The Preparation of Halogen-bridged Complexes of Platinum(II).

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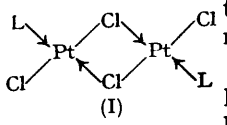
[Reprint Order No. 6328.]

General methods for the preparation of binuclear platinous chloride complexes of the type $L_2Pt_2Cl_4$ (I) have been developed, and their application to the preparation of complexes with different uncharged ligands, L, has been critically examined. Compounds containing as the ligands, L, olefins, amines, tertiary organic phosphines, arsines, and stibines, and dialkyl sulphides, selenides, and tellurides are described.

DURING an investigation of inductive and mesomeric effects in platinous complexes it became necessary to prepare a wide variety of chlorine-bridged platinous complexes of type (I) (L = any uncharged ligand), and we now report the development of existing and new methods of doing this.



(I)

Although there was considerable development of methods of preparing the halogen-bridged complexes of many metals, particularly palladium, during the 1930's (see Mann, *Ann. Reports*, 1938, **35**, 148), surprisingly few halogen-bridged platinous complexes were known before 1951, and no obviously general methods for their preparation. We then published an account of two general methods which we had developed for the preparation of halogen-bridged complexes having trialkyl-phosphines, -arsines, and -stibines as the ligand, L (Chatt, *J.*, 1951, 652). We have now developed these and other methods to give bridged complexes having as the ligands, L, substances containing nitrogen, sulphur, selenium, and tellurium as donor atoms. It seems useful therefore to summarise the methods at present available.

(1) *Reaction of Finely Powdered* $PtCl_2$ *with a Melt of* cis- *and/or* trans-L_2PtCl_2 (Chatt, *loc. cit.*) : $L_2PtCl_2 + PtCl_2 \longrightarrow L_2Pt_2Cl_4$.—This is one of the most useful general methods, but it is limited to preparations in which L_2PtCl_2 melts without decomposition (other than isomerisation) and the product has sufficient thermal stability to withstand the temperatures used. It is best suited to preparing the tri-*n*-propyl and higher homologues of the series $(PR_3)_2Pt_2Cl_4$, $(AsR_3)_2Pt_2Cl_4$, and $(R_2S)_2Pt_2Cl_4$, but it becomes increasingly difficult to apply as one descends the homologous series because the higher melting points of the simple complexes, L_2PtCl_2, and therefore higher reaction temperatures, lead to greater decomposition of the products. The corresponding bromo-complexes can be prepared by a similar reaction. Our attempts to prepare trialkylstibine, dialkyl selenide, dialkyl telluride, and amine-bridged complexes by this method yielded mainly black decomposition products.

(2) *Reaction of* cis-L_2PtX_2 *with* M_2PtCl_4 *in Solution* (X = univalent acid radical, M = alkali metal) : $L_2PtX_2 + M_2PtCl_4 \longrightarrow L_2Pt_2Cl_4 + 2MX$.—This method was used to prepare $(Et_2S)_2Pt_2Cl_4$ and $(Pr_2S)_2Pt_2Cl_4$ towards the end of the last century (Blomstrand, *J. prakt. Chem.*, 1888, **38**, 352; Klason, *Ber.*, 1895, **28**, 1493; Rudelius, *Acta Univers. Lund*, 1885—1886, **22**, Part 2, Paper 4) but these early investigators used chloro-complexes (X = Cl) which they treated with warm aqueous K_2PtCl_4. Since the mixture was not homogeneous the reactions were very slow. In the case of the lower alkyl members of the series homogeneity in aqueous solution can be obtained by employing the complexes of oxygen-acids which dissolve in water probably as aquo-ions, *e.g.*, $[(Et_2S)_2Pt(H_2O)_2]^{++}$. In this way Petren (Diss., Lund, 1898, p. 38) prepared $(Et_2Se)_2Pt_2Cl_4$ from *cis*-$(Et_2Se)_2Pt(NO_3)_2$ and K_2PtCl_4 in cold aqueous solution, and Jensen (*Z. anorg. Chem.*, 1935, **225**, 115) obtained $(Et_2S)_2Pt_2Cl_4$ and $(Pr_2S)_2Pt_2Cl_4$ similarly from the corresponding sulphates. This method has the disadvantage that the simple complexes of oxygen-acids cannot be prepared by direct methods but must be prepared from the chloro-complexes. We have therefore developed a further modification employing chloro-complexes of *cis*-configuration in ethanolic Na_2PtCl_4 solution. Jensen's and this modification have their own fields of application.

(*a*) When *cis*-$[L_2PtCl_2]$ is difficult to obtain, as in the dialkylselenide series of complexes, the *trans*-isomer is converted into an aqueous solution of the sulphate by the reaction

$$trans\text{-}[L_2PtCl_2] + Ag_2SO_4 \longrightarrow L_2PtSO_4,aq. + 2AgCl$$

with the reactants in warm aqueous suspension. This solution on treatment with aqueous K_2PtCl_4 then yields the bridged complexes.

(*b*) When *cis*-$[L_2PtCl_2]$ is readily available, it is treated in homogeneous solution with absolute ethanolic Na_2PtCl_4 at a suitable temperature until reaction is complete (about 30° for 40 hr. in the case of dialkyl sulphide complexes, and 20° for 16 hr. in the case of dialkyl telluride complexes). Since the simple dialkyl telluride complexes isomerise spontaneously, the bridged compounds may be prepared directly by adding 1 mol. of R_2Te to 1 mol. of Na_2PtCl_4 in ethanol, and keeping the solution for 16 hr. Trialkylstibine complexes are not obtained by this method, and dimethyl sulphide yields insoluble $(Me_2S)_3Pt_2Cl_4$. *trans*-$[(R_2S)_2PtCl_2]$ does react with ethanolic Na_2PtCl_4, but much too slowly to provide a preparative method. An ethanolic solution of *trans*-$[(R_2Se)_2PtCl_2]$ blackens on addition of ethanolic Na_2PtCl_4.

(3) *Thermal Decomposition of Olefin Complexes*, [un,L,$PtCl_2$] (un = olefin, *e.g.*, C_2H_4 or C_3H_6): $2[un,LPtCl_2] \longrightarrow L_2Pt_2Cl_4 + 2un$.—This is probably the method of most general applicability, but because olefin complexes are not convenient raw materials it is reserved for use when the first two methods have failed. It is the best method of obtaining the insoluble or almost insoluble bridged complexes of the lowest members of a homologous series, and the only method by which we have obtained trialkylstibine and amine-bridged complexes. Two procedures were employed, depending on the nature of the ligand, L.

(*a*) When L is a ligand of moderate to high *trans*-effect, the species *trans*-[un,$LPtCl_2$] decomposes spontaneously at a low or moderate temperature. In such a case it is sufficient to treat an acetone or dichloromethane solution of the bridged olefin complex, $un_2Pt_2Cl_4$, with the theoretical quantity of the free ligand at −75°, and allow the mixture to warm until decomposition occurs. When L contains phosphorus, arsenic, or antimony as donor atom decomposition occurs at about or below room temperature, but if it contains sulphur as donor, 50—70° is necessary for a reasonable rate of decomposition. Anderson's method (*J.*, 1936, 1042) of replacing ethylene from $(C_2H_4)_2Pt_2Cl_4$ by a less volatile olefin is a special application of this procedure. Amines (am) usually give indefinite oily products by this procedure although the remarkably stable *cis*-[am,un,$PtCl_2$] is sometimes obtained.

(*b*) To obtain amine-bridged complexes it is best to prepare *trans*-[am,un,$PtCl_2$] by the careful neutralisation with sodium hydroxide of a 3% hydrochloric acid solution of the amine hydrochloride containing K[un,$PtCl_3$], and allow it to decompose spontaneously at room temperature in a solvent in which the product, $am_2Pt_2Cl_4$, is insoluble. Light petroleum is often most satisfactory but the decomposition is slow and may require a week to several months depending on the amine and olefin present in the complex. Warming the solution speeds the reaction but causes side reactions and further decomposition of the product so that a complex mixture is obtained including, as minor product, the bridged complex. The propylene complexes decompose more quickly than the ethylene complexes and it may be that this preparation could be improved by the use of some higher olefin such as pentene.

(4) *Decomposition of the Acids* H[$LPtCl_3$]: $2H[LPtCl_3] \longrightarrow L_2Pt_2Cl_4 + 2HCl$.—These acids decompose spontaneously when their solutions are taken to dryness. However, the method is severely limited because salts containing ions of the type $[LPtCl_3]^-$ are not very common. It is the only certain method of obtaining $(C_2H_4)_2Pt_2Cl_4$ and $(C_3H_6)_2Pt_2Cl_4$ in good yields (Chatt and Duncanson, *J.*, 1953, 2939) and is doubtless the final stage in the complex series of reactions between Na_2PtCl_6 and ethanol which constitutes Anderson's preparation of $(C_2H_4)_2Pt_2Cl_4$ (*J.*, 1934, 971). The method has also been used to yield $(NH_3)_2Pt_2Cl_4$ (Klason, *J. prakt. Chem.*, 1903, **67**, 1), $(CO)_2Pt_2Br_4$, and $(CO)_2Pt_2I_4$ (Hieber, Ries, and Bader, *Z. anorg. Chem.*, 1930, **190**, 215).

(5) *Reaction of a Weakly Co-ordinating Reducing Ligand with* $PtCl_4$ *or* $PtBr_4$ *in Acetic Acid or Benzene Suspension*: $4L + 2PtCl_4 \longrightarrow L_2Pt_2Cl_4 + 2LCl_2$.—This occurs rapidly at 100° but has so far been used only to prepare olefin complexes (Kharasch and Ashford,

J. Amer. Chem. Soc., 1936, **58**, 1733). It is not convenient when the olefin is gaseous. In our hands it has not given good yields and we prefer method (3) for the preparation of higher olefin complexes. With dipentene the two methods yield different isomeric, but not bridged products (Chatt and Wilkins, *J.*, 1952, 2622).

(6) *Miscellaneous Special Methods.*—The first halogen-bridged platinous complexes to be prepared were not typical and the methods of preparation were incapable of general application. These, with their dates of discovery and most recent detailed references are :

(*a*) $2CO + 2Pt + 2Cl_2 \xrightarrow{240°} (CO)_2Pt_2Cl_4$ (1868 ; Hieber, Ries, and Bader, *loc. cit.*).

(*b*) $2PCl_5 + 2Pt \xrightarrow{>200°} (PCl_3)_2Pt_2Cl_4$ (1872 ; Arbuzov and Zoroastrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1952, 818 ; Rosenheim and Levy, *Z. anorg. Chem.*, 1905, **43**, 34).

(*c*) $2PBr_5 + 2Pt \xrightarrow{200°} (PBr_3)_2Pt_2Br_4$ (1905 ; Rosenheim and Levy, *loc. cit.*).

(*d*) $(PCl_3)_2Pt_2Cl_4 + 6ROH \xrightarrow{<20°} [P(OR)_3]_2Pt_2Cl_4$ [1872 ; see refs. to (*b*)].

(*e*) $2PF_3 + 2PtCl_2 \xrightarrow{>200°} (PF_3)_2Pt_2Cl_4$ (1950 ; Chatt and Williams, *J.*, 1951, 3061).

General Properties of the Halogen-bridged Complexes.—It is interesting to compare the general properties of the chloride-bridged complexes having as ligands the organic derivatives of nitrogen, phosphorus, arsenic, antimony, sulphur, selenium, and tellurium. The

Melting points, colours, and methods of preparation of bridged platinous complexes, $L_2Pt_2Cl_4$.

Ligand L	Method of preparation	M. p.	Colour
Piperidine *	3*b*	182—192° (decomp.)	Yellowish-orange
4-*n*-Pentylpyridine *	3*b*	121—122	,,
4-*n*-Nonylpyridine *	3*b*	132—133·5	,,
p-Toluidine *	3*b*	180—190 (decomp.)	Reddish-orange
PMe_3 *	3*a*	217—220 (decomp.)	Yellowish-orange
PEt_3	1	223—224	,,
PPr^n_3	1(3*a*)	182—183	,,
PBu^n_3 *	1	143—144	,,
PAm^n_3 *	1	121—122	,,
$PHex^n_3$ *	1	120—120·5	,,
$PPhBu^n_2$ *	1	167—171 (decomp.)	,,
$AsEt_3$ *	1	208—209 (decomp.)	Orange
$AsPr^n_3$	1	194—197 (decomp.)	,,
$AsBu^n_3$ *	1	126—127	,,
$SbMe_3$ *	3*a*	150—170 (decomp.)	Reddish-orange
$SbEt_3$ *	3*a*	130—135 (decomp.)	,,
$SbPr^n_3$	3*a*	133—134 (decomp.)	,,
Me_2S *	3*a*	200—220 (decomp.)	Mustard-yellow
Et_2S	2*b*(1)	213—230 (decomp.)	Bright yellow
Pr^n_2S	1(2*a*)	194—197 (decomp.)	,,
Bu^n_2S *	1	188—198 (decomp.)	,,
Oct^n_2S *	2*b*	148—166 (decomp.)	,,
Et_2Se	2*a*	146—147 (decomp.)	Brownish-orange
Pr^n_2Se *	2*a*(1)	76·5—77·5 (decomp.)	,,
Et_2Te *	2*b*	142 (decomp.)	Brownish-orange
Pr^n_2Te *	2*b*(1)	120—131 (decomp.)	,,

* Ligands whose bridged $PtCl_2$ compounds were previously unknown are marked *.

colours, melting or decomposition temperatures, and methods of preparation are listed in the Table.

The trialkyl-phosphine, -arsine, and -stibine chloride-bridged complexes are all beautifully crystalline substances soluble in many organic solvents such as benzene, acetone, and chloroform. Solubility increases rapidly as the homologous series is ascended from the sparingly soluble methyl to conveniently soluble propyl derivatives, then more slowly as the homologous series is ascended further. Solubility also increases on ascending the eutropic series from the phosphine to stibine complexes. Stability falls rapidly in the same series: the phosphine complexes are very stable; the arsine complexes decompose very slowly in boiling ethanolic solution and the stibine complexes decompose spontaneously in

any warm solvent. The stabilities of the stibine complexes also decrease rapidly on ascending the homologous series from the trimethyl to tri-*n*-propyl complex. This appears to be a general property of stibine complexes; it is most marked in the series $(R_3Sb)_2PdCl_2$ and to a lesser extent in the more stable series $(R_3Sb)_2PtCl_2$ (Chatt and Wilkins, *J.*, 1953, 70). The amine complexes lie between the arsine and stibine complexes in general stability and crystallise well from low-boiling solvents provided the operation is carried out rapidly.

By contrast, the bridged complexes containing sixth-group donor atoms do not give a series of complexes having well-graded properties; this is obvious even from their colours (see table). The dialkyl sulphide series of complexes is the most insoluble we have prepared. The dimethyl and diethyl sulphide complexes are practically insoluble in all solvents tried, but the dipropyl sulphide complex is slightly soluble in some boiling solvents such as chloroform and ethyl methyl ketone. Solubility increases as the homologous series is ascended. The diethyl selenide and telluride complexes, which resemble each other closely, are moderately soluble in organic solvents, those containing selenium being most soluble. In stability the sulphide are comparable with the phosphine complexes; the telluride complexes are slightly more stable than the trialkylstibine complexes, yet the selenide complexes are the least stable of any bridged series of complexes that we have prepared. Purification of the selenide complexes is difficult, and analytical purity often deteriorates on attempted recrystallisation. The bridged structure appears to be confirmed by the molecular weight of $(Et_2Se)_2Pt_2Cl_4$ (Petren, *loc. cit.*) and such bridge-splitting reactions as:

$$(Et_2Se)_2Pt_2Cl_4 + 2 \text{ piperidine} \longrightarrow 2[Et_2Se, \text{piperidine}, PtCl_2]$$

Our general experience in handling the chloride-bridged compounds indicates that the stabilities fall in the sequence: $PR_3 \sim R_2S > AsR_3 >$ amine $> R_2Te > SbR_3 > R_2Se$. In placing amines in this series it must be emphasised that the amines studied were not trialkylamines but primary, secondary, and heterocyclic amines which are known to yield stable platinous complexes; they are not strictly comparable with the organic derivatives of the other donor atoms. It seems unlikely that bridged complexes of the type $(NR_3)_2Pt_2Cl_4$ will be obtained, but if they were obtained they would probably be less stable than $(R_2Se)_2Pt_2Cl_4$ (see Chatt and Wilkins, *J.*, 1952, 4300).

Since complex salts containing two complex ions have sometimes been formulated as covalent bridged complexes (see Foss and Gibson, *J.*, 1949, 3063; Nyholm, *J.*, 1951, 1767), the conductivities of all the above types of bridged complexes were measured in nitrobenzene solution, and their covalent character was confirmed.

Only two bromide- and one iodide-bridged complexes were prepared: the former by the fusion method (1) using L_2PtBr_2, and the latter by reaction of sodium iodide (4 mols.) with the chloride-bridged complex in acetone solution (Chatt, *loc. cit.*).

Experimental

(Microanalyses marked * are by Messrs. Weiser and Ritter of Basle; the remainder are by Messrs. Brown and Olney of these laboratories.)

Most of the halogen-bridged compounds described in this section are new; those which are not new have been prepared by improved methods. The simple complexes of type L_2PtCl_2, required as starting materials for many of the preparations below, were prepared by shaking 2 equiv. of the ligand, L, with aqueous K_2PtCl_4 (Jensen, *loc. cit.*; *Z. anorg. Chem.*, 1936, **229**, 250). This reaction is slow, especially for the preparation of the higher alkyl derivatives, and so in later preparations it was accelerated by treating an ethanolic solution of Na_2PtCl_4 at room temperature, or a dilute acetic acid solution of K_2PtCl_4 at boiling temperature, with the ligand. The bromides, L_2PtBr_2, were obtained by adding potassium bromide (100% excess) to the aqueous K_2PtCl_4 solution then proceeding as in the preparation of chlorides.

Method 1. In general application a thoroughly dried, coarsely powdered mixture of the crude isomers of L_2PtCl_2 or L_2PtBr_2 is intimately mixed with finely powdered $PtCl_2$ or $PtBr_2$ (1 mol.) respectively. The mixture is then warmed in a boiling tube until it is sufficiently fluid to be stirred with a thermometer. It is stirred continuously, and the temperature maintained until the melt becomes pasty owing to separation of the higher-melting bridged product. When the reaction appears complete (about 15 min.) the melt is allowed to cool, and the solid product extracted with a suitable boiling solvent (usually acetone). The solution is then treated with

charcoal to remove traces of colloidal platinum, and filtered; the bridged compound separates as the filtrate cools. The following compounds have been prepared by this method. The temperature and time of reaction, extraction solvent, solvent used for recrystallisation (if different), and yield of pure products are given in parentheses.

Bistri-n-*butylphosphinedichloro*-μμ′-*dichlorodiplatinum* (130°, 15 min., acetone, 55·7%) (Found: C, 30·7; H, 5·8; *M*, ebullioscopic in 1·5% benzene solution, 956. $C_{24}H_{54}Cl_4P_2Pt_2$ requires C, 30·8; H, 5·8%; *M*, 937); the *tri*-n-*pentyl* analogue (110—120°; 15 min., acetone, methanol, 49%) (Found: C, 35·45; H, 6·7. $C_{30}H_{66}Cl_4P_2Pt_2$ requires C, 35·3; H, 6·5%); the *tri*-n-*hexyl* analogue (100°, 30 min. but no solidification of the melt, ethyl methyl ketone, methanol, 12%) (Found: C, 38·8; H, 7·0. $C_{36}H_{78}Cl_4P_2Pt_2$ requires C, 39·1; H, 7·1%); the (*di*-n-*butyl*)*phenyl* analogue (144°, 15 min., ethyl methyl ketone, ethanol, 10%) (Found: C, 34·3; H, 4·8. $C_{28}H_{46}Cl_4P_2Pt_2$ requires C, 34·4; H, 4·8%).

Bistriethylarsinedichloro-μμ′-*dichlorodiplatinum* (130—135°, 2 min., acetone, 50% crude) (Found: C, 17·0; H, 3·55. $C_{12}H_{30}Cl_4As_2Pt_2$ requires C, 16·8; H, 3·5%); the *tri*-n-*butyl* analogue (100°, 40 min. but no solidification of melt, ethyl methyl ketone, acetone, 50%) (Found: C, 28·0; H, 5·2%; *M*, ebullioscopic in 1·3% benzene solution, 984. $C_{24}H_{54}Cl_4As_2Pt_2$ requires C, 28·1; H, 5·3%; *M*, 1024).

Bis(di-*n*-propyl sulphide)dichloro-μμ′-dichlorodiplatinum (120°, 15 min., chloroform, 49%) (Found: C, 18·7; H, 3·7. Calc. for: $C_{12}H_{28}Cl_4S_2Pt_2$ C, 18·7; H, 3·7%); the *di*-n-*butyl* analogue (120°, 15 min., chloroform, acetone, 39%) (Found: C, 23·3; H, 4·4. $C_{16}H_{36}Cl_4S_2Pt_2$ requires C, 23·3; H, 4·4%).

Bis(*di*-n-*butyl sulphide*)*dibromo*-μμ′-*dibromodiplatinum* (120°, 15 min., ethyl methyl ketone, 42%) (Found: C, 19·5; H, 3·7. $C_{16}H_{36}Br_4S_2Pt_2$ requires C, 19·2; H, 3·6%). Bisdiethylsulphidedichloro-μμ′-dichlorodiplatinum is obtained by this method but is difficult to extract from the frozen melt because it is extremely insoluble in all solvents.

Method 2(*a*). We have prepared only two compounds by this method and the preparation of bis(diethyl selenide)dichloro-μμ′-dichlorodiplatinum is typical. *trans*-$[(Et_2Se)_2PtCl_2]$ (3 g.), prepared by shaking Et_2Se (2 mols.) with aqueous K_2PtCl_4 (1 mol.) (Petren, *loc. cit.*), was added to a suspension of Ag_2SO_4 (1·7 g.) in water (100 c.c.). The mixture was warmed to 50° and shaken for 1 hr., then the warming and shaking operation was repeated (about three times) until the selenide complex had dissolved. The mixture was shaken for a further 4 hr. to ensure complete reaction and then filtered to give a brownish-yellow solution. This on addition of K_2PtCl_4 (2·3 g.) in water (25 c.c.) yielded an immediate buff-coloured precipitate which was filtered off after a few minutes. The sticky solid thus obtained was converted into a red-brown solid by drying in a desiccator, and recrystallised from chloroform. The product decomposed at 146—147°. Petren (*loc. cit.*) gives 145° [yield 36%, calc. on the $(Et_2Se)_2PtCl_2$ used] (Found: C, 12·3; H, 2·55. Calc. for $C_8H_{20}Cl_4Se_2Pt_2$: C, 11·9; H, 2·5%). This preparation is a considerable improvement on Petren's original method, but nevertheless the bridged selenides are the most difficult series to prepare. They are very unstable in solution and not easily purified.

Bis(*di*-n-*propyl selenide*)*dichloro*-μμ′-*dichlorodiplatinum* was prepared similarly from *n*-Pr_2Se and K_2PtCl_4 and purified by dissolving it in a small amount of chloroform, adding some ether, and cooling to −70°. The red-brown powder which separated was washed with ethanol and ether, and dried [yield 10%, calc. on the $(n\text{-}Pr_2Se)_2PtCl_2$ used], decomp. 76·5—77·5° (Found: C, 16·6; H, 3·2. $C_{12}H_{28}Cl_4Se_2Pt_2$ requires C, 16·7; H, 3·3%).

Method 2(*b*). *Bis*(*diethyl sulphide*)*dichloro*-μμ′-*dichlorodiplatinum*. *cis*-$[(Et_2S)_2PtCl_2]$ (5·3 g.) and Na_2PtCl_4 (4·6 g.) in ethanol (220 c.c.) were kept at 45° for 4 hr. The yellow product which separated was filtered off from the solution, washed with ethanol then water, and dried (yield 73%) (Found: C, 13·3; H, 2·8. Calc. for $C_8H_{20}Cl_4S_2Pt_2$: C, 13·5; H, 2·8%).

Bis(*di*-n-*octyl sulphide*)*dichloro*-μμ′-*dichlorodiplatinum* is similarly obtained. A solution of Na_2PtCl_4 (0·33 g.) and *cis*-$[(Oct_2S)_2PtCl_2]$ (0·66 g.) in ethanol (30 c.c.) was kept for 24 hr., then at 45° for 6 hr. It was then filtered, and the filtrate taken to dryness at 15° under reduced pressure. The sticky brown residue was recrystallised from ethanol, then acetone (Found: C, 36·1; H, 6·4. $C_{32}H_{68}Cl_4S_2Pt_2$ requires C, 36·6; H, 6·5%).

Bis(*diethyl telluride*)*dichloro*-μμ′-*dichlorodiplatinum*. A solution of Na_2PtCl_4 (3 g.) and *cis*-$(Et_2Te)_2PtCl_2$ (5 g.) in ethanol (300 c.c.) was kept for several days at room temperature. The crystalline *complex* which formed was filtered off, washed with water, ethanol, and hot ether, and then dried (yield 40·5%) (Found: C, 10·7; H, 2·2. $C_8H_{20}Cl_4Pt_2Te_2$ requires C, 10·6; H, 2·2%).

Bis(*di*-n-*propyl telluride*)*dichloro*-μμ′-*dichlorodiplatinum* was similarly prepared as a precipitate by keeping a solution of Na_2PtCl_4 (7·4 g.) and *n*-Pr_2Te (4·14 g.) in ethanol for 16 hr. (yield

79%). It was recrystallised from acetone (Found: C, 15·6; H, 3·0. $C_{12}H_{28}Cl_4Pt_2Te_2$ requires C, 15·0; H, 2·9%).

Method 3(*a*). This method is most valuable for the preparation of the trialkylstibine and higher olefin complexes.

Bistrimethylstibinedichloro-μμ'-dichlorodiplatinum. Trimethylstibine (1·3 c.c.) was gradually added, with shaking and under nitrogen, to a solution of $(C_3H_6)_2Pt_2Cl_4$ (3 g.) in acetone (75 c.c.) at −75°. The solution on warming to room temperature and standing overnight deposited the orange crystalline bridged *compound* in poor yield. It was purified by washing it repeatedly with ethyl acetate, then dissolving it in chloroform and reprecipitating it by addition of light petroleum (Found: C, 8·7; H, 2·1. $C_6H_{18}Cl_4Pt_2Sb_2$ requires C, 8·3; H, 2·1%).

Bistriethylstibinedichloro-μμ'-dichlorodiplatinum. Triethylstibine (3·35 g.) in acetone (20 c.c.) was similarly added to $(C_3H_6)_2Pt_2Cl_4$ (4·9 g.) in acetone (60 c.c.) at −75°. The solution, after warming to room temperature and evaporation at 15 mm., left the orange crystalline *complex* which was recrystallised very rapidly from ethyl acetate (yield 35%) (Found: C, 15·3; H, 3·2. $C_{12}H_{30}Cl_4Pt_2Sb_2$ requires C, 15·2; H, 3·2%).

Bistrimethylphosphinedichloro-μμ'-dichlorodiplatinum. Propene platinous chloride (3 g.) in acetone (50 c.c.) was contained in a flask cooled to −70°, and the flask connected to a high-vacuum apparatus. The phosphine [liberated from Me_3P,AgI (3·5 g.) (Mann and Wells, *J.*, 1938, 708)] was then introduced into the flask from the vacuum-apparatus, and the mixture kept for 12 hr. at room temperature. The resulting orange solution was evaporated under reduced pressure to leave a brown gum which solidified on standing. The product was extracted from this with boiling ethyl methyl ketone, treated with a little charcoal, and filtered. The filtrate, taken to dryness under reduced pressure, deposited an orange residue which crystallised in prisms from ethyl methyl ketone and then decomposed at 217—220° (yield 3%) (Found: C, 10·9; H, 2·1. $C_6H_{18}Cl_4P_2Pt_2$ requires C, 10·5; H, 2·7%).

Bis(dimethyl sulphide)dichloro-μμ'-dichlorodiplatinum was prepared by adding dimethyl sulphide (0·7 c.c.) to $(C_3H_6)_2Pt_2Cl_4$ (3 g.) in dichloromethane (50 c.c.) at −70°. The mixture, after warming to room temperature, was evaporated to about 15 c.c., and toluene (35 c.c.) added. When this solution was boiled under reflux, the *complex* separated as a mustard-yellow crystalline solid. It was purified by extracting the impurities with boiling chloroform (yield 66%) (Found: C, 7·7; H, 1·9. $C_4H_{12}Cl_4Pt_2S_2$ requires C, 7·3; H, 1·8%). It is insoluble in all organic solvents tried except boiling ethylene dibromide, from which it crystallises with one tenaciously held molecule of solvent (Found: C, 8·2; H, 1·7. $C_4H_{12}Cl_4Pt_2S_2,C_2H_4Br_2$ requires C, 8·5; H, 1·9%).

An attempt to prepare bis-4-*n*-pentylpyridinedichloro-μμ'-dichlorodiplatinum by this method gave instead cis-*ethylene*-4-n-*pentylpyridinedichloroplatinum*. Ethylene platinous chloride (3 g.) in ethanol (25 c.c.) was cooled to −70°, and 4-*n*-pentylpyridine (1·5 g.) in ethanol (40 c.c) was added gradually with stirring. A yellow precipitate formed immediately, but after the mixture had been kept at −70° for 45 min. and then allowed to warm to room temperature, the precipitate redissolved. The solution was then kept at 60° for 16 hr., filtered from black decomposition products, and cooled to −70°. The white crystalline product which separated was recrystallised repeatedly from ethanol with a small amount of charcoal, and so obtained in silver-white plates, m. p. 142—143° (9%). This compound effervesces when in contact with aqueous potassium cyanide, and is a non-electrolyte in nitrobenzene (Found: C, 32·6; H, 4·4; N, 3·2; Cl, 16·4. $C_{12}H_{19}NCl_2Pt$ requires C, 32·5; H, 4·3; N, 3·2; Cl, 16·0%). The dielectric constant of its benzene solution indicates that it has a *cis*-configuration. In another experiment the yellow precipitate, formed immediately after mixing the reactants, was isolated and found to be *trans*-ethylene-4-*n*-pentylpyridinedichloroplatinum identical with the product described below.

Method 3(*b*). This method is most valuable for the preparation of the amine complexes.

trans-*Ethylenepiperidinedichloroplatinum.* Piperidine (1·2 c.c.) in 3% hydrochloric acid was added to a solution of $K[C_2H_4PtCl_3],H_2O$ (6 g.) in 1% hydrochloric acid (100 c.c.). The solution was carefully neutralised at 0° with 1N-sodium hydroxide, and the yellow precipitate thus obtained filtered off, washed with water, and dried. After repeated recrystallisation from light petroleum (b. p. 60—80°) it had decomp. pt. 100—105° (yield 68%) (Found: C, 22·6; H, 4·0. $C_7H_{15}NCl_2Pt$ requires C, 22·2; H, 4·0%).

Dipiperidinedichloro-μμ'-dichlorodiplatinum. A solution of the above mixed olefin–amine complex in light petroleum (b. p. 60—80°) (400 c.c.) was kept for 2 months, during which orange crystals separated from the solution. These were removed and recrystallised from chloroform (yield 48%) (Found: C, 17·2; H, 3·1; N, 4·0. $C_{10}H_{22}N_2Cl_4Pt_2$

requires C, 17·1; H, 3·2; N, 4·0%). The following pairs of compounds were similarly prepared: trans-*Ethylene*-4-n-*pentylpyridinedichloroplatinum*, thick yellow needles, m. p. 82·5—83·5° (68%) (Found: C, 32·4; H, 4·2. $C_{12}H_{19}NCl_2Pt$ requires C, 32·5; H, 4·3%). *Bis*-4-n-*pentylpyridinedichloro-μμ′-dichlorodiplatinum* (Found: C, 28·8; H, 3·6%; *M*, ebullioscopically in 1·5% benzene solution, 896. $C_{20}H_{30}N_2Cl_4Pt_2$ requires C, 28·8; H, 3·6%; *M*, 831). trans-*Ethylene*-4-n-*nonylpyridinedichloroplatinum*, thick yellow needles, m. p. 73—73·5° (90%) (Found: C, 38·7; H, 5·5. $C_{16}H_{27}NCl_2Pt$ requires C, 38·5; H, 5·5%). *Bis*-4-n-*nonylpyridinedichloro-μμ′-dichlorodiplatinum* (Found: C, 35·4; H, 4·9; N, 3·3. $C_{28}H_{46}N_2Cl_4Pt_2$ requires C, 35·7; H, 4·9; N, 3·0%).

Di-*p*-toluidinedichloro-μμ′-dichlorodiplatinum is obtained only in very small yield. *trans*-Ethylene-*p*-toluidinedichloroplatinum (Chatt, *J.*, 1949, 3340) is not soluble in light petroleum and so its 1% w/v solution in carbon tetrachloride was boiled to effect decomposition. The material underwent a complex decomposition. In general, the solution was boiled under reflux for a convenient time, filtered hot if necessary, and allowed to cool. The solids which separated were collected, and the filtrate boiled again. This was repeated, sometimes as many as twelve times. During about the first 20 hr. of boiling trans-*di*-p-*toluidinedichloroplatinum* separated. This is almost insoluble in all solvents but can be recrystallised with 70% loss from much acetone (Found *: C, 35·0; H, 3·7; N, 5·7; Cl, 14·9; Pt, 40·6. $C_{14}H_{18}N_2Cl_2Pt$ requires C, 35·0; H, 3·8; N, 5·8; Cl, 14·8; Pt, 40·6%). Its *trans*-configuration was proved by Kurnakov's reaction with thiourea (*J. prakt. Chem.*, 1894, **50**, 483). In acetone (50 c.c.) it (0·1 g.) reacted with thiourea (0·13 g., 8 mols.) at room temperature to deposit crystals of trans-*dithioureadi*-p-*toluidineplatinum dichloride*, which recrystallised from water in fine white needles, decomp. 170—180° (Found *: C, 29·65; H, 4·2; Pt, 30·8. $C_{16}H_{26}N_6S_2Cl_2Pt$ requires C, 30·4; H, 4·1; Pt, 30·8%). The cold filtrate from which the *trans*-di-*p*-toluidinedichloroplatinum had been separated was boiled for a further 6—7 hr.; then, on filtering and cooling, a quantity of reddish-orange solid separated (0·16 g.). This was extracted from insoluble *trans*-di-*p*-toluidine-dichloroplatinum with chloroform, the chloroform extract taken to dryness at 15 mm., and the residual trans-*di*-p-*toluidinedichloro-μμ′-dichlorodiplatinum* (0·08 g.) recrystallised from benzene (decomp. 190—205°) (Found *: C, 22·8; H, 2·35%; *M*, cryoscopically in *cyclo*pentadecanone, 704. $C_{14}H_{18}N_2Cl_4Pt_2$ requires C, 22·5; H, 2·4%; *M*, 747). On continued boiling of the carbon tetrachloride reaction mixture under reflux, browner products containing gradually diminishing quantities of *p*-toluidine were obtained. It appeared that a series of compounds of general formula $(C_7H_9N)_2(PtCl_2)_n$ was being produced but they were not easily separated. Fractions soluble in hot chloroform with values of n up to 6 were obtained, but this reaction requires further investigation.

The preparation of the bridged *p*-toluidine complex is slightly improved by employing as raw material crude *trans*-propene-*p*-toluidinedichloroplatinum (1 g.), prepared exactly as its ethylene analogue. The carbon tetrachloride solution of the propene complex became orange when boiled under reflux for 5 hr., and after filtration of the *trans*-di-*p*-toluidinedichloroplatinum (0·5 g.) from the hot solution the filtrate deposited the orange bridged complex (0·15 g.) on cooling (Found: C, 22·6; H, 2·5%).

cis-*Di*-p-*toluidinedichloroplatinum* was prepared for comparison with its *trans*-isomer (see above). *p*-Toluidine (0·5 g.), dissolved in a minimum of water, was added to aqueous K_2PtCl_4 (1·0 g.) and kept for two days. The product which separated recrystallised from methanol in pale yellow, felted needles, decomp. 270—280° (Found *: C, 35·1; H, 3·9; N, 5·8; Cl, 15·0; Pt, 40·4%). It is much more soluble in polar organic solvents than its *trans*-isomer, and by Kurnakov's reaction gave yellow tetrathioureaplatinum dichloride, confirming its *cis*-configuration; it had decomp. pt. 240—246° (Found: C, 8·8; H, 2·8. Calc. for $C_4H_{16}N_8Cl_2S_4Pt$: C, 8·4; H, 2·8%).

p-Toluidine complexes $[(C_7H_9N)_2PtCl_2]_n$ have previously been prepared by Gordon (*Ber.*, 1870, **3**, 174) and Cochin (*Compt. rend.*, 1878, **86**, 1402; *Bull. Soc. chim. France*, 1879, **31**, 498), but not completely characterised. From Gordon's method of preparation and the solubility of his product in alcohol his substance was probably *cis*-$[(C_7H_9N)_2PtCl_2]$, but Cochin's compound is insufficiently described to know which isomer it may have been; it was unlikely to be the analogue of Magnus salt, $Pt(NH_3)_4PtCl_4$, which he thought it to be.

The authors thank Mr. F. A. Hart, Miss J. H. Norwood, and Mr. P. F. Todd for experimental assistance.

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[*Received, April 13th*, 1955]