784. *The Constitution of Complex Metallic Salts. Part XVII.* Palladium Derivatives of* o-*Dimethylaminophenyldiethylphosphine.*

By FREDERICK G. MANN and H. R. WATSON.

Many co-ordinated derivatives of palladium with the above amine-phosphine have been prepared in order to study the conditions under which the amine-phosphine acts as a co-ordinating chelate group or as a single co-ordinating unit.

The remarkable type of tautomerism previously shown to occur with the palladium bromide derivatives of an analogous amine-arsine occurs also in the present series, and is most evident in the palladium iodide derivatives of the amine-phosphine.

The amine-phosphine reacts with potassium palladonitrite to give the normal types of complex compounds, and also (very readily) to give scarlet derivatives having the bridged μ-nitrito-μ'-hydroxo-dipalladium structure.

IN a study of the co-ordinated palladium derivatives of *o*-dimethylaminophenyldimethylarsine, Mann and Stewart[1] showed that, in many of these derivatives, the amine-arsine was acting as a chelate group, the normally weak co-ordinating power of the tertiary amine group being reinforced by that of the tertiary arsine group. A strongly co-ordinating radical, such as bromide or iodide ions, could however replace the co-ordinated amino-group by breaking the chelate ring and thus becoming itself co-ordinated. In one instance, this process could be readily reversed, the direction being dependent on the solvent and the temperature, and both isomeric compounds could exist in tautomeric equilibrium in one solvent.

In view of these results, we have examined in some detail the palladium derivatives of an analogous amine-phosphine, *o*-dimethylaminophenyldiethylphosphine (I) (see Mann and Watson[2]), and find that these derivatives illustrate clearly both the above and certain additional structural features.

For clarity of presentation, these compounds will be formulated throughout as derivatives of 4-co-ordinate palladium. The possibility that palladium adopts other co-ordination values in these derivatives is discussed below (p. 3956).

Addition of the phosphine (I) in ethanol to warm aqueous potassium palladochloride (1 equivalent) caused immediate precipitation of yellow-brown bis-(*o*-dimethylaminophenyldiethylphosphine)palladium palladochloride (II; X = Cl). This compound, when suspended in boiling ethanol, underwent slow conversion into the yellow crystalline dichloro-*o*-dimethylaminophenyldiethylphosphinepalladium (III; X = Cl), the covalent character of which is shown by its solubility in non-polar solvents and by its molecular weight in boiling chloroform.

When two equivalents of the ethanolic phosphine (I) were added to warm aqueous potassium palladochloride, the palladochloride (II; X = Cl) was initially precipitated, but rapidly dissolved to give a solution of bis-(*o*-dimethylaminophenyldiethylphosphine)-palladium dichloride dihydrate (IV; X = Cl). This compound is colourless in the solid state and in cold aqueous solution, the molar conductivity of this solution demonstrating the presence of three ions. Attempts to remove the water molecules proved unsuccessful, but only moderate dehydrating conditions could be employed, for the dichloride dihydrate when heated or when kept in a vacuum readily lost one molecule of phosphine to form the dichloro-complex (III; X = Cl).

An aqueous solution of dichloride (IV; X = Cl) when warmed developed a yellow colour, which became deeper with increasing temperature. Yellow solutions were also

---

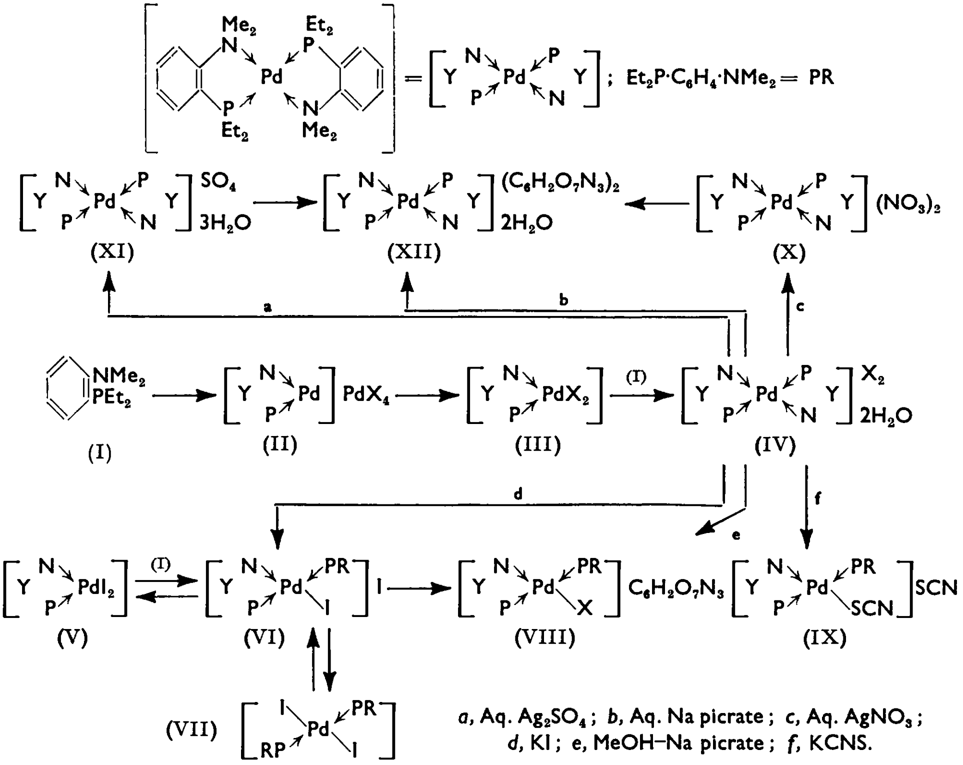
* Part XVI, Cochran, Hart, and Mann, *J.*, 1957, 2816.

[1] Mann and Stewart, *J.*, 1955, 1269.

[2] Mann and Watson, *J.*, 1957, preceding paper.

obtained in cold less polar solvents such as methanol, ethanol, chloroform, and benzene, the colour being deeper in the solvents of lower polarity (*e.g.*, solutions in benzene and toluene are deep orange-yellow). In all these organic solvents the colour became more intense as the temperature of the solutions was increased, and reverted to the original on cooling.

It is highly probable that the yellow colour is due to the formation of the isomeric monochlorobis-(*o*-dimethylaminophenyldiethylphosphine)palladium monochloride (as VI), which would almost certainly be yellow, because of the Pd–Cl group. The evidence for this isomerisation is twofold. (*a*) The solubility of the dichloride (IV; X = Cl) in cold water is very low, but increases markedly with increase in temperature. The cold saturated colourless solution, when treated with aqueous sodium picrate, deposited the corresponding dipicrate dihydrate (XII). The warm yellow aqueous solution, and the cold yellow methanolic solution, when similarly treated, deposited the monochlorobis-(*o*-dimethylaminophenyldiethylphosphine)palladium monopicrate (VIII; X = Cl). (*b*) The molar conductivity (p. 3955) of the " dichloride " in cold aqueous solution shows the presence of three ions, but that in nitrobenzene shows only two ions. In the nitrobenzene solution, therefore, the change to the " chloro-monochloride " (as VI) is apparently complete.



a, Aq. Ag_2SO_4; *b*, Aq. Na picrate; *c*, Aq. $AgNO_3$; *d*, KI; *e*, MeOH–Na picrate; *f*, KCNS.

It should be emphasised that the " chloro-monochloride " has not been isolated in the solid state. Recrystallisation of the dichloride dihydrate (IV; X = Cl) from water, methanol, ethanol, chloroform, benzene, or toluene always gave the unchanged colourless dihydrate. This is surprising, because when a warm aqueous solution is cooled the disappearance of the yellow colour is slow: for example, a solution chilled rapidly to 0° remained yellow for several minutes, indicating a slow rate of structural change.

The possible significance of the two molecules of water, which are present in several salts of type (IV), and are retained in organic solvents, is discussed below (p. 3956).

The bromo-compounds (II, III, and IV; X = Br) showed a strict analogy to the chloro-series. The methods of preparation were identical, and all three bromo-compounds have physical properties very similar to those of their chloro-counterparts. In particular, bis-(*o*-dimethylaminophenyldiethylphosphine)palladium dibromide (IV; X = Br) also crystallised as a colourless dihydrate and could not be obtained anhydrous. The cold colourless aqueous solution, which has a molar conductivity indicating the presence of three ions, developed on warming a yellow colour, which was also shown in cold organic solvents. This colour is similarly attributed to the formation of the " bromo-monobromide " (as VI): an ethanolic solution of the salt, treated with sodium picrate, deposited the corresponding bromo-monopicrate (VIII; X = Br).

The iodo-derivatives are of even greater interest (probably owing to the greater co-ordinating power of iodine), and exhibit a type of undoubted tautomerism which, in the corresponding amine-arsine series,[1] appeared in the bromo-compounds. Addition of the phosphine (I) to an ethanolic suspension of palladous di-iodide caused rapid dissolution, with the formation of the crystalline orange-red *o*-dimethylaminophenyldiethylphosphine-di-iodopalladium (V), which has the normal properties of a covalent compound, being soluble in benzene and other non-polar solvents and insoluble in water and showing a normal molecular weight in boiling chloroform.

A warm aqueous solution of the dichloride (IV; X = Cl), when added to an excess of saturated aqueous potassium iodide, deposited yellow crystals of bis-(*o*-dimethylamino-phenyldiethylphosphine)monoiodopalladium iodide (VI). This compound is stable in certain hot polar organic solvents, but in non-polar solvents is converted into the isomeric red bis-(*o*-dimethylaminophenyldiethylphosphine)di-iodopalladium (VII). The interconversion of two isomers is determined by the solvent employed. For example, the yellow isomer (VI) dissolves immediately in hot methanol, ethanol, and acetone to give yellow solutions from which it crystallises unchanged: the red isomer (VII) dissolves only slowly in these boiling solvents, giving yellow solutions, which again deposit the yellow isomer (VI). Conversely, the red isomer (VII) dissolves rapidly in boiling benzene or petroleum and separates unchanged on cooling, but the yellow isomer (VI) dissolves slowly in these boiling solvents, giving deep red solutions, which again deposit the red isomer (VII).

The equilibrium between the two forms is affected also by temperature, the formation of the red isomer being favoured at higher temperatures: the colour of solutions in the more polar solvents deepen from yellow to orange on heating. On *rapid* cooling of a hot saturated ethanolic solution, both isomers crystallise together. This occurs also on slow cooling of the deep orange solution in propan-1-ol, in which both forms are present, apparently in approximately equal proportion at room temperature.

The red isomer (VII) is thermally the more stable. It melts at 178—179° without decomposition, whereas the yellow isomer (VI) when heated steadily develops a red colour and finally melts at 177—178°, conversion into the isomer (VII) being then complete. Consequently a mixture of the isomers has the same m. p. It is noteworthy that, of the two analogous interconvertible bromo-derivatives of Mann and Stewart's amine-arsine,[1] the form corresponding to (VII) was also the more stable.

The nature of the two isomers is not in doubt, for the red isomer shows a normal molecular weight in boiling benzene, and the yellow isomer when treated in methanolic solution with sodium picrate gives bis-(*o*-dimethylaminophenyldiethylphosphine)monoiodo-palladium picrate (VIII; X = I). The ultraviolet spectra of the two isomers are distinct (p. 3958).

The orange-red di-iodo-compound (V), when treated in benzene solution with the phosphine (I), is converted necessarily into the red isomer (VII). The latter, however, slowly decomposes when its solution in petroleum is boiled, with loss of phosphine and regeneration of the compound (V).

Addition of an aqueous solution of the dichloride (IV; X = Cl) to concentrated aqueous potassium thiocyanate deposited the very pale yellow crystalline bis-(*o*-dimethylaminophenyldiethylphosphine)thiocyanatopalladium thiocyanate (IX), the constitution of which was confirmed by treating its cold aqueous or methanolic solution with sodium picrate, whereby the corresponding picrate (VIII; X = SCN) was precipitated. No indication of isomerisation of the thiocyanate (IX) was detected. Although such isomerisation would have been difficult to observe, since it would almost certainly be accompanied by very slight change in colour, it is significant that the thiocyanate has only a low solubility in boiling water and benzene, and that saturated solutions in these solvents can be boiled with undissolved thiocyanate for a considerable time without change. Isomerisation, had it occurred, would almost certainly have given the ionic dithiocyanate (IV; X = SCN) in the aqueous mixture and the covalent dithiocyanato-compound (as VII) in the benzene mixture, and the solubility of each of these compounds in the specified solvent would have been markedly greater than that of the thiocyanate (IX), a clear solution thus resulting.

The sulphate (XI), which was readily prepared by double decomposition of the dichloride (IV; X = Cl) and silver sulphate in aqueous solution, formed a pale yellow crystalline trihydrate, extremely soluble in water. Its aqueous solution, when treated with sodium picrate, deposited the bis-(*o*-dimethylaminophenyldiethylphosphine)palladium dipicrate dihydrate (XII). The yellow colour of this sulphate is difficult to explain, but it is noteworthy that the corresponding salt prepared from *o*-dimethylaminophenyldimethylarsine[1] also formed a yellow crystalline trihydrate. It is known that many hydrated sulphates have one molecule of water directly attached (probably by hydrogen bonding) to the sulphate ion.[3] If this applied to the sulphate (XI), the remaining two molecules of water may be associated with the cation, and the salt is then of the same type as the other dichelated compounds (IV; X = Cl or Br) and (XII). The ready conversion of the sulphate into the dipicrate dihydrate (XII) provides a further indication of the probable nature of these two molecules of water in the sulphate.

The colourless anhydrous dinitrate (X) was similarly prepared from the dichloride, and in aqueous solution furnished the dipicrate dihydrate (XII) identical with that obtained from the sulphate. This dinitrate is of particular importance because it demonstrates clearly that two molecules of water are not however an essential part of a salt containing the dichelated cation and simple acid radicals (cf. p. 3956).

Although the nitrito-derivatives show many similarities to the above compounds, their separate discussion is warranted by the unexpected occurrence of bridged μ-nitrito-μ'-hydroxo-dipalladium derivatives.

Interaction of the phosphine (I) and aqueous potassium palladonitrite (1 equivalent) gave an almost insoluble yellow precipitate, undoubtedly the salt (II; $X = NO_2$), which when boiled in aqueous suspension was slowly converted into the yellow crystalline dinitrito-(*o*-dimethylaminophenyldiethylphosphine)palladium (XIII), which showed a normal molecular weight in boiling chloroform. This compound (XIII) was also formed as one of the chief decomposition products of several of the bis-(amine-phosphine) complexes, *e.g.*, (XIV), (XV), and (XVIII), described below.

The dinitrito-compound (XIII), when treated with a further equivalent of the phosphine (I), afforded the very pale yellow bis-(*o*-dimethylaminophenyldiethylphosphine)-nitritopalladium nitrite monohydrate (XIV), which was also obtained by the action of sodium nitrite on the dichloride (IV; X = Cl) in aqueous solution. The structure of the nitrite (XIV) is confirmed by the action of sodium picrate in aqueous solution, the corresponding monopicrate (XVII) being precipitated.

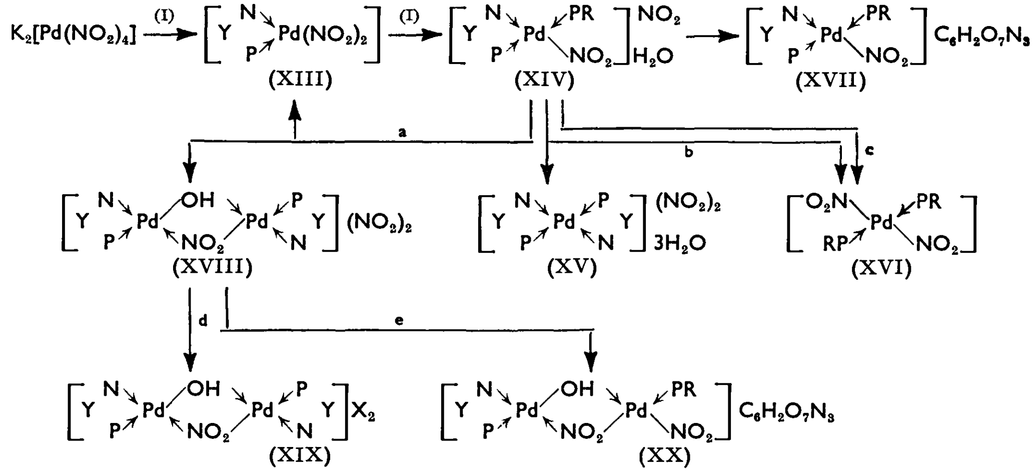
The nitrite (XIV) is stable when dry but in solution may undergo various types of decomposition. (*a*) In aqueous solution at room temperature it is slowly converted into the isomeric colourless trihydrated bis-(amine-phosphine)palladium dinitrite (XV) and the

---

[3] For specific examples, and a general discussion of this subject, see Sidgwick, "The Chemical Elements and their Compounds," Oxford, 1950, Vol. II, p. 914.

bis-(amine-phosphine)dinitritopalladium (XVI), the latter being deposited from solution. (*b*) An aqueous solution, when heated above 70°, rapidly becomes deep red, with formation of the bridged salt, bis-(amine-phosphine)-μ-nitrito-μ′-hydroxo-dipalladium dinitrite (XVIII). (*c*) In boiling benzene solution, the salt (XIV) rapidly gives the dinitrito-compound (XVI) and an unidentified yellow crystalline ionic product.

The formation of the covalent dinitrito-derivative (XVI) from the isomeric nitrito-nitrite (XIV) in cold aqueous solution was unexpected, since in all other isomeric changes investigated in this series, polar solvents have promoted the formation of the ionic isomers. The dinitrito-derivative (XVI) is typically covalent in that it is more soluble in non-polar than in polar solvents, but it crystallises unchanged from both types of solvent, and no reconversion into the salts (XIV) or (XV) was detected. It is the most stable of these three isomers, and its apparently anomalous formation in cold aqueous solution is probably determined by this comparative stability.



a, Boiling water; *b*, cold water; *c*, boiling benzene; *d*, LiX; e, Na picrate.

Both the isomeric nitrites (XIV) and (XV), when heated in aqueous solution, gave rise to the bridged salt (XVIII) together with an appreciable proportion of the dinitrito-compound (XIII). In view of the difficulties associated with the preparation of the salts (XIV) and (XV), it was found more convenient to prepare the bridged compound (XVIII) by boiling aqueous potassium palladonitrite with slightly more than two equivalents of the phosphine (I) dissolved in propan-1-ol. Under these conditions the nitrite (XIV), which is initially formed, rapidly decomposes into the bridged salt (XVIII) and the dinitrito-compound (XIII): the latter then combines with a further equivalent of the phosphine (I) to form the nitrite (XIV), which decomposes as before. The formation of the bridged salt (XVIII) thus proceeds steadily at the expense of the dinitrito-compound (XIII).

The μ-nitrito-μ′-hydroxo-bridged structure has hitherto been unknown in palladium complexes, and is of rare occurrence in other metallic salts, but Werner and Welte[4] have recorded some deep violet cobalt complexes containing this bridged system. The formation of this bridging group in these palladium derivatives (as in the cobalt compounds) causes a marked change in colour, the bridged dinitrite (XVIII) separating from aqueous solution as deep vermilion crystals, which when powdered appear deep scarlet. The evidence for the structure allotted to the salt (XVIII) is fourfold: (*a*) analytical; (*b*) that the "apparent" molecular weight in freezing urethane, a solvent of high ionising power, indicates the presence of three ions in the molecule; (*c*) that the salt is precipitated unchanged from its

---

[4] Werner and Welte, *Annalen*, 1910, **375**, 128.

aqueous solution by the addition of aqueous sodium nitrite, thus confirming the presence of nitrite ions; (*d*) that the infrared spectrum of a thoroughly dried sample showed a broad band centred at 3400 cm.$^{-1}$ (μ 2·94) attributed to the OH group; (*e*) the conductivities of aqueous and freshly prepared nitrobenzene solutions indicate a uni-bivalent salt (p. 3961).

The dinitrite (XVIII), in the solid state or in solution, is stable indefinitely in the dark, but on exposure to light the crystalline salt darkens; in cold aqueous or methanolic solution it steadily decomposes, with the liberation of palladium and formation of the dinitrito-compound (XIII) and other unidentified products.

It is noteworthy that aqueous solutions of the bridged dinitrite (XVIII), when treated with saturated aqueous solutions of lithium chloride and bromide, deposited quantitatively the scarlet dichloride (XIX; X = Cl) and dibromide (XIX; X = Br) respectively. Aqueous solutions of the dibromide, treated in turn with sodium picrate, deposited the corresponding red dipicrate [XIX; X = $O{\cdot}C_6H_2(NO_2)_3$]. In the formation of these three salts the cation has apparently remained unchanged. When however an aqueous solution of the bridged dinitrite (XVIII) was treated directly with sodium picrate, the red monopicrate (XX) was deposited, one of the chelate rings having been disrupted. It is possible therefore that the bridged dinitrite (XVIII) in aqueous solution is in equilibrium with a small proportion of the isomeric mononitrite (as XX), which furnishes the less soluble monopicrate: if so, the bridged dihalides (XIX; X = Cl or Br) either do not undergo this isomerisation in aqueous solution or, if this process does occur, the fully chelated dipicrate is here the less soluble.

There is at present no evidence for the precise disposition of the bridged NO_2 and OH groups relative to the amine and phosphine groups in the salt (XVIII), (XIX), and (XX): that indicated in these formulæ is merely regarded as the most probable.

For convenient reference, the molecular conductivities of our dichloride (IV; X = Cl) and dibromide (IV; X = Br) in water and in nitrobenzene are given in the Table. For comparison, the values for other undoubted uni-univalent and uni-bivalent salts in aqueous solutions given by Grinberg[5] and by Venanzi[6] are quoted. All determinations were made at 25° unless otherwise stated.

Compound	Solvent	Dilution (V)	Mol. conductivity (mho)	Solvent	Dilution (V)	Mol. conductivity (mho)
(IV; X = Cl)	Water	1000	217	Nitrobenzene	1036	26·0 [a]
(IV; X = Br)	,,	1000	215	,,	990	25·9 [b]
$[(NH_3)_4Pd]Cl_2$ [6]	,,	1117	260			
$[(NH_3)_4Pt]Cl_2$ [5]	,,	1000	260·2 [c]			
$[(NH_3)_4PtCl_2]Cl_2$ [5]	,,	1000	223·9			
$[(NH_3)_3PtCl]Cl$ [5]	,,	1000	115·8			
$[(NH_3)_3PtCl_3]Cl$ [5]	,,	1000	96·8			

[a] 21°. [b] 20°. [c] 17°.

It is clear that the conductivities of the salts (IV; X = Cl and X = Br) in aqueous solution approach very closely to the normal range for uni-bivalent salts and are well removed from that of uni-univalent salts. In nitrobenzene, however, the conductivities of these two salts are typical of those of uni-univalent salts, which are normally in the range of 20—30 mhos.[7]

There are possible alternative structures for certain of the above compounds which must be considered. Harris and Nyholm[8] have adduced considerable evidence that bivalent palladium, although normally showing a co-ordination number of four, can in suitable circumstances show the number five or six.

---

[5] Grinberg, " Einführung in die Chemie der Komplexverbindungen ", Verlag Technik, Berlin, 1955, p. 25.

[6] Venanzi, unpublished results.

[7] For other examples of such salts in nitrobenzene, see Kabesh and Nyholm, *J.*, 1951, 38; Harris and Nyholm, *J.*, 1956, 4375; 1957, 63; Cochran, Hart, and Mann, *J.*, 1957, 2816.

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

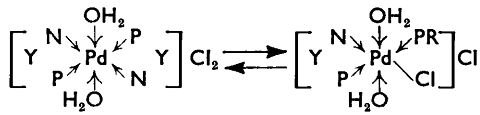
For two reasons, the significant structural feature of our colourless bis-(amine-phosphine)palladium dichloride dihydrate and the corresponding dibromide (IV; X = Cl and Br) is not the failure to remove the two molecules of water. First, this failure may be due to general instability in a vacuum or at elevated temperatures, when one equivalent of the amine-phosphine (I) is readily lost: secondly, co-ordinated salts are known, for example, the monohydrated bis-(2 : 2′-diaminodiethylamine)nickel dichloride and its cupric analogue, in which the water, although undoubtedly present as water of crystallisation, is difficult to remove even on long heating in a vacuum.[9] The striking feature of our hydrated salts (IV; X = Cl or Br) is however that they can be recrystallised unchanged from solvents such as chloroform, benzene, and toluene, conditions under which true water of crystallisation might readily be lost.

It is therefore possible that the colourless dichloride, for example, has 6-co-ordinate palladium and the structure (IVA), and that, in hot aqueous solution or in cold methanolic solution (both of which are yellow in colour) this dichloride is in equilibrium either with the isomer (IVB), in which the palladium has remained 6-co-ordinate and one $Pd \rightarrow NMe_2$ bond has been severed by the co-ordinating chlorine atom, or with the compound (IVC) in which the palladium has become 5-co-ordinate.

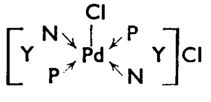
Similarly, it is possible that the yellow iodo-iodide (VI) has the 5-co-ordinate structure (VIA) and the red covalent di-iodo-isomer (VII) has the 6-co-ordinate structure (VIIA), each compound having two chelated rings; these structures, like (VI) and (VII), also provide a mechanism for the tautomerism which these compounds show in solution.

With regard to the chloro-compounds, it may be urged that structure (IVA) accounts for the lack of colour in the crystalline salt, its conductivity in aqueous solution as a uni-bivalent salt, and its conversion in cold aqueous solution into a " dihydrated " dipicrate. Structure (IVB) accounts for the yellow colour of solutions of the salt in hot water and in organic solvents, its conductivity in nitrobenzene as a uni-univalent salt, and particularly for its retention of the two molecules of water in boiling chloroform, benzene, and toluene solutions. It explains the formation of a monochloro-monopicrate, but not the fact that this salt is anhydrous, unless it is assumed that the co-ordination number of the palladium has fallen from 6 to 4 during the formation of this salt. Structure (IVC) explains the colour of the salt and its conversion into the monochloro-monopicrate, but not the retention of the water in the above boiling solvents.

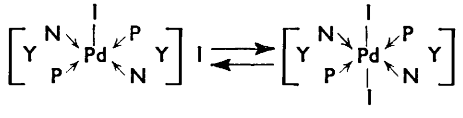
(IVA)



(IVB)



(IVC)



(VIA) (VIIA)

Against these 6- and 5-co-ordinate structures for the chloro- and bromo-derivatives, it may be urged that, although many of these bischelated palladium salts have two molecules of water, the latter are not *essential* for the formation of such salts. The anhydrous ionic dinitrate (X) must have 4-co-ordinate palladium, for nitrate ions very rarely (if ever) co-ordinate with metals: for similar reasons, the pallado-chloride and -bromide (II; X = Cl and Br) must also have 4-co-ordinate palladium. Furthermore, with regard to the iodo-derivatives, the very strong co-ordinating power of iodine would be expected to break the very weak $Pd \leftarrow NMe_2$ bond to give compounds (VI) and (VII), rather than solely to increase the co-ordination of the palladium to (normally) unstable levels as in (VIA) and (VIIA).

---

[9] Breckenridge, *Canad. J. Res.*, 1948, **26**, *B*, 11.

Decisive differentiation between these alternative structures is difficult. Evidence for a free tertiary amine group in compounds of type (VI) and (IX) would be of great value. The infrared spectra of these salts are complex, and on this point inconclusive. The fact that these salts, when treated in solution with a mixture of sodium picrate and picric acid, form only a picrate of the cation, and not in addition a picrate of the tertiary amine, is also without significance because the positive pole on the co-ordinated tertiary phosphine group considerably deactivates the tertiary amine group. This is shown by the fact that the methiodide, formed by quaternisation of the tertiary phosphine group in the amine-phosphine (I), when similarly treated gives only the phosphonium picrate, the amine group again being unaffected.[2]

The most decisive evidence for the structure, and hence the co-ordination number, of compounds such as (IV), (VI), and (VII) would be that provided by *X*-ray crystal analysis.

In many of the other compounds described above, particularly the covalent compounds (III; X = Cl and Br), (V), and (XIII), the palladium cannot be other than 4-co-ordinate.

EXPERIMENTAL

The m. p.s of certain compounds were determined by immersion in a pre-heated medium: the temperature of immersion is indicated by (T.I. — °) immediately after the m. p. Molecular weights were determined ebullioscopically, apart from that of the dinitrite (XVIII), which was determined cryoscopically.

Chloro-derivatives.—*Bis-*(o-*dimethylaminophenyldiethylphosphine*)*palladium palladochloride* (II; X = Cl). A solution of phosphine (I) (0·21 g.) in ethanol (2·5 c.c.) was added with shaking to potassium palladochloride (0·33 g., 1 mol.) in warm water. The precipitated *palladochloride*, when washed well with water and then extracted for 2 hr. with cold ethanol, formed minute yellow-brown plates, m. p. 280° (decomp.) (Found: C, 36·95; H, 5·4; N, 3·6. $C_{24}H_{40}N_2Cl_4P_2Pd_2$ requires C, 37·2; H, 5·2; N, 3·6%).

*Dichloro-*o-*dimethylaminophenyldiethylphosphinepalladium* (III; X = Cl). The palladochloride (II; X = Cl) when boiled with a large volume of ethanol for 3 hr. provided a clear solution, from which the *compound* (III; X = Cl), yellow needles, m. p. 274—275° (decomp.), was obtained on concentration (Found: C, 37·2; H, 5·2%; *M*, in $CHCl_3$, 376. $C_{12}H_{20}NCl_2PPd$ requires C, 37·2; H, 5·2%; *M*, 387).

Bis-(o-*dimethylaminophenyldiethylphosphine*)*palladium dichloride dihydrate* (IV; X = Cl). On the addition of the phosphine (I) (0·21 g.) in ethanol (2·5 c.c.) to potassium palladochloride (0·16 g., 1 mol.) in warm water (0·5 c.c.), the initial precipitate of palladochloride (II; X = Cl) rapidly redissolved, and the solution, when concentrated and cooled, deposited the *dichloride* (IV; X = Cl), colourless plates, m. p. 189—191° (evolving liquid at 181°) (Found: C, 45·6; H, 7·0; N, 4·8. $C_{24}H_{40}N_2Cl_2P_2Pd,2H_2O$ requires C, 45·7; H, 7·0; N, 4·4%).

Attempts to dehydrate the dichloride proved unsuccessful, vigorous methods being unavailable, however, as the compound lost one molecule of phosphine (I) when heated, or in a vacuum at room temperature, to form the compound (III; X = Cl). The dichloride (IV; X = Cl) is sparingly soluble in cold water, giving a colourless solution which becomes yellow on being heated, the colour change reversing on cooling. Concentrated solutions in hot water are deep yellow. The colour of solutions in organic solvents is dependent on their polarity: thus solutions in cold ethanol are pale yellow, whereas those in benzene and toluene are deep orange-yellow. From all these solutions the dichloride dihydrate crystallised unchanged.

Addition of a cold concentrated solution of the dichloride (IV; X = Cl) in ethanol to an excess of methanolic sodium picrate precipitated *monochlorobis-*(o-*dimethylaminophenyldiethylphosphine*)*palladium monopicrate* (VIII; X = Cl), m. p. 210—211° (decomp.), from methanol (Found: C, 45·9; H, 5·2; N, 9·4. $C_{30}H_{42}O_7N_5ClP_2Pd$ requires C, 45·7; H, 5·3; N, 9·0%). The use of these reagents in dilute aqueous solution gave, however, bis-(*o*-dimethylaminophenyldiethylphosphine)palladium dipicrate dihydrate (XII), m. p. 174° (decomp.), unchanged on admixture with the authentic sample from the sulphate (XI).

Bromo-derivatives.—*The palladobromide* (II; X = Br). Solutions of the phosphine (I) in ethanol and potassium palladobromide (1 mol.) in water were slowly mixed, and the precipitated *palladobromide*, when purified by thorough washing with water and prolonged extraction with cold ethanol, was obtained as a russet-brown microcrystalline powder, m. p. 276—277° (decomp.)

becoming pale buff at *ca.* 175° (Found: C, 30·5; H, 4·5; N, 3·4. $C_{24}H_{40}N_2Br_4P_2Pd_2$ requires C, 30·25; H, 4·2; N, 3·2%).

*Dibromo-*o*-dimethylaminophenyldiethylphosphinepalladium* (III; X = Br). This was prepared from the palladobromide (II; X = Br) precisely as the chloro-analogue, and obtained as canary-yellow prisms, m. p. 274° (decomp.), from methanol (Found: C, 30·0; H, 4·05; N, 3·2. $C_{12}H_{20}NBr_2PPd$ requires C, 30·25; H, 4·2; N, 2·9%).

*Bis-(*o*-dimethylaminophenyldiethylphosphine)palladium dibromide dihydrate* (IV; X = Br). Addition of the phosphine (I) in ethanol to potassium palladobromide (0·5 mol.) in hot water, followed by an excess of hot water, resulted in a yellow solution which, on cooling, deposited the *dibromide dihydrate,* colourless plates, m. p. 200—201° (decomp.) (evolving liquid at 100—180°) (from ethanol) (Found: C, 40·3; H, 6·1; N, 3·9. $C_{24}H_{40}N_2Br_2P_2Pd,2H_2O$ requires C, 40·0; H, 6·1; N, 3·9%).

The dibromide in various solvents has properties closely similar to those of the dichloride (IV; X = Cl), the colours of the solutions ranging from deep orange in benzene to colourless in cold water. The unchanged dibromide dihydrate crystallised even from non-polar solvents. Attempts to dehydrate the compound either failed or caused loss of one phosphine molecule to give (III; X = Br).

The dibromide in ethanol, treated with ethanolic sodium picrate, gave *monobromo-(*o*-dimethylaminophenyldiethylphosphine)palladium monopicrate* (VIII; X = Br), m. p. 210—213° (decomp.), from acetone–methanol (Found: C, 43·2; H, 5·0; N, 8·7. $C_{30}H_{42}O_7N_5BrP_2Pd$ requires C, 43·4; H, 5·1; N, 8·45%).

Iodo-derivatives.—o*-Dimethylaminophenyldiethylphosphinedi-iodopalladium* (V). When the ethanolic phosphine (I) was added to a suspension of palladous iodide (1 mol.) in much ethanol, a yellow colour developed rapidly in the solution, and after 1 hour's boiling under reflux all the palladous iodide dissolved. The solution, when cooled, deposited the *compound* (V), red-orange plates, m. p. 256—257° (decomp.) (Found: C, 25·5; H, 3·9%; *M,* in $CHCl_3$, 560. $C_{12}H_{20}NPPdI_2$ requires C, 25·3; H, 3·9%; *M,* 569·5). The m. p. was unchanged after recrystallisation from ethanol.

*Bis-(*o*-dimethylaminophenyldiethylphosphine)di-iodopalladium* (VII). Slow addition of the aqueous dichloride (IV; X = Cl) to an excess of concentrated aqueous potassium iodide solution gave immediately a yellow, microcrystalline precipitate, which, when collected, washed with water, and recrystallised from benzene, yielded deep ruby-red granular crystals, m. p. 178—179°, which slowly effloresced to an orange powder on exposure to air. Recrystallisation from light petroleum (b. p. 80—100°) gave the *compound* (VII), m. p. 178—179° (Found: C, 36·5; H, 5·0%; *M* in C_6H_6, 747. $C_{24}H_{40}N_2I_2P_2Pd$ requires C, 37·0; H, 5·1%; *M,* 778). The ultra-violet spectrum in the petroleum solution gave the values: $\lambda_{max.}$ 410—411, 335—337, 275·5—277·5, 221—221·5 (ε 5310, 11,990, 22,200, 33,700); $\lambda_{min.}$ 383, 315—325, 257—260, 214—216 mμ (ε 2990, 10,900, 20,400, 3200).

The di-iodo-derivative (VII) in the boiling light petroleum solution, decomposed very slowly, depositing the red insoluble crystalline compound (V), m. p. and mixed m. p. 256—257°.

Dissolution of the red di-iodo-derivative (VII) in polar solvents produced a tautomeric change, giving yellow-to-orange solutions, from which *bis-(*o*-dimethylaminophenyldiethylphosphine)iodopalladium iodide* (VI) crystallised on cooling or evaporation of solvent (Found: C, 37·4; H, 5·5. $C_{24}H_{40}N_2I_2P_2Pd$ requires C, 37·0; H, 5·1%). This salt forms canary-yellow crystals (having a very pale yellow streak), which on being heated deepen in colour and finally melt at 177—178° to a red liquid identical in colour with the fused red isomer (VII). Admixture of the two isomers causes no depression of melting point. The compound (VI) in MeOH had $\lambda_{max.}$ 362·5—365·3, 285, 214·5—216·5 (ε 3780, 21,000, 47,300) and $\lambda_{min.}$ 334—336, 256 mμ (ε 3150, 16,100).

A methanolic solution of the yellow isomer (VI), when added to saturated methanolic sodium picrate, deposited *bis-(*o*-dimethylaminophenyldiethylphosphine)iodopalladium monopicrate* (VIII; X = I), yellow platelets, m. p. 184—188° (decomp.) (T.I. 170°) (from methanol) (Found: C, 40·5; H, 5·3. $C_{30}H_{42}O_7N_5IP_2Pd$ requires C, 40·8; H, 4·8%).

A warm benzene or ethanolic solution of the di-iodo-compound (V), when treated with the phosphine (I) (1 mol.) and then concentrated and cooled, deposited the crystalline di-iodo-derivative (VII), m. p. and mixed m. p. 177—178°.

*Bis-(*o*-dimethylaminophenyldiethylphosphine)thiocyanatopalladium Thiocyanate* (IX).—A warm aqueous solution of the chloride (IV; X = Cl), when added to an excess of concentrated aqueous potassium thiocyanate, precipitated a gum, which rapidly solidified, and on crystallisation from much water afforded the *thiocyanate* (IX), very pale yellow needles, m. p. 221—222° (decomp.) (Found: C, 48·45; H, 6·6. $C_{26}H_{40}N_4S_2P_2Pd$ requires C, 48·7; H, 6·2%). The colour and m. p. were unchanged on further recrystallisation. The salt is readily soluble in warm ethanol and methanol, but only very sparingly soluble in boiling benzene. The addition of its warm methanolic solution to an excess of saturated methanolic sodium picrate caused no precipitation after 12 hr., but evaporation of the solution to small bulk and dilution with a large excess of water precipitated (o-*dimethylaminophenyldiethylphosphine*)*thiocyanatopalladium monopicrate* (VIII; X = SCN), deep yellow-grey plates, m. p. 169—170° (decomp.) (from water) (Found: C, 46·2; H, 5·4. $C_{31}H_{42}O_7N_6SP_2Pd$ requires C, 45·9; N, 5·2%). This salt was also prepared in cold aqueous solution, but owing to the great dilution it separated as a suspension, which was collected in a centrifuge.

Bis-(o-*dimethylaminophenyldiethylphosphine*)*palladium Sulphate Trihydrate* (XI).—Warm aqueous solutions of the chloride (IV; X = Cl) (0·252 g.) and silver sulphate (0·125 g., 1 mol.) were mixed, shaken vigorously, and filtered. The pale yellow filtrate was evaporated in a vacuum-desiccator at room temperature, giving a hygroscopic gum. The gum was redissolved in water, and the solution allowed to evaporate under atmospheric conditions for 3 weeks, giving large well-formed crystals in a deep yellow gummy matrix. The crystals and matrix were not separable, for the crystals dissolved more readily than the gum on being washed with solvents. Finally, a methanolic solution of the mixture was cautiously diluted with ether, and then deposited the pale yellow *sulphate trihydrate* (XI), m. p. 127—132° (decomp., slow heating), 171—173° (decomp., T.I. 122°) (Found: C, 42·5; H, 7·2. $C_{24}H_{40}O_4N_2SP_2Pd,3H_2O$ requires C, 42·8; H, 6·8%).

The corresponding dipicrate (XII), prepared by mixing cold aqueous solutions of the sulphate and of sodium picrate, was recrystallised twice from boiling ethanol, the solution on each occasion rapidly becoming deep green, but depositing the crystalline *dipicrate dihydrate* (XII), bright yellow plates, m. p. 176° (decomp., liquid evolved *ca.* 130°, much prior shrinking), the green colour remaining in the mother-liquor (Found: C, 42·1; H, 4·7. $C_{36}H_{44}O_{14}N_8P_2Pd,2H_2O$ requires C, 42·5; H, 4·7%). It is possible that the green colour, which faded to pale brown after some hours, was due to minute quantities of colloidal palladium. Attempts to dehydrate the dipicrate by heating it *in vacuo* over phosphoric anhydride proved unsuccessful, the results indicating loss of the phosphine (I).

Bis-(o-*dimethylaminophenyldiethylphosphine*)*palladium Dinitrate* (X).—Aqueous solutions of the chloride (IV; X = Cl) (0·211 g.) and silver nitrate (0·113 g., 2 mols.) were mixed, shaken for 1·5 hr., and filtered, and the colourless filtrate was evaporated in a vacuum-desiccator at room temperature. The residue, a partly crystallised gum, when recrystallised from chloroform–ethyl acetate, gave the colourless *dinitrate* (X), m. p. 208—209° (decomp.) (Found: C, 44·2; H, 5·8; N, 8·6. $C_{24}H_{40}O_6N_4P_2Pd$ requires C, 44·4; H, 6·2; N, 8·4%).

The dipicrate (XII), prepared from the dinitrate as described above, had m. p. 174° (decomp.), unchanged on admixture with the dipicrate prepared from the sulphate. Crystallisation of this picrate from ethanol again resulted in the formation of a deep green colour in the solution.

Nitrito-derivatives (*Unbridged*).—(o-*Dimethylaminophenyldiethylphosphine*)*dinitritopalladium* (XIII). Addition of the phosphine (I) in ethanol to potassium palladonitrite (1 mol.) in water precipitated a very pale yellow microcrystalline solid, almost certainly bis-(*o*-dimethylaminophenyldiethylphosphine)palladium palladonitrite (as II; X = NO_2). This compound, in a suspension in boiling water, was very slowly converted into the dinitrito-compound (XIII). The conversion was accompanied by deposition of much palladium, and the yield of the compound (XIII) was low.

The compound was better prepared from bis-(*o*-dimethylaminophenyldiethylphosphine)-nitritopalladium mononitrite (XIV) (see below), which in boiling water decomposed into the nitrito-derivative (XIII) and the bridged compound (XVIII). On cooling of the aqueous solution, the two compounds crystallised and when collected were readily separated by extraction with cold methanol, in which (XVIII) is very soluble and (XIII) insoluble. The *dinitrito*-compound (XIII) formed yellow plates, m. p. 218° (decomp.), from methanol (Found: C, 35·1; H, 4·9%; *M*, in $CHCl_3$, 435. $C_{12}H_{20}O_4N_3PPd$ requires C, 35·2; H, 4·9%; *M*, 408).

Bis-(o-*dimethylaminophenyldiethylphosphine*)*nitritopalladium nitrite* (XIV). The phosphine (I) was added to a suspension of the compound (XIII) (1 mol.) in ethanol, which when warmed to 50° slowly gave a clear solution. Evaporation to dryness in a desiccator gave a gum, which was triturated with dry ether and placed immediately in a vacuum-desiccator. [If the gum is exposed to the air, it deliquesces, forming a solution of isomeric dinitrite (XV) (see below).] The dry gum was dissolved in acetone, and an excess of dry ether added. Well-formed, very pale yellow (almost colourless) crystals of the *nitrite monohydrate*, m. p. 139·5—140° (decomp. to deep red liquid), crystallised during 12 hr. (Found: C, 45·3; H, 6·3; N, 8·6. $C_{24}H_{40}O_4N_4P_2Pd$ requires C, 45·3; H, 6·5; N, 8·7%).

This compound was readily deposited when saturated aqueous sodium nitrite was added very slowly to a stirred, cold aqueous solution of the dichloride (IV; X = Cl) and, when washed with ice-water and dried, had m. p. and mixed m. p. 140° (decomp. as before). It is moderately soluble in cold water, and more so in hot water, from which it can be crystallised provided the solution temperature is kept below 65°. In aqueous solution above 70° it is rapidly decomposed (see below). The cold aqueous solution when set aside slowly deposits a small proportion of the isomeric dinitrito-compound (XVI), the main proportion being converted into the isomeric dinitrite (XV). The compound (XIV), when boiled with benzene, is converted into (XVI) and an unknown yellow compound.

The mononitrite (XIV), when added to sodium picrate, both in aqueous solution, gave an immediate yellow precipitate of the *monopicrate* (XVII), m. p. 178° (decomp.) after crystallisation from ethanol (Found: C, 45·6; H, 5·6; N, 10·4. $C_{30}H_{42}O_9N_6P_2Pd$ requires C, 45·1; H, 5·3; N, 10·5%).

Bis-(o-*dimethylaminophenyldiethylphosphine*)*palladium dinitrite trihydrate* (XV). An aqueous solution of the nitrite (XIV) when set aside for two days deposited a small quantity of the compound (XVI). The filtrate, when evaporated to dryness in a vacuum-desiccator, gave a residual gum which when stirred with a small quantity of acetone partly dissolved and partly crystallised. More crystals were deposited when ether was added to the solution. The colourless crystals of the *dinitrite trihydrate* (XV) when collected had m. p. 130—132° (decomp. to red liquid, becoming brown) (Found: C, 43·0; H, 6·8. $C_{24}H_{40}O_4N_4P_2Pd,3H_2O$ requires C, 43·3; H, 6·6%). The crystals were insoluble in cold benzene, but extremely soluble in cold water, the solution becoming irreversibly deep red on boiling. Attempts at recrystallisation from various solvents resulted in decomposition.

Bis-(o-*dimethylaminophenyldiethylphosphine*)*dinitritopalladium* (XVI). A suspension of the nitrite (XIV) in a large volume of benzene was heated under reflux on a water-bath for 4 hr. (Heating over a free flame caused decomposition of the solid which had separated on the side of the flask.) The solution was filtered hot to remove much brown residue, and then evaporated to dryness. Trituration of the resulting gum with ether afforded the crystalline *dinitrito*-compound (XVI), which on recrystallisation from benzene and then from chloroform–ethyl acetate was colourless and had m. p. 152·5° (decomp.) (Found: C, 46·4; H, 6·4; N, 9·2. $C_{24}H_{40}O_4N_4P_2Pd$ requires C, 46·7; H, 6·5; N, 9·2%). It is insoluble in water, readily soluble in cold chloroform and hot benzene.

The brown residue from the hot filtration was dissolved in a small quantity of cold ethanol which was filtered to remove a trace of the compound (XIII), m. p. and mixed m. p. 218°. The filtrate was evaporated to dryness, and the resulting deep yellow crystals, when recrystallised repeatedly from hot water, had a constant m. p. 267—270° (decomp. much previous charring), but inconsistent analytical results were obtained with different samples. The presence of nitrite ion was demonstrated by adding saturated sodium nitrite solution to a cold aqueous solution of the compound, thus depositing the crystalline original compound, m. p. and mixed m. p. being identical. A picrate, prepared by admixture of aqueous solutions of the compound and of sodium picrate, had m. p. 157° after crystallisation from aqueous ethanol, but also gave inconsistent analytical values.

Nitrito-compounds (*Bridged*).—*Bis-*(o-*dimethylaminophenyldiethylphosphine*)-μ-*nitrito*-μ′-*hydroxo-palladium dinitrite* (XVIII). This compound can be prepared by boiling an aqueous solution of the nitrite (XIV) (see above). More conveniently, a solution of the phosphine (I) in a small quantity of propan-1-ol was added to aqueous potassium palladonitrite (1 mol.) which was then boiled under reflux in a nitrogen atmosphere and shaded from the light. A red colour developed after 5 min., and the reaction was complete after 2 hr. The deep cherry-red solution on cooling deposited the bridged compound (XVIII) with a small quantity of the dinitrito-compound (XIII). The crystals were collected and extracted with the minimum quantity of cold methanol. The undissolved compound (XIII) was then collected, and the filtrate when diluted with ether deposited the *dinitrite* (XVIII), bright scarlet needles, m. p. 140° (decomp.) (Found: C, 36·4; H, 5·5; N, 8·9%; *M*, cryoscopic in urethane, 257. $C_{24}H_{41}O_7N_5P_2Pd_2$ requires C, 36·6; H, 5·2; N, 8·9%; *M*, 787). The salt crystallises from water in deep vermilion-red crystals, of identical composition and m. p. It is sparingly soluble in cold water but extremely soluble in cold methanol and ethanol. The molecular conductivity of an aqueous solution of the dinitrite (XVIII) at 20° was 228 mhos (*V*, 3010) and was constant over 30 min. The conductivity of a nitrobenzene solution at 20°, determined 1·5 min. after preparation, was 42·6 mhos (*V*, 1930) and fell to zero during 45 min., although the red colour of the solution appeared unaltered after 2 hr. It is clear therefore that the nitrite exists as a uni-bivalent salt in aqueous solution, and also initially in nitrobenzene solution, in which it apparently undergoes conversion into a null-valent product. Harris and Nyholm [8] cite a number of uni-bivalent salts, the molecular conductivities of which in nitrobenzene are in the range 38—58 mhos.

The *dichloride* (XIX; X = Cl) was precipitated when a saturated aqueous lithium chloride solution was slowly added to a cold aqueous solution of the dinitrite (XVIII), and when collected, washed with ice-water and then with much ether, was obtained as bright scarlet plates, m. p. 113—114° (Found: C, 37·5; H, 5·7; N, 5·3. $C_{24}H_{41}O_3N_3Cl_2P_2Pd_2$ requires C, 37·6; H, 5·3; N, 5·5%). The *dibromide* (XIX; X = Br), similarly prepared by using lithium bromide, and recrystallised from water, formed deep scarlet needles, m. p. 108—109° (Found: C, 33·8; H, 4·9; N, 4·7. $C_{24}H_{41}O_3N_3Br_2P_2Pd_2$ requires C, 33·7; H, 4·8; N, 4·9%), readily soluble in methanol and ethanol, and precipitated unchanged when the cold aqueous solution is treated with concentrated hydrobromic acid. Neither the dichloride nor the dibromide in the solid state or in solution was affected by light.

When warm aqueous solutions of the dibromide and of sodium picrate were slowly mixed, the *dipicrate* (XIX; X = $C_6H_2O_7N_3$) separated as fine red crystals, m. p. 103° after thorough washing with water and drying (Found: C, 37·5; H, 4·5. $C_{36}H_{45}O_{17}N_9P_2Pd_2$ requires C, 37·5; H, 3·9%).

Addition of an aqueous solution of the dinitrite (XVIII) to saturated aqueous sodium picrate deposited the *bis(amine-phosphine)-μ-nitrito-μ′-hydroxo-nitritopalladium monopicrate* (XX), red needles, m. p. 118—119° (prior shrinking) (from ethanol) (Found: C, 37·3; H, 4·0; N, 10·1, 10·2. $C_{30}H_{43}O_{10}N_7P_2Pd_2$ requires C, 37·2; H, 4·4; N, 10·1%).

We are greatly indebted to Dr. L. M. Venanzi for conductivity measurements, and to Albright and Wilson, Ltd., for a grant (to H. R. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, April 4th,* 1957.]