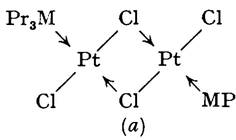
140. *The Nature of the Co-ordinate Link. Part II. Halogen-bridged, Binuclear Platinous Complexes. The Co-ordinating Affinity of the Tertiary Alkyls of Group V Elements for Platinous Chloride.*

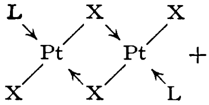
By J. Chatt.


(*a*)

Halogen-bridged compounds of type (*a*) (M = P, As, and Sb) have been prepared. No evidence of geometric isomerism has been observed in this series of complexes, and only the *trans*-symmetrical forms were found. Neither simple nor bridged tri-*n*-propylamine complexes could be obtained, but the unsymmetrical *trans*-$[MPr_3,NPr_3,PtCl_2]$ (M = P and As) have been prepared. With *p*-toluidine the bridged complexes yielded the unsymmetrical *trans*-$[C_7H_7{\cdot}NH_2,MPr_3,PtCl_2]$ as in the reaction with the corresponding palladous bridged complexes, but with 2 : 2′-dipyridyl the salt $[MPr_3,dpy,PtCl]^+[Pr_3M,PtCl_3]^-$ was obtained (M = P and As only). The phosphine salt was stable, but the arsine salt decomposed in solution to $(AsPr_3)_2PtCl_2$ and dpy $PtCl_2$ at room temperature. The stibine bridged compound behaved as do the palladium compounds and produced $(SbPr_3)_2PtCl_2$ and dpy $PtCl_2$ immediately on reaction with dipyridyl. Attempts to prepare a bismuthine complex were unsuccessful.

On the basis of the observed stabilities of these compounds, the co-ordinating affinity of these ligands towards platinous chloride is considered to be in the order $PPr_3 > AsPr_3 > SbPr_3 > NPr_3 > BiPr_3$. It was shown by attempting to place ethylene in this series that the relative co-ordinating affinity of ligands is very sensitive to the nature of the ligands already attached to the metal.

We intend to measure the dipole moments of a number of unsymmetrical *trans*-compounds of the type $LL'PtX_2$ (L = neutral ligands; X = univalent acid radicals), to obtain a more quantitative measure of the part played by filled *d* orbitals in co-ordination to platinous salts (Chatt, *J.*, 1949, 3340; *Nature*, 1950, **165**, 637). The readiest synthesis of these complexes appears to lie through the bridged complexes according to the reaction :


$$+ 2L' = 2LL'PtX_2$$

Accordingly, a series of platinous halogen-bridged complexes of general formula $(MPr^n{}_3,PtX_2)_2$ (M = P, As or Sb) has been prepared and is now described in view of its interest.

Although one of the first binuclear complexes to be isolated, namely, $(COPtCl_2)_2$ (Schützenberger, *Bull. Soc. chim.*, 1870, **14**, 17), was a halogen-bridged platinum complex, the number of known platinous complexes of this class is surprisingly small, except for two or three organic sulphide derivatives and one selenide derivative, which are too insoluble in organic solvents for thorough chemical investigation (Jensen, *Z. anorg. Chem.*, 1935, **225**, 124); the few that are known cannot be considered typical. They contain unusual ligands, for example, CO, PCl_3, $P(OEt)_3$ (Schützenberger, *Bull. Soc. chim.*, 1872, **17**, 482; **18**, 148), C_2H_4 (Anderson, *J.*, 1934, 971), and PF_3 (Chatt, *Nature*, *loc. cit.*). The CO, PCl_3, and PF_3 complexes are decomposed at once by moisture and the bridged structure is assumed. The olefin co-ordination complexes are less sensitive to moisture, yet are not very stable or amenable to study. The bridged complexes of phosphorus trichloride and triethyl phosphite were investigated by Rosenheim and his co-workers (*Z. anorg. Chem.*, 1903, **37**, 394; 1905, **43**, 35), who showed that the complex $P(EtO)_3,PtCl_2$ is dimeric and studied its reaction with amines.

The halogen-bridged structure was put forward in 1923 by Pfeiffer (" Anorganischen Chemie," pp. 56, 170) but the existence of such a structure was not confirmed until it was shown by complete *X*-ray crystal-structure determination to exist in diethylmonobromogold $(Et_2AuBr)_2$(Burawoy, Gibson, Hampson, and Powell, *J.*, 1937, 1690), and in dibromobis(trimethylarsine)-μμ′-dibromodipalladium $(AsMe_3,PdBr_2)_2$ and its chlorine analogue (Mann and

Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169). Since then, easily soluble tertiary phosphine and arsine halogen-bridged complexes containing many other metals, particularly from the second and the third long series of the Periodic Table, have been prepared and studied, yet platinous bridges have received no further study because no general synthetic method had been found.

Platinous bridged complexes are of especial interest. The simple platinous complexes, L_2PtX_2, are the most rigid of all planar complex compounds as shown by the existence of a large number of stable *cis*- and *trans*-isomers; hence, if geometric isomerism exists amongst bridged complexes, it is most probably to be found in the platinous series. Also, rearrangement of platinous complexes during reaction is less likely to occur than in any other planar complex compounds. Hence, it is interesting to compare their reactions with typical reactions in the similar palladium series, where there is lability of geometric isomers and rearrangements take place spontaneously (Mann, *Ann. Reports*, 1938, **35**, 150; Chatt and Mann, *J.*, 1939, 1622).

*Preparation and Properties of Bridged Platinous Complexes of Tri-*n*-propyl-phosphine, -arsine, and -stibine.*—The tertiary phosphine and arsine bridged complexes are most conveniently prepared by direct reaction of powdered platinous chloride with a crude mixture of the *cis*- and *trans*-simple complexes at the lowest possible reaction temperature :

$$(PPr_3)_2PtCl_2 + PtCl_2 = (PPr_3)_2Pt_2Cl_4$$

Dichlorobis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum is thus prepared at 165° (Chatt, *J.*, 1950, 2301), and the arsenic analogue at 125°, the temperature being gradually raised to 150° as reaction proceeds. This reaction has also been applied to prepare the di-*n*-propyl sulphide bridged derivative at 120—150°, but neither *p*-toluidine nor tertiary stibine bridged complexes could be prepared by this method.

A second general method is provided by the reaction of the ligand with a solution of ethyleneplatinous chloride at or below room temperature :

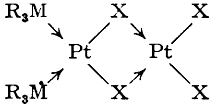
$$(C_2H_4)_2Pt_2Cl_4 + 2L = L_2Pt_2Cl_4 + 2C_2H_4$$

The yields are not good, and L_2PtCl_2 is also a major product. Dichlorobis(tri-*n*-propylstibine)-μμ′-dichlorodiplatinum has been prepared by this method, as has also the phosphorus analogue, but tri-*n*-propylamine gave only a yellow solution which on concentration under reduced pressure at room temperature yielded an intractable, unstable yellow oil.

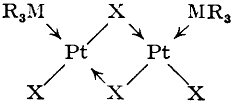
The three Group V derivatives form a well-graded series, the properties of which are summarised below. They are soluble in many organic solvents—acetone, alcohol, benzene, chloroform, etc.—but are rather less soluble and much paler in colour than the corresponding palladium compounds, which otherwise they resemble closely.

Substance.	M. p.	Colour.	Soly. in org. solvents.	Stability.
$(PPr_3)_2Pt_2Cl_4$	180—182°	Pale orange	Increases from the phosphine to the stibine complex	Stable
$(AsPr_3)_2Pt_2Cl_4$	156·5—157·5	Reddish-orange		Decomp. very slowly in boiling alcohol
$(SbPr_3)_2Pt_2Cl_4$	133—134 (decomp.)	Reddish-orange		Decomp. rapidly in boiling EtOH, $COMe_2$, or CCl_4

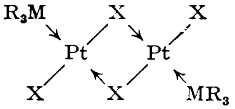
The above is the first stibine bridged complex to be isolated, and in view of its low stability it seems doubtful whether bridged stibine complexes of any other metallic chloride will exist at room temperature. No attempt was made to prepare the tri-*n*-propylbismuthine analogue.



(I.)



(II.)



(III.)

Search for Geometric Isomerism amongst these Halogen-bridged Complexes.—Pfeiffer (*loc. cit.*) pointed out the possibility that bridged complexes of this type might exist in three isomeric forms (I), (II), and (III), but there is no proved case where such isomers containing platinum or any other metal have been isolated. On the basis of the empirical knowledge that the simple platinous complexes show geometric isomerism to a greater extent than any other, it has often been suggested that such isomers would be found in the platinous series. Dichloro-bis(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum, the most stable of these bridged complexes, has been prepared by the following four methods at temperatures ranging from $-70°$ to $165°$ in an attempt to obtain such isomers :

(1) (*a*) *trans*-$(PPr_3)_2PtCl_2 + PtCl_2 = (PPr_3)_2Pt_2Cl_4$ (165°)
    (*b*) *cis*-$(PPr_3)_2PtCl_2 + PtCl_2 = (PPr_3)_2Pt_2Cl_4$ (165°)
(2) $(C_2H_4)_2Pt_2Cl_4 + 2PPr_3 = (PPr_3)_2Pt_2Cl_4 + 2C_2H_4$ ($-70°$ to 10°)
(3) $(PPr_3)_2Pt_2Cl_8 + 2SnCl_2 = (PPr_3)_2Pt_2Cl_4 + 2SnCl_4$ (20°)

Careful fractionation of the products has revealed no evidence of isomerism.

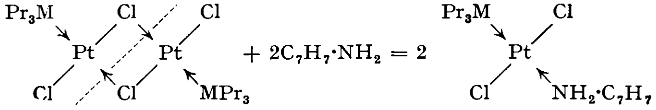
I am indebted to C. W. Bunn and R. de P. Daubeny for a powder *X*-ray examination of the above bridged phosphine complex. They found that it is isomorphous with, and has the same unit cell size as, the corresponding palladium compound (Mann and Purdie, *J.*, 1936, 884). It must thus have the *trans*-symmetrical structure (III), which has been assigned to this class of bridged palladium compound (Mann and Wells, *loc. cit.*). If either of the *cis*-isomers (I) or (II) had been produced in any of the above reactions, it is unlikely that they would have escaped detection because their dipole moments would be sufficiently high to render them much less soluble than this symmetrical isomer in non-polar solvents.

The above bridged tetrachloride, $(PPr_3)_2Pt_2Cl_4$, was also converted into the orange tetrabromide by boiling it in aqueous-alcoholic solution with 100% excess of ammonium bromide, and almost quantitatively into the bright red tetraiodide by treating its acetone solution with sodium iodide in acetone. The tetrabromide was more conveniently prepared directly by method (I), using crude bis(tri-*n*-propylphosphine)dibromoplatinum and platinous bromide. Again no evidence of isomerism was found.

If this isomerism exists amongst halogen-bridged complexes, the only remaining compounds which might show it are the bridged complexes of platinous halides with primary amines $(R{\cdot}NH_2)_2Pt_2Cl_4$. Compounds of this type with any metal are, however, almost unknown, and no general synthetic method of preparation has been developed.

Reactions of the Above Bridged Complexes with p-*Toluidine and with* 2 : 2′-*Dipyridyl.*—For comparison with the reactions of the bridged palladium compounds, *p*-toluidine and 2 : 2′-dipyridyl were chosen as typical reagents.

Reaction with p-*toluidine.* With *p*-toluidine at room temperature each of the three bridged compounds reacted immediately :



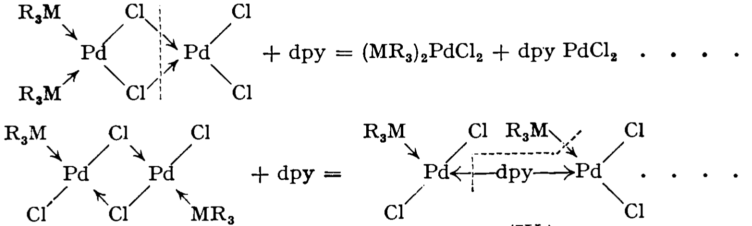
Only the *trans*-isomer was isolated in each case. This result is exactly analogous to the reactions of the palladous bridged complexes, but contrasts with the results of Rosenheim and Levy (*Z. anorg. Chem.*, 1905, **43**, 35) who obtained white and yellow isomeric substances, presumably *cis*- and *trans*-isomers, by splitting the ethyl phosphite complex, $[(EtO)_3P]_2Pt_2Cl_4$, with primary amines. Of the unsymmetrical products, $MR_3,C_7H_7{\cdot}NH_2,PtCl_2$, the phosphorus and the arsenic compound are stable but the stibine complex decomposes in a vacuum at 0·1 mm. pressure.

Although we were unable to prepare tri-*n*-propylaminoplatinous chlorides, either simple or bridged, because the products of every reaction tried decomposed rapidly, we obtained tri-*n*-propylaminotri-*n*-propylphosphinedichloroplatinum as a stable, beautifully crystalline yellow solid closely resembling *trans*-$(PPr_3)_2PtCl_2$, by the reaction

$$(PPr_3)_2Pt_2Cl_4 + 2NPr_3 = 2(PPr_3,NPr_3PtCl_2)$$

This is apparently the first complex of a trialkylmono-amine with platinous salts ever recorded; although Jensen (" Om de Koordinativt Firegyldige Metallers Stereokemi," Reitzels Forlag, Copenhagen, 1937; *Z. anorg. Chem.*, 1936, **229**, 228) claims to have prepared some, he has never published details. Evidently, tertiary amine platinous complexes are very unstable as compared with their phosphorus and even antimony analogues. The less stable tripropylarsine–tripropylamine analogue was also prepared. When tri-*n*-propylbismuthine was added to a benzene solution of the bridged phosphine tetrachloride there was no change in colour or other evidence of the formation of tri-*n*-propylbismuthinetri-*n*-propylphosphinedichloroplatinum but fairly rapid reduction to metallic platinum occurred.

Reactions with 2 : 2′-*dipyridyl.* (i) In the palladium series the reaction with 2 : 2′-dipyridyl was apparently a vertical splitting of the *cis*-isomer type (I), as in (A), but this explanation was later abandoned in favour of the scheme (B). It was supposed that the dipyridyl first reacted, each nitrogen atom independently, splitting the bridge to form an unstable intermediate (IV) which, because of the strongly chelating tendency of the dipyridyl, splits, as shown by the broken line, to give the products of equation (A) (Chatt, Mann, and Wells, *J.*, 1938, 2089).



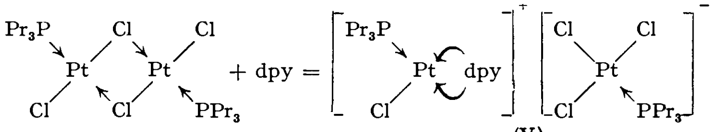
(A)

(B)

(IV.)

(ii) The reaction of dipyridyl with the platinum bridged complexes was of particular interest because the intermediate, which has not the structure (IV) but is ionic, was isolated from the reaction with both the phosphine and arsine bridged complexes. The stibine complex, however, reacted rapidly and completely after the manner of the palladium complexes.

(iii) The reaction of dipyridyl with the phosphine bridged complex occurred as follows in benzene solution :



(V.)

The salt, tri-*n*-propylphosphinedipyridylchloroplatinum tri-*n*-propylphosphinetrichloroplatinite (V), separated almost quantitatively in beautiful yellow leaflets, readily recrystallised from alcohol. It is dissociated in freezing nitrobenzene solution as shown by molecular-weight determination; the electrical conductivity in nitrobenzene solution at 25° followed Ostwald's dilution law fairly well over the concentration range $2{\cdot}7$—50×10^{-3} mols. per litre. The best value of Λ_{∞} thus calculated was 18·95 mhos. At very low concentrations, however, some second weak ionisation must become significant because the molar conductivity rose rapidly to 30 mhos as the concentration was decreased from 0·27 to $0{\cdot}013 \times 10^{-3}$ mols. per litre.

The reaction is thus exactly analogous to that found by Foss and Gibson (*J.*, 1949, 3063) for the reaction of dipyridyl with diethylmonobromogold. The analogy is carried further in that a second molecule of dipyridyl, which might be expected to react with the salt (V), yielded

$$[PPr_3,dpy,PtCl]^+[PPr_3PtCl_3]^- + dpy = 2[PPr_3,dpy,PtCl]^+Cl^-$$

an equilibrium from which only the starting materials, (V) and dipyridyl, could be isolated. The same behaviour was observed with the gold salt $[dpy,Et_2Au]^+[Et_2AuBr_2]^-$.

(iv) The arsine bridged complex reacts with dipyridyl in an analogous manner, except that the reaction

$$(AsPr_3)_2Pt_2Cl_4 + dpy = (AsPr_3)_2PtCl_2 + dpy\ PtCl_2$$

occurs as a very minor side reaction and the arsine salt $[AsPr_3,dpy,PtCl]^+[AsPr_3,PtCl_3]^-$ is contaminated with a few small yellow and red needles of dipyridyldichloroplatinum. This salt is much less stable than its phosphine analogue. In boiling alcohol it decomposes rapidly :

$$[AsPr_3,dpy,PtCl]^+[AsPr_3,PtCl_3]^- = (AsPr_3)_2PtCl_2 + dpy\ PtCl_2\downarrow$$

In $2{\cdot}5 \times 10^{-3}$M-nitrobenzene solution it has a molecular conductivity (extrapolated to zero time) of 17·7 mhos at 25°, but the conductivity falls to half its value in 90 mins. owing to the above decomposition. In more concentrated nitrobenzene solution at room temperature, long brilliant red needles of $dpy,PtCl_2$ separate as the decomposition proceeds. These then change into the yellow form spontaneously.

(v) The only reaction observed with the stibine bridged complex was :

$$(SbPr_3)_2Pt_2Cl_4 + dpy = (SbPr_3)_2PtCl_2 + dpy\ PtCl_2\downarrow$$

and this is complete in about five minutes. The dpy,$PtCl_2$ was deposited almost entirely in the red form. The stibine salt analogous to (V) is probably an unstable intermediate, thus bringing this reaction into line with those observed in the phosphorus and the arsenic series. The same mechanism is also probable for the corresponding reactions in the palladium series.

The Co-ordinating Affinity of Group V Ligands and Ethylene.—The order of stabilities of the phosphine, arsine, and stibine salts analogous to (V) is striking evidence of the rapidly decreasing strength of the $R_3M \longrightarrow Pt$ bond as we pass along the series M = P, As, and Sb. This order is observed in all the known complexes of the trialkyls of these elements, and may be universally true. When we consider the failure to obtain simple or bridged complexes of tri-*n*-propylamine, and the complete failure of Jensen (*Z. anorg. Chem.*, 1936, **229**, 234) and ourselves to obtain any platinous tertiary bismuthine complex, it seems that the strength of co-ordination to platinous salts is in the order $PR_3 > AsR_3 > SbR_3 > NR_3 > BiR_3$. Great care must be exercised in assigning a co-ordinating affinity in this qualitative manner. This may be illustrated by attempting to place ethylene in the above series. If we consider the bridged complexes $L_2Pt_2Cl_4$, ethyleneplatinous chloride, $(C_2H_4)_2Pt_2Cl_4$, decomposing at 180—190°, is more stable than its analogous propylstibine complex, decomposing at 133—134°. In solution also, the stibine complex has the lower stability, whereas there is no question that the arsine complex has a much greater stability; the co-ordinating affinity appears to be $AsPr_3 > C_2H_4 > SbPr_3$.

When we consider the only known forms of the simple complexes L_2PtCl_2 the order is reversed; the stibine complex melts without decomposition at 80—81° (Jensen, *Z. anorg. Chem.*, 1936, **229**, 247), whereas the ethylene complex decomposes at −10° (Chatt and Wilkins, *Nature*, 1950, **165**, 859), even in an atmosphere of ethylene. The order now appears to be $SbPr_3 > C_2H_4 > NPr_3$.

If we consider the mixed compounds $PPr_3,C_2H_4,PtCl_2$ and $PPr_3,NPr_3,PtCl_2$, we have so far failed to prepare the former because the product always loses part of its ethylene, but the latter is readily prepared; the order thus appears to be $NPr_3 > C_2H_4 > BiPr_3$.

Thus the position of ethylene depends, not only on the metal and on its valency, but also on the class of compound we choose for the comparison. The strength of co-ordination of any particular ligand is thus very sensitive to the nature of the other groups attached to the metal, and it appears misleading to place ligands in order of co-ordinating strengths either generally or with reference to a particular metal, unless we also define minutely the type of complex.

As a further example of co-ordinating affinity, the above orders can be contrasted with the series $NMe_3 > PMe_3 > AsMe_3 > C_2H_4$ (private communication from Herbert C. Brown, Purdue University; Chatt, *J.*, 1949, **3340**) observed for co-ordination to trimethylborine, which appears to be fundamentally different from co-ordination to platinum(II) (Chatt, *Nature*, *loc. cit.*).

EXPERIMENTAL.

* Microanalysis by Mr. W. Brown, Butterwick Research Laboratories, † by Mr. H. R. Thomas, Imperial Chemical Industries Limited, Paints Division, Slough, ‡ by Dr. G. Weiler and Dr. F. B. Strauss, Oxford, § by Mr. F. Weisser, Basle.

*Preparation of Dichlorobis(tri-*n*-propylarsine)-μμ′-dichlorodiplatinum.*—This *compound* was prepared in the same manner as its phosphorus analogue at 125—150° (Chatt, *J.*, 1950, 2306) and recrystallised from alcohol; yield 41%, m. p. 156·5—157·5° (Found: C*, 23·0; H*, 4·7. $C_{18}H_{42}Cl_4As_2Pt_2$ requires C, 23·0; H, 4·5%). The corresponding bright yellow bridged di-*n*-propyl sulphide compound, prepared by the same method at 120—150° and recrystallised from acetone, had m. p. 194—197° (decomp.). It appears to be identical with Jensen's product (*Z. anorg. Chem.*, 1935, **225**, 125), obtained by reaction of *cis*-$(SPr_2)_2PtCl_2$ with aqueous alcoholic potassium chloroplatinite (Found: C*, 18·7; H*, 3·7. Calc. for $C_{12}H_{28}Cl_4S_2Pt_2$: C, 18·75; H, 3·7%).

*Preparation of Dichlorobis-(tri-*n*-propylstibine)-μμ′-dichlorodiplatinum.*—Solutions of tri-*n*-propylstibine (3·5 g., 2 mols.) in acetone (15 c.c.) and ethyleneplatinous chloride, $(C_2H_4PtCl_2)_2$ (4·10 g., 1 mol.) in acetone (50 c.c.) were prepared under a nitrogen atmosphere and cooled to −70°. The stibine solution was then slowly added, with swirling, to the solution of the platinum compound, through a syphon tube operated by the nitrogen pressure. The mixed solution was now allowed to warm to room temperature, and the acetone removed under 15 mm. pressure. A residual, sticky, orange-red solid was extracted with a little ethyl acetate, and the solid residue of the *complex* was quickly recrystallised from acetone; yield 2·10 g., m. p. 133—134° (decomp.) (Found: C*, 20·75; H*, 4·05. $C_{18}H_{42}Cl_4Pt_2Sb_2$ requires C, 20·9; H, 4·1%).

*Preparation of Dichlorobis-(tri-*n*-propylphosphine)-μμ′-dichlorodiplatinum (Tetrachloro-compound).*—Methods (1) and (3) (see p. 654) are described by Chatt (*J.*, 1950, 2305). Method (2) is analogous to the preparation of the bridged stibine complex. Ethyleneplatinous chloride $(C_2H_4PtCl_2)_2$ (2·8 g.) in acetone (50 c.c.) was treated at −63° with an acetone (10 c.c.) solution of tri-*n*-propylphosphine (1·51 g., 2 mols.). There was change of colour and yellow crystals separated. These dissolved as the solution warmed to room temperature and a little gas was evolved. The solution was now evaporated at 15 mm. pressure to about 8 c.c., whereupon slow separation of an amorphous-looking, rather dirty solid set in. This was removed, but the slow separation of the solid continued and overnight about 90 mg. of light yellowish material were obtained. It was insoluble in all solvents tried and blackened rapidly in boiling water and in boiling dioxan. It was purified as far as possible by thorough extraction with acetone. When heated in a m. p. tube it showed no change except gradual darkening, becoming grey at 150° and black at 160°. Its analysis corresponded to diethylenedichloroplatinum contaminated with 10·75% of platinum (Found: C§, 13·4; H§, 2·1; Cl§, 19·7; Pt§, 65·05. Calc. for $C_4H_8Cl_2Pt$: C, 14·9; H, 2·5; Cl, 22·0; Pt, 60·6%) and it may be the *cis*-isomer, but is possibly a polymeric substance. It effervesces at once with potassium cyanide solution, as do all ethyleneplatinous complexes. If we assume the sample contained 10·75% of metallic platinum as impurity, the corrected analysis figures are: C, 15·0; H, 2·31; Cl, 22·1; Pt, 60·8%. We were unable to obtain purer material or appreciably better yields, except of inferior material, for a more thorough investigation. The substance is interesting because it is the first example of what may possibly be a simple non-ionic bisolefin complex. The mother-liquor from which the material had separated, on standing for a week, deposited a further 0·75 g. of black insoluble material. This was removed, and the mother-liquor taken to dryness under 15 mm. pressure. The *trans*-$(PPr_3)_2PtCl_2$ contained in it was extracted with ether, then the residue, recrystallised from acetone, yielded 0·7 g. of pure tetrachloro-compound. The ether extract was evaporated to dryness, and the residue recrystallised from alcohol, yielding 0·8 g. of pure *trans*-$(PPr_3)_2PtCl_2$, m. p. alone and mixed with an authentic specimen 83—85°. This preparation was repeated, but the products were worked up rapidly; instead of 0·75 g. of black insoluble material, 0·66 g. of unchanged ethyleneplatinous chloride was recovered. In a further experiment carried out in benzene at room temperature, in spite of a careful search no evidence of $C_2H_4,PPr_3,PtCl_2$, *cis*-$(PPr_3)_2PtCl_2$, or isomers of the tetrachloro-compound, $(PPr_3)_2Pt_2Cl_4$, was obtained.

Preparation of trans-*Bis*(*tri*-n-*propylphosphine*)*dibromoplatinum.*—This was prepared in the same way as the chloro-compound by reaction of the phosphine (2 mols., 2·3 g.) with aqueous potassium bromoplatinite (1 mol.) (Jensen, *Z. anorg. Chem.*, 1936, **229**, 240). The product was almost entirely soluble in ether, leaving a small white residue; this after recrystallisation from methyl alcohol had m. p. 160—161·5° and is presumably the *cis*-isomer, but there was insufficient for analysis. The ethereal extract on evaporation yielded a yellow residue of trans-*bis*(*tri*-n-*propylphosphine*)*dibromoplatinum*, which was pure after three recrystallisations from methyl alcohol and had m. p. 96—97° (1·5 g.) (Found: C†, 31·9; H†, 6·2. $C_{18}H_{42}Br_2P_2Pt$ requires C, 32·0; H, 6·3%).

Preparation of Dibromobis-(*tri*-n-*propylphosphine*)-*μμ'-dibromodiplatinum* (*Tetrabromo-compound*).—Prepared in the same way as its chlorine analogue (method 1) at 210°, the *tetrabromo*-compound was obtained in orange crystals, m. p. 167—168° (from acetone) (Found: C†, 20·9; H†, 4·15. $C_{18}H_{42}Br_4P_2Pt_2$ requires C, 21·0; H, 4·1%). It was also obtained by replacing the chlorine in its chlorine analogue by bromine: 0·46 g. (8 mols.) of ammonium bromide in water (1 c.c.) was added to 0·5 g. (1 mol.) of the tetrachloro-compound in alcohol (15 c.c.), and the mixture boiled under reflux for 1¾ hours. The product was taken to dryness at 15 mm. pressure, and the residue extracted with boiling water. The orange residue, recrystallised twice from alcohol, was the pure tetrabromo-compound, m. p. 167—168° (0·3 g.).

Preparation of Di-iodobis(*tri*-n-*propylphosphine*)-*μμ'-di-iododiplatinum* (*Tetraiodo-compound*).—Sodium iodide (2·14 g., 4·5 mols.) in acetone (20 c.c.) was added to a solution of the tetrachloro-compound (2·68 g., 1 mol.) in acetone (120 c.c.), and the whole boiled under reflux for 40 minutes. The solution was filtered hot, and the filtrate deposited 2·07 g. of almost pure *tetraiodo*-compound on cooling. Recrystallised (acetone), it had m. p. 200—201° (yield 1·42 g.) (Found: C‡, 17·7; H‡, 3·4; Pt†, 32·0, 32·2. $C_{18}H_{42}I_4P_2Pt_2$ requires C, 17·7; H, 3·5; Pt, 32·0%). A further 2·1 g. of crude product were obtained from the mother-liquors.

Reaction of p-*Toluidine with the Bridged Tri*-n-*propylphosphine, -arsine, and -stibine Tetrachloro-compounds.*—The reaction with the phosphine complex has already been described (Chatt, *J.*, 1950, 2309). The reactions with the arsine and stibine compounds in benzene were exactly analogous. trans-p-*Toluidinotri*-n-*propylarsinedichloroplatinum* (recryst. from ligroin, b. p. 80—100°; yield 75%) was obtained in well-formed, yellow, granular crystals, m. p. 94° (Found: C*, 33·3; H*, 5·1; N*, 2·55. $C_{16}H_{30}NCl_2AsPt$ requires C, 33·3; H, 5·2; N, 2·4%). The light orange *stibine* analogue (recryst. from ligroin, b. p. 60—80°; yield 37%) had m. p. 69°. A sample decomposed on attempted drying at 0·1 mm. pressure, but was dried in a vacuum-desiccator (15 mm.) over sulphuric acid (Found: C*, 31·0; H*, 4·8; N*, 2·6. $C_{16}H_{30}NCl_2PtSb$ requires C, 30·8; H, 4·8; N, 2·2%).

Preparation of Tri-n-*propylaminetri*-n-*propylphosphinedichloroplatinum.*—Tripropylamine (0·83 g., 2 mols.) in benzene (5 c.c.) was added to the tetrachloro-compound (2·48 g., 1 mol.) in benzene (45 c.c.) at 25°. There was a change of colour from orange to yellow and a rise of temperature of 2·5°. Evaporation at 15 mm. pressure and room temperature gave the yellow crystalline *complex*, which was pure after one recrystallisation from methyl alcohol, and then had m. p. 114—115° (yield 1·72 g.) (Found: C‡, 38·0; H‡, 7·1; N*, 2·4. $C_{18}H_{42}NCl_2PPt$ requires C, 38·0; H, 7·4; N, 2·5%). The yellow *tri-propylarsine* analogue, similarly obtained, had m. p. 104—105° (decomp.), dependent on the rate of heating (Found: C*, 35·1; H*, 6·8; N*, 2·4. $C_{18}H_{42}NCl_2AsPt$ requires C, 35·2; H, 6·9; N, 2·3%). In an attempt to obtain tri-*n*-propylbismuthinetri-*n*-propylphosphinedichloroplatinum in the same manner, the reaction mixture darkened and finally deposited metallic platinum during the evaporation at room temperature. No pure substance was isolated.

Reaction of 2 : 2'-*Dipyridyl with the Bridged Tri*-n-*propyl-phosphine, -arsine, and -stibine Tetrachloro-compounds.*—The phosphine tetrachloro-compound (1 g., 1 mol.) in benzene (25 c.c.) was treated with 2 : 2'-dipyridyl (0·183 g., 1 mol.) in benzene (5 c.c.) at room temperature. The colour immediately changed to yellow and pure *tri*-n-*propylphosphinedipyridylchloroplatinum tri*-n-*propylphosphinetrichloroplatinite* started to separate in beautiful, bright yellow scales. Next morning, 1·04 g. of product were filtered off. It melted sharply with decomposition anywhere in the range 170—180° according to the rate of heating; recrystallisation from acetone or alcohol did not improve the product (Found: C*, 33·2; H*, 4·95; N*, 2·84%; *M*, cryoscopically in nitrobenzene, 671 in 0·818% and 735 in 1·786% solution. $C_{28}H_{50}N_2Cl_4P_2Pt_2$ requires C, 33·35; H, 5·0; N, 2·78%; *M*, 1009). The values of *M* correspond to a dissociation (α) of 50·4% and 37·3%, respectively. The molecular conductivity (Λ_v) at 25°, measured with a Mullard conductance bridge, varies with molar concentration as in the table, which also shows the values of Ostwald's dissociation constant, *K*, calculated on the basis that Λ_∞ = 18·95. Values recorded in heavy type are constant to the accuracy of the measurements.

Concn. × 10^4	0·135	0·270	2·70	13·5	26·85	78·6	131	196·5	268·5	393	524	1026	1861
Λ_v, mhos ...	30·6	28·1	21·8	18·6	16·75	13·9	12·5	10·9	9·98	9·15	8·00	5·535	3·72
K × 10^3 ...	—	—	—	77	18·1	**15·9**	**16·8**	**15·4**	**15·7**	**17·4**	**16·2**	12·4	8·9

A solution in nitrobenzene showed no change in conductivity after 3 days.

The *arsine* analogue, similarly prepared, was contaminated with a little dipyridyldichloroplatinum. It was purified by dissolution in chloroform at room temperature, filtration, and reprecipitation of the pale yellow, slightly orange product with ethyl alcohol. It blackens on heating to 260—280°, and decomposes on attempted recrystallisation from hot solvents (Found: C*, 30·65; H*, 4·5; N*, 2·75. $C_{28}H_{50}N_2Cl_4As_2Pt_2$ requires C, 30·65; H, 4·6; N, 2·55%).

The molar conductivity of a 2·5 × 10^{-3}M.-solution of the arsine salt in nitrobenzene solution, initially almost identical with that of the phosphine salt, decreases rapidly with time; then, as it approaches zero, only very slowly. The variation of molar conductivity with time at 25° is :

Time, mins.	0	6	8	12	16	30	60
Λ_v, mhos	17·7 extrap.	16·8	16·4	15·8	15·2	13·2	10·6
Time, mins.	100	175	393	536	1108	2843	10·5 days
Λ_v, mhos	8·31	5·76	2·77	1·98	0·857	0·356	0·185

*Attempt to prepare Tri-*n*-propylphosphine-ethylenedichloroplatinum,* $PPr_3,C_2H_4,PtCl_2$.—The first reaction tried was $(C_2H_4)_2Pt_2Cl_4 + 2PPr_3 = 2C_2H_4,PPr_3PtCl_2$, as described on p. 657, but no sign of formation of the desired product was obtained.

The reaction of tripropylphosphine with aqueous potassium ethylenetrichloroplatinite was partially successful: $(C_2H_4)_2Pt_2Cl_4$ was dissolved in 50 c.c. of a solution of potassium chloride (0·76 g., 2 mols.) in water, and filtered; propylphosphine (1·61 g., 2 mols.) was next added together with a little alcohol used to wash out the propylphosphine from its container, and the whole shaken together for ½ hour. Some ethylene was evolved, and a yellow solid separated and was filtered off and dried (yield 3·15 g.; m. p. 97—100°). Extraction with ether removed a portion of *trans*-$(PPr_3)_2PtCl_2$ (m. p. 85—87° alone or mixed with an authentic specimen), leaving an ether-insoluble yellow substance, m. p. 105—111° (efferv.) for different preparations. This substance was too unstable to be purified by recrystallisation. It was insoluble in ether and very soluble in acetone, and very small quantities could be recrystallised quickly from ethyl alcohol or carbon tetrachloride without improvement in purity. In attempts to recrystallise larger quantities, only the bridged complex $(PPr_3)_2Pt_2Cl_4$, m. p. 181·5—183° alone or mixed with an authentic specimen, separated from the cold solution. In composition the product approximated to the *molecular compound* $(PPr_3)_2PtCl_2,PPr_3,C_2H_4PtCl_2$ (Found: C‡, 34·1; H‡, 6·3. $C_{29}H_{67}Cl_4P_3Pt_2$ requires C, 33·5; H, 6·5%).

The author thanks Mr. F. A. Hart for experimental assistance.

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[*Received, November* 19*th*, 1950.]