frac{M \times 49{\cdot}33}{W_c}\left(\frac{\varepsilon_s - 1}{\varepsilon_s + 2} - \frac{\varepsilon_B - 1}{\varepsilon_B + 2}\right)$$

In compounds such as these where the total polarisations are of the order 2000 c.c., the atom polarisations can be ignored. Our determinations are listed in Table 4.

TABLE 4

Substance	W_e, g.	ΔC, $\mu\mu$F	ε_s	${}_0P$, c.c.	$\mu = 0{\cdot}2212\sqrt{{}_0P}$, D.	
$(PEt_3)_2PtCl_2$ $M = 502{\cdot}5$	0·0418	1·112	2·297	2432	10·91	10·9
	0·0426	1·129	2·298	2424	10·89	
	0·0521	1·376	2·303	2407	10·85	
	0·0540	1·436	2·305	2426	10·89	
$(AsEt_3)_2PtCl_2$ $M = 590{\cdot}3$	0·0365	0·832	2·291	2455	10·96	10·9
	0·0376	0·852	2·2915	2433	10·91	
	0·0432	0·967	2·294	2403	10·84	
	0·0590	1·340	2·3025	2433	10·91	
$(SbEt_3)_2PtCl_2$ $M = 684{\cdot}0$	0·0896	1·630	2·309	2252	10·50	10·45
	0·0961	1·723	2·311	2219	10·42	
	0·0995	1·792	2·313	2231	10·45	

In the examination of the $(PEt_3)_2PtCl_2$ equilibrium, slightly different values of the equilibrium constant were obtained depending on whether the *cis*- or the *trans*-complex was isomerised (see Part V). In the arsine series, the values obtained by isomerisation of both the *cis*- and the *trans*-complexes are identical within experimental error. The values obtained by isomerisation of the *trans*-complexes have been given most weight because the *cis*-compound is too insoluble in benzene to give sufficient concentration for very accurate measurements. Even in presence of a trace of triethylarsine, 1—1·5 g. of *cis*-isomer required 1—2 hours' vigorous shaking to dissolve it with isomerisation.

Only the *cis*-isomer of $(SbEt_3)_2PtCl_2$ is available, but solubility increases as the series of complexes is ascended from M = P to M = Sb, and in addition more dilute solutions of the stibine complex could be used because the equilibrium lies much farther to the *cis*-side; thus no difficulty was experienced with solubility.

The triethylstibine complex isomerised to give the same equilibrium concentrations whether the isomerisation was spontaneous or catalysed by a trace of triethylarsine. In the former case, equilibrium was reached in about 18 hr. but with the catalyst it was complete in 10 min. The fact that the same equilibrium position was reached under such very different conditions is evidence that the isomerisation is probably free from any important side reactions.

The authors thank Mr. D. J. Odds for experimental assistance.

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