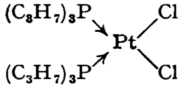
471. *The Nature of the Co-ordinate Link. Part I. The Non-ionic Complex Compounds of Tri-*n*-propylphosphine with Platinic and Platinous Chlorides.*

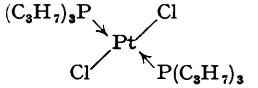
By J. Chatt.

The non-ionic simple complexes *cis*-$[(C_3H_7)_3P]_2PtCl_2$ (I), *trans*-$[(C_3H_7)_3P]_2PtCl_2$ (II), and the bridged complex $[(C_3H_7)_3P,PtCl_2]_2$ (III) have been oxidised to the corresponding platinic complexes (IV), (V), and (VI), which have all been characterised.

Chlorination of the simple complexes is easy and clean but that of the bridged complex does not go cleanly. The *cis*-platinic complex (IV) is much more labile than its platinous analogue and isomerises in benzene solution, slowly at room temperature, rapidly on boiling. Thermal decomposition of both the *cis*- and *trans*-platinic complexes yields a mixture of *cis*- and *trans*-platinous complexes from each isomer, indicating a *cis*-elimination of the chlorine atoms. The simple platinic complexes are surprisingly resistant to reduction by sulphur dioxide but each yields a mixture of the *cis*- and *trans*-platinous complexes by stannous chloride reduction. The bridged platinic complex (III) is on the other hand easily reduced. Its properties contrast with those of the bridged platinous complex in that the bridge is very weak and is split by ether and other oxygen-containing solvents, rather like the bridge in aluminium chloride. The platinic bridged complex also shows catalytic activity not shown by any other of these six complexes. It is suggested that the *d* orbitals of the platinum atom take part in a resonance which stabilises the platinous bridge but is less likely to take place in a platinic bridge because another *d* orbital is now involved in principal valency formation. Tri-*n*-propylhydroxyphosphonium chloroplatinate, chloroplatinite, and tetrachloro-$\mu\mu'$-dichlorodiplatinite are described.

Hitherto only two series of complex compounds of tertiary phosphines with platinum chlorides have been described. In the *n*-propyl series they are *cis*- and *trans*-bis(tri-*n*-propylphosphine)dichloroplatinum (I and II). Their configurations have been determined by dipole-moment measurements (Jensen, *Z. anorg. Chem.*, 1936, **229**, 250).


(I.)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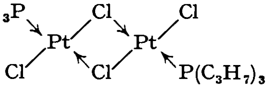

(III.)

The third platinous complex, dichlorobis(tri-*n*-propylphosphine)-μμ'-dichlorodiplatinum (III), was first obtained by reaction of the phosphine with ethyleneplatinous chloride $(C_2H_4PtCl_2)_2$ but is more conveniently prepared by the direct reaction at about 165° of finely powdered platinous chloride with the crude mixture of (I) and (II) prepared by Jensen's method. This compound is a platinum analogue of the palladium compounds described by Mann (*Ann. Reports*, 1938, **35**, 150; Chatt and Mann, *J.*, 1939, 1622), but could not be obtained by the method available in the palladium series (Mann and Purdie, *J.*, 1936, 880).

The properties of this class of compound will not be described here; other members have been prepared and isomerism in this series is at present under investigation.

It has been observed (Nyholm, *Quart. Reviews*, 1949, **3**, 343) that the most stable halogen-bridged complex compounds are those in which the metal, which is usually multivalent, exists in one of its lower valency states. In view of the ready and clean halogenation of the simple complex compounds of tertiary arsines with platinous halides to the corresponding platinic compounds (Nyholm, *J.*, 1950, 843), it was of interest to see whether the bridged platinous complex compounds were so easily and cleanly oxidised and whether the halogen bridge would survive such treatment.

Chlorination of the bridged complex (III) was, however, far from clean; some propylphosphine was oxidised away from the platinum atom, and the properties of the derived platinic complex (VI) were very different from those of the platinous bridged complex (III). On the basis of the formulæ as written, (I), (II), and (III), there is no obvious reason why (III) should behave so differently on chlorination; consequently, the oxidation of these three substances was of immediate interest for the light it might throw on the detailed structure of the halogen bridge.

Chlorination of the Platinous Complexes (I), (II), and (III).—When the simple compounds (I) and (II) were treated in benzene solution at 0—5° with the theoretical quantity of chlorine in carbon tetrachloride solution, the oxidation proceeded smoothly and cleanly. The crystalline platinic derivatives crystallised from the reaction mixture as Nyholm described for the simple arsine complexes (*J.*, *loc. cit.*). There was only very slight chlorination of the benzene, as shown by a slight fume of hydrogen chloride. Some isomerisation of the *cis*-compound (IV) also occurred during the chlorination :

$$cis\text{-}(PPr_3)_2PtCl_2 + Cl_2 = 70\%\ cis\text{-}(PPr_3)_2PtCl_4 + 30\%\ trans\text{-}(PPr_3)_2PtCl_4$$
$$trans\text{-}(PPr_3)_2PtCl_2 + Cl_2 = trans\text{-}(PPr_3)_2PtCl_4$$

These chlorinations can be effected most conveniently by passing an excess of chlorine into the benzene solutions, then immediately filtering off the *cis*-product or removing the excess of chlorine by partial evaporation under 15 mm. pressure in the preparation of the *trans*-isomer.

The products *cis*- and *trans*-bis(tri-*n*-propylphosphine)tetrachloroplatinum (IV) and (V) are beautifully crystalline substances less soluble in benzene and more strongly coloured than their progenitors. Unlike the simple platinic derivatives of tertiary arsines studied by Nyholm (*J.*, *loc. cit.*) they both decompose on melting. The *cis*-isomer melts at 123—125°, immediately resolidifies, and remelts over a long range at 175—200°. The *trans*-isomer melts at 175—185° depending on the rate of heating.

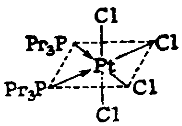
The *cis*-configuration was assigned to the greenish-yellow isomer, and the *trans*-configuration to the golden-yellow isomer, on the basis of the following contrasting properties :

cis-$(PPr_3)_2PtCl_4$.	*trans*-$(PPr_3)_2PtCl_4$.
Obtained only by chlorination of *cis*-$(PPr_3)_2PtCl_2$.	Obtained as the only product in the chlorination of *trans*-$(PPr_3)_2PtCl_2$.
Insoluble in cold benzene and non-polar solvents.	Fairly soluble in cold benzene and most organic solvents.
Labile, converted into its isomer in boiling solvents.	Not labile; no physical conditions caused isomerisation.
Develops a cloudiness with silver nitrate in aqueous acetone.	Stable to silver nitrate.

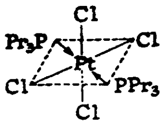
The chlorination of the bridged complex (III) was in marked contrast. In benzene solution considerable chlorination of the benzene occurred even when the theoretical quantity of chlorine was used. A deliquescent yellow oil separated. The benzene solution decanted from the oil yielded ultimately only a very small quantity of hexachlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum, (VI), together with a little unchanged (III). When an excess of chlorine was used, very rapid chlorination of the benzene occurred and the oil was the only product.

The preparation of (VI) was therefore carried out in chloroform solution by using the theoretical quantity of chlorine. Even then only a yield of about 30% was obtained, together with gummy and oily by-products and a small quantity of the salt, $[PPr_3{\cdot}OH]_2[Pt_2Cl_6]$. This must be a secondary hydrolysis product derived from tri-*n*-propylphosphine dichloride, indicating that in this chlorination some of the phosphine is oxidised away from the metal atom.

Hexachlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum (VI) is either insoluble, or decomposes, in all organic solvents tried, so neither its complexity nor its configuration could be established. To retain the octahedral configuration of groups round the platinum atoms the dimeric formula $(PPr_3PtCl_4)_2$ was assumed. The existence of a halogen bridge in the molecule is supported by the orange colour in contrast to the yellow colours of the simple platinic derivatives. The *trans*-configuration is probable because the simple platinic derivatives were found to be much more labile than their platinous analogues and the halogen bridged platinous derivatives are so labile that only the *trans*-symmetrical forms have so far been isolated.



(IV.)



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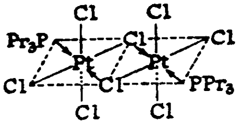
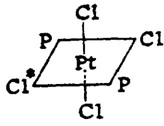


(VI.)



(VII.)

The following four comparative studies of the above six complex compounds have been made:

(1) *Isomerisation of* (IV) *into* (V), (I) *into* (II), *and* (II) *into* (I).—The co-ordinating groups in the *cis*-platinic complex (IV) show a very much greater lability than in the corresponding platinous complex (I). In boiling benzene isomerisation occurs rapidly, and even at room temperature a suspension of (IV) in benzene showed 25% isomerisation in 5 days. In boiling acetone 20% isomerisation was found after 1 hour and none of the *cis*-isomer remained after 15 hours.

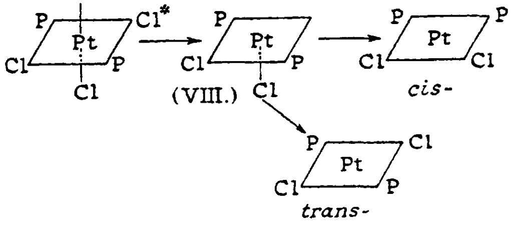
In contrast *cis*-$(PPr_3)_2PtCl_2$ (I) was isomerised only to the extent of 55% after being held in a molten condition for 2¾ hours at 160° and 88% at 195°. The reverse change occurred in the same time to the extent of 6·5% at 160° and 3·5% at 195°. No isomerisation of the *cis*-isomer occurred during 15 hours' boiling of its acetone solution.

(2) *Thermal Decomposition of* cis- *and* trans-$(PPr_3)_2PtCl_4$, (IV and V).—The thermal decomposition of the *trans*-platinic complex (V) provided an example of the production of a *cis*-isomer by the thermal decomposition of a compound of *trans*-configuration:

$$\textit{trans}\text{-}(PPr_3)_2PtCl_4 \xrightarrow[\text{for 15 mins.}]{\text{heat at 195°}} 9\%\ \textit{cis-} + 14\%\ \textit{trans}\text{-}(PPr_3)_2PtCl_2 + 77\%\ \text{black oily substances}$$

This transformation can be explained only on the basis of a *cis*-elimination of the chlorine atoms. If a *trans*-elimination occurred, *i.e.*, the removal of the starred atoms in (VII), it would lead at once without any rearrangement of the molecule to *trans*-$(PPr_3)_2PtCl_2$. In this event the quantity of *cis*-material in the product could not exceed the equilibrium concentration (~4%) and would most probably be of the order of ½% because equilibrium is only very slowly established.

A *cis*-elimination on the other hand leaves an intermediate (VIII) in which the groups are not in a planar configuration, and during the subsequent rearrangement either a *cis*- or a *trans*-configuration could be assumed by the molecule:—



It was also found that stannous chloride reduction of *trans*-$(PPr_3)_2PtCl_4$ produced a mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$, so it may be that a *cis*-elimination rule is applicable to these platinic complexes as the classical *trans*-elimination rule is to the platinous ammines (Werner, *Z. anorg. Chem.*, 1893, **3**, 267).

The thermal decomposition of *cis*-$(PPr_3)_2PtCl_4$ (IV) also produced a similar mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$. The decomposition occurred at 135—140°, a lower temperature than was possible with the *trans*-isomer, and the product was free from black and oily by-products. The decomposition occurred as follows:

$$3\ cis\text{-}(PPr_3)_2PtCl_4 = 2(PPr_3)_2PtCl_2 + \underset{\text{(IX.)}}{[PPr_3Cl]_2[PtCl_6]}$$

The salt (IX) was isolated as it hydrolysis product tri-*n*-propylhydroxyphosphonium chloroplatinate, $[PPr_3{\cdot}OH]_2[PtCl_6],2H_2O$, also obtained by direct synthesis by the following series of reactions:

$$PPr_3 + Cl_2 = PPr_3Cl_2;\ 2PPr_3Cl_2 + H_2PtCl_6 = [PPr_3Cl]_2[PtCl_6] + 2HCl;$$
$$[PPr_3Cl]_2[PtCl_6] + 4H_2O = [PPr_3{\cdot}OH]_2[PtCl_6],2H_2O + 2HCl$$

This salt was also characterised as its anhydrous chloroplatinite $[PPr_3{\cdot}OH]_2[PtCl_4]$ and its tetrachloro-μμ′-dichlorodiplatinite $[PPr_3{\cdot}OH]_2[Pt_2Cl_6]$ obtained during chlorination of (III).

That the decomposition of *cis*-$(PPr_3)_2PtCl_4$ occurs at a lower temperature and more cleanly than its *trans*-isomer indicates that isomerisation does not occur before decomposition. Isomerisation does occur simultaneously, however, and 40—50% of the *trans*-platinic complex was isolated together with the above products.

The isomerisation and thermal decomposition reactions are summarised in the following diagram:

$$\begin{tikzcd}
trans\text{-}(PPr_3)_2PtCl_2 \arrow[r, shift left, "Cl_2"] \arrow[dr, leftrightarrow, "\text{i. in fused state}" near start] & trans\text{-}(PPr_3)_2PtCl_4 \arrow[l, shift left, "\text{t.d. } 195°"] \arrow[d, shift left, "\text{t.d. } 195°"] \\
cis\text{-}(PPr_3)_2PtCl_4 \arrow[u, "\text{t.d. } 135°"] \arrow[r, shift left, "Cl_2"] \arrow[ur, "\text{i. in hot } C_6H_6"' near start] & cis\text{-}(PPr_3)_2PtCl_2 \arrow[l, shift left, "\text{t.d. } 135°"] \arrow[u, shift left, "Cl_2"]
\end{tikzcd}$$

(i. = Isomerisation. t.d. = Thermal decomposition.)

(3) *Reduction of the Platinic Complexes* (IV), (V), *and* (VI) *to the Corresponding Platinous Compounds.*—The simple platinic complexes showed unexpected resistance to reduction. The *cis*-isomer was rather more easily reduced than the *trans*-isomer and stannous chloride was the only satisfactory reducing agent used. A mixture of *cis*- and *trans*-$(PPr_3)_2PtCl_2$ was produced in each case. The product obtained from the *cis*-platinic complex contained 64%, and that from the *trans*-platinic complex 15%, of the *cis*-platinous complex.

By way of contrast the bridged platinic complex (VI) showed a marked tendency to revert to the platinous state. Even if it was allowed to remain in a sticky condition damped with acetone or some similar solvent the bridged platinous complex (III) would start to crystallise from the gum after a few days.

Under comparable conditions reduction by various reducing agents occurred as below. The sulphur dioxide (20% excess) and the stannous chloride reductions were carried out in aqueous acetone.

Reducing agent.	(IV.)	(V.)	(VI.)
KI	I_2 very slowly liberated	No free I_2	I_2 liberated comparatively rapidly
Boiling acetone ...	5—10% Redn. (14 hrs.)	No redn. (14 hrs.)	25% Redn. (4 hrs.)
SO_2 (5 days)	15% Redn.	<5% Redn.	30% Redn.
$SnCl_2$	Redn.	Redn.	Redn.

(4) *Comparison of the Properties of the Platinous and the Platinic Bridged Complexes* (III) *and* (VI).—The properties of these bridged complexes are in marked contrast. Dichlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum (III), like the corresponding palladium compounds, is easily soluble in organic solvents and easily recrystallised. The platinic bridged complex (VI)

is only sparingly soluble in all the organic solvents tried, with the exception of acetone and similar substances which split the bridge. It could not be recrystallised.

The bridge in the platinic complex (VI) is very much weaker than in the platinous complex (III). The former is readily split by oxygen-containing solvents such as esters, alcohol, acetone, and ether. Thus a solution in ether on evaporation under reduced pressure produces the very beautifully crystalline, yellow etherate which is extremely soluble in ether. It loses ether on exposure to the air, or more rapidly in a vacuum, thus reverting to the orange bridged complex (VI) :

$$\text{(VI.)}\quad (PPr_3PtCl_4)_2 + 2Et_2O \rightleftharpoons 2Et_2O,PPr_3,PtCl_4$$

This reaction was used for the isolation and purification of (VI). A similar substance (not analysed) was obtained from acetone solution. It follows that all the reactions of the platinic bridged complex taking place in solution are really the reactions of such substances as the above etherate and acetonate.

Etherates in the platinous series are unknown and the platinous bridge is not split by ether; it is, however, split by the more strongly co-ordinating molecule, *p*-toluidine, in the same manner as the corresponding palladium compounds (Mann and Purdie, *J.*, 1936, 876) :

$$(PPr_3,PtCl_2)_2 + 2CH_3\cdot C_6H_4\cdot NH_2 = 2PPr_3,CH_3\cdot C_6H_4\cdot NH_2,PtCl_2 \quad \text{(X.)}$$

The platinic bridged complex gives a similar product in ether solution :

$$PPr_3,Et_2O,PtCl_4 + CH_3\cdot C_6H_4\cdot NH_2 = \underset{\text{(XI.)}}{PPr_3,CH_3\cdot C_6H_4\cdot NH_2,PtCl_4} + Et_2O$$

(XI) has also been obtained by direct chlorination of (X).

The platinic bridge is split by concentrated hydrochloric acid, in which the compound (VI) dissolves in about an hour to give a yellow solution. The product or products were not identified. The bridged platinous complex is not affected after being in contact with the acid for a few days, but dissolves gradually during a few months.

The bridged platinic complex (VI) is also a powerful catalyst for the polymerisation of acetaldehyde, further emphasising its electron-seeking character. Neither the bridged platinous complex (III) nor the simple platinic complexes (IV and V) react in this manner. The bridged platinic complex also acts as a catalyst in the chlorination of benzene.

This work has raised two interesting points : (1) In the bridged series of complexes the platinous state has a much greater stability relative to the platinic state than it has in the simple complexes. (2) The bridge in the platinic bridged complex, if it exists, is so weak that it shows considerable resemblance to the bridge in aluminium chloride and this resemblance is extended to the catalytic activity of bridged platinic complexes.

The difference in behaviour between the simple and bridged complexes towards chlorination receives no explanation on the basis of formulæ (I), (II), and (III), in which the platinum atoms are in exactly similar states. Neither can the difference be explained on steric grounds, because even if there was not room for four chlorine atoms to add to the molecule (III), two should readily attach themselves to one of the platinum atoms. If we consider the probable dimensions of the molecule it is found that there is room for all four added chlorine atoms with negligible overlap of the van der Waals radii.

We must look to the detailed structure of the platinous bridge itself for an explanation of its stability. It appears to be stabilised in some manner, perhaps by a resonance which is not possible, or possible only to a lesser extent, in the platinic and the aluminium chloride bridges. The usual formulation, as in formula (III), of the halogen bridge is not entirely satisfactory on empirical grounds (Jensen and Asmussen, *Z. anorg. Chem.*, 1944, **252**, 234) and the above work further emphasises its unsatisfactory character, although it produces no support for the type of resonance proposed by Jensen.

The comparative resistance to chlorination, shown by the bridged platinous complex, suggests that the resonance involves filled *d* orbitals on the metal atom, thus reducing their availability for raising the valency state of the metal. When the metal has been oxidised to the platinic state, their availability for resonance in the bridge is reduced, thus reducing the stability of the bridge. The platinic halogen bridge is thus closer to that in aluminium chloride where there are no filled *d* orbitals. Both these halogen rings are split by ether and like substances, and the acceptor properties of the metal promote catalytic activity. Perhaps it is significant that the metals which form the most stable halogen bridged structures, *viz.*, Pd^{II}, Pt^{II}, Au^{III}, and to a lesser extent Zn, Cd, Hg and Cu, are heavy metals at the end of the transition series where the *d* orbitals are on an energy level close to the *s* and *p* levels. Also, most stable halogen bridges are formed by metals showing square co-ordination, thus having a natural angle of 90° which is just that between *d* orbitals and would favour the formation of dative double bonds (Chatt, *Nature*, 1950, **165**, 637).

EXPERIMENTAL.

Microanalyses: * by Drs. Weiler and Strauss, Oxford; † by Messrs. Weisser and Ritter, Basle; ‡ by Mr. Thomas, I.C.I. Paints Division, Slough; § by Mr. Brown, Butterwick Research Laboratories; ‖ by Dr. Chambers, British Rubber Producers Research Association, Welwyn Garden City.

cis- *and* trans-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum* (I and II).—Jensen (*loc. cit.*) obtained a mixture of these compounds by reaction of tri-*n*-propylphosphine with aqueous potassium chloroplatinite. The quantity of the *trans*-isomer is variable, rarely greater than 20% and usually less than 10% of the mixture. Consequently, Jensen's method was used to prepare the *cis*-isomer. The *trans*-isomer was prepared by reaction of the phosphine with the bridged platinous complex (III) (0·5 mol.) in chloroform solution. The mixture of isomers thus obtained contained 85% of the *trans*-isomer. The m. p.s of the pure isomers were *cis*-, 150—151°; *trans*-, 85—86°. Jensen records 149—150° and 82—82·5°, respectively.

Dichlorobis(*tri*-n-*propylphosphine*)-*μμ'*-*dichlorodiplatinum* (III).—A mixture of the dry crude isomeric bis(tri-*n*-propylphosphine)-dichloroplatinums (11·45 g.) prepared by Jensen's method and finely powdered platinous chloride (5·5 g., 5% excess) was heated with stirring to 165° for 15 minutes, the melt becoming pasty. The product, when cold, was dissolved in hot acetone, boiled with a very little charcoal, filtered, and evaporated to crystallisation. Almost pure *dichlorobis*(*tri*-n-*propylphosphine*)-*μμ'*-*dichlorodiplatinum* (III), 12·5 g., m. p. 180—182°, separated in beautiful yellowish-orange needles. Recrystallised from acetone, it had m. p. 181·5—183° (Found: C*, 25·6; H*, 5·02; Cl†, 16·7; Pt†, 45·9%; *M*, ebullioscopic in 1·44% benzene solution, 837; in 2·72%, 859. $C_{18}H_{42}Cl_4P_2Pt_2$ requires C, 25·4; H, 5·0; Cl, 16·6; Pt, 45·9%; *M*, 853). It is readily soluble in cold benzene and chloroform, moderately soluble in cold acetone and alcohol, but insoluble in ligroin and dry ether. It is, however, soluble in wet ether. The same product is obtained when the above preparation is made from either the pure *cis*- or the pure *trans*-isomer.

Chlorination of cis-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum* (I).—A carbon tetrachloride solution of chlorine (21·7 c.c.; 0·423 g. of Cl_2) was added to a benzene solution of (I) [90 c.c.; 3·5 g. of (I)] at 5—6°. The colourless solution became yellow, and on standing overnight fine yellow needles of cis-*bis*(*tri*-n-*propylphosphine*)*tetrachloroplatinum* (IV) (1·74 g.) separated. It was recrystallised from alcohol rapidly (to minimise isomerisation); m. p. 123—127° (decomp.), resolidifying and remelting at 178—200° (Found: C‡, 32·8; H‡, 6·1%; *M*, ebullioscopic in 0·942% benzene solution, 555; in 1·66%, 578; in 0·89% acetone, 695; in 1·64%, 602. $C_{18}H_{42}Cl_4P_2Pt$ requires C, 32·9; H, 6·4%; *M*, 657·5). The benzene filtrate, after evaporation of the benzene at the pump, yielded a sticky residue from which 1·0 g. of the *trans*-isomer (V) was recovered by recrystallisation from acetone.

The above *cis*-platinic complex (IV) is most readily prepared by passing chlorine through the benzene solution of (I) with cooling, seeding the solution with (IV), immediately filtering off the crystalline precipitate, and recrystallising it from alcohol.

Chlorination of trans-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum* (II).—When (II) (3 g.) was treated with chlorine (0·36 g.) as above, there was immediate deepening of colour and golden-yellow crystals separated. The mixture was evaporated under reduced pressure and the residue, recrystallised from acetone, yielded 2·28 g. of pure trans-*bis*(*tri*-n-*propylphosphine*)*tetrachloroplatinum*, m. p. 174—180° (decomp.) depending on the rate of heating (Found: C*, 32·9; C‡, 33·1; H*, 6·4; H‡, 6·15%; *M*, ebullioscopic in 1·08% benzene solution, 645; in 2·55%, 633; in 1·16% acetone 545; in 2·58%, 597. $C_{18}H_{42}Cl_4P_2Pt$ requires C, 32·9; H, 6·4%; *M*, 657·5). This compound is also most readily prepared by reaction of excess gaseous chlorine on a benzene solution of (II), followed immediately by evaporation under reduced pressure and treatment as above.

The solubilities of these two isomeric platinic complexes are as follows:

		Ether.	Alcohol.	Acetone.	Benzene.
cis	Cold	i	ss	vs	i
	Hot	i	vs	vs	vs
trans	Cold	i	ss	ss	vs
	Hot	i	ms	ms	vs

(i = insoluble, ss = slightly soluble, ms = moderately soluble, vs = very soluble.)

Chlorination of Dichlorobis(*tri*-n-*propylphosphine*)-*μμ'*-*dichlorodiplatinum* (III).—(III) (5 g.) in chloroform (100 c.c.) was chlorinated at 0° by slow addition of 30·4 c.c. of a carbon tetrachloride solution of chlorine (0·85 g. = 2 mols.) with shaking. The solution, from which some oil had separated, was kept for 5 minutes, and the chloroform then removed by distillation at 18 mm. pressure. The sticky orange residue was repeatedly extracted by long shaking with ether until the extract was colourless and a small quantity of sticky reddish-brown solid " A " remained. This extraction is slow and it is best if the ether is not quite anhydrous.

The ethereal solution was then evaporated to dryness at 15—20 mm. pressure, and the sticky yellow residue immediately extracted thrice with a little fresh dry ether to remove the very soluble part. A small residue of unoxidised (III) remained. The solution contained the main product, *diethyl ether–tri*-n-*propylphosphinetetrachloroplatinum*, $Et_2O,PPr_3,PtCl_4$, together with oily by-products, and the separation is rather difficult. Care must be taken not to decompose this etherate by excessive drying of ether because the ***hexachlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum*** (VI) thus produced dissolves again only slowly in ether and will be removed mixed with unchanged (III).

The concentrated ethereal extract was evaporated to crystallisation at 15—20 mm. pressure. The yellow crystalline paste was pressed free from oily products on the filter and then washed with a very little ether. The solid etherate thus obtained was immediately dissolved in a little ether and caused to crystallise slowly by cautious addition of ligroin (b. p. 60—80°) until crystallisation just started. It was then set aside in an almost closed vessel so that slow evaporation of the ether caused large lemon-yellow crystals to develop during the course of about 6 hours. There was also a slight separation of gummy material, and this apparently coated some of the crystals with a very thin skin, thus preserving them from decomposition in air for some time (1—3 hours) after they had been removed from the solution. The crystals were therefore dried in air for 1½ hours and those which had not effloresced were analysed (Found: C‡, 26·2; H‡, 5·5; Pt‡, 34·3; loss on drying for 8 hours at 10^{-5} mm. Et_2O‡, 13·65. $C_{13}H_{31}OCl_4PPt$ requires C, 27·3; H, 5·5; Pt, 34·2; Et_2O, 13·0%). On being heated, the compound reddens owing to loss of ether at 80—140°, and melts with decomposition at about 150°. It is very soluble in cold ether, acetone, hydroxylic organic solvents, and concentrated hydrochloric acid; it is less soluble in chloroform, slightly soluble in benzene, and insoluble in *cyclo*hexane and carbon tetrachloride. The hydrochloric acid solution deposits a yellow oil on dilution and this oil dissolves on further dilution. The dilute acid solution liberates iodine immediately on addition of potassium iodide.

The orange residue which remained after drying the etherate *in vacuo* as above was pure hexachlorobis(tri-*n*-propylphosphine)-*μμ′*-dichlorodiplatinum (VI), m. p. 150—151·5° (decomp.) (Found: C‡, 21·7; H‡, 4·4. $C_{18}H_{42}Cl_8P_2Pt_2$ requires C, 21·7; H, 4·3%). It is most easily obtained by dissolving the crude solid etherate, which has been freed from oil, in ether (0·5 g. in 3 c.c.), then reprecipitating it in the form of fine crystals by cautious addition of about an equal volume of ligroin. These crystals effloresce even during filtration and washing and lose all their ether on standing overnight over sulphuric acid in a vacuum desiccator to yield pure (VI). This substance is almost insoluble in all except oxygen-containing solvents. It dissolves in ethyl acetate, acetone, and alcohol, and slowly in ether to give yellow solutions, presumably containing complexes of a similar nature to the etherate. This was confirmed by taking the molecular weight of (VI) ebullioscopically in acetone. It was found to be approximately half the formula weight [Found: *M*, in 1·42% solution, 410; in 2·34%, 422. Calc. for $\frac{1}{2}(C_{18}H_{42}Cl_8P_2Pt_2)$: *M*, 497].

The small quantity of sticky brown solid "A" (above) was extracted with chloroform to leave a residue of crude *tri-*n*-propylhydroxyphosphonium tetrachloro-μμ′-dichlorodiplatinite* $[PPr_3{\cdot}OH]^+{}_2[Pt_2Cl_6]^{=}$. This substance is very soluble in acetone, alcohol, and such solvents but insoluble in non-polar solvents. It was purified by solution in a minimum of methyl ethyl ketone, from which it could be caused to crystallise in fine reddish-brown needles by cautious addition of glacial acetic acid; yield 0·2 g. It had m. p. 150—159° (decomp.), and slowly became black in contact with ordinary air but was stable for about a month in dry air. It blackened during ¾ hour at 80° *in vacuo* at 10^{-1} mm. pressure (Found: C†, 22·6; H†, 4·6; Cl†, 22·1, 22·2, 22·5; P†, 6·3; Pt†, 40·8, 40·7. $C_{18}H_{44}O_2Cl_6P_2Pt_2$ requires C, 22·6; H, 4·6; Cl, 22·2; P, 6·5; Pt, 40·8%).

It was further characterised by treatment of 0·166 g. in cold aqueous solution with tetrammino-platinous chloride, $Pt(NH_3)_4Cl_2,H_2O$, to form the chloride:

$$[PPr_3{\cdot}OH]_2Pt_2Cl_6 + 2Pt(NH_3)_4Cl_2 = 2PPr_3(OH)Cl + 2Pt(NH_3)_4PtCl_4\downarrow$$

This was too deliquescent to be isolated in so small a quantity as was obtained from the above reaction, but by addition of the theoretical quantity of hydrochloroplatinic acid, evaporation to dryness in a desiccator, and crystallisation of the residue from concentrated hydrochloric acid, the chloroplatinate was obtained in hydrated orange needles, m. p. 84—85° alone and mixed with an authentic specimen (see tri-*n*-propylphosphine hydroxy-salts, p. 2308). The green Magnus's salt obtained in the above reaction was identified by analysis (Found: N‡, 9·2. Calc. for $H_{12}N_4Cl_4Pt_2$: N, 9·3%).

Attempts to chlorinate (III) in benzene solution by using the theoretical quantity of chlorine in carbon tetrachloride solution were partly successful but an appreciable part of the chlorine was used in chlorinating the benzene because the chlorinated product is a very active catalyst for this chlorination. The use of an excess of chlorine gas causes rapid liberation of hydrogen chloride which destroys any (VI) produced, and solid products formed by chlorination of the benzene soon start to separate. This result is in marked contrast to the chlorination of simple tertiary phosphine and arsine derivatives which occurs cleanly in benzene solution.

*Separation of the Simple Platinous and Platinic Chloride Complexes of Tri-*n*-propylphosphine,* (I), (II), (IV), *and* (V).—In the following experiments it was necessary to separate mixtures of two or more of the above substances. This was easily accomplished by extraction with organic solvents according to the scheme below.

Solid mixture of (I), (II), (IV), *and* (V). Extract by shaking with cold benzene for one hour.

Residue. (IV) — *Filtrate contains* (I), (II), *and* (V). Evaporate to dryness at room temperature under reduced pressure, and extract the dry solids with as little cold MeOH as is judged necessary to dissolve (I) and (II).

Residue. (V) — *Filtrate contains* (I) *and* (II). Evaporate to dryness as above and extract with Et_2O.

Residue. (I) — *Filtrate contains* (II). Recover by evaporation.

If the original mixture of (I), (II), (IV), and (V) is sticky owing to the presence of other substances, the separation is not so clean as is indicated above. Interference occurs particularly at the extraction with methyl alcohol, which extracts some of (V) together with (I) and (II), so repeated extraction of later residues becomes necessary.

In the following experiments these compounds and the platinous bridged complex (III), whenever they were isolated, were identified by mixed m. p. with authentic specimens.

Isomerisation of cis-*Bis*(*tri*-n-*propylphosphine*)*tetrachloroplatinum* (IV).—(a) *In cold benzene.* The *cis*-platinic derivative (IV) (0·5 g.) was suspended in cold benzene (50 c.c.) and kept, with occasional shaking, for 5 days. The maximum room temperature was 17°. The unchanged *cis*-isomer (0·35 g.) was then filtered off, and the solution yielded 0·15 g. of crude *trans*-isomer. (b) *In boiling acetone.* The *cis*-platinic derivative (IV) (2·14 g.) in 50 c.c. of acetone was boiled for 55 minutes, then 25 c.c. were removed for analysis according to the above scheme. After a further 13 hours' boiling, the second 25 c.c. were also analysed. From the former, 0·86 g. of *cis*- and 0·21 g. of *trans*-isomer were recovered. In the second case no *cis*-isomer remained (cf. reduction by acetone).

Isomerisation of cis- *and* trans-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum,* (I) *and* (II).—(a) *Isomerisation in a molten condition.* Samples of each platinous isomer were kept at about 160° and at 195° for 2¾ hours. Isomerisation occurred as follows :

Temp.	Starting material.	Products, g.		Isomerisation. %.
		cis-.	*trans*-.	
160°	1·0 g., *cis*-	0·43	0·53	55
160	1·05 g., *trans*-	0·068	0·94	6·7
195	0·31 g., *cis*-	0·036	0·25	87
195	0·7 g., *trans*-	0·024	0·64	3·5

These approximate figures show that the equilibrium moves towards the side of *trans*-$(PPr_3)_2PtCl_2$ at higher temperatures, hence heat must be evolved in the change from *trans*- to *cis*-. It is intended to investigate this and similar equilibria further.

(b) *Attempted isomerisation in boiling acetone.* When 1 g. of the *cis*-platinous isomer in 15 c.c. of acetone was boiled for 15 hours, no isomerisation occurred and 0·95 g. of unchanged material was recovered.

Thermal Decomposition of the trans-*Platinic Complex* (V).—(V) (1 g.) was heated to 190° for 15 minutes. The temperature was then raised to 200° for 2 minutes to clarify the melt, and the product, a sticky brown oil, yielded a solid mixture of 0·12 g. of *trans*- and 0·08 g. of *cis*-$(PPr_3)_2PtCl_2$ on addition of a little alcohol and keeping overnight. In a repeat experiment the oil was first extracted with benzene but no residue of $[PPr_3Cl]_2PtCl_6$ remained (cf. next experiment).

Thermal Decomposition of the cis-*Platinic Complex* (IV).—(IV) (1·54 g.) was kept at 135—140° for 10 minutes, then cooled, and the product extracted with benzene. A residue of buff-coloured solid " B " remained. Analysis of the benzene solution according to the scheme on p. 2307 yielded the *trans*-platinic complex (V) (0·67 g.), the *cis*-platinous complex (I) (0·13 g.), and the *trans*-platinous complex (II) (0·23 g.). The substance " B " is a salt, very soluble in water and alcohol. It was recrystallised thrice from very little concentrated hydrochloric acid with final cooling in ice-water. The solubility of the salt increases so rapidly in the range 0—20° that it is essential to keep the solution cold and filter it through a well-cooled funnel. In this way pure tri-*n*-propylhydroxyphosphine chloroplatinate $[PPr_3{\cdot}OH]_2[PtCl_6],2H_2O$ was obtained in well-formed efflorescent orange needles. It had m. p. 84—85° alone and mixed with the synthetic specimen (see below). This material was also converted into the platinite, m. p. 100—102° (decomp.) alone and mixed with a synthetic specimen (see below).

Tri-n-*propylhydroxyphosphonium Salts.—Direct synthesis.* Chlorine (1·13 g.) in glacial acetic acid (43·7 c.c.) was run into a solution of tri-*n*-propylphosphine (2·5 g.) in glacial acetic acid (15 c.c.) with ice-cooling. To this solution was immediately added $H_2PtCl_6,4{\cdot}05H_2O$ (3·77 g.) in the acid (10 c.c.). A red oil separated and was caused to crystallise by seeding with the chloroplatinate " B " from the above preparation. It was twice recrystallised as above from concentrated hydrochloric acid, and the crystals were air-dried for 4½ hours. Crystals which had not effloresced were analysed. *Tri*-n-*propylhydroxyphosphonium chloroplatinate* thus obtained had m. p. 84—85° (Found : C*, 27·1; H*, 6·05. $C_{18}H_{48}O_4Cl_6P_2Pt$ requires C, 27·1 ; H, 6·06%).

The chloroplatinite was prepared as follows. Potassium chloroplatinite (0·39 g.) in water (2 c.c.) was mixed with a cold solution of the hydroxy-chloroplatinate (0·75 g., 1 mol.) in water (8 c.c.) and the precipitated potassium chloroplatinate removed. The aqueous filtrate was evaporated to dryness in a vacuum desiccator over sulphuric acid, and the residue extracted with alcohol, leaving a small residue of potassium chloroplatinate. The alcoholic extract was evaporated to dryness at 15 mm. pressure, and the residue, thrice recrystallised from acetone, yielded pure *tri*-n-*propylhydroxyphosphonium chloroplatinite,* m. p. 101—102° (decomp.) dependent on the rate of heating (Found : C§, 31·1; H§, 6·35; O‖, 5·05. $C_{18}H_{44}O_2Cl_4P_2Pt$ requires C, 31·3 ; H, 6·4 ; O, 4·6%).

Reduction of the Platinic Complexes (IV, V, VI).—(a) *With potassium iodide.* 5—10 Mg. of each solid were ground with 2—3 c.c. of potassium iodide solution containing starch. A faint violet colour developed with the *cis*-isomer (IV) after 5—10 minutes. No change at all occurred with the *trans*-isomer. A violet colour developed immediately with the bridged complex (VI), becoming almost black after 10 minutes. A drop of thiosulphate solution decolourised the solution from both (IV) and (VI).

(b) *With boiling acetone.* The *cis*-platinic complex (IV) (1·07 g.) in 25 c.c. of acetone was boiled under reflux for 14 hours, then concentrated to about 5 c.c. ; 0·41 g. of *trans*-$(PPr_3)_2PtCl_4$ crystallised out and was removed. The filtrate was evaporated to dryness, and the sticky residue analysed according to the scheme on p. 2307. No *cis*-platinic (IV) or *cis*-platinous (I) complexes could be detected, but 0·05 g. of *trans*-platinous complex (II) was isolated. A sticky residue remained. Because the *cis*-complexes are most easily isolated and purified, we can be certain that the quantity here, if any, is negligible, but the residue undoubtedly contained more of both the *trans*-complexes. It seems probable that, by-products being ignored, 90% isomerisation and 10% reduction to the *trans*-platinous complex represents the course of this reaction.

The *trans*-platinic complex (V) (2·5 g.) was similarly treated; 2·32 g. of unchanged material was recovered and no other platinous or platinic complexes were detected in the small sticky residue.

The bridged platinic complex (VI) (0·3 g.), similarly treated in 10 c.c. of acetone, blackened rather rapidly, so after 4 hours it was evaporated to yield a black pasty oil from which 0·06 g. of pure bridged platinous complex (III) was obtained by washing away the oil with a very little acetone.

(c) *With sulphur dioxide in aqueous acetone.* The *cis*-platinic complex (IV) (0·9 g.) in 110 c.c. of acetone and 30 c.c. of water was treated with 0·105 g. of sulphur dioxide (20% excess) in 10 c.c. of acetone and kept for 4¾ days. The acetone and excess of sulphur dioxide were removed at 15 mm. pressure, and the solid (0·61 g.) which separated from the aqueous solution was filtered off. The pale yellow aqueous solution gave a slight test for sulphate and contained acid sulphito-platinum complexes which were not investigated. The water-insoluble solid was analysed according to the above scheme and contained 0·08 g. of unchanged *cis*-platinic complex, 0·32 g. of *trans*-platinic complex, 0·13 g. of *cis*-platinous complex, and 0·03 g. of *trans*-platinous complex.

The *trans*-platinic complex (0·73 g.) in 60 c.c. of acetone and 4 c.c. of water was similarly treated with 0·085 g. of sulphur dioxide in 15 c.c. of acetone. 0·63 G. of water-insoluble material, from which were obtained 0·55 g. of pure unchanged *trans*-platinic complex and 0·02 g. of *trans*-platinous complex, but no *cis*-isomers, was recovered. The aqueous solution from this experiment was not coloured and gave only the faintest test for sulphate.

The bridged platinic complex (VI) (0·5 g.) in 25 c.c. each of acetone and water was treated with 0·075 g. of sulphur dioxide in 10 c.c. of acetone and kept for 5 days. Evaporation of the solution as above yielded 0·31 g. of water-insoluble material. The aqueous solution gave a good test for sulphate. The 0·31 g. of solid yielded a residue of 0·13 g. of the platinous bridged complex (III) by extraction with a little acetone, and the acetone extract was taken to dryness. The residue from the extract was dissolved in ether and 0·02 g. of *p*-toluidine added. This caused *p*-toluidine–tri-*n*-propylphosphinetetrachloroplatinum to separate, m. p. 144—145° (decomp.), indicating that the acetone-soluble part of the 0·31 g. of solid was largely unreduced starting material.

(d) *With stannous chloride.* Hydrated stannous chloride (0·53 g.) in water and acetone (5 c.c. each) containing one drop of concentrated hydrochloric acid was gradually added at room temperature to a solution of 1·5 g. of *cis*-platinic complex (IV) in 20 c.c. of acetone and 3 c.c. of water. The solution became paler, with a transient orange coloration, as each addition was made. The solution was now warmed to 40—50° for 10 minutes and then kept at room temperature for ¾ hour. The acetone was removed at 15 mm. pressure, and the remaining aqueous suspension filtered. The solid (1·11 g.) thus obtained yielded 0·72 g. of *cis*- and 0·39 g. of *trans*-platinous isomers (I and II).

When the *trans*-platinic complex (V) (1·5 g.) in 115 c.c. of acetone (it is less soluble than the *cis*-isomer) was similarly treated with an identical solution of stannous chloride, the solution became paler and after addition of a little water it was worked up as above. 1·32 G. of solid were recovered which, by analysis as above, contained 0·32 g. of unchanged *trans*-platinic complex, 0·13 g. of *cis*-, and 0·74 g. of *trans*-platinous complexes (I and II).

The platinic bridged complex (VI) (0·3 g.) in 4 c.c. of acetone and 0·6 c.c. of water, similarly treated, reddened at once when the addition of stannous chloride was made. The colour faded slowly at room temperature but rapidly and completely on warming. Worked up as above, 0·26 g. of water-insoluble solid was recovered. This was separated by recrystallisation from ethyl acetate into 0·13 g. of pure bridged platinous complex (III) and a sticky intractable residue.

Reaction of p-*Toluidine with the Platinous Bridged Complex* (III).—*p*-Toluidine (0·27 g., 1·05 mols.) in benzene (3 c.c.) was added to a solution of (III) (1 g.) in benzene (30 c.c.). The colour changed immediately from orange to yellow. The solution was evaporated to dryness at 15 mm. pressure, and the residual yellow oil (0·2 g.) crystallised at once on addition of ether. Careful fractionation of the product from methyl alcohol showed that only one geometric isomer was present, presumably of *trans*-configuration [compare the reaction of PPr_3 with (III), p. 2306]. trans-p-*Toluidine–tri*-n-*propylphosphinedichloroplatinum* (X) is thus obtained in lemon-yellow prisms, m. p. 110·5—111·5° (Found: C§, 36·1; H§, 5·7%; *M*, ebullioscopic in benzene, in 1·36% solution 470; in 2·16%, 485. $C_{16}H_{30}NCl_2PPt$ requires C, 36·0; H, 5·7%; *M*, 533).

Reaction of p-*Toluidine with the Etherate from the Platinic Bridged Complex* (VI).—Diethyl ether–tri-*n*-propylphosphinetetrachloroplatinum (0·9 g.) in ether (9 c.c.) was treated with *p*-toluidine (0·16 g.) in ether (4 c.c.). Golden-yellow crystals started to separate at once, and after 24 hours were filtered off. One recrystallisation from alcohol gave 0·51 g. of pure p-*toluidine–tri*-n-*propylphosphinetetrachloroplatinum* (XI), m. p. 147—151° (decomp.) (Found: C†, 31·5; H†, 5·1. N†, 2·4; Cl†, 23·4; Pt†, 32·2%; *M*, ebullioscopic in benzene, in 1·48% solution, 569; in 1·96% solution, 540; in 1·23%, 550; in 2·00%, 573. $C_{16}H_{30}NCl_4PPt$ requires C, 31·9; H, 5·0; N, 2·3; Cl, 23·4; Pt, 32·2%; *M*, 604). Because of the lability of platinic complexes this substance must have a *trans*-configuration.

Chlorination of p-*Toluidine–tri*-n-*propylphosphinedichloroplatinum* (X).—(X) (1·42 g.) in benzene (15 c.c.) was treated with chlorine (0·189 g.) in carbon tetrachloride solution (3·29 c.c.) with ice-cooling, and kept for 40 minutes. The solution was now evaporated to dryness under 15 mm. pressure, leaving a residue of 1·64 g. of sticky crystalline solid. Twice recrystallised from ethyl alcohol, it yielded pure *p*-toluidine–tri-*n*-propylphosphinetetrachloroplatinum (0·76 g.), m. p. 147—151° (decomp.) alone and mixed with an authentic specimen.

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