

351. *The Constitution of Complex Metallic Salts. Part XIX.* The 2-Phenylisophosphindoline Derivatives of Platinum(II), Palladium(II), and Nickel(II).*

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2-Phenylisophosphindoline shows a marked ability to combine with halides of transitional metals to form complexes in which the metal shows an unusual co-ordination number. The phosphine will combine with the dihalides of the metals named in the title to form (a) normal compounds, $[(R_3P)_2MX_2]$ (M = metal, X = halogen, R_3P = isophosphindoline molecule), and (b) compounds of type $(R_3P)_3MX_2$. The study of the tris(phosphine) palladium compounds in particular is complicated by the existence of the dichloro- and dibromo-members in isomeric and readily interconvertible forms. Crystallographic evidence shows that one of the dibromo-members has a covalent structure, $[(R_3P)_3PdBr_2]$, although this and other members in certain solvents act as salts, $[(R_3P)_3PdX]X$. There is some evidence that the dibromo- and di-iodo-platinum(II) members can have a similar covalent structure, although also acting as salts in solution. The stable dihydrated dichloro- and dithiocyanato-members almost certainly have the structure $[(R_3P)_3(H_2O)_2PtX]X$, in which the platinum shows a co-ordination number of 6. The nickel compounds are unstable in solution, and their structure in the crystalline state awaits investigation.

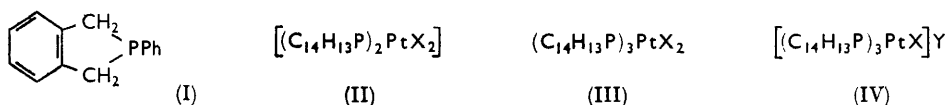
2-PHENYLISOPHOSPHINDOLINE (I) was first prepared by Mann, Millar, and Stewart¹ by a synthesis giving only a 4% yield; the phosphine available was sufficient to show that it

* Part XVIII, Mann and H. R. Watson, *J.*, 1958, 2772.

¹ Mann, Millar, and Stewart, *J.*, 1954, 2832.

combined with palladium dihalides to give normal covalent derivatives (V; X = Cl or I) and a second type of derivative which could not be adequately investigated. A greatly superior synthesis of the phosphine (I)² enabled the palladium dihalide derivatives to be investigated in detail. It was shown³ that the second type of derivative was a tris-(phosphine)dihalogenopalladium, of which the dichloro-form existed in two colourless and one orange dihydrates (VI) and one red monohydrate, the dibromo-form in orange and red (solvent-free) isomers (VIII), and the di-iodo-form in one crimson form (X). This investigation has now been extended to the derivatives of bivalent platinum, palladium, and nickel, which are most conveniently discussed in this order.

The phosphine (I) (2 equivalents) reacts with potassium tetrachloroplatinate(II) in aqueous ethanol to give an insoluble precipitate, undoubtedly the salt $[(C_{14}H_{13}P)_4Pt][PtCl_4]$, which undergoes rearrangement to the colourless crystalline bis(phosphine)dichloroplatinum (II; X = Cl). This compound, when treated in aqueous acetone with a solution

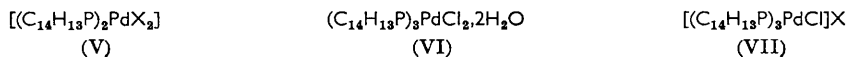


of the appropriate sodium salt, affords the corresponding dibromo-, di-iodo-, and dithiocyanato-compounds (II; X = Br, I, or SCN). All these compounds are colourless except the yellow di-iodo-compound (II; X = I), all are solvent-free and give non-conducting solutions in nitrobenzene; the dichloro- and dibromo-members give normal molecular weights in dichloromethane solution.

Each of these compounds in hot acetone solution combines with a third molecule of the phosphine to give tris(phosphine) compounds of type (III). The colourless dichloro- and dithiocyanato-members (III; X = Cl or SCN) form dihydrates which cannot be dehydrated without loss of phosphine; the colourless dihydrated dibromo-member is converted in boiling benzene into the yellow anhydrous compound; the deep orange di-iodo member is solvent-free.

The dibromo-member (III; X = Br), both hydrated and anhydrous, and the di-iodo-member show normal molecular weights in dichloromethane solution at 29°, and are therefore apparently not ionised in this solvent. All four members, however, give solutions in nitrobenzene having molar conductivities, Λ_m , of 20.9—23.2 mhos at 23°; these are normal values for uni-univalent salts. Further, the three dihalogeno-members (III; X = Cl, Br, or I) in ethanolic solution react with sodium picrate and with sodium perchlorate to give salts such as (IV; X = Cl, Y = C₆H₂N₃O₇) and (IV; X = Cl, Y = ClO₄), which also give nitrobenzene solutions having conductivities in the range 22.0—29.7 mhos. It is clear therefore that in certain solvents these tris(phosphine) compounds can act as salts of the general type (IV). Their probable structure is discussed below.

Palladium dihalides when treated with the phosphine (2 equivalents) also give "normal" compounds of type (V). These are analogous to the platinum(II) compounds (II), but each member is darker in colour than its platinum(II) analogue; thus, the bis(phosphine)-dichloropalladium (V; X = Cl) is yellow and the dibromo-member is yellowish-orange;



the di-iodo-member (V; X = I) forms deep orange plates, when prepared by the dissociation in cold benzene of the tris(phosphine)di-iodopalladium (X) described below. The dinitro-member (V; X = NO₂) forms very pale greenish-yellow (almost colourless) crystals.

² Mann, Millar, and H. R. Watson, *J.*, 1958, 2516.

³ Mann and H. R. Watson, *Chem. and Ind.*, 1958, 1264.

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The phosphine (3 equivalents) reacts with potassium tetrachloro- and tetrabromopalladate(II) to give various isomeric forms under specific conditions (see Experimental section), which can be briefly summarised.

The Colourless Dichloride Dihydrate (VI), m. p. 140°.—The addition of the phosphine in hot ethanol to hot aqueous potassium tetrachloropalladate(II) ultimately gives a colourless dihydrated tris(phosphine) derivative (VI), m. p. 140°, which is also formed by combination of the phosphine (1 equivalent) with the dichloro-compound (V; X = Cl), a process which is reversed when compound (VI) is heated in a vacuum. The compound (VI) can be recrystallised unchanged from methanol, ethanol, and acetone, although the solutions in these solvents are yellow; no dissociation apparently occurs under these conditions, for the compounds (V; X = Cl) and (VI) are, respectively, only very slightly, and fairly freely, soluble in these solvents. However, the addition of ether to the three solutions causes dissociation with precipitation of the dichloro-compound (V; X = Cl). The addition of aqueous potassium tetrachloropalladate(II) (0.5 mol.) to an aqueous ethanolic solution of the compound (VI), m. p. 140°, gives an immediate pale buff precipitate, probably the salt $[(C_{14}H_{13}P)_3ClPd]_2[PdCl_4]$, which is rapidly converted into the dichloro-compound (V; X = Cl). Furthermore, an ethanolic solution of the compound (VI) when treated with aqueous sodium perchlorate gives a colourless crystalline chloro-perchlorate monohydrate (VII; X = ClO₄), and with ethanolic sodium picrate gives a yellow chloro-picrate monohydrate (VII; X = C₆H₂N₃O₇). Nitrobenzene solutions of the dichloride, the chloro-perchlorate, and the chloro-picrate had conductivities 18.3, 24.0, and 19.7 mhos, respectively. These results show that the dichloro-compound, m. p. 140°, can act in solution as a salt of type (VII); they give no evidence, however, to show that these "mixed" salts are true derivatives of the colourless solute or of the yellow product which is always present in its solutions.

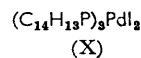
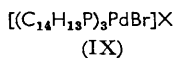
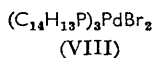
The Colourless Chloride Dihydrate (VI), m. p. 219°.—When a warm solution of the dichloride, m. p. 140°, in aqueous ethanol was treated with aqueous potassium or lithium chloride and cooled, the dichloride separated unchanged; treatment of the warm solution with dilute hydrochloric acid, however, caused the yellow colour to fade considerably, with the deposition of a colourless isomer (VI), m. p. 219° (decomp.). This form can be recrystallised from ethanolic hydrochloric acid, but attempted recrystallisation from aqueous ethanol gives the form of m. p. 140°. The stability of the high-melting form in solution is apparently dependent on the presence of hydrochloric acid.

The Orange Chloride Dihydrate (VI), m. p. 130—131°.—The dichloro-compound, m. p. 140°, is highly soluble in chloroform, giving red solutions which, when diluted with ether, rapidly precipitate a third dihydrated isomer as orange crystals, m. p. 130—131° (melting to a red liquid, the process reversing on cooling); the crystals give a yellow-orange "streak." Warm solutions of this form, in solvents other than chloroform, deposit the colourless form, m. p. 140°; the isomeric change is not instantaneous, because very rapid crystallisation from aqueous ethanol gives a mixture of the orange and the colourless forms.

The Red Chloride Monohydrate, m. p. 216—220°.—The addition of ether under nitrogen to a solution of the dichloride, m. p. 140°, in methanol-acetone containing free phosphine causes the deposition of separate red and colourless crystals. Cold ethanol extracts the colourless crystals, leaving deep scarlet crystals (having a bright orange streak) of a monohydrated dichloro-compound (as VI), m. p. 216—220°. This form dissolves readily in chloroform, from which the orange form can be isolated as before; the scarlet form is only slightly soluble in cold ethanol or acetone, but solutions in these hot solvents when diluted with water and cooled deposit the colourless form, m. p. 140°.

The Isomeric Dibromides (VIII).—The addition of the phosphine (3.2 equivalents) in ethanol to a warm aqueous solution of potassium tetrabromopalladate(II) gives ultimately a precipitate of mixed orange and red crystals. A hot methanolic solution of this mixture containing a trace of free phosphine, when concentrated and cooled, deposits the deep

orange crystalline dibromide (giving an orange streak), m. p. 216—220° (decomp.), having the composition (VIII). This compound can also be prepared by mixing methanol-acetone solutions of the dichloride (VI), m. p. 140°, and lithium bromide, followed by the



addition of water. This orange dibromide can be recrystallised by the slow evaporation of its methanolic solution at 50°, but it slowly dissociates, giving the dibromide (V; X = Br) in boiling methanol, ethanol, and acetone solutions, to which a trace of the free phosphine must therefore be added for recrystallisation purposes. The orange dibromide, when heated under reduced pressure, ultimately gives the pure dibromide (V; X = Br). Nitrobenzene solutions of the orange dibromide have low conductivities, for example, at 20° and V 547, $\Lambda_m = 4.2$ mhos, but cold acetone or methanol solutions when treated with sodium perchlorate or picrate deposit the bromo-perchlorate (IX; X = ClO₄) or the bromopicrate (IX; X = C₆H₂N₃O₇), having Λ_m 24.2 and 22.0 mhos, respectively. The structure of the dibromide in solution may therefore depend largely on the solvent employed.

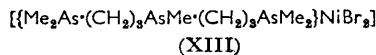
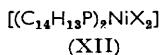
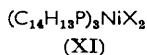
When a hot saturated acetone solution of the orange dibromide is treated with the free phosphine, the solution changes in colour from orange to deep ruby-red, and on concentration an isomeric deep red crystalline dibromide (with a crimson streak), m. p. 223—224°, is deposited. The cautious addition of hot water to a hot dilute methanol, acetone, or dimethylformamide solution of the orange dibromide causes a striking separation of the pure red needles from the orange solution; as the solution cools, a mixture of the red and the orange form separates. The red dibromide dissolves in pure organic solvents to give an orange solution, presumably of the orange dibromide, but it may be recrystallised from these solvents if a relatively high proportion of the free phosphine is present. In the crystalline state, however, the red form is apparently the more stable; samples of the orange form, which had been stored for five years in tubes closed with Cellophane-covered corks, underwent complete conversion into the red form in the neighbourhood of the corks. The structure of the red form is discussed below.

The phosphine (3 equivalents) combines exothermically with palladium(II) iodide in chloroform, to give an intense red solution, from which the deep vermilion di-iodide (X) can be obtained. This compound, when suspended or dissolved in many cold solvents, or when heated under reduced pressure, readily dissociates, forming the di-iodide (V; X = I); it is stable in these solvents only in the presence of 5—10% of the free phosphine. It dissolves readily in chloroform giving solutions which are however stable even when hot, and which are unaffected at room temperature for long periods if stored under dry nitrogen.

An acetone solution of the di-iodo-compound (X) containing some of the free phosphine, when treated with aqueous sodium perchlorate, gave the crystalline orange tris(phosphine)-iodopalladium perchlorate, sufficiently stable for recrystallisation; its molecular conductivity in nitrobenzene, 27.8 mhos, shows its ionic character.

A solution of the di-iodo-compound (X) in nitrobenzene has a molecular conductivity of *ca.* 5 mhos, but an accurate value cannot be obtained, for the degree of dissociation to the di-iodo-compound (V; X = I) and the phosphine is unknown. It is highly probable, however, that the compound (X) is covalent, in contrast to the iodo-perchlorate.

The addition of the phosphine (3 equivalents) to hydrated nickel chloride, each in ethanolic solution, rapidly afforded deep bottle-green crystals of the tris(phosphine)-dichloronickel monohydrate (XI; X = Cl). This compound was apparently stable in chloroform solution, but when heated with most other solvents it gave the deep brick-red crystalline bis(phosphine)dichloro-compound (XII; X = Cl). The anhydrous deep green dibromo- and di-iodo-compounds (XI; X = Br or I) were similarly prepared, and when



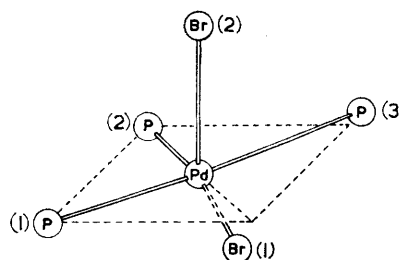
heated in ethanolic solution gave the brick-red dibromo-compound (XII; X = Br) and the chocolate-brown di-iodo-compound (XII; X = I), respectively. All the compounds of types (XI) and (XII) gave non-conducting solutions in nitrobenzene.

Discussion of Structure.—It is probable that all our tris(phosphine) derivatives of platinum, palladium, and nickel could have a structure in certain organic solvents which is different from that in the crystalline state. Moreover, certain apparently isomeric members, such as the tris(phosphine)dichloropalladium compounds (VI; X = Cl), have a definite identity in the crystalline state but in solution rapidly give one form alone or possibly an equilibrium mixture of forms; this is shown by the fact that all four forms of this dichloride give the same pale yellow colour in acetone or ethanolic solutions, from each of which the same chloro-perchlorate (VII; X = ClO₄) and chloro-picrate (VII; X = C₆H₂N₃O₇) are precipitated. Consequently, only indirect information is available for the structure of even the most stable compounds in solution. Decisive information for the structure in the crystalline state is available only for the red form of the dibromide, (R₃P)₃PdBr₂ (VIII).

Tris(phosphine)dibromopalladium (VIII) (red form).—The essential stereochemistry of this compound has been determined by X-ray crystallography (see Figure). The atomic

Tris(phosphine)dibromopalladium (VIII) (red form).

The rectangle can be considered to be drawn in the ideal plane defined by the atoms Pd, P(1), P(2), and P(3), which are nearly coplanar, although the atom P(3) is slightly raised above this plane.



co-ordinates are listed in Table 1, and the relevant interatomic distances and angles in Table 2. It is thus evident that this 5-co-ordinated palladium complex has the form of

TABLE 1.

Atomic co-ordinates.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pd	−0.096	0.193	0.179	P(1)	0.022	0.230	0.263
Br(1)	−0.113	0.055	0.233	P(2)	−0.118	0.323	0.155
Br(2)	0.099	0.178	0.091	P(3)	−0.198	0.141	0.094

TABLE 2.

Bond lengths (Å) and bond angles.

Pd-Br(1)	2.52	Br(1)-Pd-P(1)	87°	Br(1)-Pd-Br(2)	105°
Pd-Br(2)	2.93	P(1)-Pd-P(2)	90	P(1)-Pd-Br(2)	91
Pd-P(1)	2.30	P(2)-Pd-P(3)	97	P(2)-Pd-Br(2)	92
Pd-P(2)	2.19	P(3)-Pd-Br(1)	88	P(3)-Pd-Br(2)	84
Pd-P(3)	2.28				

a distorted square pyramid. The Br(1) atom deviates by about 0.1 Å from the plane defined by atoms Pd, Br(2), and P(2), and is depressed about 10° below the least-squares plane through atoms Pd, P(1), P(2), and P(3). The configuration of this molecule is very similar to that of the 5-co-ordinated nickel compound (XIII)⁴ in which the atom corresponding to the atom Br(1) (cf. Figure) is displaced further from the plane of the square, presumably because of the greater steric effect of the arsenic ligands. A square-pyramid

⁴ Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415; cf. Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

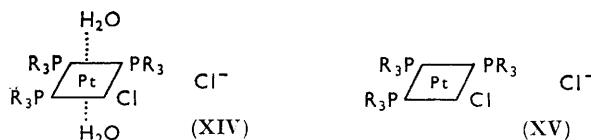
structure was deduced⁵ for the compound $(Et_3P)_2NiBr_3$ on the basis of magnetic and dipole measurements.

Daudel and Bucher⁶ indicated that a square-pyramidal arrangement should be favoured if, in the combination dsp^3 , the d -orbital has a lower energy than the s - and p -orbitals, in this case by the use of $4d5s5p^3$ -bonds. They also pointed out that the apical bond should be weak, and our results agree with this theory, the Pd-Br(2) distance being 2.93 Å whilst the Pd-Br(1) distance is 2.52 Å. Linnett and Mellish,⁷ however, favour the formation of a trigonal bipyramid but admit that the probabilities of formation of either structure are almost equal.

To this evidence of structure, the following points can be added regarding the tris(phosphine) compounds. (a) Preliminary crystal-structure work showed that the diiodide, $(R_3P)_3PdI_2$, is not isomorphous with the red dibromide, $(R_3P)_3PdBr_2$. (b) X-Ray powder photographs show that the orange and red forms of the dibromide, $(R_3P)_3PdBr_2$, are not isomorphous; the platinum dibromide and di-iodide compounds, $(R_3P)_3PtBr_2$ (anhydrous) and $(R_3P)_3PtI_2$, are probably isomorphous, but are not isomorphous with either form of the palladium dibromide.

The very low conductivities of nitrobenzene solutions of the orange palladium dibromide indicate a covalent structure, but in ethanolic solution its chemical properties show an ionic structure (IX; X = Br) or a mobile equilibrium of both structures. The structure of the red form in solution cannot be studied because of its ready conversion into the orange form.

The great stability towards dehydration of the tris(phosphine)dichloroplatinum dihydrate, $(R_3P)_3PtCl_2 \cdot 2H_2O$, indicates that in the solid state it may have the octahedral cation as in (XIV); the fact that in ethanolic solution it gives a chloro-picrate dihydrate and an anhydrous chloro-perchlorate may indicate that in solution it exists as an equilib-



rium mixture of the chlorides of the cations in (XIV) and (XV). The molecular weights of the white (dihydrated) and the pale yellow (anhydrous) dibromo-compound (III; X = Br) in dichloromethane agree closely with those of the un-ionised compounds, and indicate that the former also has the structure (XIV). The anhydrous compound is also reasonably soluble in benzene, in which it may therefore have a covalent structure, in nitrobenzene it forms a conducting solution, and in ethanol it also acts as a salt, giving the bromo-picrate and -perchlorate. These factors also apply to the di-iodide, which has a high solubility in benzene, but acts as a salt in nitrobenzene and ethanol. Both of these compounds (III; X = Br or I) may therefore exist as 5-covalent derivatives of platinum, possibly similar in type to the red palladium dibromide (cf. Figure), and also as salts of type (XV), the form in solution being determined primarily by the solvent.

There is considerable evidence that the dithiocyanate, $(R_3P)_3Pt(SCN)_2 \cdot 2H_2O$, even in the solid state, has a structure of type (XIV), namely, (a) its resistance to dehydration, and (b) its infrared spectrum which shows sharp bands at 2110 (co-ordinated unbridged SCN) and at 2066 cm^{-1} (ionic SCN); the normal values for these SCN groups are 2100—2120⁸ and 2040—2070 cm^{-1} ,⁹ respectively. The spectrum also has two sharp, but weak, bands at 3400 and 3600 cm^{-1} , the latter (in particular) indicating co-ordinated water.

⁵ Jensen and Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.

⁶ Daudel and Bucher, *J. Chim. phys.*, 1945, **42**, 6.

⁷ Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 665.

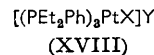
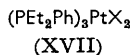
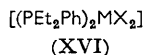
⁸ Chatt and Duncanson, *Nature*, 1956, **178**, 997.

⁹ Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253, who record the values 2040 and 2070 cm^{-1} for the SCN band in potassium and barium thiocyanate, respectively.

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In the bis(phosphine) series, the application of Nyholm's collected arguments,¹⁰ based on colour and solubility in solvents, for the structure of the compounds $[(Et_3As)_2PtX_2]$ and $[(MePh_2As)_2PtX_2]$ (X = halogen) indicates that our colourless compounds, $[(R_3P)_2PtX_2]$ (X = Cl or Br), have the *cis*-configuration, whilst the di-iodide is probably *trans*. Our palladium compounds, $[(R_3P)_2PdX_2]$, have almost certainly the normal *trans*-configuration. Finally, our nickel compounds, $[(R_3P)_2NiX_2]$, have the typical deep red (dichloride and dibromide) and dark brown (di-iodide) colours of similar *trans*-planar bis(trialkylphosphine)dihalogenonickel compounds; ^{11,12} this configuration is supported by the diamagnetic properties of the compound $[(R_3P)_2NiBr_2]$.

Since diethylphenylphosphine also tends to stabilise complex metallic derivatives in which the metal has an unusual co-ordination number, derivatives of the phosphine with platinum, palladium, and nickel were briefly investigated. This phosphine with platinum(II) halides forms "normal" derivatives of type (XVI; M = Pt, X = Cl, Br, or I),



and also tris(phosphine) derivatives of type (XVII; X = Cl, Br, or I), of which only the dichloride is hydrated. In solution these compounds act as salts (XVIII), since the dichloride and dibromide in nitrobenzene have Λ_m 20.3 and 22.5 mhos; further, the dibromide and di-iodide in methanolic solution react with sodium tetraphenylborate to give the bromo- and the iodo-tetraphenylborate (XVIII; X = Br, Y = Ph₄B) and (XVIII; X = I, Y = Ph₄B), which in nitrobenzene solution have Λ_m 26.5 and 25.7 mhos, respectively. These compounds have properties similar to those of the compound (AsMePh₂)₃PtBr₂ studied by Nyholm.¹³

Potassium tetrabromopalladate(II) and hydrated nickel bromide reacted with the phosphine (2 equivalents) to give the normal derivatives (XVI; M = Pd, X = Br) and (XVI; M = Ni, X = Br), respectively. These compounds gave non-conducting solutions in nitrobenzene, and all attempts to induce the addition of a third equivalent of the phosphine failed.

In the above compounds, and in other metallic series to be described, diethylphenylphosphine shows a much weaker power than 2-phenylisophosphindoline to form reasonably stable complexes in which the metal shows an unusual co-ordination number. This power was not apparent in the palladium dihalide derivatives of 1-ethylphosphindoline,¹⁴ 1-ethyl-1,2,3,4-tetrahydrophosphinoline or the isomeric 2-ethylisophosphinoline,¹⁵ or dibenzylphenylphosphine.¹ It appears, therefore, that this power is mainly dependent on purely steric factors; in the isophosphindoline (I), the symmetric incorporation of the phosphorus atom in the 5-membered ring tends to pull the two CH₂-P bonds together and thus enhance the steric freedom and consequent reactivity of the tertiary phosphorus atom. This factor would not apply to 1-ethylphosphindoline, in which the phosphorus atom is directly joined to the benzene ring, or to the two phosphinolines, in which the phosphorus atom is part of a hydrogenated and almost strainless 6-membered ring.

A possible second factor is indicated by the apparent inability of triphenylphosphine and triethylphosphine to form tris(phosphine) metallic derivatives; in the former phosphine the phosphorus is too electronegative and phosphorus-metal σ -bonding is restricted, and in the latter the lack of electronegative substituents allows insufficient π -character in the phosphorus-metal bond. In the isophosphindoline (I), and in diethylphenylphosphine,

¹⁰ Nyholm, *J.*, 1950, 843; cf. Jensen, *Z. anorg. Chem.*, 1936, 229, 225.

¹¹ Jensen, *Z. anorg. Chem.*, 1936, 229, 265.

¹² Venanzi, *J.*, 1958, 719; Coussmaker, Hutchinson, Mellor, Sutton, and Venanzi, *J.*, 1961, 2705; Browning, Davies, Morgan, Sutton, and Venanzi, *J.*, 1961, 4816.

¹³ Nyholm, *J.*, 1950, 848.

¹⁴ Mann and Millar, *J.*, 1951, 2205.

¹⁵ Beeby and Mann, *J.*, 1951, 411.

the phosphorus atoms carry groups which provide a favourable balance between σ -bonding and π -bonding to the metal, the phosphindoline showing the above steric factor in addition. The metallic derivatives of the (unknown) 2-methylisophosphindoline, in which both these factors would be modified, should prove of great interest.

EXPERIMENTAL

The 2-phenylisophosphindoline (I), when required for small-scale preparations, could be kept in a calibrated glass syringe, or a micrometer syringe, under nitrogen in a desiccator without deterioration. The term "the phosphine" refers to this phosphine unless otherwise stated. Operations involving the use of the free phosphine in solution were conducted under nitrogen.

Molecular weights were determined in dichloromethane solution by the vapour-pressure thermistor technique at 29–30°; whenever sufficient solution remained, it was evaporated to ensure that the solute was recovered unchanged. The molar conductivities, Λ_m , were determined at 23° and V 1000, unless otherwise stated.

The term "petroleum" refers to light petroleum of b. p. 60–80°.

Platinum Compounds.—*Bis(phosphine)dichloroplatinum* (II; X = Cl). The phosphine (0.424 g., 2 mol.) in ethanol (8 ml.) was added dropwise with shaking to a solution of potassium tetrachloroplatinate(II) (0.424 g.) in water (10 ml.), giving immediately a pink insoluble precipitate, which was collected, washed with water, and digested with hot dimethylformamide until a clear solution was obtained. Dilution with hot water, and cooling, gave the crystalline *product*, m. p. 286–287° (from aqueous acetone) (Found: C, 48.3; H, 3.4%; M , 674. $C_{28}H_{26}Cl_2P_2Pt$ requires C, 48.7; H, 3.7%; M , 690).

A solution of this compound (0.2 g.) in boiling acetone (20 ml.) was treated with saturated aqueous sodium bromide (2 ml.) and sufficient water to give a complete solution. This was boiled under reflux for 20 min., diluted with hot water and cooled, giving the *dibromo-compound* (II; X = Br), m. p. 292–293° from aqueous acetone (Found: C, 43.1; H, 3.2%; M , 785. $C_{28}H_{26}Br_2P_2Pt$ requires C, 43.1; H, 3.3%; M , 779). A mixture of the dichloro- and dibromo-compound had m. p. 270°. The yellow *di-iodo-compound*, similarly prepared and recrystallised, had m. p. 268–268.5°, fusing to a red liquid (Found: C, 38.3; H, 3.0. $C_{28}H_{26}I_2P_2Pt$ requires C, 38.5; H, 3.0%). The *dithiocyanato-compound* had m. p. 240–240.5° (Found: C, 48.8; H, 3.8; N, 3.8. $C_{30}H_{26}N_2P_2PtS_2$ requires C, 49.0; H, 3.5; N, 3.8%).

Tris(phosphine)dichloroplatinum dihydrate (IV; X = Y = Cl).—A solution of the dichloro-compound (II; X = Cl) (0.23 g.) in boiling acetone (8 ml.) was added to the phosphine (0.075 g., 1 mol.) in acetone (2 ml.). The mixture, which had become pale yellow, was boiled for 10 min., diluted with petroleum, and cooled; it deposited the *product*, m. p. 183–184°, fusing to a yellow liquid, after crystallisation from acetone-petroleum (Found: C, 53.5; H, 4.9. $C_{48}H_{39}Cl_2P_3Pt \cdot 2H_2O$ requires C, 53.7; H, 4.6%); Λ_m 21.6. The solubility of this salt in dichloromethane was too low for molecular weight determinations.

The dibromo-compound (II; X = Br) similarly gave the *dihydrated dibromo-compound* (IV; X = Y = Br), m. p. 234–236° (becoming yellow at 130° with apparent dehydration, and fusing to an orange liquid), after crystallisation as before (Found: C, 49.3; H, 3.9%; M , 1046. $C_{48}H_{39}Br_2P_3Pt \cdot 2H_2O$ requires C, 49.0; H, 4.2%; M , 1027), Λ_m 20.9 mhos. A benzene solution of this compound, when boiled under reflux for 15 min., became deep yellow, and when diluted with petroleum deposited the yellow crystalline *anhydrous dibromide* (IV; X = Y = Br), m. p. 234–236° (Found: C, 50.5; H, 4.1%; M , 980. $C_{42}H_{39}Br_2P_3Pt$ requires C, 50.8; H, 4.0%; M , 991).

The *di-iodo compound* (IV; X = Y = I), when similarly prepared and recrystallised from benzene, had m. p. 229–230° (Found: C, 46.6; H, 4.0%; M , 1065. $C_{48}H_{39}I_2P_3Pt$ requires C, 46.5; H, 3.6%; M , 1085), Λ_m 23.2 mhos. The *dihydrated di-thiocyanato compound* (IV; X = Y = SCN) had m. p. 204–204.5° (from acetone-petroleum) (Found: C, 53.4; H, 4.8. $C_{44}H_{39}N_2P_3PtS_2 \cdot 2H_2O$ requires C, 53.7; H, 4.7%), Λ_m 22.3 mhos.

The following picrates were prepared by the action of saturated ethanolic sodium picrate on a warm ethanolic solution of the appropriate dihalogeno-compound (IV); the perchlorates were similarly prepared using sodium perchlorate; all were recrystallised from acetone-petroleum containing a trace of free phosphine. *Trisphosphine-chloroplatinum picrate dihydrate*

(IV; X = Cl, Y = C₆H₂N₃O₇), m. p. 224—225° (decomp.) (Found: C, 51.2; H, 3.9; Cl, 3.4; N, 4.0. C₄₈H₄₁ClN₃O₇P₃Pt·2H₂O requires C, 51.4; H, 4.0; Cl, 3.1; N, 3.8%), Λ_m 23.5 mhos; the *bromo-picrate*, m. p. 228—229° (decomp.) (Found: C, 50.2; H, 3.4; N, 3.7. C₄₈H₄₁BrN₃O₇P₃Pt requires C, 50.6; H, 3.5; N, 3.6%), Λ_m 29.7 mhos; the *iodo-picrate*, m. p. 221—223° (decomp.) (Found: C, 48.3; H, 3.2; N, 3.4. C₄₈H₄₁IN₃O₇P₃Pt requires C, 48.55; H, 3.5; N, 3.5%), Λ_m 23.2 mhos; the *chloro-perchlorate*, colourless, m. p. 267—268° (yellow melt) (Found: C, 52.05; H, 4.1. C₄₂H₃₉Cl₂O₄P₃Pt requires C, 52.2; H, 4.05%), Λ_m 23.2 mhos; the *bromo-perchlorate*, colourless, m. p. 263—264° (orange melt) (Found: C, 49.8; H, 3.85. C₄₂H₃₉BrClO₄P₃Pt requires C, 49.9; H, 3.85%), Λ_m 22.6 mhos; the *iodo-perchlorate*, pale yellow, m. p. 254—255° (red melt) (Found: C, 48.0; H, 3.8. C₄₂H₃₉ClIO₄P₃Pt requires C, 47.7; H, 3.7%), Λ_m 22.0 mhos.

Palladium Compounds.—*Bis(phosphine)dichloropalladium* (V; X = Cl). When a small excess of the phosphine in ethanol was added to a cold aqueous solution of potassium tetrachloropalladate(II), the *product* was immediately precipitated, and after recrystallisation from acetone gave yellow needles, m. p. 258—262° (decomp.) (lit.,¹ 256—260°) (Found: C, 55.55; H, 4.8. Calc. for C₂₈H₂₆Cl₂P₂Pd: C, 55.85; H, 4.4%). It crystallised from chloroform as a very pale yellow *trichloromethanate*, m. p. 266—268° (decomp.) (Found: C, 48.5; H, 3.8. C₂₈H₂₆Cl₂P₂Pd·CHCl₃ requires C, 48.3; H, 3.7%); on exposure to the air the crystals slowly effloresce, giving the parent compound.

The addition of the phosphine (0.20 g.) in ethanol (20 ml.) to potassium tetrabromopalladate(II) (0.28 g., 0.55 mol.) in warm water (30 ml.) precipitated a reddish-brown solid, which was dissolved in boiling acetone (150 ml.). The solution, when filtered, concentrated, and cooled, gave a crystalline mixture of a pale yellow-orange and a deep russet-red compound, the latter almost certainly the salt [(C₁₄H₁₃P)₄Pd][PdBr₄]. The mixture was digested with boiling water for 4 hr. to convert this salt into the covalent compound, and recrystallisation of the insoluble residue from acetone gave the yellowish-orange *dibromo-compound* (V; X = Br), m. p. 271—272° (decomp.) (Found: C, 48.7; H, 3.9. C₂₈H₂₆Br₂P₂Pd requires C, 48.7; H, 3.8%), readily soluble in chloroform and sparingly soluble in other common solvents.

The di-iodo-member (V; X = I) was most readily prepared by addition of the tris(phosphine)-di-iodide (X) to cold benzene, in which it rapidly decomposed to give the compound (V; X = I), deep orange plates, m. p. 268° (decomp.) (from much benzene) (Found: C, 42.9; H, 3.9. Calc. for C₂₈H₂₆I₂P₂Pd: C, 42.8; H, 3.35%). Mann *et al.*¹ record this compound as deep crimson crystals, m. p. 246—248°, when prepared by the action of potassium iodide on the di-chloride (VI) in aqueous ethanol.

The addition of the phosphine (0.28 g., 2 mol.) in ethanol (4 ml.) to potassium tetranitropalladate(II) (0.25 g.) in water (7 ml.), deposited yellow crystals, which after extraction with boiling ethanol (4 ml.) left the pale yellow-green *dinitro-compound* (V; X = NO₂), m. p. 180—181° (vigorous decomp., darkening at 165°) (from acetone-chloroform) (Found: C, 53.7; H, 4.5; N, 4.6. C₂₈H₂₆N₂O₄P₂Pd requires C, 53.95; H, 4.2; N, 4.5%).

Tris(phosphine)dichloropalladium. (a) *The colourless dichloride dihydrate* (VI), m. p. 140°. The dropwise addition of the phosphine (0.50 g., 3 mol.) in hot ethanol (10 ml.) to potassium tetrachloropalladate(II) (0.26 g.) in hot water (3 ml.) gave a precipitate, which dissolved to a deep yellow solution when the mixture was boiled for 5 min. When the solution was diluted with warm water (5 ml.) and allowed to cool, the *dichloride* (VI) crystallised, m. p. 140° (decomp. to a scarlet liquid) (from aqueous ethanol and then ethanol) (Found: C, 59.0; H, 4.8; Pd, 12.4, 12.8%; *M*, 645. C₄₂H₃₉Cl₂P₃Pd·2H₂O requires C, 59.4; H, 5.1; Pd, 12.6%; *M*, 849), Λ_m 18.3 mhos. The compound can also be prepared by the addition of the phosphine (1 mol.) to a suspension of the dichloro-compound (V; X = Cl) in hot ethanol; the resultant clear yellow solution, when diluted with water and cooled, deposits the dichloride, m. p. 140° (decomp.).

A sample of the dichloride, heated at 135°/0.005 mm. for 3 hr., gave a residue of the dichloride (V; X = Cl), m. p. and mixed m. p. 266—267° (decomp.) (from acetone), and a distillate of the phosphine (I), identified as the methiodide, m. p. and mixed m. p. 206—208° (decomp.) (lit.,^{1,2} 207—209°, 208—210°).

The addition of saturated aqueous sodium perchlorate to an orange solution of the dichloride (VI) in acetone caused rapid fading of the colour and the deposition of the colourless *chloro-perchlorate monohydrate* (VII; X = ClO₄), m. p. 251° (decomp.); it was recrystallised (a) by the addition of just sufficient water to a boiling ethanolic suspension to give a

clear solution or (b) from acetone-petroleum [Found: (a) C, 56.2; H, 4.7; (b) C, 56.5; H, 4.8. $C_{42}H_{39}Cl_2O_4P_3Pd, H_2O$ requires C, 56.3; H, 4.6%], Λ_m 24.0 mhos. The addition of an excess of ethanolic sodium picrate to an ethanolic solution of the dichloride containing a trace of the free phosphine gave the *chloro-picrate monohydrate* (VII; $X = C_6H_2N_3O_7$), m. p. 206–207° (decomp.) (from acetone-petroleum) (Found: C, 56.2; H, 4.3; Cl, 3.7; N, 4.2. $C_{48}H_{41}ClN_3O_7P_3Pd, H_2O$ requires C, 56.25; H, 4.1; Cl, 3.5; N, 4.1%), Λ_m 19.7 mhos.

(b) *The colourless dichloride dihydrate* (VI), m. p. 219°. When 2N-hydrochloric acid (0.5 ml.) was added to a solution of the previous chloride (0.3 g.) in warm 50% aqueous ethanol (30 ml.), the yellow colour faded and the cooled solution deposited the colourless crystalline isomeric *dichloride*, m. p. 219° (decomp., becoming red with partial melting at 170°, and pale yellow at ca. 200°) (from ethanol-hydrochloric acid) (Found: C, 59.5; H, 4.9%).

(c) *The orange dichloride dihydrate* (VI), m. p. 130–131°. Ether (4 ml.) was added to a stirred solution of the chloride (0.2 g.), m. p. 140°, in pure chloroform (3 ml.), causing immediate separation of the orange *dichloride*, m. p. 130–131° (Found: C, 59.2; H, 5.3; Pd, 13.2%).

(d) *The red dichloride monohydrate*, m. p. 216–220°. Ether (10 ml.) was added under nitrogen to a yellow solution of the chloride (0.04 g.), m. p. 140°, in methanol (0.75 ml.)-acetone (4 ml.) containing the free phosphine (ca. 0.02 g.). Deposition of red and colourless crystals continued for 1.5 hr.; the mother-liquor was decanted, and the residual crystals extracted with cold ethanol (10 ml.) until the colourless crystals were dissolved. The undissolved deep scarlet crystals of the *dichloride*, when washed again with ethanol, had m. p. 216–220° (becoming pale yellow with partial melting at 185–191°) (Found: C, 60.4, 60.7; H, 5.3, 5.1. $C_{42}H_{39}Cl_2P_3Pd, H_2O$ requires C, 60.6; H, 5.1%. The second values were obtained from a sample dried at 70°/0.05 mm. for 7 hr.).

The orange bromide (VIII). The phosphine (0.34 g., 3.2 mol.) in ethanol (7 ml.) was added to a warm solution of potassium tetrabromopalladate(II) (0.25 g.) in water (3 ml.), which was heated under reflux until the yellowish-brown precipitate had almost completely dissolved. The hot filtered solution deposited a mixture of orange and red crystals, which were collected and dissolved in hot methanol containing the free phosphine (ca. 0.02 g.); this solution, when concentrated and cooled, deposited well-formed orange crystals (0.35 g.) of the *dibromide* (VIII), m. p. 216–220° (decomp., becoming red at 150–180° and then yellow) (Found: C, 55.6; H, 4.8; Pd, 11.4%; *M*, 780. $C_{42}H_{39}Br_2P_3Pd$ requires C, 55.8; H, 4.3; Pd, 11.8%; *M*, 902.5). When solutions of the chloride (VI), m. p. 140°, and lithium bromide, each in ethanol-acetone (3:7 v/v), were mixed, the colour changed from yellow to deep orange; addition of water precipitated the orange dibromide, m. p. and mixed m. p. 216–220° (from methanol). It is noteworthy in this preparation that the initial orange precipitate can be extracted with ether, and the residue from the evaporated extract, when crystallised from methanol, gives the orange dibromide which is then insoluble in ether.

Saturated aqueous sodium perchlorate, when added to an ethanolic solution of the dibromide, deposited the *tris(phosphine)bromopalladium perchlorate monohydrate* (IX; $X = ClO_4$), pale cream crystals, m. p. 222–223° (decomp.) (from acetone-petroleum) (Found: C, 53.9; H, 4.35. $C_{42}H_{39}BrClO_4P_3Pd, H_2O$ requires C, 53.6; H, 4.35%), Λ_m 24.2 mhos. The use of ethanolic sodium picrate deposited the orange *bromo-picrate* (IX; $X = C_6H_2N_3O_7$), m. p. 199–200° (decomp.) (from acetone-petroleum) (Found: C, 55.1; H, 4.1; N, 3.9. $C_{48}H_{41}BrN_3O_7P_3Pd$ requires C, 54.8; H, 3.9; N, 4.0%), Λ_m 22.0 mhos.

The red dibromide (VIII). The free phosphine was added to a hot saturated acetone solution of the orange bromide, to give an approximately 3% solution (v/v) of the phosphine. The deep ruby-red solution, when concentrated and cooled, gave deep red crystals of the *dibromide* (VIII), m. p. 223–224° (decomp., becoming yellow with partial fusion at 180°) (Found: C, 55.25; H, 4.5; Pd, 11.6%).

The di-iodide (X). The free phosphine (0.32 g., 3 mol.) was added under nitrogen to a suspension of palladium(II) iodide (0.18 g.) in chloroform (12 ml.), giving a warm clear deep red solution which was heated under reflux for 1 hr., concentrated to ca. 3 ml., and set aside. The large black crystals when collected rapidly lost chloroform, giving the vermilion *di-iodide* (X), m. p. 180–220° (decomp. to pale red liquid), m. p. 194° (to deep vermilion liquid) when immersed at 190° (from acetone containing 5% of the phosphine) (Found: C, 51.0; H, 4.25; Pd, 10.35. $C_{42}H_{39}I_2P_3Pd$ requires C, 50.6; H, 3.9; Pd, 10.7%).

An acetone-phosphine solution of the di-iodide, when treated with an excess of saturated

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ethanolic sodium picrate, deposited the deep orange *tris(phosphine)iodopalladium picrate monohydrate*, m. p. 180—181° (decomp.) (Found: C, 52·8; H, 3·7; N, 4·0. $C_{48}H_{41}IN_3O_7P_3Pd \cdot H_2O$ requires C, 52·5; H, 3·7; N, 3·8%), Λ_m 20·8 mhos.

Nickel Derivatives.—*Tris(phosphine)dichloronickel monohydrate* (XI; X = Cl). When the phosphine (0·31 g., 3 mol.) was added to nickel chloride hexahydrate (0·12 g.), each dissolved in ethanol (5 ml.), the solution became deep green and rapidly deposited the *dichloro-compound* (XI; X = Cl) (0·22 g.), deep bottle-green crystals, m. p. 170—172° (becoming reddish-brown at ca. 150° with partial fusion), after thorough washing with cold methanol (Found: C, 64·7; H, 5·4; Ni, 7·7%; M , 650. $C_{42}H_{30}Cl_2NiP_3 \cdot H_2O$ requires C, 64·6; H, 5·2; Ni, 7·5%; M , 784). The crystals when added to hot benzene gave a reddish-brown solution, which on dilution with ether deposited the *bis(phosphine)dichloronickel* (XII; X = Cl), brick-red plates, m. p. 218—220° (from acetone) (Found: C, 60·5; H, 4·65. $C_{28}H_{26}Cl_2NiP_2$ requires C, 60·7; H, 4·7%). This compound was also prepared by the interaction of nickel chloride and the phosphine (2 mol.) in boiling ethanol.

The *dibromo-compound* (XI; X = Br) was similarly prepared as deep green crystals, m. p. 190—191° (Found: C, 59·2; H, 4·4%; M , 725. $C_{42}H_{30}Br_2NiP_3$ requires C, 59·0; H, 4·5%; M , 855); its ethanolic solution when boiled deposited the *dibromo-compound* (XII; X = Br), brick-red needles, m. p. 225—227° (from acetone) (Found: C, 51·7; H, 4·3%; M , 620. $C_{28}H_{26}Br_2NiP_2$ requires C, 51·6; H, 4·3%; M , 643). Nickel iodide dihydrate similarly gave the dark green *di-iodo-compound* (XI; X = I), m. p. 192—194° after washing with ethanol and ether (Found: C, 51·5; H, 4·0%; M , 797. $C_{42}H_{30}I_2NiP_3$ requires C, 52·0; H, 4·2%; M , 949); its ethanolic solution when boiled gave the brown *di-iodo-compound* (XII; X = I), m. p. 199—200° (Found: C, 45·6; H, 3·6%; M , 720. $C_{28}H_{26}I_2NiP_2$ requires C, 45·7; H, 3·8%; M , 737).

Derivatives of Diethylphenylphosphine.—*Platinum(II) compounds.* The compounds of type (XVI) were prepared precisely as the analogous platinum(II) compounds (II), and when treated in acetone solution with the phosphine (1·5 mol.) gave the *tris(diethylphenylphosphine) compounds* of type (XVII). The members of type (XVI), all recrystallised from aqueous acetone, were: the *dichloro* member, colourless needles, m. p. 205—206° (Found: C, 40·6; H, 5·0; Cl, 11·7. $C_{20}H_{30}Cl_2P_2Pt$ requires C, 40·0; H, 5·0; Cl, 11·85%); the *dibromo* member, colourless needles, m. p. 193—194° (Found: C, 35·1; H, 4·3. $C_{20}H_{30}Br_2P_2Pt$ requires C, 34·9; H, 4·4%); the *di-iodo* member, yellow needles, m. p. 158—159° (Found: C, 31·0; H, 3·8. $C_{20}H_{30}I_2P_2Pt$ requires C, 30·8; H, 3·8%).

The members of type (XVII) were; the *dichloro* member (XVII; X = Cl), colourless crystals, m. p. 119—120° (decomp.) (from acetone-petroleum containing a trace of the free phosphine) (Found: C, 45·8; H, 6·2. $C_{30}H_{45}Cl_2P_3Pt \cdot H_2O$ requires C, 45·9; H, 6·0%), Λ_m 20·3 mhos; the *dibromo* member (XVII; X = Br), pale yellow crystals, m. p. 121—122° (decomp.), recrystallised as before (Found: C, 41·9; H, 5·5. $C_{30}H_{45}Br_2P_3Pt$ requires C, 42·1; H, 5·2%), Λ_m 22·5 mhos, which reacted with methanolic sodium tetraphenylborate to give the *bromo-tetraphenylborate* (XVIII; X = Br, Y = $C_{24}H_{20}B$), colourless plates, m. p. 136—137° (Found: C, 57·9; H, 6·0. $C_{54}H_{65}BBrP_3Pt \cdot H_2O$ requires C, 58·2; H, 6·0%); Λ_m 26·5 mhos; the *di-iodo* member was obtained as an orange gum, which, in methanol containing a trace of the phosphine, gave the *iodo-tetraphenylborate* (XVIII; X = I; Y = $C_{24}H_{20}B$), pale yellow plates, m. p. 121—122° (Found: C, 56·9; H, 5·8. $C_{54}H_{65}BI_3P_3Pt$ requires C, 56·8; H, 5·7%), Λ_m 25·7 mhos.

Bis(diethylphenylphosphine)dibromopalladium formed yellow needles, m. p. 203—204° (from methanol) (Found: C, 40·5; H, 5·1. $C_{20}H_{30}Br_2P_2Pd$ requires C, 40·2; H, 5·1%). *Bis(diethylphenylphosphine)dibromonickel* formed garnet-red needles, m. p. 114—115° (lit.,¹⁶ 114—116°) (from ethanol) (Found: C, 43·7; H, 5·0. Calc. for $C_{20}H_{30}Br_2NiP_2$: C, 43·5; H, 5·4%).

Crystallographic Data.—*Tris(2-phenylisophosphindoline)dibromopalladium* (VIII) (red form), $C_{42}H_{30}Br_2P_3Pd$, $M = 902·5$, Orthorhombic disphenoidal, $a = 11·70$, $b = 16·28$, $c = 20·63$, all $\pm 0·02$ Å, $U = 3930$ Å³, $D_m = 1·54 \pm 0·04$ (by flotation), $Z = 4$, $D_c = 1·48$; $F(000) = 1808$. Space group, $P2_12_12_1$ (D_2^4 , No. 19). Cu K_α -radiation, single-crystal photographs. Absorption coefficient for X-rays ($\lambda = 1·542$ Å) $\mu = 78·7$ cm.⁻¹.

Considerable difficulty was experienced in the determination of the crystal density owing to slow dissolution in the trichloroethylene-bromoform mixture.

Experimental measurements. Rotation, oscillation, and equi-inclination Weissenberg

¹⁶ Chatt and Shaw, *J.*, 1960, 1718.

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photographs were taken, and the average size of the crystal specimen employed was about $0.3 \times 0.2 \times 0.1$ mm. The reciprocal lattice was explored by recording the intensities of the $(0kl)$ — $(5kl)$ layers together with the $(h0l)$ and $(hk0)$ layers, using the multiple-film technique¹⁷ for correlation of strong and weak reflections. Intensities were estimated visually using the step-wedge technique, and the usual Lorentz, polarisation, and rotation factors applied. Corrections for absorption were also made using a programme written for EDSAC II by Wells¹⁸ according to the method of Busing and Levy.¹⁹ In the case of the higher-layer Weissenberg photographs, there was a considerable difference in spot shape and size on either side of the film, and allowance was made for this effect by an empirical analysis of the extended and contracted spots. 1012 independent structure factors were finally evaluated by the mosaic crystal formula.

Analysis of the structure.—The positions of the palladium and bromine atoms were determined by analysis of a three-dimensional sharpened Patterson function. Using the atomic scattering factor curves of Thomas and Umeda²⁰ for palladium and bromine, a set of structure factors were computed for which the *R*-factor was 37.4%. Phase angles calculated from the palladium and bromine positions were then associated with the observed structure amplitudes, and a three-dimensional Fourier synthesis computed. Inspection of this electron-density map immediately yielded the positions of the three phosphorus atoms. Inclusion of their contribution to the structure-factor calculation, using the scattering curve of Freeman and Watson,²¹ lowered the *R*-factor to 29.7%.

Refinement of the structure is proceeding by Fourier and difference-Fourier syntheses in an effort to locate the positions of the carbon atoms. The present *R*-factor, with 21 of the total 42 carbon atoms included in the calculation, is 23.8%.

Two maps showing the relative positions of the molecules, one being the $(hk0)$ projection viewed down the *c*-axis and the other the $(0kl)$ projection viewed down the *a*-axis, show that in no case does a Br atom of one molecule approach within bonding distance of the Pd atom of another molecule. There is, therefore, no tendency to form an octahedral structure by the apical Br(2) atom (see Figure) co-ordinating with the Pd atom of an adjacent molecule, as in the compounds of composition $\text{Pt}(\text{NH}_3)_2\text{Br}_3$ ²² and $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$.²³ The displacement of the Br(1) atom is most probably caused by the steric effect of the phosphine molecules.

A full account of the structure will be published later.

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¹⁷ Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

¹⁸ Wells, *Acta Cryst.*, 1960, **13**, 722.

¹⁹ Busing and Levy, *Acta Cryst.*, 1957, **10**, 180.

²⁰ Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 239.

²¹ Freeman and R. E. Watson, unpublished work, noted in "International Tables for X-ray Crystallography," Vol. III, p. 202, ed. Macgillavry and Rieck, Kynoch Press, Birmingham, 1962.

²² Brosset, *Arkiv Kemi., Min., Geol.*, 1948, **25**, A, No. 19, 14 pp.

²³ Cohen and Davidson, *J. Amer. Chem. Soc.*, 1951, **73**, 1955.