The Constitution of Complex Metallic Salts. Part XV. Palladium Derivatives of* o-*Dimethylaminophenyldimethylarsine.*

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A number of co-ordinated palladium derivatives of the above amine-arsine have been prepared, and the conditions under which it can thus form a chelate ring with the metal have been investigated.

It is well known that simple aliphatic tertiary amines will not usually co-ordinate with metallic salts. If however a molecule contains a tertiary amine group and another more strongly co-ordinating group, situated so that the two groups could co-operate to form a chelate ring, the co-ordinating power of the tertiary amine group may be considerably strengthened. For example, triethylamine does not co-ordinate with metallic salts, but 2 : 2′ : 2″-triaminotriethylamine forms stable salts such as $[Cl_2PtN(C_2H_4{\cdot}NH_2)_3]Cl_2$, $[NiN(C_2H_4{\cdot}NH_2)_3]SO_4$, and $[(SCN)_2CoN(C_2H_4{\cdot}NH_2)_3]SCN$, in all of which the tertiary amine group is firmly co-ordinated (Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 446; Mann, *J.*, 1926, 482; 1929, 409). Simple aliphatic tertiary phosphines and arsines, in contrast to the amines, co-ordinate readily and stably with many metals, particularly with palladium and platinum (cf. Mann and Purdie, *J.*, 1935, 1549; 1936, 873; Mann, Purdie, and Wells, *J.*, 1936, 1503; 1937, 1828; Chatt, *J.*, 1950, 2301; Chatt and Wilkins, *J.*, 1951, 2532).

It was therefore of great interest to investigate the co-ordination of palladium salts with *o*-dimethylaminophenyldimethylarsine (I), a compound in which the tertiary amine and the arsine group are ideally orientated for chelation [cf. *o*-phenylenebis(dimethylarsine); Chatt and Mann, *J.*, 1939, 1622]; the amine group might thus be enabled to co-ordinate with the palladium, although the N–Pd bond would certainly be much weaker than the As–Pd bond.

The arsine (I) is a colourless liquid prepared by the interaction of dimethyliodoarsine and the Grignard derivative of *o*-bromodimethylaniline: it readily forms a monomethiodide, in which undoubtedly the arsine group has become quaternised.

The arsine (I) in ethanolic solution reacted with hot aqueous potassium palladochloride to give an almost insoluble dark green product; digestion of this product with much boiling water or ethanol ultimately gave a clear solution which deposited the pale yellow crystalline dichloro-(*o*-dimethylaminophenyldimethylarsine)palladium (II). This compound is only slightly soluble in boiling water, ethanol, acetone, or benzene. When however an excess of the arsine was used, the orange-red crystalline monochlorobis(*o*-dimethylaminophenyldimethylarsine)palladium monochloride (III) was obtained. This monochloride could also be obtained by the action of the free arsine on the compound (II): conversely, when the monochloride (III) was slowly heated in an open vessel almost to its normal m. p., some of the arsine was lost and the compound (II) regenerated. The monochloride (III) has the normal properties of a salt: it is freely soluble in cold water, moderately so in cold ethanol, but almost completely insoluble in boiling acetone and benzene. The fact that only one chlorine is ionic, and therefore that only one amine-arsine molecule is chelated to the palladium, is clearly demonstrated by mixing cold aqueous solutions of the chloride (III) and of sodium picrate (in excess), by which means the crystalline monopicrate (IV; $X = Cl$) is precipitated.

The identity of the insoluble dark green product was not investigated: it may well be the palladochloride of the salt (III).

Similarly the arsine (I) when treated with potassium palladobromide gave a brown insoluble product which on digestion with boiling ethanol furnished the yellowish-orange crystalline dibromo-(*o*-dimethylaminophenyldimethylarsine)palladium (V) which is insoluble in boiling water and only very sparingly soluble in the common hot organic solvents, including dioxan. Treatment of either this compound or potassium palladobromide with the appropriate amount of the free arsine (I) produced deep ruby-red crystals

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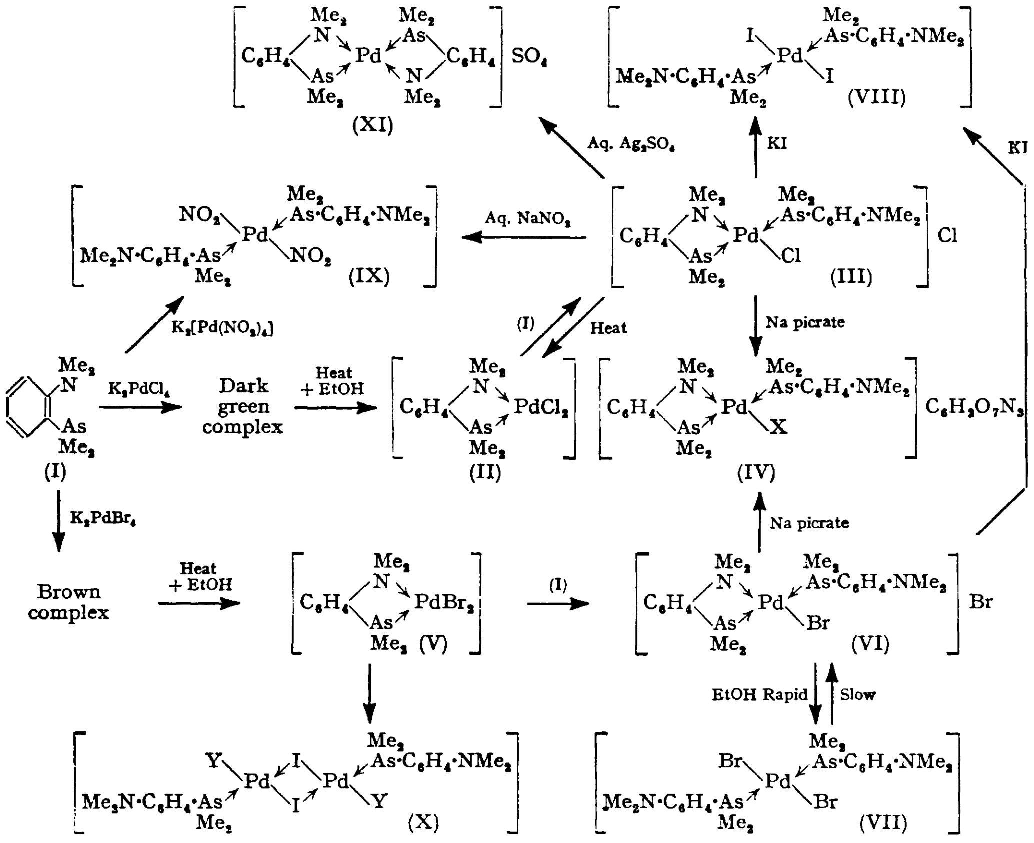
of monobromobis-(*o*-dimethylaminophenyldimethylarsine)palladium monobromide (VI), m. p. 170—172°. This salt is readily soluble in warm water (from which it can be recrystallised unchanged), moderately so in hot ethanol, slightly soluble in boiling acetone, and perceptibly more so in boiling benzene. Its constitution was also shown by its conversion into the crystalline monopicrate (IV; X = Br).



The monobromide (VI) was isolated by slow recrystallisation from ethanolic solution. When, however, recrystallisation from ethanol was performed as rapidly as possible, or when a suspension in benzene was boiled until clear, then concentrated and cooled, the non-ionic isomeric dibromobis-(*o*-dimethylaminophenyldimethylarsine)palladium (VII) was obtained as orange-yellow crystals, also of m. p. 170—172°. This isomer has the properties of a true covalent compound: it dissolves readily in cold benzene, is much more soluble in ethanol than the monobromide (VI), and only very slowly dissolves in boiling water, with conversion into the monobromide (VI). The interconversion of the two compounds is a ready process: the isomer (VII) always recrystallises unchanged from benzene, but slow recrystallisation from ethanol (in which the two isomers must exist in equilibrium) furnishes the monobromide (VI). Moreover, their identical m. p.s indicate a complete thermal conversion into one form which proves to be the isomer (VII). The equilibrium which exists in ethanolic solution between the compounds (VI) and (VII) represents a very rare type of tautomerism.

Aqueous or aqueous-ethanolic solution of the monochloride (III) or the monobromide (VI) when treated with potassium iodide deposited the orange-red di-iodobis-(*o*-dimethylaminophenyldimethylarsine)palladium (VIII). This compound shows no ionic properties: it is insoluble in boiling water, moderately soluble in ethanol and readily soluble in cold acetone and benzene, and in the last solvent shows a normal molecular weight.

The chloro-, bromo-, and iodo-compounds in this diarsine series thus show a noteworthy transition, since in the chloro-series apparently only the salt (III) can be obtained, whereas in the bromo-series the salt (VI) and the covalent isomer (VII) can be isolated, and in the iodo-series only the covalent form (VIII) is obtained. The absence of an iodo-derivative having the chelated arsine ring system is striking.

Treatment of an aqueous solution of potassium palladonitrite, $K_2[Pd(NO_2)_4]$, with the arsine (I), or of a similar solution of the monochloride (III) with sodium nitrite, produced dinitritobis-(*o*-dimethylaminophenyldimethylarsine)palladium (IX), as very pale yellow (almost colourless) crystals. The covalent structure (IX) is shown by the solubilities of this compound in water, ethanol, acetone, and benzene, which are closely similar to those of the di-iodo-compound (VIII): moreover, the compound (IX) also shows a normal molecular weight in benzene. The chelated ring in the monochloride (III) must therefore be broken at the N–Pd link during the above reaction, as in the similar preparation of the derivative (VIII). The fact that a fundamental change in structure has thus occurred is shown by mixing cold moderately concentrated aqueous solutions of (III) and of sodium nitrite: the mixture remains clear for some time before the insoluble dinitrito-compound (IX) begins to separate; and even if more concentrated cold solutions are employed, only a faint turbidity initially appears, although separation of (IX) is now less delayed.

When an ethanolic solution of the compound (IX) was treated with an excess of sodium iodide in acetone, heavy well-formed crystals of the di-iodo-derivative (VIII) slowly separated.

The dibromo-compound (V) is converted, when its suspension in aqueous potassium iodide is boiled for several hours, into a deep orange compound of empirical formula $C_{10}H_{16}NBrIAsPd$: the similar use of an acetone solution of sodium iodide gives a deep red product of composition $C_{10}H_{16}NI_2AsPd$. There is insufficient evidence to determine the structure of these compounds. They may be the simple chelated bromo-iodo- and di-iodo-compounds corresponding to (II) and (V), but it is more probable that they are the bridged compounds dibromobis-(*o*-dimethylaminophenyldimethylarsine)-μμ′-di-iododipalladium (X; Y = Br) and the di-iodo-μμ′-di-iodo-analogue (X; Y = I), respectively, for the following reasons. (*a*) The potassium iodide, employed in excess in the above preparation, would be unlikely to form a mixed bromo-iodo-compound of type (V) but, since the stability of halogen atoms in the bridged condition is known to increase in the order $Cl < Br < I$, the formation of the compound (X; Y = Br) is not unexpected. This reaction would have some analogies to that shown by dichlorobistri-*n*-butylphosphine-μμ′-dichlorodipalladium when heated in an aqueous-ethanolic suspension with an excess of potassium oxalate; the bridged chlorine atoms are replaced by a bridged oxalate radical, but the unbridged chlorine atoms are unaffected (Mann and Purdie, *loc. cit.*). (*b*) The compounds (II) and (V) blacken and decompose without melting, whereas the above red iodo-compound melts to a clear red liquid which only slowly decomposes. (*c*) The formation of the compound (VIII) indicates that the co-ordinating power of the iodine atom disrupts the N–Pd link, a process which in this series must lead to the bridged derivatives. The high molecular weights and low solubilities of the two compounds precluded decisive molecular-weight determinations.

The reason why the above halogeno- and nitrito-compounds contain no derivative having two molecules of the arsine chelated to one atom of palladium is apparently that the co-ordinating power of chlorine and bromine is sufficiently strong to break one of the two rings [cf. (III) and (VI)], whilst that of iodine and the nitro-group suffices to break both [cf. (VIII) and (IX)]. An anion of very weak co-ordinating power, which therefore would not enter the metallic complex, should allow the two chelate rings to exist. This we find to be the case. The chloride (III), when treated in aqueous solution with an equivalent of silver sulphate, gave the hydrated crystalline bis-(*o*-dimethylaminophenyldimethylarsine)palladium sulphate (XI): the fact that the water molecules had not co-ordinated with the palladium with rupture of the N–Pd link was shown by the conversion of the sulphate into the crystalline anhydrous dipicrate (as XI).

The co-ordinated derivatives of dialkyl-*o*-dimethylaminophenylphosphines and of dialkyl-(*o*-dialkylphosphinophenyl)arsines with various metals will be described later.

EXPERIMENTAL

Molecular weights were determined ebullioscopically.

o-*Dimethylaminophenyldimethylarsine* (I).—A solution of *o*-bromodimethylaniline (10·6 g.) in ether (45 c.c.) was slowly added to magnesium (1·6 g.) under ether (5 c.c.) in a nitrogen atmosphere. The resulting Grignard solution was boiled under reflux for 30 min., and then cooled in ice-water with stirring whilst a solution of dimethyliodoarsine (12·5 g., 1·02 mols.) in ether (30 c.c.) was added dropwise. A heavy dark oil separated, but slowly dissolved when the mixture was boiled for 2 hr.: the product was then cooled as before and hydrolysed with aqueous ammonium chloride. The dried ethereal layer on distillation gave the *arsine* (I), a colourless mobile refractive liquid (7·9 g., 68%), b. p. 110—114°/11 mm., having an unpleasant odour (Found: N, 6·1. $C_{10}H_{16}NAs$ requires N, 6·2%).

The arsine in ethereal solution readily gave a colourless *monomethiodide*, m. p. 221—222° (from methanol–ether) (Found: C, 36·0; H, 4·9; N, 4·1. $C_{11}H_{19}NIAs$ requires C, 35·9; H, 5·1; N, 3·8%): this salt gave a yellow *monomethopicrate*, m. p. 179—181° (from ethanol) (Found: C, 43·7; H, 4·3; N, 12·4. $C_{17}H_{21}O_7N_4As$ requires C, 43·5; H, 4·2; N, 12·0%).

Chloro-derivatives.—(*a*) Hot concentrated aqueous potassium palladochloride was treated with just sufficient of the arsine (I) in ethanol to discharge its colour. The precipitated dark green product was collected and boiled with a large volume of water until a clear solution was obtained: the crystals which separated on cooling were recrystallised from much ethanol, and afforded *dichloro-*(o-*dimethylaminophenyldimethylarsine*)*palladium* (II), glistening pale yellow plates, which darkened and became black at 215—220° but gave no effervescence below 320° (Found: C, 29·8; H, 3·9%; *M*, in ethylene dichloride, 380. $C_{10}H_{16}NCl_2AsPd$ requires C, 29·8; H, 3·9%; *M*, 402·7).

(*b*) Solutions of potassium palladochloride (0·5 g.) in water (5 c.c.) and of the arsine (I) (0·7 g., 2 mols.) in ethanol (5 c.c.) were mixed and boiled until a clear solution was obtained, 50% aqueous ethanol being added when necessary. The solution was evaporated to dryness and the residue extracted with boiling absolute ethanol. The filtered extract, when diluted with ether and vigorously scratched, deposited *monochlorobis-*(o-*dimethylaminophenyldimethylarsine*)-*palladium monochloride* (III), which, when carefully recrystallised from ethanol by the addition of ether, formed beautiful orange-red prisms, m. p. 187—188° (decomp.) (Found: C, 38·3; H, 5·1; N, 4·5. $C_{20}H_{32}N_2Cl_2As_2Pd$ requires C, 38·2; H, 5·1; N, 4·4%). Mixing cold aqueous solutions of this salt and of sodium picrate precipitated the *monopicrate* (IV; X = Cl), yellow needles, m. p. 171—172°, from ethanol (Found: C, 38·2; H, 4·0; N, 8·6. $C_{26}H_{34}O_7N_5ClAs_2Pd$ requires C, 38·0; H, 4·1; N, 8·5%): the presence of chlorine in this salt was confirmed.

When a finely powdered sample of the monochloride (III) was slowly heated to *ca.* 160°, it became pale yellow as amine-arsine was lost with conversion into the compound (II), which then could be readily recrystallised from ethanol. When a hot ethanolic solution of the compound (II) was treated with the arsine (1 mol.), the solution immediately became deep orange and, when considerably concentrated, cooled, and diluted with ether, deposited the pure monochloride (III), m. p. 186—187° (decomp.), alone and mixed.

Bromo-derivatives.—(*a*) The addition of an ethanolic solution of the arsine (I) to a hot concentrated aqueous solution of potassium palladobromide until the colour of the latter had faded precipitated a dark khaki-coloured product, which, when collected and digested with much boiling ethanol, ultimately gave an almost clear solution. The filtered cooled solution deposited *dibromo-*(o-*dimethylaminophenyldimethylarsine*)*palladium* (V), yellowish-orange needles, which began to blacken at *ca.* 220° and effervesced at 240° (Found: C, 24·7; H, 3·5; N, 3·1%; *M*, in ethylene dibromide, 470. $C_{10}H_{16}NBr_2AsPd$ requires C, 24·4; H, 3·2; N, 2·8%; *M*, 491·7).

(*b*) An ethanolic solution of the arsine (I) was added to a vigorously stirred hot concentrated solution of potassium palladobromide until a clear yellow solution containing a slight excess of (I) was obtained. The solution, diluted with a small amount of water and cooled, deposited *monobromobis-*(o-*dimethylaminophenyldimethylarsine*)*palladium monobromide* (VI), which on slow crystallisation from ethanol formed ruby-red prisms, m. p. 170—172° (decomp.) (Found: C, 33·5; H, 4·5; N, 4·2. $C_{20}H_{32}N_2Br_2As_2Pd$ requires C, 33·5; H, 4·4; N, 3·9%). This salt crystallised unchanged when its warm aqueous solution was cooled. This aqueous solution, when added to aqueous sodium picrate, precipitated the *monopicrate* (IV; X = Br), yellow crystals (from ethanol), m. p. 174—175° (Found: C, 36·3; H, 4·0; N, 8·2. $C_{26}H_{34}O_7N_5BrAs_2Pd$ requires C, 36·1; H, 3·9; N, 8·1%); the presence of bromine was confirmed.

A hot concentrated ethanolic solution of the monobromide (VI), when rapidly cooled with vigorous stirring and scratching, deposited *dibromobis*-(o-*dimethylaminophenyldimethylarsine*)-*palladium* (VII), orange-yellow tablets, m. p. 170—172° (decomp.) (Found: C, 33·8; H, 4·5; N, 4·0. $C_{20}H_{32}N_2Br_2As_2Pd$ requires C, 33·5; H, 4·4; N, 3·9%). A suspension of the monobromide (VI) in benzene when boiled slowly dissolved and the clear solution on cooling deposited the isomer (VII). The monobromide (VI), when heated just above its m. p. and then cooled, was converted into the isomer (VII) without change of m. p.: this conversion was shown in particular by the ready solubility of the product in cold benzene, in which the monobromide (VI) is very slightly soluble.

Iodo-derivative.—An excess of aqueous potassium iodide, when added to a cold aqueous solution of the monochloride (III), precipitated *di-iodobis*-(o-*dimethylaminophenyldimethylarsine*)-*palladium* (VIII), deep orange-red crystals, m. p. 206—207° (decomp.) from ethanol (Found: C, 29·4; H, 4·1%; *M* in benzene, 780. $C_{20}H_{32}N_2I_2As_2Pd$ requires C, 29·6; H, 3·9%; *M*, 810·5). The same compound was obtained when the monobromide (VI) in aqueous-ethanol solution was used.

Nitrito-derivative.—A warm stirred concentrated aqueous solution of potassium pallado-nitrite, when treated with a slight excess of the arsine (I) in ethanol, readily deposited *dinitritobis*-(o-*dimethylaminophenyldimethylarsine*)*palladium* (IX), very faint greenish-yellow (almost colourless) crystals, m. p. 180° (decomp.), from ethanol (Found: C, 37·2; H, 5·3; N, 8·5%; *M* in benzene, 640. $C_{20}H_{32}O_4N_4As_2Pd$ requires C, 37·0; H, 4·9; N, 8·6%; *M*, 648·8). A cold aqueous solution of the monochloride (III), when mixed with an excess of sodium nitrite solution, remained initially clear and then slowly deposited the compound (IX) which, after crystallisation from ethanol, had m. p. 179—180° (decomp.), unchanged on admixture with the above sample.

An ethanolic solution of the compound (IX), when diluted with a small excess of a saturated acetone solution of sodium iodide, slowly deposited crystals of the di-iodo-compound (VIII), m. p. 206° (decomp.), unchanged by admixture with the above authentic compound.

Bridged Compounds.—(*a*) The finely powdered dibromo-compound (V), when digested for several hours with boiling aqueous potassium iodide, was converted into *dibromobis*-(o-*dimethylaminophenyldimethylarsine*)-$\mu\mu'$-*di-iododipalladium* (X; Y = Br), deep orange crystals, m. p. 229—230° (decomp.), from ethanol (Found: C, 22·0; H, 2·9; N, 2·9. $C_{20}H_{32}N_2Br_2I_2As_2Pd_2$ requires C, 22·2; H, 2·9; N, 2·6%).

(*b*) When the compound (V) was similarly digested for 4 hr. with an excess of sodium iodide in acetone, a marked change in colour occurred, and the solution, when concentrated and diluted with water, deposited the *di-iodo*-$\mu\mu'$-*di-iodo*-analogue (X; Y = I), deep red crystals, m. p. 221—222° (slow decomp.), from ethanol (Found: C, 20·6; H, 2·7; N, 2·3. $C_{20}H_{32}N_2I_4As_2Pd$ requires C, 20·5; H, 2·7; N, 2·3%).

The Sulphate (XI).—Warm aqueous solutions of the chloride (III) (34 mg.) and silver sulphate (17 mg., 1 mol.) were mixed, vigorously shaken, and filtered. The filtrate, evaporated in a desiccator at room temperature, deposited hydrated clear pale yellow plates, which were very soluble in water, methanol, ethanol, and acetone, but insoluble in boiling benzene. When confined in a vaccum over phosphoric anhydride, they rapidly underwent partial dehydration to *bis*-(o-*dimethylaminophenyldimethylarsine*)*palladium sulphate trihydrate* (XI), a fine very pale buff coloured powder, m. p. 178—180° (decomp.) (Found: C, 33·8; H, 5·5. $C_{20}H_{32}O_4N_2SAs_2Pd,3H_2O$ requires C, 33·9; H, 5·4%). The addition of this sulphate to sodium picrate, both in cold aqueous solution, precipitated the *dipicrate* (as XI), a dark yellow micro-crystalline powder, m. p. 188—190° (decomp.), after crystallisation from water containing a small proportion of ethanol (Found: C, 37·75; H, 3·9; N, 11·1. $C_{32}H_{36}O_{14}N_8As_2Pd$ requires C, 37·9; H, 3·6; N, 11·1%).

Great accuracy is not claimed for the determination of the molecular weights of the compounds (II) and (V), owing to their very low solubility in boiling solvents: the values obtained however leave no doubt concerning the order of the molecular weights.

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