The Reaction of Binuclear Halogen-bridged Complexes of Platinum(II) with Monoamines.

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The reactions of a number of amines (am) with bridged compounds $L_2Pt_2X_4$ are described:

$$L_2Pt_2X_4 + 2am \rightleftharpoons 2[L,amPtX_2]$$

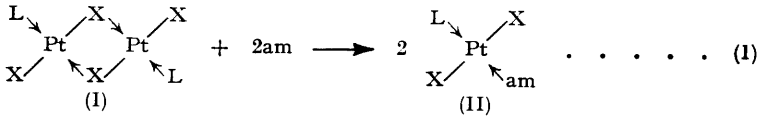
The uncharged ligands, L, are of the types C_2H_4, amines, PR_3, $P(OR)_3$, AsR_3, SbR_3, R_2S, R_2Se, and R_2Te, and the halogen, X, is usually chlorine.

When X is chlorine or bromine the equilibrium lies well to the side of the "mixed" product, unless the amine is very weakly basic, or sterically hindered. In the iodide series the equilibrium lies more to the left-hand side and the crystalline mixed complex can be difficult to isolate because $L_2Pt_2X_4$ is usually the least soluble component.

Generally the reaction proceeds rapidly to give "mixed" complexes of *trans*-configuration except when L is an amine. The reaction is then very slow, and the product a mixture of *cis*- and *trans*-isomers unless the amine is strongly hindered (the *trans*-isomer may then be the only product). The directing effects of the ligands, L, are most strongly marked in the reactions: (*a*) of ethylene with the amine bridged complex, $am_2Pt_2Cl_4$, which gives exclusively *cis*-$[C_2H_4,amPtCl_2]$, and (*b*) of an amine with the ethylene-bridged complex, $(C_2H_4)_2Pt_2Cl_4$, which gives only the *trans*-isomer.

The chloro-complexes *trans*-$[L,amPtCl_2]$ have moderate to high stabilities except when L is C_2H_4, SbR_3, R_2Se, or R_2Te; then dissociation and disproportionation occur easily.

A SERIES of complex compounds of the type *trans*-$[L,amPtCl_2]$ (II) (L = a wide variety of uncharged ligands, am = ammonia or a monoamine, and X = a halogen) was required for the study of inductive and mesomeric effects in complex compounds of platinum(II). The reaction of binuclear halogen-bridged complexes (Chatt and Venanzi, *J.*, 1955, 2787) with amines was therefore investigated as a general preparative method. This "bridge-splitting" reaction may generally be represented as follows although the product does not necessarily have a *trans*-configuration.



The ligands, L, were chosen to have as great a variety of donor atoms as possible and were of the types: C_2H_4, amines, PR_3, $P(OR)_3$, AsR_3, SbR_3, R_2S, R_2Se, and R_2Te. Since we desired products soluble in carbon tetrachloride the sizes of the alkyl groups (R) were so chosen as to give this solubility.

The addition of ammonia and amines to compounds of the empirical formula, $LPtCl_2$ (now known to be dimeric), is one of the earliest known properties of such compounds. However, an excess of ammonia or amine was usually employed and the products were often more complex than indicated by reaction 1. Nevertheless a simple compound, now known to be *cis*-$[P(OEt)_3,p$-toluidine$PtCl_2]$, was isolated (Schützenberger and Fontaine, *Bull. Soc. chim. France*, 1872, **18**, 101). Rosenheim and Levy (*Z. anorg. Chem.*, 1905, **43**, 34) later prepared both the white *cis*- and the yellow *trans*-$[P(OEt)_3,PhNH_2PtCl_2]$ by treating $\{P(OEt)_3\}_2Pt_2Cl_4$ with aniline in hot and cold ethanolic solution respectively. The configurations were assigned by Troitskaya (*Zhur. priklad. Khim.*, 1953, **26**, 781). Of the bridged complexes of the sixth-group alkyls, Petren (Diss., Lund, 1898, p. 40) reported

that Svensson obtained [Et_2S,pyridine$PtCl_2$] from $(Et_2S)_2Pt_2Cl_4$ and pyridine, but in the selenide series only disproportionation occurred leading to $(Et_2Se)_2PtCl_2$ and (pyridine)$_2$-$PtCl_2$. Klason (*Ber.*, 1904, **37**, 1349) also prepared this substance, now known to be *trans*-[Et_2S,pyridine$PtCl_2$], which he noted is converted into its *cis*-isomer on melting.

More recently it was shown by Mann and his co-workers (*Ann. Reports*, 1938, **35**, 148; Chatt and Mann, *J.*, 1939, 1622) that similar bridge-splitting reactions occur in the analogous series of palladium(II) bridged complexes and by Chatt (*J.*, 1951, 652) for the bridged series $(MPr^n_3)_2Pt_2Cl_4$ (M = P, As, and Sb).

The investigation to be described is concerned mainly with the reactions of a variety of amines with chloro-bridged complexes, $L_2Pt_2Cl_4$, having as great a diversity of donor atoms in the ligands, L, as possible. Generally the reaction proceeds very satisfactorily at room temperature with the reactants in acetone solution or with the bridged complex in acetone suspension. The yield of crude *trans*-[L,am$PtCl_2$] is often almost quantitative. However, considerable loss of product usually occurs during the purification by recrystallisation because the compounds *trans*-[L,am$PtCl_2$] which we prepared tend to have inconveniently high solubilities in organic solvents.

In carrying out the bridge-splitting reaction it is preferable to use the stoicheiometric quantity of amine because an excess facilitates the formation of by-products.

In general, the bridge-splitting reaction appears to be reversible but at the normal concentrations of reactants used in preparative work the equilibrium lies well to the side of the mixed complex, *trans*-[L,am$PtCl_2$]. This is certainly true of the splitting of $(PPr^n_3)_2Pt_2Cl_4$ by *p*-toluidine (Chatt and Hart, *J.*, 1953, 2363). However, when a weakly basic or sterically hindered amine is used to split the bridge the position of equilbrium lies so far in favour of the bridged complex as to cause difficulty in isolating the mixed complex.

Thus no diphenylamine complex could be isolated from the reaction of that amine with $(PPr^n_3)_2Pt_2Cl_4$ although the equilibrium (2) contains an appreciable proportion of the diphenylamine complex.

$$(PPr^n_3)_2Pt_2Cl_4 + 2Ph_2NH \rightleftharpoons 2\textit{trans}\text{-}[PPr^n_3,Ph_2NHPtCl_2] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In general, in these circumstances, only the original bridged complex can be isolated because it is the least soluble component of the mixture; the equilibrium must lie well to the right-hand side to allow the isolation of the mixed complex.

Factors Dependent on the Halide Bridge.—The effect of different halogens in the bridged system was investigated only in the series $(PPr^n_3)_2Pt_2X_4$ (X = Cl, Br and I). The equilibrium appears to lie increasingly in favour of the bridged complex as chlorine is replaced by bromine, and bromine by iodine. The bromides $(PPr^n_3)_2Pt_2Br_4$ and $(Bu^n_2S)_2Pt_2Br_4$ were both split and the products isolated as with the chlorides. However, the stability of the iodo-bridged system is so far in favour of the bridged complex that it is sometimes difficult to isolate the crystalline product, *trans*-[PPr^n_3,amPtI_2]. Even when *trans*-[L,amPtI_2] is prepared directly (from the corresponding chloride and potassium iodide in acetone solution) it is so labile that it tends to lose amine and form the bridged iodide before it can be isolated. The preparation of *trans*-[L,amPtI_2] where " am " is a volatile amine, *e.g.*, ammonia, is therefore especially difficult.

Factors Dependent on the Ligand L.—Only the chloro-bridged complexes were investigated in detail. The ligand, L, determines to some extent the configuration of the product. In the substitution reactions of complex ions of platinum(II) in aqueous solution, some ligands already present in the complex ion tend to direct incoming groups into the *cis*-positions to themselves. Others direct them into the *trans*-positions (see Quagliano and Schubert, *Chem. Rev.*, 1952, **50**, 201). *cis*-Substitution is slow and *trans*-substitution is rapid, somewhat analogous to *meta*- and *ortho-para*-substitution in benzene chemistry. Of the ligands, L, examined in this study, amines are known to be most strongly *cis*-directing and ethylene most strongly *trans*-directing. The relative strengths of the *trans*-directing effects of the remainder are not known with any certainty (see Chatt and Williams, *J.*, 1951, 3061; Hel'man and Karandashova, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**,597).

All the bridged complexes, except those of the amines, react rapidly to give only the *trans*-isomer in the bridge-splitting reaction, although isomerisation may sometimes occur

subsequently. The contrast between the rates at which the olefin and amine chloro-bridged complexes were split is, however, very marked. Amines react almost instantaneously with a solution of $(C_2H_4)_2Pt_2Cl_4$ at −70° and in the one example which has been investigated (with 4-*n*-pentylpyridine) the immediate product had a *trans*-configuration (Chatt and Venanzi, *loc. cit.*). On the other hand amines, am, react extremely slowly with solutions of the amine-bridged complexes, $am'_2Pt_2Cl_4$. With stoicheiometric proportions at room temperature the reaction was not complete after a week and so it was carried out at the boiling point of acetone (½ hr.) with an excess of the amine. Under both of these conditions the product was a mixture of *cis*- and *trans*-[am',amPtCl$_2$], although we cannot be certain whether both isomers were produced directly in the reaction, or whether one was formed from the other by subsequent isomerisation. However, the directing effects of amines and olefins are strikingly illustrated by the two bridge-splitting reactions (3) and (4) in dichloromethane and ethanol respectively; each leads to only one of the two possible isomeric products.

$$(pip)_2Pt_2Cl_4 + 2C_2H_4 \xrightarrow{15°} cis\text{-}[C_2H_4,pipPtCl_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$(C_2H_4)_2Pt_2Cl_4 + 2pepy \xrightarrow{-70°} trans\text{-}[C_2H_4,pepyPtCl_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(pip = piperidine; pepy = 4-*n*-pentylpyridine)

The nature of the ligands, L, also has considerable effect on the stabilities of the mixed complexes, as is discussed below.

Factors Dependent on the Amine.—In general the amines used showed very similar behaviour when the chloro-bridged systems were split. The only marked differences were that sterically hindered amines, *e.g.*, 2 : 6-dimethylaniline, gave only the *trans*-isomer on fission of the amine-bridged complexes, $am_2Pt_2Cl_4$, and it was not always possible to isolate the product when weakly basic amines were used to split the bridge, as discussed above.

The splitting of amine-bridged complexes, possibly because of the more drastic conditions necessary for a reasonable rate of reaction, does not always give well-defined products, this depending to some extent on the amine used to split the bridge. Thus (4-*n*-pentylpyridine)$_2Pt_2Cl_4$ with 4-*n*-dodecylaniline gives only brown tars, yet with 2 : 6-dimethylaniline and 2 : 6-dibromo-4-*n*-dodecylaniline the bridge-splitting reactions were normal.

Properties of the Complexes of the Type trans-[L,amPtCl$_2$].—The new compounds of *trans*-configuration prepared by the bridge-splitting reaction (1) are listed in the Table. The most complete series are the *p*-toluidine and piperidine complexes where the effects of changing the ligands, L, may be compared, and the tri-*n*-propylphosphine complexes containing different amines.

All the compounds listed are beautifully crystalline. Those containing the lighter donor atoms, N, P, S, and Cl, are yellow with a trace of green or red, but the colours deepen towards red on ascending any group of donor atoms in the Periodic Table. This is most marked in the halide series, quite marked in the phosphorus group, but scarcely obvious with changing donor atoms of the sixth group. The complexes containing phosphines and phosphites as ligands, L, are qualitatively the most stable, but those containing a primary or a secondary amine, a 4-alkylpyridine, a sulphide, or an arsine are also very stable. The olefin and stibine complexes are less stable and in solution some of them decompose slowly with loss of the olefin and amine respectively. The selenide and telluride complexes tend to disproportionate, *e.g.*:

$$trans\text{-}[R_2Te,\ p\text{-}Me{\cdot}C_6H_4{\cdot}NH_2,PtCl_2] \longrightarrow (R_2Te)_2PtCl_2 + (p\text{-}Me{\cdot}C_6H_4{\cdot}NH_2)_2PtCl_2 \quad . \quad (5)$$

For this reason their *p*-toluidine complexes were obtained only in an impure state and are not recorded in the table. Nevertheless their piperidine analogues are sufficiently stable to be obtained pure. In contrast, the *p*-toluidine are more stable than the piperidine complexes when olefins or stibines constitute the ligand, L.

All the compounds listed dissolve readily in organic solvents except low-boiling petroleum. Generally solubilities increase in passing from phosphine to stibine, from

sulphide to telluride, and from chloro- to iodo-complexes. Also the complexes of the phosphorus group tend to be more soluble and to crystallise better than those of the sulphur group with an equal number of carbon atoms.

New complex compounds of the type trans-[L,amPtX$_2$]

(L = uncharged ligand, am = amine, X = halogen.)

L	am	X	M. p.	Colour
PEt_3	*p*-Toluidine	Cl	137·5—138·5°	Greenish-yellow
PBu^n_3	,,	,,	58·5—59·5	,,
$P(OEt)_3$	,,	,,	92—93	,,
Pr^n_2S	,,	,,	115—116·5	Orange-yellow
Bu^n_2S	,,	,,	85·5—87	,,
Bu^n_2S	,,	Br	98—98·5	Orange
4-*n*-Pentylpyridine	Piperidine	Cl	129·5—131	Greenish-yellow
PPr^n_3	,,	,,	125·5—127	,,
PPr^n_3	,,	Br	141—142	Deep yellow
PPr^n_3	,,	I	128·5—129·5	Deep orange
$P(OMe)_3$	,,	Cl	98—99	Greenish-yellow
$AsPr^n_3$	,,	,,	96·5—98	Mustard-yellow
$SbEt_3$	,,	,,	76—77	Yellowish-orange
Et_2S	,,	,,	71—72·5	Orange
Et_2Se	,,	,,	65—66·5	,,
Et_2Te	,,	,,	60·5—61·5	,,
PPr^n_3	NH_3	,,	99—99·5	Greenish-yellow
,,	$Me·NH_2$	,,	58·5—59	,,
,,	$CH_2Ph·NH_2$	,,	71—72	,,
,,	Et_2NH	,,	96—96·5	,,
,,	$Ph·NH_2$	,,	120—120·5	,,
,,	*p*-$Cl·C_6H_4·NH_2$	,,	144—145	,,
,,	*p*-$NO_2·C_6H_4·NH_2$	,,	115—116·5	Yellow
,,	*p*-$Ph·C_6H_4·NH_2$	,,	129—130	Greenish-yellow
,,	*p*-$MeO·C_6H_4·NH_2$	,,	118—119	Yellow
,,	2 : 6-Dimethylaniline	,,	126—126·5	Greenish-yellow
,,	PhMeNH	,,	88·5—89·5	,,
,,	NH_3	I	62·5—63·5	Orange-red
4-*n*-Pentylpyridine	2 : 6-Dibromo-4-*n*-dodecylaniline	Cl	105—106	Greenish-yellow
4-*n*-Nonylpyridine	2 : 6-Dimethylaniline	,,	131·5—132·5	,,
PEt_3	$Et·NH_2$	,,	63—64	,,
PBu^n_3	*o*-$Me·C_6H_4·NH_2$	,,	83—84·5	,,
Bu^n_2S	2 : 6-Dimethylaniline	,,	120·5—121·5	Deep yellow
$AsPr^n_3$	NH_3	,,	91—92	Mustard-yellow

Experimental

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

The bridged complexes, $L_2Pt_2X_4$ (I), were prepared as described by Chatt and Venanzi (*loc. cit.*).

The bridge-splitting reaction (1) was usually carried out by treating one equivalent of $L_2Pt_2Cl_4$, dissolved or suspended in acetone, with two equivs. of amine at room temperature. In many cases reaction was immediate, but with the more insoluble bridged complexes the suspension was shaken for several hours to complete the reaction. This was generally accompanied by a lightening in colour. The solution was then taken to dryness under reduced pressure in the cold and the residue recrystallised. In many cases oils remained after the evaporation but generally they solidified on storage. In the worst cases the oils were induced to crystallise by dissolving them in ether and evaporating the solution in the cold under reduced pressure. The crude products were purified by recrystallisation from light petroleum (b. p. 60—80°) (charcoal). When a different procedure was necessary to split the bridge or to purify the products, this is described under the appropriate product below. The low yields are caused by the small scale of the reaction (2—3 g. of bridged complex) and high solubilities of the products in all organic solvents. All the products are non-electrolytes, as shown by conductivity experiments in nitrobenzene. Their molar conductivities were of the order 10^{-8} mho.

The *trans*-configurations of the products are evident from their solubilities in carbon tetrachloride, ether, and other non-polar solvents. Few of the corresponding *cis*-isomers are known but those known are much less soluble in non-polar solvents and are very much paler.

The *trans*-configuration of two typical members *trans*-[PEt_3,*p*-toluidine$PtCl_2$] and *trans*-[Et_2Se,piperidine$PtCl_2$] were checked by measuring their $\Delta\varepsilon/f$ in benzene solution ($\Delta\varepsilon$ = the increment in dielectric constant due to the solute, f = mol. fraction of solute). The values obtained were 40 and 54 respectively, which is reasonable for unsymmetrical compounds of *trans*-configuration. Symmetrical compounds of *cis*-configuration, *e.g.*, *cis*-[$(PPr^n_3)_2PtCl_2$], have values of the order 160—170 (Chatt and Wilkins, *J.*, 1953, 70).

The products from the bridge-splitting reactions were: trans-p-*Toluidinetriethylphosphinedichloroplatinum*, needles (from ethanol, then methanol) (yield, 40%) (Found: C, 31·7; H, 5·1. $C_{13}H_{24}NCl_2PPt$ requires C, 31·8; H, 4·9%).

trans-p-*Toluidinetri*-n-*butylphosphinedichloroplatinum*, needles (yield, 60%) (Found: C, 39·4; H, 6·3. $C_{19}H_{36}NCl_2PPt$ requires C, 39·6; H, 6·3%).

trans-p-*Toluidine*(*triethyl phosphite*)*dichloroplatinum* [prepared by adding *p*-toluidine in ethanol to a concentrated ethanolic solution of $\{P(OEt)_3\}_2Pt_2Cl_4$ then cooling to −70°; the product separated at once, was filtered off, and recrystallised from light petroleum] (yield, 30%) (Found: C, 29·0; H, 4·5. $C_{13}H_{24}O_3NCl_2PPt$ requires C, 29·05; H, 4·5%).

trans-p-*Toluidine*(*di*-n-*propyl sulphide*)*dichloroplatinum*, recrystallised from *cyclo*hexane, then benzene (yield, 20%) (Found: C, 32·0; H, 4·9. $C_{13}H_{23}NCl_2SPt$ requires C, 31·8; H, 4·7%).

trans-p-*Toluidine*(*di*-n-*butyl sulphide*)*dichloroplatinum* [oily and difficult to purify; spontaneous evaporation of its dichloromethane solution gave a product which recrystallised from light petroleum (b. p. 60—80°) in needles] (yield, 20%) (Found: C, 34·8; H, 5·3. $C_{15}H_{27}NCl_2SPt$ requires C, 34·7; H, 5·2%).

trans-p-*Toluidine*(*di*-n-*butyl sulphide*)*dibromoplatinum* (yield, 16%) (Found: C, 29·4; H, 4·4. $C_{15}H_{27}NBr_2SPt$ requires C, 29·6; H, 4·5%).

trans-*Piperidine*-4-n-*pentylpyridinedichloroplatinum*: (piperidine)$_2Pt_2Cl_4$ (2·4 g.) in acetone (50 c.c.) was boiled under reflux for 30 min. with 4-*n*-pentylpyridine (1·5 c.c.); the solution was then taken to dryness under reduced pressure and the *trans*-isomer extracted from the residue with boiling ether; the ethereal extract was then taken to dryness under reduced pressure and the pure product obtained in greenish-yellow needles by repeated recrystallisation of the residue from ethanol. The yield was 15% (Found: C, 36·1; H, 5·2. $C_{15}H_{26}N_2Cl_2Pt$ requires C, 36·0; H, 5·2; N, 5·6%); the *trans*-configuration was confirmed by Kurnakov's reaction with thiourea (*J. prakt. Chem.*, 1894, **50**, 483; see also Chatt and Venanzi, *loc. cit.*). The ether-insoluble part from this bridge-splitting reaction was recrystallised from carbon tetrachloride and cis-*piperidine*-4-n-*pentylpyridinedichloroplatinum* obtained in pale yellow plates, m. p. 156—157° (yield, 8%) (Found: C, 35·9; H, 5·1; N, 5·7%); the *cis*-configuration was confirmed by Kurnakov's reaction. The very low yields of these pure *trans*- and *cis*-isomers were due to difficulties in purification, but from the initial crude separation with ether the *cis*-isomer appeared to predominate in the mixture. Where the bridge-splitting reaction was repeated at room temperature with the theoretical quantity of amine, reaction was not complete after 7 days but again both isomeric products were obtained.

trans-*Piperidinetri*-n-*propylphosphinedichloroplatinum*, prisms (yield, 25%) (Found: C, 32·9; H, 6·1. $C_{14}H_{32}NCl_2PPt$ requires C,32·9; H, 6·3%).

trans-*Piperidinetri*-n-*propylphosphinedibromoplatinum* prisms (from ethanol) (yield, 30%) (Found: C, 27·9; H, 5·4. $C_{14}H_{32}NBr_2PPt$ requires C, 28·0; H, 5·4%).

trans-*Piperidinetri*-n-*propylphosphinedi-iodoplatinum*, prisms (from ethanol) (33%) (Found: C, 24·1; H, 4·6. $C_{14}H_{32}NI_2PPt$ requires C, 24·2; H, 4·6%).

trans-*Piperidine*(*trimethyl phosphite*)*dichloroplatinum*: $[P(OMe)_3]_2Pt_2Cl_4$ (2·5 g.), prepared by Schützenberger's method (*loc. cit.*, 1872), in methanol (10 c.c.) was treated with piperidine (0·6 c.c.) at −70°; the yellow precipitate was separated, washed with cold methanol, and dried; repeated recrystallisation from light petroleum (b. p. 60—80°) gave plate-like crystals of the pure *compound* (yield, 50%) (Found: C, 20·4; H, 4·2. $C_8H_{20}O_3NCl_2PPt$ requires C, 20·2; H, 4·2%).

trans-*Piperidinetri*-n-*propylarsinedichloroplatinum*, prisms (30%) (Found: C, 30·4; H, 5·65. $C_{14}H_{32}NCl_2AsPt$ requires C, 30·3; H, 5·8%).

trans-*Piperidinetriethylstibinedichloroplatinum*, prisms (20%) (Found: C, 23·45; H, 4·5. $C_{11}H_{26}NCl_2PtSb$ requires C, 23·6; H, 4·7%): this compound was readily purified in the normal manner when operations such as recrystallisation were carried out rapidly; nevertheless the infrared spectrum of its freshly prepared solution in carbon tetrachloride changed fairly rapidly with time, indicating spontaneous decomposition. The N–H band at 3235 cm.$^{-1}$ due to the complex decreased in intensity with time, whilst a new band appeared at 3177 cm.$^{-1}$.

trans-*Piperidine*(*diethyl sulphide*)*dichloroplatinum*, plates [from *cyclo*hexane, then light petroleum (b. p. 60—80°)] (30%) (Found : C, 24·35; H, 4·8. $C_9H_{21}NCl_2SPt$ requires C, 24·5; H, 4·8%).

trans-*Piperidine*(*diethyl selenide*)*dichloroplatinum*, plates (14%) (Found : C, 22·1; H, 4·3. $C_9H_{21}NCl_2PtSe$ requires C, 22·1; H, 4·3%).

trans-*Piperidine*(*diethyl telluride*)*dichloroplatinum*, plates (30%) (Found : C 20·4; H, 4·0. $C_9H_{21}NCl_2PtTe$ requires C, 20·1; H, 3·9%).

trans-*Amminotri*-n-*propylphosphinedichloroplatinum* (prepared in ethanol), plates (60%) (Found : C, 24·6; H, 5·5; N, 3·3. $C_9H_{24}NCl_2PPt$ requires C, 24·4; H, 5·6; N, 3·2%).

trans-*Methylaminetri*-n-*propylphosphinedichloroplatinum*, obtained as an oil and induced to crystallise by keeping its concentrated ethanol solution at −70° for 15 hr., and purified by partial evaporation of its light petroleum (b . p. 40—60°) solution from which it separated in prisms (30%) (Found : C, 26·2; H, 5·6. $C_{10}H_{26}NCl_2PPt$ requires C, 26·3; H, 5·7%).

trans-*Benzylaminetri*-n-*propylphosphinedichloroplatinum*, plates (50%) (Found : C, 36·0; H, 5·6. $C_{16}H_{30}NCl_2PPt$ requires C, 36·0; H, 5·7%).

trans-*Diethylaminetri*-n-*propylphosphinedichloroplatinum*, plates (from methanol) (85%) (Found : C, 31·3; H, 6·4. $C_{13}H_{32}NCl_2PPt$ requires C, 31·3; H, 6·5%).

trans-*Anilinetri*-n-*propylphosphinedichloroplatinum*, needles from ethanol (yield, 35%) (Found : C, 34·3; H, 5·3; N, 3·0. $C_{15}H_{28}NCl_2PPt$ requires C, 34·7; H, 5·4; N, 2·7%).

trans-p-*Chloroanilinetri*-n-*propylphosphinedichloroplatinum*, plates from methanol (yield, 30%) (Found : C, 32·5; H, 4·85; N,2·7. $C_{15}H_{27}NCl_3PPt$ requires C, 32·5; H, 4·9; N, 2·5%).

trans-p-*Nitroanilinetri*-n-*propylphosphinedichloroplatinum*, prisms from ethanol (yield, 25%) (Found : C, 31·7; H, 4·7. $C_{15}H_{27}O_2N_2Cl_2PPt$ requires C, 31·9; H, 4·8%).

trans-4-*Diphenylylaminetri*-n-*propylphosphinedichloroplatinum*, needles from ethanol (yield, 40%) (Found : C, 42·1; H, 5·5. $C_{21}H_{32}NCl_2PPt$ requires C, 42·35; H, 5·4%).

trans-p-*Anisidinetri*-n-*propylphosphinedichloroplatinum*, prisms from methanol (yield, 50%) (Found : C, 34·7; H, 5·6; N, 2·8. $C_{16}H_{30}ONCl_2PPt$ requires C, 35·0; H, 5·5; N, 2·55%).

trans-2 : 6-*Dimethylanilinetri*-n-*propylphosphinedichloroplatinum*, needles (40%) (Found : C, 37·0; H, 5·9. $C_{17}H_{32}NCl_2PPt$ requires C, 37·3; H, 5·9%).

trans-N-*Methylanilinetri*-n-*propylphosphinedichloroplatinum*, prisms from methanol (yield, 25%) (Found : C, 36·1; H, 5·6. $C_{16}H_{30}NCl_2PPt$ requires C, 36·0; H, 5·7%).

trans-*Amminotri*-n-*propylphosphinedi-iodoplatinum* : its chloro-analogue (2 g.) in acetone (50 c.c.) was shaken for several hours with finely divided potassium iodide (1·6 g.); the red solution was filtered and taken to dryness under reduced pressure; the residual oil, which solidified on storage, was extracted with light petroleum (b. p. 40—60°) [the residue was $(PPr^n_3)_2Pt_2I_4$, m. p. 185—190°, alone and mixed with an authentic specimen]; the light petroleum solution was taken to dryness under reduced pressure and the residual solid repeatedly crystallised from light petroleum (b. p. 40—60°) forming prisms (yield, 35%) (Found : C, 17·3; H, 3·85. $C_9H_{24}NI_2PPt$ requires C, 17·3; H, 3·9%).

trans-4-n-*Pentylpyridine*-2 : 6-*dibromo*-4-n-*dodecylanilinedichloroplatinum*, prepared by shaking a suspension of the pentylpyridine-bridged complex and the aniline in ethanol until all had dissolved to a yellow solution, was isolated in the usual manner and recrystallised from ethanol in plates (20%) (Found : C, 40·2; H, 5·2; N, 3·4. $C_{28}H_{44}N_2Cl_2Br_2Pt$ requires C, 40·3; H, 5·3; N, 3·4%). The reaction of formation appears to be reversed in carbon tetrachloride because the infrared spectrum of the above mixed complex in carbon tetrachloride solution showed the slow development of absorption bands at 3490 and 3392 cm.$^{-1}$ attributable to free 2 : 6-dibromo-4-*n*-dodecylaniline.

trans-4-n-*Nonylpyridine*-2 : 6-*dimethylanilinedichloroplatinum* (similarly prepared), needles from ethanol (yield, 20%) (Found : C, 44·6; H, 6·3; N, 4·9. $C_{22}H_{34}N_2Cl_2Pt$ requires C, 44·6; H, 5·8; N, 4·7%).

trans-*Ethylaminetriethylphosphinedichloroplatinum*, needles (50%) (Found : C, 22·7; H, 5·2. $C_8H_{22}NCl_2PPt$ requires C, 22·4; H, 5·2%).

trans-o-*Toluidinetri*-n-*butylphosphinedichloroplatinum*, needles (30%) (Found : C, 39·5; H, 6·1. $C_{19}H_{36}NCl_2PPt$ requires C, 39·6; H, 6·3%).

trans-2 : 6-*Dimethylaniline*(*di*-n-*butyl sulphide*)*dichloroplatinum*, needles (40%) (Found : C, 36·3; H, 5·4; N, 3·0; S, 6·1. $C_{16}H_{29}NCl_2SPt$ requires C, 36·0; H, 5·5; N, 2·6; S, 6·0%).

trans-*Amminotri*-n-*propylarsinedichloroplatinum*, plates (yield, 75%) (Found : C, 22·3; H, 4·8. $C_9H_{24}NCl_2AsPt$ requires C, 22·2; H, 5·0%).

An attempt to prepare *trans*-piperidine(di-*n*-propyl sulphide)dichloroplatinum by the bridge-splitting reaction led to an oil. Treatment with a further two mols. of piperidine caused slow

separation of *dipiperidine(di-n-propyl sulphide)chloroplatinum chloride* $[pip_2,PPr^n_3PtCl]Cl$, of unknown, but probably *cis*-, configuration. It was purified by washing it with light petroleum (b. p. 60—80°) and repeated recrystallisation from carbon tetrachloride. The salt formed white prisms, melting at 122—123·5° to a yellow oil (Found: C, 34·6; H, 6·5; N, 5·2. $C_{16}H_{36}N_2Cl_2SPt$ requires C, 34·6; H, 6·5; N, 5·05%).

Attempts to prepare trans-*Diphenylaminetri*-n-*propylphosphinedichloroplatinum.*—$(PPr^n_3)_2Pt_2Cl_4$ (0·5 g.) in benzene (50 c.c.) was treated with diphenylamine (0·7 g.). There was no colour change but on evaporating the benzene a partly crystalline residue remained. Its ethanol solution deposited orange crystals, which after one recrystallisation from acetone had m. p. 179—181° alone and mixed with $(PPr^n_3)_2Pt_2Cl_4$ of m. p. 182°. $(PPr^n_3)_2Pt_2Cl_4$ is almost insoluble in carbon tetrachloride but dissolves more readily in presence of diphenylamine (2 mols.); however, the desired product cannot be isolated from the solution. That reaction occurred between the bridged complex and diphenylamine was also shown by decrease in the intensity of the N–H stretching band of the free amine at 3433 cm.$^{-1}$ on addition of the bridged complex to a carbon tetrachloride solution of the amine, whilst another broader band appeared at 3214 cm.$^{-1}$, probably due to the complex $[Ph_2NH,PPr^n_3PtCl_2]$.

Reaction 3.—$(Piperidine)_2Pt_2Cl_4$ (0·42 g.) in chloroform (50 c.c.) was shaken in an ethylene atmosphere. A solid slowly separated during about 18 hr. This was recrystallised from ethyl methyl ketone (charcoal), to give pure cis-*piperidine-ethylenedichloroplatinum* in yellowish-white needles, decomp. 180—185° (yield, 77%) (Found: C, 22·4; H, 4·05. $C_7H_{15}NCl_2Pt$ requires C, 22·2; H, 4·0%). This is very much less soluble in organic solvents than its *trans*-isomer (Chatt and Venanzi, *loc. cit.*).

Reaction 4.—This is described by Chatt and Venanzi (*loc. cit.*).

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