

458. *Phosphido- and Arsenido-bridged Complexes of Platinum(II).*

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A number of phosphido-bridged complexes and a diphenylarsenido-bridged complex of the type *trans*-[Pt₂Cl₂{(P,As)R₂}(PPrⁿ₃)₂] have been prepared for comparison with the corresponding thio-bridged complexes. They differ in many ways, in particular, no *cis*-isomers were obtained. By replacing the terminal chlorine by phenyl groups, *cis*-isomers containing phosphido-, bromo-, iodo-, and mixed-bridge systems were obtained, *e.g.*, *cis*-[PtBr₂Ph₂(PPrⁿ₃)₂] and *cis*-[Pt₂(PPh₂)(SPh)Ph₂(PPrⁿ₃)₂]. These have low dipole moments, as compared with their mononuclear analogues, especially when there are sulphur or halogen atoms in the bridging position *trans* to the terminal tri-*n*-propylphosphine group. It is suggested that the ring has a pseudo-aromatic character, especially when the bridging atoms have a non σ -bonding pair of electrons. Strong mesomeric drift of these electrons into the *trans*-terminal phosphine group then occurs so reducing the moment.

A dihydride, *trans*-[Pt₂H₂(PPh₂)₂(PEt₃)₂], was prepared and the Pt-H stretching frequency is the lowest observed, suggesting that the bridging phosphido-group has an even stronger *trans*-effect than cyanide ion. It also appears to be the strongest bridging group for platinum(II).

THE recent development of easy methods for preparing secondary phosphines has stimulated interest in their metal derivatives.¹ The subject has recently been summarized by Hayter,² who described a number of palladium(II) derivatives. In this Paper, we describe a number of platinum(II) derivatives, containing bridging dialkylphosphido-, diarylphosphido-, and diarylarsenido-groups, prepared for comparison with the corresponding bridged alkyl- and aryl-thio-complexes.³

The thio-bridged platinum complexes [Pt₂Cl₂(SR')₂(PPrⁿ₃)₂] (R' = an alkyl or aryl group) are interesting because they exist as *cis*- and *trans*-isomers, [(XIII) and (XIV); Chart 1], which show a peculiar stability relationship. Both isomers can be isolated, and when R' is ethyl or cyclohexyl the *cis*-isomer is much the more stable. On the other hand, when R' is an aryl group, the *trans*-isomer is the more stable. Addition of a trace of tri-*n*-propylphosphine to solutions of the isomers causes spontaneous isomerization. Compounds having only one bridging thio-group exist only in the *cis*-form (XV).

There is no obvious explanation of these unexpected stability relationships, and it was of interest to see whether the phosphido-bridged complexes, having a PR₂ group (R = an alkyl or aryl group) in place of SR' groups, show similar peculiarities. However, the phosphido- (and arsenido-) bridged complexes differ considerably from their thio-analogues, and the *cis*-isomers show no unusual stability relative to the *trans*. Indeed *cis*-isomers of [Pt₂Cl₂(PR₂)₂(PPrⁿ₃)₂] were unobtainable, just as in the halogeno-bridged series [Pt₂X₄(PPrⁿ₃)₂] (I; X = Cl, Br, or I).

Nevertheless, compounds (VIII) and (XI) showed considerable variation of dipole moment according to the nature of the groups X and Y, respectively, and it is evident that there is strong interaction of the *d_π*- and *p_π*-orbitals of the atoms in the inorganic ring, when X and Y has a non-bonding electron pair, perhaps producing a pseudo-aromatic system, in which mesomeric electron drifts, compensating the inductive dipole moments in (VIII) and (XI), can occur. This effect is especially marked when, as in (XI), the halogen, or sulphur, bridging atom is *trans* to the terminal phosphorus atoms. Then it appears that strong mesomeric electron drift occurs into a *d*-orbital of the positively-charged PPrⁿ₃ group from the *trans*-bridging sulphur or halogen atom. We shall return to this point after describing the formation and reactions of the phosphido- and arsenido-bridged complexes, summarized in Chart 1.

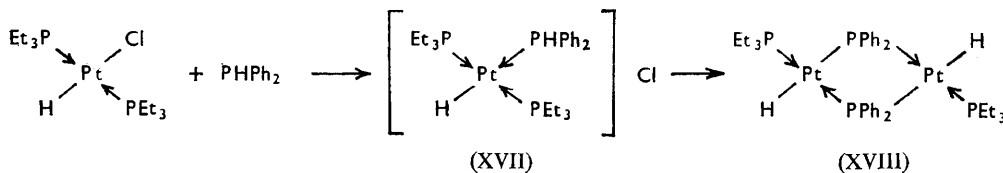
¹ *E.g.*, Issleib and Wenschuh, *Z. anorg. Chem.*, 1960, **305**, 15, and references therein.

² Hayter, *J. Amer. Chem. Soc.*, 1962, **84**, 3046.

³ Chatt and Hart, *J.*, 1960, 2807, and references therein.

diphenylphosphine in presence of a base the binuclear complex (III; R = Ph) was obtained in low yield. Although terminal diphenylphosphido-groups have been observed in the palladium(II) series of complexes² it seems unlikely that they can exist in the platinum(II) series except under very special circumstances, the tendency to occupy bridging positions between platinum atoms being too strong.

This elimination of a tertiary phosphine by a phosphido-group has been used to prepare the dihydride (XVIII). Neither (XVIII) nor its *n*-propyl analogue was obtained by reduction of the phosphido-bridged complexes (III; L = PPr₃ or PEt₃, R = Ph) but on treatment of *trans*-[PtHCl(PEt₃)₂]⁵ with diphenylphosphine in benzene a yellow solution, presumably of the ionic intermediate (XVII), was obtained. This on treatment with a base gave a strong smell of triethylphosphine, and the dihydride (XVIII) eventually crystallized from the solution.



This hydride is the first having phosphorus *trans* to hydrogen in the platinum(II) series of hydrides, and the Pt-H stretching frequency (2005 cm⁻¹) is the lowest observed, even lower⁶ than in *trans*-[PtH(CN)(PEt₃)₂] (2041 cm⁻¹). Since $\nu(\text{Pt-H})$ appears to follow an inverse relation to the *trans*-effect of the ligand in *trans*-position to the hydrogen,⁶ it would seem that the bridging phosphido-group in the platinumous series has a *trans*-effect even greater than that of cyanide ion.

All attempts to obtain a monophosphido-monochloro-bridged complex, corresponding to the thio-bridged complex (XV) or its *trans*-isomer, failed, as did attempts to obtain a monothiomonophosphido-bridged complex with terminal halogen atoms. The phosphido-bridged product always contained two phosphido-bridges, which provides another reason for preferring structure (a) for (XVI; R = Ph).

All the compounds mentioned above except the dihydride contain terminal chlorine atoms. These tend to have considerable ionic character when they are *trans* to phosphorus, and so are somewhat labile. This lability could be partly responsible for our inability to obtain *cis*-isomers, or monophosphido-bridged complexes. We decided therefore to attempt to obtain them by replacing the terminal chlorine atoms by organic groups, which, because of their great ligand field strength, might tighten the binding in the complex, and if *cis*-isomers could be isolated, they would certainly exhibit no lability through slight ionization of the phenyl groups. Phenyl groups could be inserted in place of chlorine in the terminal position⁷ and by this device we were able to obtain some *cis*-isomers, and some mixed phosphido-halogeno-, and phosphido-thio-bridged systems.

The binuclear series of platinum(II) aryls have not been described previously, although an isolated dimethyl binuclear derivative of palladium(II) is known.⁸ We now describe binuclear aryl derivatives of platinum(II) having phosphorus, arsenic, sulphur, bromine, and iodine in the bridging positions and tri-*n*-propylphosphine in terminal positions. The reaction sequences are set out in Chart 1.

The compounds having symmetrically bridged arrangements are readily obtained by reaction of the corresponding terminal halides with phenyl-lithium or, in certain cases,

⁵ Chatt and Shaw, *J.*, 1962, 5075.

⁶ Chatt, Duncanson, and Shaw, *Chem. and Ind.*, 1958, 859.

⁷ Chatt and Hayter, *J.*, 1961, 772.

⁸ Calvin and Coates, *J.*, 1960, 2008.

phenylmagnesium bromide. The diphosphides (III; R = Et and R = Ph) react with phenyl-lithium affording *trans*-[Pt₂(PR₂)₂Ph₂(PPrⁿ₃)₂] (V; R = Et and R = Ph). *trans*-[Pt₂(SR')₂Ph₂(PPrⁿ₃)₂] (VII; R' = Et or Ph) may be obtained similarly except that the starting materials may have either *cis*-(XIII) or *trans*-(XIV) configuration, and no evidence of a *cis*-isomer was found in the product from either. In view of this result it is surprising that only *cis*-[Pt₂Br₂Ph₂(PPrⁿ₃)₂] (VI; X = Br) could be isolated, following reaction of the tetrabromide (I; X = Br) with phenyl-lithium. This was readily converted into the di-iodide (VI; X = I) by an excess of sodium iodide, but the dichloro-analogue is apparently unstable since only the disproportionation product *trans*-[PtPh₂(PPrⁿ₃)₂] (XIX) was obtained from (I; X = Cl) and phenyl-lithium.

cis-[Pt₂Br₂Ph₂(PPrⁿ₃)₂] proved to be a useful starting material for a series of *cis*-isomers. Although reaction with an excess of lithium thiophenolate or lithium diphenylphosphide affords only the *trans*-isomers (VII; R' = Ph) and (V; R = Ph), respectively, the slow addition of exactly one equivalent of reagent gave the unsymmetrically bridged *cis*-isomers, (IX; R' = Ph, X = Br) and (VIII; R = Ph, X = Br). Similarly prepared were *cis*-[Pt₂BrI(Ph)₂(PPrⁿ₃)₂] and *cis*-[Pt₂Br(AsPh₂)Ph₂(PPrⁿ₃)₂] (XI; Y = I, and Y = AsPh₂). Stepwise replacement of the second bromide ion takes place with retention of configuration except that only *trans*-[Pt₂(SR')₂Ph₂(PPrⁿ₃)₂] (VII) could be obtained from (IX). This is a most curious anomaly since it was in the series of di-*u*-thio-complexes that the formation of the *cis*-isomers (XIII) by stepwise addition of the thiol to [Pt₂Cl₄(PPrⁿ₃)₂] was first observed.³ Thus preparation of the *cis*-isomer of (VII) failed where on the basis of previous experience, it seemed most likely to succeed. *cis*-[Pt₂(PPh₂)(SPh)Ph₂(PPrⁿ₃)₂] (X; R = R' = Ph) could be obtained from either (VIII; R = Ph, X = Br) or (IX; R' = Ph, X = Br); it is noteworthy that although most of these complexes are one of two or three possible isomers, all the preparative reactions appear to be stereospecific and give only one product.

cis-[Pt₂(PPh₂)₂Ph₂(PPrⁿ₃)₂] (XII; R = Ph) was also prepared from (VIII; R = Ph, X = Br) and completes the only *cis*-*trans* pair of the series. It is thermally the less stable isomer, and just above its melting point it resolidifies as the high-melting *trans*-isomer.

The isomerization of such compounds as [PtCl₂(PPrⁿ₃)₂] in solution, induced by a trace of tri-*n*-propylphosphine as catalyst, is believed to occur through an ionic intermediate, *e.g.*, [PtCl(PPrⁿ₃)₃]Cl, and indeed [PtPh₂(PEt₃)₂] does not isomerize in the presence of a trace of triethylphosphine.⁹ Thus it is not surprising that these complexes, having stable phosphido-bridges and terminal phenyl groups, are not isomerized by a trace of the phosphine, and we were unable to find a catalyst which caused isomerization under suitably mild conditions to allow the study of the thermodynamic equilibrium between *cis*- and *trans*-isomers of the phosphido-bridged complexes.

The reason for the stability of certain configurations, *e.g.*, *cis*-[Pt₂Br₂Ph₂(PPrⁿ₃)₂], remains obscure, but the dipole moments uncover some interesting features of the bonding. In the series of unsymmetrically bridged *cis*-isomers, the structural assignments are based on a comparison of the phenylthio- and diphenylphosphido-complexes with their *p*-tolyl analogues. The tertiary phosphine ligands lie at the positive end of the dipole, and as the $\overset{+}{\text{C}}\text{H}_3\text{-}\overset{-}{\text{C}}_{\text{ar}}$ bond moment in (VIII; R = *p*-tolyl, X = Br) serves to reduce the total moment the P(*p*-tolyl)₂ group must be in the *trans*-position to the $\overset{-}{\text{P}}\text{-}\overset{+}{\text{P}}$ bond. On the basis of the similarity in dipole moments and infrared spectra the diphenylarsenido-complex (XI; Y = AsPh₂) may also be assigned to this configuration (*cis*-PBrP). The same argument may be applied to the pair of arylthio-complexes (IX; X = Br, R' = Ph and R' = *p*-tolyl), where sulphur is the ligand atom *trans* to the tertiary phosphine groups. Following the general rule that iodine appears to be

⁹ Chatt and Shaw, *J.*, 1959, 4020.

more negative than bromine in platinum(II) derivatives,⁹ the dipole moment of (VIII; R = Ph, X = I) is lower than that of the corresponding bromide. For this reason, also, *cis*-[Pt₂BrI(Ph₂(PPrⁿ)₂)] (XI; Y = I) likewise belongs to the group of *cis*-PBrP isomers since the dipole is higher than that of both the dibromide (VI; X = Br) and the di-iodide (VI; X = I). Finally the structure of (X; R = R' = Ph) was also confirmed (*cis*-PSP) by synthesis of the *p*-tolyl analogue (X; R = *p*-tolyl, R' = Ph), where the effect of hyperconjugation again reduces the total dipole moment.

The *cis*-isomers discussed above have dipole moments much lower than would be expected on the basis of the moments of mononuclear organic derivatives of platinum(II).⁹ Only *cis*-[Pt₂(PPh₂)₂Ph₂(PPrⁿ)₂] (XII; R = Ph) ($\mu = 6.35$ D) has a moment comparable with that of the corresponding mononuclear complex, *cis*-[PtPh₂(PPrⁿ)₂] ($\mu = 7.15$ D) while in most cases the values are much lower dropping to 4.05 D in *cis*-[Pt₂Br₂Ph₂(PPrⁿ)₂] (VI; X = Br).

These preparations have yielded two related series of *cis*-isomers (VIII) and (XI). Within each series the dipole moments vary differently with respect to the variable groups X and Y and in (XI) show no relation to what would be expected on the basis of the relative negativities of X and Y (see Table I, where X and Y are listed in order of increasing electronegativity).

TABLE I.

Variation of dipole moment with the groups X and Y in the series of compounds (VIII) and (XI).

X or Y	AsPh ₂	PPH ₂	SPh	I	Br	Debye units
in (VIII)	—	6.35	5.95	4.35	4.65	
in (XI)	5.10	4.65	3.95	4.25	4.05	..

In series (VIII), the group X is on the same side of the molecule as the positively charged phosphine ligands and so the dipole moments of the molecules (VIII) should fall as X becomes more electronegative. This is observed except that the bromide (X = Br) has a higher moment than the iodide.

In series (XI), the group Y is on the negative side of the molecule and increased electronegativity of Y should cause the moment to increase. The observed sequence is almost the converse of this, although there are irregularities whereby the SPh compound has the lowest moment, and the iodide a higher moment than the bromide. Evidently, mesomeric effects are very strong in this series (XI) to reverse the sequence expected from the inductive moments in the molecules.

The fact that the moments of the iodide and bromide occur in the wrong sequence according to their electronegativities is general in the complex chemistry of platinum(II),⁹ and of other transition metals having filled non-bonding *d*-orbitals. It might arise because iodine with its greater *trans*-effect repels more negative charges on to the *trans*-ligand atom than does bromine (cf. hydrogen as a ligand¹⁰); or because there is a greater compatibility in size of the *d*-orbitals between platinum and iodine, allowing greater mesomeric drift of electrons from the *d*-orbitals of the platinum atom into those of the iodine atom in spite of its lower electronegativity, or because the larger iodine atom sterically repels the positively charged PR₃ groups in *cis*-positions so increasing their contribution to the molecular dipole moment by angular distortion.⁹ All three effects may operate, but in any case the anomalous sequence of the polarity of the bromide and iodides is not peculiar to the binuclear compounds.

The strong mesomeric effects invoked to explain the low moments might occur through π -type molecular orbitals in the plane of the complex (*xy*) or π -type molecular orbitals above and below the plane. The π -type molecular orbitals in the plane of the complex arise from a combination of the *d*_{xy}-orbitals of the platinum and ligand atoms, and *p*_x- and/or

¹⁰ Chatt, *Proc. Chem. Soc.*, 1962, 318.

p_y -orbitals of the terminal ligand atoms, when these have suitably orientated non-bonding lone pairs. They cannot involve the p_x - or p_y -orbitals of the bridging atoms because those p -orbitals are used in σ -bonding. The π -molecular orbitals of the phenyl group would interact with this π -system only, because the phenyl groups are sterically held perpendicular to the plane of the complex. Molecular models show that rotation about the Pt-Ph bond is completely restricted by the *cis*- PPr^n_3 and PR_2 groups in (VIII), and remains quite limited in the case of the *cis*-bromide (XI; Y = Br). The interaction would probably result in electron withdrawal from the platinum atoms into anti-bonding orbitals of the phenyl groups as in the mononuclear complexes, *cis*- $[\text{PtPh}_2(\text{PR}_3)_2]$.⁹ In the above π -type system there is nothing which does not occur in the similar π -system of mononuclear complexes. As compounds of the types *cis*- $[\text{PtPh}_2(\text{PR}_3)_2]$, *cis*- $[\text{PtClPh}(\text{PR}_3)_2]$, and *trans*- $[\text{PtClPh}(\text{PR}_3)_2]$ and a few corresponding bromides show no gross anomaly in their dipole moments, it seems we must look to the π -type orbitals above and below the molecular plane for the source of the anomalies in the dipole moments of the binuclear complexes.

These molecular orbitals arise from the combination of the d_{xz} -, d_{yz} -, and p_z -orbitals on the platinum and ligand atoms. The new feature, which cannot occur in the mononuclear complexes, is provided by the overlap of orbitals including p -orbitals on adjacent atoms around the four-membered ring perhaps producing a pseudo-aromatic system to which the terminal phosphorus atoms are conjugated through their d_{xz} - or d_{yz} -orbitals.

When PPh_2 or AsPh_2 are bridging groups, the ring π -type system is limited to the overlap of filled d_{xz} -, d_{yz} -, and perhaps vacant high energy p_z -orbitals on the platinum atoms, with vacant d_{xz} - and d_{yz} -orbitals of high energy on the bridging atoms. These altogether contain eight electrons, provided by the platinum atoms. Because of the differences in energy of the sets of orbitals on the two sorts of atoms, mixing will be poor. The electron drift must be from the platinum to bridging atoms and so mesomeric drift from the platinum to terminal phosphorus atoms will be weak and the dipole moments high, comparable with those of corresponding mononuclear complexes.

When sulphur or halogen atoms are bridging groups, the ring π -type orbitals are compounded with greater electrical symmetry from the filled low energy p_z -orbitals and higher energy vacant d_{xz} - and d_{yz} -orbitals on the bridging atoms, and vacant high energy p and filled low energy d_{xz} - and d_{yz} -orbitals on the platinum atoms. These altogether contain 12 electrons, four from the bridging atoms and eight from the platinum atoms. The synergetic effects of electron release in the d -orbitals from the platinum to the bridging atom and from the p -orbitals of the bridging atoms to the platinum atoms will tend to reduce the difference in energy of the π -type orbitals on the two types of atoms so that good mixing may occur giving a pseudo-aromatic system compounded from the six orbitals Pt d_{xz} , d_{yz} , and p_z and S or halogen d_{xz} , d_{yz} , and p_z , with good delocalization of the 12 electrons.

The positively charged terminal PPr^n_3 groups will be conjugated to this system through their d_{xz} - and d_{yz} -orbitals, and will be able mesomerically to withdraw electrons from it. Because of the symmetry of d -orbitals the withdrawal would be expected mainly from the atom in *trans*-position to the terminal phosphorus. This electron withdrawal into the positively charged terminal phosphorus atoms would account for the low dipole moments of the bridged derivatives containing bridging atoms in *trans*-position to the PPr^n_3 groups and having a lone pair of electrons. The moments should be lower, the more readily available are the p -electrons from the bridging groups; thus (XI; Y = SPh) has the lowest moment and highest energy filled p_z -orbital, *i.e.*, most electron releasing p -orbital. When the SPh group or halogen atom occurs in *cis*-position to the PPr^n_3 groups as in (X), electron release to the PPr^n_3 groups may be small, just as in benzene mesomeric effects are not transmitted between *meta*-positions, but our measurements would be insensitive to this, because the electrons would drift mesomerically from the bridging atom on the positive side of the molecule to the phosphorus atoms on the same side. This mesomeric

drift if it occurred would scarcely affect the moment. Thus, in compounds (VIII) moments of inductive origin would appear to be dominant even if strong mesomeric drift to the PPr_3 groups occurred.

The contribution of the filled p_z -orbital to the stability of the ring in these aryl derivatives may be a vital factor with weakly co-ordinating groups in the bridge. We suggest that the chloro-bridged complex (VI; $\text{X} = \text{Cl}$) could not be obtained because the electronegative chlorine atom was not sufficiently forthcoming with its p -electrons, *i.e.*, the energy level of the p_z -orbital was too low for good mixing.

EXPERIMENTAL

Small samples of ether solutions containing known weights of phenyl-lithium were dispensed into glass ampoules under dry nitrogen, sealed, and stored at -20° before use. These reagents were subsequently handled in a nitrogen dry-box, as also were all reaction mixtures containing free phosphines. Samples of lithium diphenylarsenide, lithium diphenylphosphide, and lithium thiophenolate were prepared by admixture of phenyl-lithium (in ether) and an equivalent of the appropriate hydride added as a known volume of a standard solution in benzene. Diphenylarsine and di-*p*-tolylphosphine were prepared according to methods given in refs. 11 and 12. All the compounds were crystalline and sharp-melting, except the series of sulphur compounds (IX). These were generally obtained as well-defined crystals following chromatography but still had wide melting ranges. Melting points (Table 2) were determined on a Kofler apparatus and are corrected. Microanalyses are by the analytical department of the Akers Research Laboratories.

cis-Dichloro(diphenylphosphine)(tri-*n*-propylphosphine)platinum(II), (II; $\text{R} = \text{Ph}$).—Diphenylphosphine (0.64 g.) was added to the tetrachloride (I; $\text{X} = \text{Cl}$) (1.45 g.) in ethanol (40 ml.), and when the orange colour had been dispelled, the solvent was removed from the solution at 10 mm. The product was purified by two recrystallizations from methanol (1.14 g.) (Found: C, 41.4; H, 5.3. $\text{C}_{21}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pt}$ requires C, 41.2; H, 5.2%).

cis-Dichloro(diethylphosphine)(tri-*n*-propylphosphine)platinum(II), (II; $\text{R} = \text{Et}$).—It was obtained from a similar preparation and crystallized as long needles from methanol (Found: C, 30.4; H, 6.3. $\text{C}_{13}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pt}$ requires C, 30.2; H, 6.2%). This derivative of diethylphosphine was stable in solution but that of diphenylphosphine slowly eliminated hydrogen chloride with formation of the phosphido-complex (III; $\text{R} = \text{Ph}$). In general, the binuclear complexes were obtained by reaction of (II), prepared *in situ*, with a base, typically sodium ethoxide.

trans-Dichloro-di- μ -(diphenylphosphido)-bis(tri-*n*-propylphosphine)diplatinum(II) (III; $\text{R} = \text{Ph}$).—A solution in ethanol (400 ml.) of the tetrachloro-compound (I; $\text{X} = \text{Cl}$) (8.4 g.), and diphenylphosphine (3.8 g.) was kept for 1 hr., then sodium ethoxide was added (prepared from 0.48 g. of sodium). After removal of the ethanol by distillation, the crude product was separated from sodium chloride by extraction with benzene and evaporation of the filtered solution. Addition of acetone to the resultant red gum precipitated substantially pure compound (III; $\text{R} = \text{Ph}$) which crystallized (chloroform-acetone) as fine needles (3.9 g.), which were soluble in benzene or chloroform but insoluble in alcohols, acetone, or petroleum. Yields vary in the range 35–45% (Found: C, 43.8; H, 5.4%; M , ebullioscopically in 1.009% benzene solution, 1211. $\text{C}_{42}\text{H}_{62}\text{Cl}_2\text{P}_4\text{Pt}_2$ requires C, 43.8; H, 5.4%; M , 1152).

trans-Dichloro-di- μ -(diethylphosphido)-bis(tri-*n*-propylphosphine)diplatinum(II) (III; $\text{R} = \text{Et}$).—This was obtained from the tetrachloride (2.2 g.) and diethylphosphine (0.48 g.) after reaction with sodium ethoxide (0.35 g.), and the crude product, after removal of sodium chloride, crystallized from methanol (1.0 g.) as prisms (Found: C, 32.5; H, 6.5%; M , ebullioscopically in 0.735% benzene solution, 985. $\text{C}_{26}\text{H}_{62}\text{Cl}_2\text{P}_4\text{Pt}_2$ requires C, 32.5; H, 6.5%; M , 959).

The method was also extended to *trans*-dichloro-di- μ -(diphenylarsenido)-bis(tri-*n*-propylphosphine)diplatinum(II) (IV) which was prepared from the tetrachloride (1.42 g.), diphenylarsine (0.81 g.), and sodium ethoxide (0.27 g.). The complex crystallized from chloroform-acetone (0.27 g.) (Found: C, 40.6; H, 5.0. $\text{C}_{42}\text{H}_{62}\text{As}_2\text{Cl}_2\text{P}_2\text{Pt}_2$ requires C, 40.7; H, 5.0%).

trans-Di- μ -(diphenylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II), (V; $\text{R} =$

¹¹ Cookson and Mann, *J.*, 1947, 618.

¹² Niedergall and Langerfeld, *Ber.*, 1962, 95, 64.

Ph).—A solution in dry benzene (25 ml.) of the compound, (III; R = Ph; 1.07 g.), was added to phenyl-lithium (2.04 mmoles) in ether (3 ml.), and was maintained at reflux for 45 min., after which lithium salts were removed with water. The organic phase was separated, dried, and evaporated to leave a white solid, which was then crystallized from a minimum volume of hot benzene, forming prisms (0.7 g.) (Found: C, 52.9; H, 6.1%; *M*, ebullioscopically in 1.131% benzene solution, 1184. $C_{54}H_{72}P_4Pt_2$ requires C, 52.5; H, 5.9%; *M*, 1235). The compound was also prepared in 10% yield by the reaction of (VI; X = Br) with two equivalents of $LiPPh_2$. Similarly prepared was trans-*di-μ*-(diethylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (V; R = Et), which crystallized as prisms from benzene (70% yield) (Found: C, 43.8; H, 6.9%; *M*, ebullioscopically in 1.185% benzene solution, 1005. $C_{38}H_{72}P_4Pt_2$ requires C, 43.8; H, 6.95%; *M*, 1043).

cis-sym-*Di-μ*-bromo-diphenylbis(tri-*n*-propylphosphine)diplatinum(II), (VI; X = Br).—Phenyl-lithium (1.39 mmoles) in ether (2 ml.) was added dropwise to the tetrabromo-compound, (I; X = Br; 0.65 g.), in benzene (15 ml.) at 20°, during 5 min. and with constant agitation. The reaction mixture, which became very dark during the addition, was kept for 30 min., and then hydrolysed with water. The dried organic layer was stripped of solvent and afforded a dark brown oil from which the product commenced to crystallize on addition of acetone (10 ml.). After 24 hr., the pale solid was recrystallized from acetone (0.19 g.). This material was sufficiently pure to use as starting material for other preparations. Analytically pure material was obtained by chromatography on neutral alumina, benzene being used as eluent. Yields of 30% were obtained from batches of up to 5 g. of tetrabromide (Found: C, 35.5; H, 5.1%; *M*, ebullioscopically in 1.631% benzene solution, 1028. $C_{30}H_{52}Br_2P_2Pt_2$ requires C, 35.2; H, 5.1%; *M*, 1024). It was also obtained by the action of phenylmagnesium bromide on the tetrabromide (23% yield) or on the tetrachloride (I; X = Cl) (21% yield), where all four chloride ions are replaced by two phenyl groups and two bromide ions. However, the reaction between the tetrachloride (I; X = Cl; 0.94 g.) in benzene (15 ml.) and phenyl-lithium (2.44 mmoles) in ether (4 ml.) yielded trans-diphenylbis(tri-*n*-propylphosphine)platinum(II) (XIX), which crystallized from acetone (0.19 g.) (Found: C, 53.4; H, 7.7. $C_{30}H_{52}P_2Pt$ requires C, 53.7; H, 7.8%).

cis-Diphenylbis(tri-*n*-propylphosphine)platinum(II).—This was prepared by the method of Chatt and Shaw¹³ (Found: C, 54.0; H, 7.9. $C_{30}H_{52}P_2Pt$ requires C, 53.7; H, 7.8%).

cis-*PBrP*-sym-*μ*-Bromo-*μ*-iodo-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (XI; Y = I).—The compound (VI; X = Br; 0.214 g.) and sodium iodide (2.08 mmoles) were refluxed in acetone (150 ml.) for 2 hr., after which the solvent was removed and the residue partitioned between benzene and water. The organic layer was dried, and after the benzene had been distilled away, the product crystallized from acetone as plates (Found: C, 33.7; H, 5.0. $C_{30}H_{52}BrIP_2Pt_2$ requires C, 33.6; H, 4.9%). In the same way cis-sym-*di-μ*-iodo-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VI; X = I) was prepared from the bromo-compound (VI; X = Br; 0.319 g.) and sodium iodide (*ca.* 10 mmoles) (Found: C, 32.0; H, 4.7. $C_{30}H_{52}I_2P_2Pt_2$ requires C, 32.2; H, 4.7%).

cis-*PBrP*-sym-*μ*-Bromo-*μ*-(diphenylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VIII; R = Ph, X = Br).—The diphenyl-dibromide (VI; X = Br) was used as the starting material for the preparation of a number of compounds and in each case the method followed closely the synthesis of (VIII; R = Ph, X = Br). Lithium diphenylphosphide was prepared from phenyl-lithium (1.96 mmoles) in ether (2 ml.) and diphenylphosphine (3.60 ml.; 0.544*N*-solution in benzene), and the yellow solution was added dropwise to (VI; X = Br; 2.0 g.) in benzene (40 ml.). This addition was carried out at 20° during 10 min., and with constant agitation after which the solution was kept for 30 min. Water was added and the benzene layer was separated, dried, and evaporated to leave a gummy solid which crystallized from acetone (1.3 g.) (Found: C, 44.7; H, 5.55%; *M*, cryoscopically in 1.71% benzene solution, 1143. $C_{42}H_{62}BrP_3Pt_2$ requires C, 44.6; H, 5.5%; *M*, 1129).

Similarly prepared were:

cis-*PBrP*-sym-*μ*-Bromo-*μ*-(*di-p*-tolylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VIII; R = *p*-tolyl, X = Br) from the diphenyldibromide (VI; X = Br; 0.68 g.) and lithium *di-p*-tolylphosphide (0.661 mmole) in 34% yield after crystallization from ethanol (Found: C, 45.8; H, 5.85. $C_{44}H_{66}BrP_3Pt_2$ requires C, 45.6; H, 5.7%).

¹³ Chatt and Shaw, *J.*, 1959, 705.

cis-PIP-sym- μ -(Iodo- μ -(diphenylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VIII; R = Ph, X = I) by conversion of the corresponding bromide (VIII; R = Ph, X = Br) by metathesis with sodium iodide in acetone solution. The compound crystallizes from acetone (Found: C, 43.2; H, 5.3. $C_{42}H_{62}IP_3Pt_2$ requires C, 42.9; H, 5.3%).

cis-PBrP-sym- μ -Bromo- μ -(diphenylarsenido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (XI; Y = AsPh₂) from the bromo-compound (VI; X = Br; 0.72 g.) and lithium diphenylarsenide (0.700 mmole) in 55% yield after crystallization from ethanol as leaflets (Found: C, 43.2; H, 5.4. $C_{42}H_{62}AsBrP_2Pt_2$ requires C, 43.0; H, 5.3%).

cis-PBrP-sym- μ -Bromo- μ -(phenylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (IX; R' = Ph, X = Br) from the bromo-compound (VI; X = Br; 0.83 g.) and lithium thiophenolate (0.808 mmole) in 40% yield after crystallization from acetone (Found: C, 41.3; H, 5.4%; *M*, cryoscopically in 1.20% benzene solution, 974. $C_{36}H_{57}BrP_2Pt_2S$ requires C, 41.0; H, 5.45%; *M*, 1053). This compound was also obtained by refluxing equivalents of (VII; R' = Ph) and (VI; X = Br) in benzene for 2 hr. The mixture was subjected to chromatography on alumina, benzene being used as eluent, and a single fraction containing only (IX; R' = Ph, X = Br) was collected. This method was also applied to the reaction of (VII; R = *p*-tolyl; 58 mg.) with (VI; X = Br; 53 mg.) to yield *cis*-PBrP-sym- μ -bromo- μ -(*p*-tolylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (IX; R' = *p*-tolyl, X = Br). The product was crystallized three times from chloroform-methanol (42 mg.) (Found: C, 41.1; H, 5.5. $C_{37}H_{59}BrP_2Pt_2S$ requires C, 41.6; H, 5.6%).

cis-PSP-sym- μ -(Diphenylphosphido)- μ -(phenylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (X; R = R' = Ph) from the compound (VIII; R = Ph, X = Br; 0.27 g.) and lithium thiophenolate (0.236 mmole), in 70% yield after crystallization from acetone (Found: C, 49.7; H, 5.8. $C_{45}H_{67}P_3Pt_2S$ requires C, 49.7; H, 5.8%), or from (IX; R' = Ph, X = Br; 0.62 g.) and lithium diphenylphosphide (0.586 mmole) in 43% yield.

cis-PSP-sym- μ -(Di-*p*-tolylphosphido)- μ -(phenylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (X; R = *p*-tolyl, R' = Ph) from the compound (VIII; R = *p*-tolyl, X = Br; 0.40 g.) and lithium thiophenolate (0.344 mmole) in 70% yield after crystallization from ethanol, forming prisms (Found: C, 50.7; H, 6.0. $C_{50}H_{71}P_3Pt_2S$ requires C, 50.6; H, 6.0%).

cis-sym-Di- μ -(diphenylphosphido)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (XII; R = Ph) from (VIII; R = Ph, X = Br; 0.65 g.) and lithium diphenylphosphide (0.606 mmole) in 49% yield after crystallization from benzene-ethanol (Found: C, 52.9; H, 5.85. $C_{34}H_{72}P_4Pt_2$ requires C, 52.6; H, 5.9%).

trans-Di- μ -(phenylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VII; R' = Ph) from (IX; R' = Ph, X = Br; 0.265 g.) and lithium thiophenolate (0.250 mmole) in 39% yield after crystallization from acetone (Found: C, 46.6; H, 5.9%; *M*, cryoscopically in 1.14% benzene solution, 1017. $C_{42}H_{62}P_2Pt_2S_2$ requires C, 46.4; H, 6.1%; *M*, 1083), or from (VI; X = Br; 0.60 g.) and lithium thiophenolate (1.85 mmoles) in 35% yield. The compound was also prepared from either (XIII; R = Ph) or (XIV; R = Ph) by reaction with two equivalents of either phenyl-lithium or phenylmagnesium bromide. *trans*-Di- μ -(ethylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VII; R' = Et) was also obtained from both *cis*- and *trans*-dichlorides (XIII and XIV; R' = Et) by reaction with two equivalents of phenyl-lithium at 20°. The products were crystallized from chloroform-ethanol at -20° and at all times during their manipulation were rigorously protected from possible thermal isomerization (Found: C, 41.2; H, 6.3. $C_{34}H_{62}P_2Pt_2S_2$ requires C, 41.3; H, 6.3%).

Similarly prepared was *trans*-di- μ -(*p*-tolylthio)-diphenylbis(tri-*n*-propylphosphine)diplatinum(II) (VII; R' = *p*-tolyl) (Found: C, 47.6; H, 6.0. $C_{44}H_{66}P_2Pt_2S_2$ requires C, 47.6; H, 6.0%).

Chloro(diphenylphosphido)platinum(II) (XVI; R = Ph).—(I; X = Cl; 0.318 g.) and (III; R = Ph; 0.430 g.) were refluxed in toluene (15 ml.) for 4 hr., after which the precipitate of (XVI) was removed at the centrifuge, washed with benzene, and dried at 0.1 mm. (0.32 g.). No further purification was possible (Found: C, 35.0; H, 3.1. $C_{12}H_{10}ClPPt$ requires C, 34.7; H, 2.4%). The toluene was distilled from the supernatant liquid and the residue of *trans*-dichlorobis(tri-*n*-propylphosphine)platinum(II) was recrystallized from petroleum (b. p. 30–40°) at -20°. It had m. p. and mixed m. p. 84–86°. Compound (XVI; 0.28 g.) was heated under nitrogen with tri-*n*-propylphosphine (4.0 g.) at the boiling point of the latter until a clear solution was obtained. On cooling, long needles of (III; R = Ph) crystallized. These had m. p. 255–258° and were characterized by mixed m. p. and i.r. spectrum.

trans-Dihydrido-di- μ -(diphenylphosphido)-bis(triethylphosphine)diplatinum(II) (XVIII). To

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hydrido-chlorobis(triethylphosphine)platinum(II) (1.0 g.) in benzene (15 ml.) was added diphenylphosphine (2.18 mmoles). After 15 min. ethanol (25 ml.) containing sodium ethoxide [from sodium (50 mgm.)] was added, causing a red coloration. The solvents were immediately removed at *ca.* 15 mm. and the *product* was extracted with a small volume of chloroform. Dilution with methanol (10 volumes) and refrigeration at -20° gave the *complex* (XVIII) as elongated prisms (Found: C, 43.5; H, 5.5%; *M*, cryoscopically in 0.690% benzene solution, 960. $C_{36}H_{52}P_4Pt_2$ requires C, 43.3; H, 5.2%; *M*, 999). Yields were variable and in some experiments a complex having more than two platinum atoms was isolated. In a similar experiment *cis*-dichlorobis(tri-*n*-propylphosphine)platinum(II) (1.0 g.) was treated with diphenylphosphine (1.87 mmoles) in benzene (50 ml.). The yellow solution was kept for 2 days and

TABLE 2.

Melting points and dipole moments in benzene at 25° .

$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	T ^P	E ^P	O ^P	μ
<i>cis</i> -[PtCl ₂ (PPr ⁿ) ₂ (HPhPh ₂)] (II; R = Ph), m. p. 142°.							
3.102	20.83	—	—	—	—	—	—
3.997	20.99	—	(0.53)	2525 *	(129)	2377 *	10.8 *
<i>cis</i> -[PtCl ₂ (PPr ⁿ) ₂ (HPEt ₂)] (II; R = Et), m. p. 208°.							
2.816	25.20	—	—	—	—	—	—
2.989	25.30	—	(0.53)	2551 *	(100)	2437 *	10.9 *
<i>trans</i> -[Pt ₂ Cl ₂ (PPh ₂) ₂ (PPr ⁿ) ₂] (III; R = Ph), m. p. 259°.							
4.242	0.690	—	—	—	—	—	—
4.268	0.695	—	(0.57)	350 *	(285)	22 *	1.05 *
<i>trans</i> -[Pt ₂ Cl ₂ (PEt ₂) ₂ (PPr ⁿ) ₂] (III; R = Et), m. p. 235°.							
2.601	0.761	—	—	—	—	—	—
3.880	0.757	—	(0.57)	304 *	(226)	43.5 *	1.45 *
<i>trans</i> -[Pt ₂ Cl ₂ (AsPh ₂) ₂ (PPr ⁿ) ₂] (IV), m. p. 262°.							
2.330	0.777	—	—	—	—	—	—
3.152	0.758	—	—	—	—	—	—
10.83	—	9.23	—	—	—	—	—
12.53	—	8.69	—	—	—	—	—
4.737	—	—	0.606	—	—	—	—
6.436	—	—	0.590	381.7	262.8	79.5	1.95
<i>trans</i> -[Pt ₂ (PEt ₂) ₂ Ph ₂ (PPr ⁿ) ₂] (V; R = Et), m. p. 247°.							
2.104	0.378	—	—	—	—	—	—
2.650	0.402	—	(0.47)	287 *	(250)	0 *	0 *
<i>trans</i> -[Pt ₂ (PPh ₂) ₂ Ph ₂ (PPr ⁿ) ₂] (V; R = Ph), m. p. 275°.							
2.406	0.434	—	—	—	—	—	—
2.524	0.493	—	(0.47)	357 *	(309)	1 *	0.25 *
<i>trans</i> -[Pt ₂ (SPh) ₂ Ph ₂ (PPr ⁿ) ₂] (VII; R = Ph), m. p. 174°.							
1.613	0.568	—	—	—	—	—	—
2.017	0.533	—	(0.47)	331 *	(257)	35 *	1.3 *
<i>trans</i> -[Pt ₂ (SEt) ₂ Ph ₂ (PPr ⁿ) ₂] (VII; R = Et), m. p. 182.5°.							
2.863	0.629	—	—	—	—	—	—
3.321	0.629	—	(0.47)	316 *	(227)	55 *	1.65 *
<i>trans</i> -[Pt ₂ (S- <i>p</i> -tolyl) ₂ Ph ₂ (PPr ⁿ) ₂] (VII; R = <i>p</i> -tolyl), m. p. 188°.							
3.397	0.551	—	(0.47)	339 *	(266)	34 *	1.3 *

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TABLE 2. (Continued.)

<i>cis</i> -[Pt ₂ (PPh ₂) ₂ Ph ₂ (PPr ⁿ ₃) ₂] (XII; R = Ph), m. p. 198° (resolidifies).							
2·656	3·982	—	—	—	—	—	—
3·403	3·976	—	(0·47)	1175 *	(309)	820 *	6·35 *
<i>cis</i> -[Pt ₂ Br ₂ Ph ₂ (PPr ⁿ ₃) ₂] (VI; X = Br), m. p. 209°.							
2·050	2·092	—	—	—	—	—	—
2·179	2·091	—	—	—	—	—	—
17·51	—	6·61	—	—	—	—	—
22·74	—	6·54	—	—	—	—	—
5·851	—	—	0·637	—	—	—	—
7·294	—	—	0·610	563·4	195·7	338·3	4·05
<i>cis</i> -[Pt ₂ I ₂ Ph ₂ (PPr ⁿ ₃) ₂] (VI; X = I), m. p. 186° (orange).							
2·294	2·043	—	—	—	—	—	—
3·301	2·014	—	—	—	—	—	—
22·27	—	7·55	—	—	—	—	—
7·019	—	—	0·634	—	—	—	—
7·025	—	—	0·636	597·8	216·0	349·4	4·15
<i>cis</i> -[Pt ₂ BrIPh ₂ (PPr ⁿ ₃) ₂] (XI; Y = I), m. p. 197° (orange).							
2·631	2·163	—	—	—	—	—	—
3·014	2·195	—	(0·63)	605 *	(206)	368 *	4·25 *
<i>cis</i> -[Pt ₂ Br(PPh ₂)Ph ₂ (PPr ⁿ ₃) ₂] (VIII; R = Ph; X = Br), m. p. 145°.							
3·841	2·588	—	—	—	—	—	—
4·224	2·582	—	(0·58)	741 *	(259)	444 *	4·65 *
<i>cis</i> -[Pt ₂ Br(P- <i>p</i> -tolyl) ₂ Ph ₂ (PPr ⁿ ₃) ₂] (VIII; R = <i>p</i> -tolyl, X = Br), m. p. 136°.							
2·934	2·150	—	—	—	—	—	—
3·096	2·221	—	(0·58)	672 *	(268)	364 *	4·2 *
<i>cis</i> -[Pt ₂ I(PPh ₂)Ph ₂ (PPr ⁿ ₃) ₂] (VIII; R = Ph, X = I), m. p. 151°.							
2·379	2·292	—	—	—	—	—	—
3·155	2·259	—	(0·61)	693 *	(264)	389 *	4·35 *
<i>cis</i> -[Pt ₂ Br(AsPh ₂)Ph ₂ (PPr ⁿ ₃) ₂] (XI; Y = AsPh ₂), m. p. 151°.							
1·539	2·820	—	—	—	—	—	—
1·856	2·857	—	—	—	—	—	—
15·11	—	8·66	(0·60)	819 *	246	536 *	5·1 *
<i>cis</i> -[Pt ₂ Br(SPh)Ph ₂ (PPr ⁿ ₃) ₂] (IX; R' = Ph, X = Br), m. p. 131—141°.							
1·464	2·039	—	—	—	—	—	—
1·696	2·053	—	(0·58)	584 *	(232)	317 *	3·95 *
<i>cis</i> -[Pt ₂ Br(S- <i>p</i> -tolyl)Ph ₂ (PPr ⁿ ₃) ₂] (IX; R' = <i>p</i> -tolyl, X = Br), m. p. 140—147°.							
1·552	1·667	—	(0·58)	514 *	(237)	241 *	3·45 *
<i>cis</i> -[Pt ₂ (SPh)(PPh ₂)Ph ₂ (PPr ⁿ ₃) ₂] (X; R = R' = Ph), m. p. 159°.							
2·093	3·713	—	—	—	—	—	—
3·002	3·735	—	(0·47)	1047 *	(283)	722 *	5·95 *
<i>cis</i> -[Pt ₂ (SPh)(P- <i>p</i> -tolyl) ₂ Ph ₂ (PPr ⁿ ₃) ₂] (X; R = <i>p</i> -tolyl, R' = Ph), m. p. 149°.							
2·993	3·065	—	—	—	—	—	—
3·056	3·070	—	(0·47)	925 *	(292)	590 *	5·35 *
<i>trans</i> -[Pt ₂ H ₂ (PPh ₂) ₂ (PPr ⁿ ₃) ₂] (XVIII), m. p. 174° (yellow).							
2·291	0·812	—	—	—	—	—	—
2·746	0·814	—	(0·47)	354 *	(238)	81 *	2·0 *
<i>cis</i> -[PtPh ₂ (PPr ⁿ ₃) ₂], m. p. 158°.							
2·581	8·732	—	—	—	—	—	—
2·789	8·860	—	(0·46)	1236 *	(163)	1048 *	7·15 *
<i>trans</i> -[PtPh ₂ (PPr ⁿ ₃) ₂], m. p. 184°.							
1·355	0·360	—	(0·46)	182 *	(163)	— *	0 *

Calc. by using the estimated values of densities and refractivities given in parentheses (see ref. 9).

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then ethanol containing sodium ethoxide [from sodium (40 mg.)] was added. (III; R = Ph) was then isolated (0.15 g.) by the procedure described above and was shown to be identical (mixed m. p. and i.r. spectra) with material obtained by that method.

M. p.s and dipole moments are recorded in Table 2. The last were determined as previously,^{9,10} where the symbols are explained. In general the $\Delta\epsilon$ values became steady after the usual short interval required for the attainment of thermal equilibrium and the pure compounds therefore show no tendency to isomerize in cold benzene solution. The two arylthio-complexes (IX; R' = Ph or R' = *p*-tolyl, X = Br) proved to be exceptional, since $\Delta\epsilon$ was time-dependent and decreased slowly, the initial rate being about 2% per hour. The recorded dipole moments are the initial values.

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