562. *Five-co-ordinate Palladium*(II) *and Platinum*(II)

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Ionic complexes formed by bivalent palladium and platinum in which the metal atom is bonded to four donor atoms from group VA were investigated. The following new compounds have been prepared and studied: $PdX_2,2L$ where for $L = Ph_2P{\cdot}C_2H_4{\cdot}PPh_2$, X = Cl, I, and ClO_4 and for $L = Ph_2As{\cdot}C_2H_4{\cdot}AsPh_2$, X = Cl, Br, and ClO_4; $PtX_2,2L$ where $L = Ph_2P{\cdot}C_2H_4{\cdot}PPh_2$, $Ph_2As{\cdot}C_2H_4{\cdot}AsPh_2$, and X = Cl, Br, NO_3, and ClO_4; and $Pt(NO_3)_2,4Ph_3Sb$. Molar conductivities and conductimetric titrations in non-aqueous solvents indicate that the halides of the arsine complexes show a more pronounced tendency toward ionic association, *e.g.*, $[Pd(diarsine)_2]Cl_2 \rightleftharpoons [PdCl(diarsine)_2]Cl$ than do the corresponding phosphine complexes. Such association was entirely absent from amine complexes. The stibine nitrate exhibited extensive association to a five-co-ordinate complex. It is concluded that the tendency of the ligand donor atoms to confer upon the central atom the ability to engage in pentaco-ordination increases in the sequence N < P < As < Sb.

IN addition to complexes with the familiar square planar configuration of bivalent palladium and platinum, a variety of complexes have been described in which these metals show five- and even six-co-ordination. It was long suspected [1] that palladium forms bonds to six nitrogen atoms in bis-(1,2,3-triaminopropane)palladium(II) iodide. Subsequently, Harris and Nyholm [2] prepared a number of palladium complexes of the di(tertiary arsine), $o\text{-}C_6H_4(AsMe_2)_2$, and showed that many of them contain a five-co-ordinate metal atom in nitrobenzene solution and may be formulated as $[Pd(Diarsine)_2X]Y$. *X*-Ray structure determinations showed $Pd(Diarsine)_2I_2$ to be 6-co-ordinate in the solid state. However, Porai-Koshits and his co-workers [3] have argued that the iodide ions in such compounds are simply close-packed rather than covalently bound to the metal atom. Somewhat later, investigations were extended to platinum(II) which likewise exhibits 5-co-ordination under similar conditions.[4] Chiswell and Livingstone [5] obtained similar results with bisdimethyl-*o*-(methylthio)phenylarsine complexes of platinum. The platinum(II) atom might possibly be regarded as six-co-ordinate even in the ammine known as Wolfram's red salt in which neighbouring $Pt^{II}(EtNH_2)_4$ and $Pt^{IV}(EtNH_2)_4$ groups appear to share a chlorine atom.[6] By using tri- and tetra-arsines and analogous phosphines as ligands, the schools of Venanzi [7,8,9] and Nyholm [10] have induced platinum and palladium to adopt 5-co-ordination, probably in trigonal bypyramidal arrangement. The only five-co-ordinate di(tertiary phosphine) complex so far reported is $[PdCl\{C_6H_4(PEt_2)_2\}_2]Cl$.[11]

Nyholm and his co-workers [2,4,10] have variously suggested effective charge of the central atom, back-bonding to the arsenic atoms, and orbital hydridisation energies as factors which may be predominant in determining the relative tendencies toward association in arsine complexes of nickel, palladium, and platinum. The present Paper describes a comparison of similar amines, phosphines, arsines, and a stibine which affords a further study of these factors.

Palladium Complexes.—The di(tertiary phosphine), 1,2-bisdiphenylphosphinoethane,

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[1] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78.

[2] Harris and Nyholm, *J.*, 1956, 4375.

[3] Porai-Koshits, Bokii, and Kukina, *Zhur. struct. Khim.*, 1961, **2**, 327.

[4] Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

[5] Chiswell and Livingstone, *J.*, 1960, 1071.

[6] Craven and Hall, *Acta Cryst.*, 1961, **14**, 475.

[7] Brewster, Savage, and Venanzi, *J.*, 1961, 3699.

[8] Savage and Venanzi, *J.*, 1962, 1548.

[9] Hartley, Venanzi, and Goodall, *J.*, 1963, 3930.

[10] Barclay, Nyholm, and Parish, *J.*, 1961, 4433.

[11] Chatt, Hart, and Watson, *J.*, 1962, 2537.

and the analogous arsine, 1,2-bisdiphenylarsinoethane, hereinafter designated " diph " and " dias " and referred to as diphosphine and diarsine respectively, reacted readily with alkali tetrachloropalladate to produce [$PdCl_2$(diph)] and [$PdCl_2$(dias)] which were at least partly in the form of salts of the Magnus type. The salts were easily converted into the mononuclear species by a brief heating with 1 : 1 ethanol–hydrochloric acid. The mono-substituted complexes took up a second mol. of diphosphine or diarsine to form deeply yellow-coloured salts. Perchlorate salts were prepared from aqueous solutions of the chlorides by the addition of perchloric acid. The Table lists the molar conductivities of several palladium salts containing nitrogen, phosphorus, and arsenic as ligand donor atoms. Attempts to prepare salts of tetrakistriphenylstibinepalladium(II) were unsuccessful. The solutions of the halides $Pd(dias)_2X_2$ were a strong yellow, which has been suggested as characteristic of palladium–halogen bonds.[2] Solutions of salts of the type $Pd(diph)_2X_2$ are less strongly coloured, the chloride showing only an extremely faint yellow tint at the concentration employed.

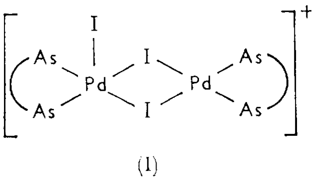
The molar conductivities in nitromethane of the phosphine halides at 5×10^{-4}M shown in the Table are somewhat lower than the value obtained for the perchlorate, a salt which is most likely to be completely dissociated. The values for the most highly dissociated compounds fall in the range 180—205 ohm^{-1} $cm.^{-1}$. In nitromethane, the palladium halide arsine complexes were partially decomposed to the monodiarsinepalladium complexes. This was evident from the marked increase in conductivity which occurred when additional diarsine was added to the solution. No increase was observed for similar additions to $Pd(dias)_2Cl_2$ in methanol and when excess of diphosphine was added to solutions of the phosphine complexes. A very slight drop in specific resistance was accounted for by the inherent conductivity of these complexing agents or traces of impurity in them.

Conductimetric titration of bisdiarsinepalladium(II) perchlorate with tetraethylammonium chloride in nitromethane revealed that there is no stoicheiometric equivalence point. The plot of conductivity against added chloride indicated the existence of competing equilibria, the following being most likely:

$$Pd(dias)_2^{2+} + Cl^- \rightleftharpoons PdCl(dias)_2^{+} \qquad (1)$$

$$2Pd(dias)_2^{2+} + 3Cl^- \rightleftharpoons Pd_2Cl_3(dias)_2^{+} + 2\ dias \qquad (2)$$

The titration with iodide ion shown in Figure 1(*a*) provided an end-point at 1·5 g.-ion of iodide for each g.-atom of palladium taken. The half-integral value indicates that a complex was formed which contained an even number of palladium atoms. The simplest reaction having the correct stoicheiometry is that analogous to (2). The specific conductivity of the solution at the end-point was almost the same as that of the initial solution which is evidence that the product of the reaction, if binuclear, was a uni-univalent electrolyte. The proposed structure (I) contains one 5-co-ordinate palladium atom. A second iodide ion is not added presumably because the remaining single positive charge is insufficient and too diffuse, being shared by the two palladium atoms, to hold another anion. The titration in nitromethane of $[Pd(diph)_2]^{2+}$ with iodide ion shown in Figure 1(*b*) just barely provides evidence of association, a result which is consonant with the high molar conductivity of $Pd(diph)_2I_2$.



(I)

In methanol the compounds $Pd(diph)_2X_2$ exist as bi-univalent electrolytes but the arsine complexes behave essentially as uni-univalent electrolytes, the bromide having a conductivity close to the expected value of about 80 ohm^{-1} $mole^{-1}$ for such salts. The characteristic molar conductivities of strong electrolytes in methanol are about the same as in nitromethane at a concentration of 5×10^{-4}M.

Platinum Complexes.—The diarsine and diphosphine react with alkali tetrachloroplatinate(II) to produce salts of the Magnus type which are converted slowly into the mononuclear species [$PtCl_2$(dias)] and [$PtCl_2$(diph)] by treatment with boiling ethanol–hydrochloric

Molar conductivities of complexes in various solvents

		Molar conductivity (ohm^{-1}) at 25° ($C = 5 \times 10^{-4}$M)		
		in MeOH	in $MeNO_2$	
$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2](ClO_4)_2$	I			46·2 [a]
$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl]Cl$	II			25·7 [a]
$Pd(C_5H_5N)_4Cl_2$	III	Insol.	4 [b]	
$Pd(diph)_2(ClO_4)_2$	IV	Insol.	195	
$Pd(diph)_2Cl_2$	V	167	164	
$Pd(diph)_2Br_2$	VI	171	162	
$Pd(diph)_2I_2$	VII	174	169	
$Pd(dias)_2(ClO_4)_2$	VIII	Insol.	188	
$Pd(dias)_2Cl_2$	IX	111	41 [c]	
$Pd(dias)_2Br_2$	X	86	55 [c]	
$Pt(C_5H_5N)_4(ClO_4)_2$	XI	Insol.	203	
$Pt(C_5H_5N)_4Cl_2$	XII	193	Insol.	
$Pt(diph)_2(NO_3)_2$	XIII	185	205	
$Pt(diph)_2(ClO_4)_2$	XIV	Insol.	194	
$Pt(diph)_2Cl_2$	XV	185	204	
$Pt(diph)_2Br_2$	XVI	185	190	
$Pt(dias)_2(NO_3)_2$	XVII	176	179	
$Pt(dias)_2(ClO_4)_2$	XVIII	Insol.	180	
$Pt(dias)_2Cl_2$	XIX	157	95	
$Pt(dias)_2Br_2$	XX	152	104	
$Pt(SbPh_3)_4(NO_3)_2$	XXI	132		117 [d]

[a] In nitrobenzene. Value from ref. 2. [b] Complex decomposed to non-electrolyte. [c] Complex decomposed, see text. [d] Measurement in dimethylformamide as insoluble in $MeNO_2$.

acid. The bis-substituted salts are more stable than the corresponding palladium compounds and unlike these may be handled without dissociation of neutral ligand in solvents of only medium polarity. The molar conductivities of the platinum complexes are shown in the Table.

Tetrapyridineplatinum(II) chloride is a strong bi-univalent electrolyte in methanol and a titration of the perchlorate salt with iodide ion in nitromethane shows no inflexion. Even though the halides are insoluble in this solvent, there was no precipitation during the reaction. Similarly all four salts of the bisdiphosphineplatinum ion are bi-univalent electrolytes in methanol and nitromethane. However, titration of the nitrate salt in the latter solvent revealed a slight inflexion at 1·5 g.-ions of added iodide ion which suggests an equilibrium analogous to (2) but lying rather far to the left.

The bis-diarsineplatinum(II) halides exhibit molar conductivities in methanol which are significantly lower than that of the corresponding nitrate and in nitromethane the values are closer to those characteristic of uni-univalent salts. Titration of bis-diarsineplatinum(II) nitrate with tetraethylammonium chloride in nitromethane revealed a pronounced end-point at 1·0 g.-ion.

Attempts to prepare 1,2-bisdiphenylstibinoethane were unsuccessful so recourse was had to a triphenylstibine complex of platinum. The bis(triphenylstibine)dichloroplatinum complex was substituted further by triphenylstibine when the chloride was removed by the addition of silver nitrate, giving tetrakis(triphenylstibine)platinum(II) nitrate. The compound dissolved only sparingly in nitromethane but readily in dimethylformamide. Its molar conductivity in this solvent was very much lower than those (150—170 ohm^{-1}) found for other nitrates and perchlorates and was unaffected by adding triphenylstibine to the solution. The conductivity in methanol is very low for a nitrate. A titration in methanol with chloride ion gave a sharp end-point at one equivalent. This is ambiguous in that the reaction may have consisted of chloride-ion substitution of one stibine molecule. The non-linear plot of molar conductance μ against the square-root of concentration for methanol solutions shown in Figure 2 is characteristic for a weak electrolyte above a concentration of 4×10^{-4}M. The dropping away at lower concentration was verified by a duplicate determination of the curve on a different sample and is undoubtedly due to loss of stibine. Ion-pairing is very extensive at a concentration of 10^{-3}M.

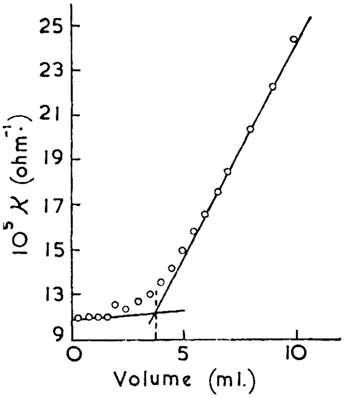


FIGURE 1(*a*). Conductimetric titration of $[Pd(dias)_2](ClO_4)_2$ (25 ml. of 5×10^{-4}M solution) with $(C_2H_5)_4NI$ (5×10^{-3}M) in nitromethane. Broken line shows calculated equivalence point

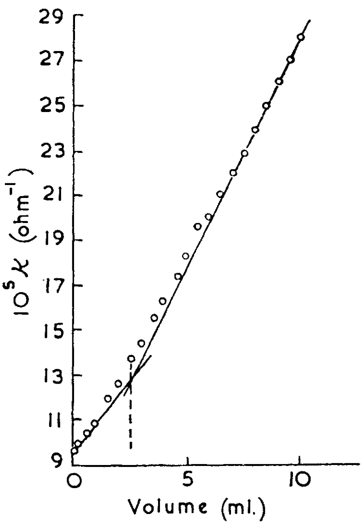


FIGURE 1(*b*). Conductimetric titration of $[Pd(diph)_2](ClO_4)_2$ (25 ml. of 5×10^{-4}M solution) with $(C_2H_5)_4NI$ (5×10^{-3}M) in nitromethane. Broken line shows calculated equivalence point

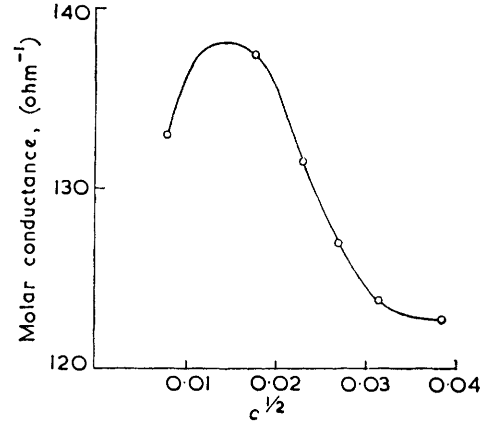


FIGURE 2. Plot of molar conductance of $[(Ph_3Sb)_4Pt](NO_3)_2$ in methanol against (concentration)$^{-2}$

DISCUSSION

The greater tendency, previously observed, on the part of palladium(II) to form 5-co-ordinate species is seen to apply to diphosphine complexes as well as to those of diarsine. The influence of ligand donor atoms in promoting five-co-ordination increases in the order $N < P < As < Sb$ for the types of ligand used in the present study. Nitrogen showed no such tendency while antimony promoted five-co-ordination in platinum to such a high degree that even the nitrate was largely in the associated form. Chatt and his co-workers have demonstrated the effect of the electronegativity of ligand donor atoms upon the effective charge on platinum(II) and palladium(II) atoms [12] as indicated by changes in the N–H stretching frequency of a co-ordinated amine. The controlling factor in the present phenomenon is clearly not a simple inductive effect governing the coulombic attraction of the anion by the central atom for this should be greatest for nitrogen-containing complexes, rather than least.

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[12] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

The suggestion has been made [10] that since the separation between the outer atomic orbitals of free atoms increases with increasing effective nuclear charge, it should be more difficult to hybridise the additional *p*-orbital in going from dsp^2 to dsp^3 hybridisation when the charge on the central atom of a complex is increased. The high electronegativity of nitrogen should therefore favour four-co-ordination in amine complexes whereas dsp^3 hybridisation may be increasingly permitted by the less electronegative donor atoms. However, it is difficult to see why the enhanced coulombic effect of increased charge would not outweigh the reorganisation energy as it apparently does in forming four-co-ordinate complexes from the free ions. Thus, even though the effective nuclear charge of platinum is greater than that of palladium, the total bond energy in $PtCl_4^{2-}$ is estimated to be some 22 kcal. mole^{-1} greater than that of $PdCl_4^{2-}$ the heats of formation of K_2PdCl_4 and K_2PtCl_4 [13] being used, with the assumption that the lattice energies of the salts, *i.e.*, the heats of the reactions $2K^+ \text{ (gas)} + [MCl_4^-]\text{(gas)} \longrightarrow K_2[MCl_4]\text{(cryst.)}$ are equal.

An alternative explanation is to be found by assuming that the Group V donor atoms engage in π-bonding with the metal atom to an increasing extent in going from nitrogen to antimony. There is no certain evidence of this but evidence [14] was given for a corresponding trend down the series of halogens. Also, dipole moments of the molecules *cis*-$PtCl_2L_2$, where L is R_3P, R_3As, or R_3Sb, do not increase in this order as expected when electron drift in the σ-bonds alone is considered.[15] A parallel increase in back-donation could result in the near constancy in the dipole moments.

Substitution in the direction N ⟶ Sb should weaken the σ-bonding. It follows that σ-bonding should be most important for lighter donor atoms and π-bonding relatively of more importance with the heavier ones. If a negatively charged anion is now added to a fifth co-ordination position to form a tetragonal pyramidal complex, the resultant reduction in the charge on the central atom will raise the energy of σ-bonding orbitals (a_{1g}, b_{1g}, e_u) and lower that of π-bonding orbitals (e_g, b_{2g}) to the original four ligand atoms. In the case that σ-bonding is much more important than π-bonding, this effect will destabilise the complex and the addition of a fifth ligand will occur to a relatively small extent, if at all. If, on the other hand the σ-bonding is weak, the further weakening (increase in energy) resulting from an increased co-ordination would necessarily be proportionately small and may be offset by the effect of adding the new electron pair to the complex and by strengthening of the π-bonds. The a_{1g} orbital will be raised very much in energy upon adding the new ligand but at the same time the a_{2u} orbital becomes bonding. It appears that in this way it is possible for halide ions to be bonded more firmly in solution to the less electronegative complexes. Adams *et al.*[16] have shown recently that the metal–chlorine assymmetric stretching frequency in complexes of the type *trans*-$PtCl_2L_2$ is practically independent of L where L is a ligand containing N, P, As, or Sb. The frequency is very dependent upon L in the corresponding *cis* complexes, however. This may be taken as support for the present contention that decreasing the electronegativity of the basal ligands does not necessarily result in a " loosening " of an apical acido-group.

The arsine perchlorates have a lower molar conductivity than the phosphine perchlorates. The same relation obtains between the nitrate salts of platinum arsine and phosphine. Thus the metal arsine cations have a slightly smaller mobility than the corresponding metal phosphines. As the *X*-ray diffraction patterns of the crystalline compounds reveal that the ionic sizes are identical to within experimental error in all four cases, the difference suggests that there is either some ion-pairing or that solvent molecules are actually more strongly bound to the arsines. In either case the observation is in agreement with the general tendency toward 5-co-ordination.

Livingstone and Wheelahan [17] recently demonstrated that bisdipyridylplatinum(II) or

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[13] Biltz and Grimm, *Z. anorg. Chem.*, 1925, **145**, 63.
[14] Westland and Westland, *Canad. J. Chem.*, 1961, **39**, 324.
[15] Chatt and Wilkins, *J.*, 1952, 4300.
[16] Adams, Chatt, Garrett, and Westland, *J.*, 1964, 734.
[17] Livingstone and Wheelahan, *Austral. J. Chem.*, 1964, **17**, 219.

bis-(1,10-phenanthroline)platinum(II) ion tends to form an ion pair with chloride ion. This is in contrast to the behaviour of the tetrapyridineplatinum(II) ion and leads to the conclusion that the enforced planarity of the dipyridyl group promotes back-bonding much more than pyridine which is free to rotate about the metal–nitrogen bond axis.

EXPERIMENTAL

Conductance measurements were carried out with an a.c. bridge on compounds dissolved in dried solvents and the values obtained were corrected for the conductivity of the pure solvents. Microanalyses were performed by Dr. C. Daessle, Montreal.

*Dichloro-*1,2-*bisdiphenylphosphinoethanepalladium,* $[PdCl_2\{C_2H_4(PPh_2)_2\}]$.—Potassium tetrachloropalladate(II) (10 g.) in dimethylformamide (100 c.c.) was treated with diphosphine, $C_2H_4(PPh_2)_2$ (12·2 g., 1 mol.) in methylene chloride (60 c.c.). Upon warming, the solution turned yellow and a solid formed upon dilution with water. Recrystallisation by dissolving in dimethylformamide and diluting with ether gave the white *product* (15 g.), m. p. >360° (Found: C, 54·0; H, 4·4. $C_{26}H_{24}Cl_2P_2Pd$ requires C, 54·2; H, 4·2%).

Di-(1,2-*bisdiphenylphosphinoethane*)*palladium Dichloride* (V).—The compound $[PdCl_2\{C_2H_4(PPh_2)_2\}]$ (1·5 g.) in hot dimethylformamide (25 c.c.) was treated with the diphosphine (1·04 g., 1 mol.). The solution immediately turned deep yellow and precipitation began. Ether was added to further the precipitation and the solid so formed was recrystallised from dimethylformamide to yield a white *dichloride* (1·0 g.), m. p. 283—300° (Found: C, 63·6; H, 5·1. $C_{52}H_{48}Cl_2P_4Pd$ requires C, 64·1; H, 5·0%).

Di-(1,2-*bisdiphenylphosphinoethane*)*palladium Dibromide* (VI).—The compound $[PdCl_2\{C_2H_4(PPh_2)_2\}]$ (2·0 g.) in warm dimethylformamide (25 c.c.) was treated with $BaBr_2$ (1·15 g., 1 mol.) in dimethylformamide (15 c.c.). Upon adding ether to the resultant solution crystals were formed which were separated and washed with water to remove $BaCl_2$. The residue was recrystallised by dissolving in dimethylformamide and adding ether. The solid so obtained (2·1 g.) was dissolved in hot dimethylformamide (50 c.c.) and the diphosphine (1·26 g., 1 mol.) added. A deep yellow solution was formed from which a fine yellow precipitate began to separate upon cooling. Precipitation was furthered by the addition of ether. Recrystallisation from 1 : 1 benzene–ethanol yielded the *dibromide* (2·7 g.), m. p. 247—249·5° (Found: C, 58·8; H, 4·6. $C_{52}H_{48}Br_2P_4Pd$ requires C, 58·7; H, 4·55%).

Di-(1,2-*bisdiphenylphosphinoethane*)*palladium Di-iodide* (VII).—A solution of (V) in ethanol was added to a large excess of sodium iodide in water. The yellow precipitate which formed was collected, washed with water, and recrystallised from 1 : 1 ethanol–water to give the pure *di-iodide,* m. p. 281·5—284·5: (Found: C, 54·0; H, 4·6. $C_{52}H_{48}I_2P_4Pd$ requires C, 54·0; H, 4·2%).

Di-(1,2-*bisdiphenylphosphinoethane*)*palladium Diperchlorate* (IV).—A solution of the chloride $[Pd\{C_2H_4(PPh_2)_2\}_2]Cl_2$ in ethanol was added to an excess of dilute perchloric acid. The precipitate which formed was collected, washed with water, and dried at 100° under vacuum giving a quantitative yield of the *perchlorate,* m. p. 328—333° (decomp.) (Found: C, 56·6; H, 4·4. $C_{52}H_{48}Cl_2O_8P_4Pd$ requires C, 56·7; H, 4·4%).

*Dichloro-*1,2-*bisdiphenylarsinoethanepalladium,* $[PdCl_2\{C_2H_4(AsPh_2)_2\}]$.—Potassium tetrachloropalladate(II) (4·05 g.) in dimethylformamide (100 c.c.) was heated with the diarsine (6·0 g., 1 mol.) in methylene chloride (20 c.c.) and concentrated hydrochloric acid (100 c.c.). The reaction yielded a fine yellow precipitate which recrystallised twice from dimethylformamide to give the *complex* (5·2 g.) as bright yellow crystals, m. p. >340° (Found: C, 47·2; H, 3·5. $C_{26}H_{24}As_2Cl_2Pd$ requires C, 47·1; H, 3·6%).

Di-(1-2-*bisdiphenylarsinoethane*)*palladium Dichloride* (IX).—The complex $[PdCl_2\{C_2H_4(AsPh_2)_2\}]$ (2·5 g.) in hot dimethylformamide (5 c.c.) was treated with diarsine (1·8 g., 1 mol.) in methylene chloride (5 c.c.). The mixed solutions immediately became orange and upon cooling in ice a yellow solid separated. The *product* (1·45 g.), recrystallised from methanol, had m. p. 231—250° (decomp.). It was decomposed when a large volume of ether was used to aid crystallisation to give monosubstituted compound and free diarsine (Found: C, 63·6; H, 5·1. $C_{52}H_{48}As_4Cl_2Pd$ requires C, 64·1; H, 5·0%).

Di-(1,2-*bisdiphenylarsinoethane*)*palladium Dibromide* (X).—The chloro-complex $[PdCl_2\{C_2H_4(AsPh_2)_2\}]$ (1·0 g.) was treated in a manner analogous to that followed in the preparation of the phosphine salt (VI). The product (0·49 g.), recrystallised from methanol, had m. p. 210—225° (decomp.) (Found: C, 50·7; H, 4·2. $C_{52}H_{48}As_4Br_2Pd$ requires C, 50·4; H, 3·9%).

Di-(1,2-*bisdiphenylarsinoethane*)*palladium Diperchlorate* (VIII).—Prepared similarly to (IV) from $[Pd\{C_2H_4(AsPh_2)_2\}_2]Cl_2$, the *compound* decomposed at 338·5° (Found: C, 48·9; H, 3·8. $C_{52}H_{48}As_4Cl_2O_8Pd$ requires C, 48·9; H, 3·8%).

Dichloro-1,2-*bisdiphenylphosphinoethaneplatinum* $[PtCl_2\{C_2H_4(PPh_2)_2\}]$.—Sodium tetrachloroplatinate(II) (4 g.) in ethanol was treated with diphosphine (3·5 g., 1 mol.) in methylene chloride. A pink precipitate formed immediately which was collected and washed with water. The solid was heated with equal volumes of concentrated hydrochloric acid and ethanol under reflux for 4 hr. whereupon a white complex was formed. The residue was separated, washed with ethanol, and recrystallised from hot dimethylformamide by the addition of equal volumes of light petroleum and diethyl ether to provide the pure *product* (3·0 g.), m. p. >360° (Found: C, 46·7; H, 3·7. $C_{26}H_{24}Cl_2P_2Pt$ requires C, 47·0; H, 3·6%).

Di-(1,2-*bisdiphenylphosphinoethane*)*platinum Dichloride* (XV).—The compound $[PtCl_2\{C_2H_4(PPh_2)_2\}]$ (2·8 g.) in dimethylformamide (60 c.c.) was treated with diphosphine (1·7 g., 1 mol.) in chloroform (10 c.c.). A few c.c. of water were added to clarify the solution and methanol (75 c.c.) was added followed by diethyl ether (700 c.c.). A precipitate was formed which was recrystallised from hot dimethylformamide by the addition of methanol to give the *dichloride* (4·3 g.). It was dried at 100° under vacuum and had m. p. 268·5—272° (Found: C, 59·0; H, 4·5. $C_{52}H_{48}Cl_2P_4Pt$ requires C, 58·8; H, 4·55%).

Di-(1,2-*bisdiphenylphosphinoethane*)*platinum Dibromide* (XVI).—The chloride $[Pt\{C_2H_4(PPh_2)_2\}_2]Cl_2$ (2·0 g.) in water (100 c.c.) was passed down a column of Dowex 1 ion-exchange resin in the bromide form. The effluent was evaporated and the residue recrystallised from hot dimethylformamide and dried under vacuum at 100° to give pure *dibromide* (1·5 g.), m. p. 301—316° (Found: C, 54·0; H, 4·3. $C_{52}H_{48}Br_2P_4Pt$ requires C, 54·2; H, 4·2%).

Di-(1,2-*bisdiphenylphosphinoethane*)*platinum Dinitrate* (XIII).—The compound $[Pt\{C_2H_4(PPh_2)_2\}_2]Cl_2$ (1·0 g.) in hot water (50 c.c.) was treated with potassium nitrate (0·2 g.) in water (5 c.c.). The immediate precipitate was collected, washed with water, and dried at 100° under vacuum to yield the *dinitrate* (0·82 g.), m. p. 310—311° (decomp.) (Found: C, 56·7; H, 4·6. $C_{52}H_{48}N_2O_6P_4Pt$ requires C, 56·0; H, 4·3%).

Di-(1,2-*bisdiphenylphosphinoethane*)*platinum Diperchlorate* (XIV).—Prepared similarly to the palladium analogue (IV), the *perchlorate* had m. p. 367° (Found: C, 52·1; H, 4·1. $C_{52}H_{48}Cl_2O_8P_4Pt$ requires C, 52·4; H, 4·1%).

Dichloro-1,2-*bisdiphenylarsinoethaneplatinum*, $[PtCl_2\{C_2H_4(AsPh_2)_2\}]$.—Prepared as for $[PtCl_2\{C_2H_4(PPh_2)_2\}]$ from 2·2 g. of sodium tetrachloroplatinate(II), the *product* (2·2 g.) had m. p. 331—335° (decomp.), and formed glistening white platelets (Found: C, 41·0; H, 3·4. $C_{26}H_{24}As_2Cl_2Pt$ requires C, 41·5; H, 3·2%).

Di-(1,2-*bisdiphenylarsinoethane*)*platinum Dichloride* (XIX).—The compound $[PtCl_2\{C_2H_4(AsPh_2)_2\}]$ (0·7 g.) in dimethylformamide (10 c.c.) was added to the diarsine (0·45 g., 1 mol.) in chloroform (3 c.c.), whereupon a yellow colour appeared immediately. An equal volume of ethanol followed by light petroleum (b. p. 60—80°, 100 c.c.) gave slowly a white precipitate, which was recrystallised from dimethylformamide to give the pure *dichloride* (0·6 g.), m. p. 200—200·5° (Found: C, 50·2; H, 3·9. $C_{52}H_{48}As_4Cl_2Pt$ requires C, 50·4. $C_{52}H_{48}As_4Cl_2Pt$ requires C, 50·4; H, 3·9%).

Di-(1,2-*bisdiphenylarsinoethane*)*platinum Dibromide* (XX).—This was prepared in 42% yield from the chloro-complex $[PtCl_2\{C_2H_4(AsPh_2)_2\}]$ in a manner analogous to the preparation of (VI) except that the final recrystallisation was from dimethylformamide. The *dibromide* consisted of white crystals, m. p. 210·5—212° (Found: C, 47·2; H, 3·7. $C_{52}H_{48}As_4Br_2Pt$ requires C, 47·05; H, 3·6%).

Di-(1,2-*bisdiphenylarsinoethane*)*platinum Dinitrate* (XVII).—This *compound*, prepared in 70% yield as for the phosphine analogue (XIII), was a white powder, m. p. 292—295° (Found: C, 48·2; H, 3·7. $C_{52}H_{48}As_4N_2O_6Pt$ requires C, 48·4; H, 3·7%).

Di-(1,2-*bisdiphenylarsinoethane*)*platinum Diperchlorate* (XVIII).—This *product*, prepared in quantitative yield as for (IV), was a white powder, m. p. 314·5° (decomp.) (Found: C, 45·8; H, 3·7. $C_{52}H_{48}As_4Cl_2O_8Pt$ requires C, 45·7; H, 3·5%).

Tetrakis(*triphenylstibine*)*platinum Dinitrate* (XXI).—Dichlorobis(triphenylstibine)platinum (1·0 g.) and triphenylstibine (0·73 g., 2 mol.) in acetone (50 c.c.) were shaken with finely ground

$AgNO_3$ (0·395 g., 2 mol.). The resulting precipitate was separated and the solution evaporated under reduced pressure to give a cream-coloured *product* (0·21 g.) twice recrystallised from ethanol. It had m. p. 147—151° (decomp.) (Found: C, 49·85; H, 3·6. $C_{72}H_{60}N_2O_6PtSb_4$ requires C, 49·95; H, 3·5%).

I thank Mrs. A Strickland, Mrs. J. Pluščec, and Mrs. O. Vitorovič for experimental assistance. The work was supported by the National Research Council (Canada).

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[*Received, April* 15*th*, 1964.]