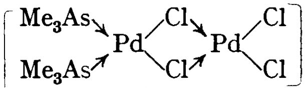
129. *The Constitution of Complex Metallic Salts. Part VII. The Structure and Configuration of the Bridged Derivatives of Trimethylarsine with Palladous Halides.*

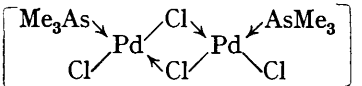
By Frederick G. Mann and Alexander F. Wells.

It has previously been shown that the bridged derivatives of the trialkyl-phosphines and -arsines with palladous halides, *e.g.*, $[R_3P,PdCl_2]_2$ and $[R_3As,PdCl_2]_2$, exist in the solid state as only one of the three theoretically possible isomeric forms (I—III below): in organic solvents all three forms are apparently present in tautomeric equilibrium. Crystallographic examination of the isomorphous trimethylarsine members, $[Me_3As,PdCl_2]_2$ and $[Me_3As,PdBr_2]_2$, proves that these compounds have a planar molecule with a centre of symmetry, and must therefore be the isomer (III). The dimensions of these molecules and their orientation in the crystal have been determined. The significance of these results is discussed.

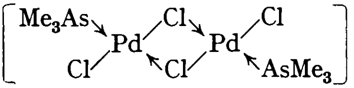
In Part IV (Mann and Purdie, J., 1936, 873) the constitution of the trialkyl-phosphine and -arsine derivatives of various palladous salts, having the molecular formulæ $[R_3P,PdX_2]_2$ and $[R_3As,PdX_2]_2$ where X is a univalent acid radical, was discussed, and a considerable volume of evidence was adduced to show that in these compounds the two palladium atoms are linked or "bridged" through two acid radicals. It followed that the trimethylarsinepalladous chloride member, $[Me_3As,PdCl_2]_2$, for example, should theoretically exist in three isomeric forms, *viz.*, the unsymmetrical form (I), and the *cis*- and *trans*-members of the symmetrical form (II and III, respectively). It was shown, however, that such isomerism did not apparently occur in the solid state, since each compound examined was crystallographically homogeneous and (except the lower homologous members) of sharp melting point. Moreover, the *n*-butylphosphine and the *n*-butylarsine members were isomorphous, and therefore the two homologous series had identical structures in the solid state. In organic solvents, however, these compounds gave a number of reactions indicating clearly the existence of both the unsymmetrical (I) and the symmetrical (II and III) forms, and it followed that in such solutions these isomeric forms exist apparently in tautomeric equilibrium.



(I.)



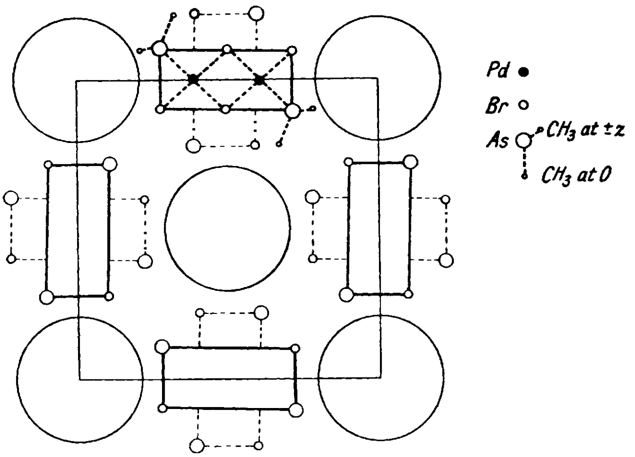
(II.)



(III.)

In order to determine which of the three isomeric forms exists in the solid state, a crystallographic examination has now been made of dichlorobis(trimethylarsine)-μ-dichlorodipalladium (I—III) and of the analogous bromine *compound* $[Me_3As,PdBr_2]_2$. These compounds were selected because it was essential to examine the first member of the homologous series in order to minimise complications caused by the alkyl groups: furthermore, the methylarsine derivatives were more readily accessible than the methylphosphine derivatives, and the arsenic atom more suitable for *X*-ray detection than the lighter phosphorus atom. (For investigation of the reactions of this class of compound in solution, the butyl members were earlier used because of their higher solubility and greater thermal stability.) The tetrachloride and the tetrabromide were obtained from various solvents as very fine needles: the best-developed crystals were obtained in each case from dioxan, from which the two compounds separated as isomorphous tetragonal prisms. A complete *X*-ray examination has been made of the tetrabromide. It was first established that the molecules—apart from the alkyl groups—are planar (in accordance with formulæ I—III) and that the crystals are built up of parallel layers of such molecules. The molecule, furthermore, possesses a diad axis of symmetry perpendicular to the plane of the molecule and therefore must have the *trans*-symmetrical structure such as (III). The orientation of the molecules in the crystal was then determined: this is depicted diagrammatically in Fig. 1, which shows the relative position of four such molecules in one plane, and that of the corresponding four molecules in the plane below. The relative position of the atoms in the molecule was finally determined (Fig. 2), and conclusive

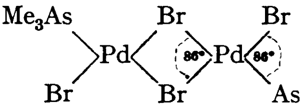
FIG. 1.



Projection of the structure of [Me$_3$As,PdBr$_2$]$_2$ *on* (001)—*diagrammatic. Molecules at z* = 0 *are distinguished by heavy unbroken lines, those at z* = $\frac{1}{2}$ *by light dotted lines. The heavy dotted lines indicate the bonds in one molecule at z* = 0; *the palladium atoms and the bridged bromine atoms are shown in this molecule only. The large circles* (*radius* 3·45 A.) *represent the possible position of dioxan molecules.*

proof of the *trans*-symmetrical formula thus obtained. The palladium atoms are therefore definitely bridged by bromine atoms, and the four-membered ring thus produced has an angle of 86° at the palladium atoms: the opposite angle in each case, between the arsenic-palladium-bromine atoms, has the same value. The distance between the palladium atoms and neighbouring bromine atoms (bridged and unbridged) has a constant value, 2·45 A., that between palladium and neighbouring arsenic atoms being slightly greater, 2·50 ± 0·05 A.

FIG. 2.

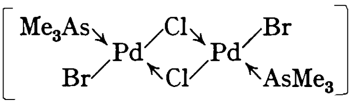


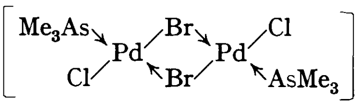
Configuration and dimensions of the dibromobis(trimethylarsine)-μ-dibromodipalladium molecule.
Interatomic distances: Pd–Br, 2·45 A.; Pd–As, 2·50 ± 0·05 A.

An interesting point arose in connexion with the purification of these compounds. When the tetrachloride and tetrabromide were recrystallised from alcohol, the fine needles, when dried in a vacuum desiccator for 3—4 hours, were pure. When these compounds were recrystallised from dioxan, similar but larger and better-formed needles were obtained, which however usually still contained traces of dioxan even after 24 hours in a vacuum desiccator. These last traces of dioxan were then slowly lost in the desiccator (most rapidly from the smallest crystals), but the crystal form and structure of the compounds were unaffected by this loss of solvent: hence the dioxan could not have been originally chemically combined with the palladium molecule. The explanation of this phenomenon is that the orientation of the molecules in the crystal (Fig. 1) gives rise to cylindrical tunnels in the crystal parallel to the *c* axis, *i.e.*, at right angles to the layers of the planar molecules. The molecules of a solvent (if not too large) may therefore occupy these tunnels without appreciable distortion of the crystal structure, such molecules having clearly no linkage or constant proportion to the palladium molecules. The comparatively small and readily volatile molecules of alcohol are quickly lost from these tunnels when the crystals are placed in a vacuum. The cyclic molecules of dioxan have a diameter approximating to that of these tunnels, and the escape of these larger and less volatile molecules must obviously be a much slower process. The growth of the crystals in dioxan does, however, cause a slight change in the cell dimensions: thus the needles of the tetrachloride from alcohol and dioxan are isomorphous, but the needles from dioxan have cell dimensions 1·5% greater than those of the needles from alcohol. This movement of solvent molecules through tunnels in the crystal structure is not a novel phenomenon, and this example is probably closely parallel to that of the water molecules in the zeolite crystals.

Since the configuration of these bridged palladium compounds was thus accurately known, it was of interest to investigate a similar compound having mixed acid radicals, and for this purpose the *dichloride-dibromide* compound, $[Me_3As,PdClBr]_2$, was prepared; it was obtained by the action of ammonium palladochloride on *dibromobis(trimethylarsine)-palladium*, $[(Me_3As)_2PdBr_2]$, and separated readily from alcohol in needles very similar to, but not isomorphous with, those of the tetrachloride and tetrabromide. After this main crop had been removed, the mother-liquor on standing deposited small quantities of compact monoclinic crystals; when these crystals were collected, the disturbance of the solution owing to the filtration caused the more rapid separation of fine rhombic needles. Three forms of this compound were thus obtained. The rhombic needles contained 8 molecules of $[Me_3As,PdClBr]_2$ in the cell and were therefore not further investigated. The monoclinic crystals, however, had only 2 molecules in the cell and these molecules possessed a centre of symmetry: they must therefore have the structure (IV) or (V), and are of the same isomeric form as the tetrachloride and tetrabromide. The reactions of the tributylphosphine dichloride-dibromide, $[Bu_3{}^{\alpha}P,PdClBr]_2$, which have been studied and will be described in a subsequent communication, give strong evidence that the bridging in this molecule is through the bromine atoms, and by analogy it is probable that the monoclinic crystals of the trimethylarsine compound have the structure (V). It should be noted, however, that each of the three isomeric forms of the trimethylarsine tetrachloro-compound (I, II, and III) can theoretically give rise to four isomeric compounds when two of the four chlorine atoms are replaced by bromine, and the dichloride-dibromide may be formulated therefore in twelve isomeric forms.

(IV.)

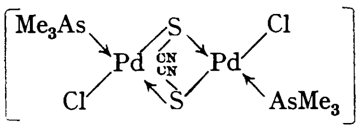


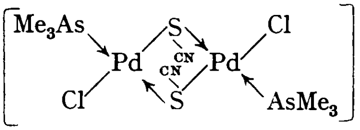


(V.)

Other mixed compounds of this type, such as the *dichloride-dithiocyanate*, $[Me_3As,PdCl(SCN)]_2$ (VI), and the *dibromide-dithiocyanate*, $[Me_3As,PdBr(SCN)]_2$, have now been prepared for investigation. These two compounds were obtained by the action of ammonium palladochloride and palladobromide respectively on *dithiocyanatobis(trimethylarsine)palladium*, $[(Me_3As)_2Pd(SCN)_2]$, and it is known (Mann and Purdie, *loc. cit.*) that in such compounds the palladium atoms are bridged through the thiocyanate groups. An additional cause of isomerism will arise in such compounds, however, as the tetrahedral disposition of the co-ordinated sulphur atoms will cause the — CN groups to adopt either the *cis*- or the *trans*-position (VIA and VIB respectively) relative to the plane of the molecule.

(VIA.)

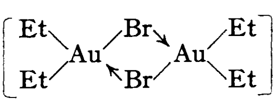


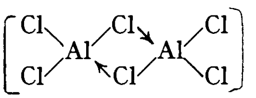


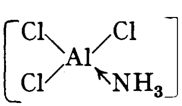
(VIB.)

Dichlorobis(trimethylphosphine)-μ-dichlorodipalladium, $[Me_3P,PdCl_2]_2$, has also been prepared for crystallographic investigation; it separates as large, well-formed, monoclinic crystals, which are therefore not isomorphous with those of the trimethylarsine analogue. The fact that, in the homologous phosphine and arsine palladium compounds, isomorphism is not shown by the methyl members but is shown by the *n*-butyl members is not surprising, since as each series is ascended the effect of the six increasingly large alkyl groups will tend more and more to minimise the difference in the inorganic portion of the molecules.

This elucidation of the structure of the tetrachloride and tetrabromide, together with the fact that Burawoy, Gibson, Hampson, and Powell (J., 1937, 1690) have found a similar structure for diethylmonobromogold (VII), gives decisive proof of the existence of the bridged linking of metallic atoms through acid radicals and other similar groups, a type of linking first used in 1905 by Werner (" Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," 1st edtn., pp. **63**, **71**, **188**), who later extended its use considerably *

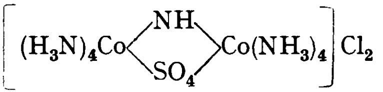

(VII.)

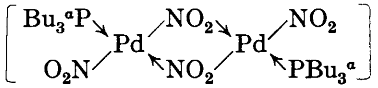

(VIII.)

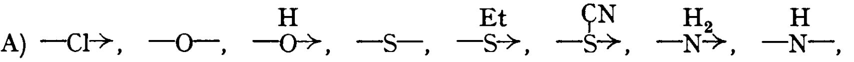

(IX.)

(*op. cit.*, 2nd edtn., 1909, p. 185 *et seq.*). There is little doubt that this type of linking is commoner than has been supposed, and that it exists, not only in compounds such as $[CO,PtCl_2]_2$ and $[C_2H_4,PtCl_2]_2$, but also in several volatile metallic chlorides which exhibit immediately above their boiling point a vapour density corresponding to a bimolecular form. Chief among the latter are aluminium chloride (VIII) (Werner, *op. cit.*, 5th edtn., 1923, p. 285), gallium trichloride, and ferric chloride. The bridged linkage in these metallic chlorides is clearly not of great stability, since at higher temperatures the vapour density falls to that required for the unassociated chloride; for instance, the density of aluminium chloride vapour corresponds at 430° to Al_2Cl_6 and at 800° to $AlCl_3$, similar results being obtained for ferric and gallium chlorides (Friedel and Crafts, *Compt. rend.*, 1888, **106**, 1764; **107**, 301, 306; Nilson and Pettersson, *Z. physikal. Chem.*, 1889, **4**, 222; Biltz and Meyer, *Z. anorg. Chem.*, 1928, **176**, 23). When, however, aluminium chloride reacts with ammonia, the stable volatile trichloroamminoaluminium (IX) is formed; this compound has now the " unimolecular " formula, since the aluminium atom has acquired five electrons and the bridged formulation is thus no longer possible; gallium trichloride behaves similarly (Klemm, Clausen, and Jacobi, *ibid.*, 1931, **200**, 343, 367; Klemm, Tilk, and Jacobi, *ibid.*, 1932, **207**, 187). The fact that aluminium chloride shows a molecular weight corresponding to $AlCl_3$ when dissolved particularly in co-ordinating solvents such as pyridine and ether may be due to simple dissociation, but is more probably due to the formation of soluble compounds similar to (IX) by linkage with solvent molecules.

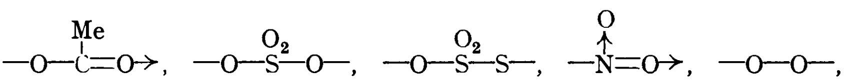
In all the bridged compounds discussed above, the nature of the bridging group has allowed (i) the simultaneous operation of a covalent and a co-ordinate link from this group, (ii) the formation of a 4-membered ring. Consideration of the chief groups known to bridge metallic atoms shows that many such groups bridge, however, by the operation of two covalent links: such groups occur more frequently in the 6-co-ordination salts, such as octammino-μ-imino-μ-sulphatodicobaltic chloride (X). Moreover, the nature of many bridging groups necessarily entails (if more than one group is present in the molecule) a bridged ring containing more than four atoms. Thus the bridging groups in (A) can all give 4-membered rings when two such groups bridge two metallic atoms, the type of linkages involved being indicated. The groups in (B) necessarily give rings with more than four atoms under similar conditions. The groups noted under (B) are the acetate group, which by resonance gives a symmetrical linkage; the sulphate and thiosulphate groups; the nitro-group, in which one of the oxygen atoms must co-ordinate to the metal,


(X.)


(XI.)

(A) 

$$-Cl\rightarrow,\ -O-,\ -\overset{H}{O}\rightarrow,\ -S-,\ -\overset{Et}{S}\rightarrow,\ -\overset{CN}{S}\rightarrow,\ -\overset{H_2}{N}\rightarrow,\ -\overset{H}{N}-,$$

(B) 

$$-O-\overset{Me}{C}{=}O\rightarrow,\ -O-\overset{O_2}{S}-O-,\ -O-\overset{O_2}{S}-S-,\ -\overset{\overset{O}{\uparrow}}{N}{=}O\rightarrow,\ -O-O-,$$

since the nitrogen atom has no unshared pair of electrons available; the peroxide group, which gives a linkage of great stability, but may belong to the (A) group and have the

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* It is of interest to note that formulæ precisely similar to (I) and (III) were suggested in 1909 by Werner (*op. cit.*, p. 52) for the compound $[PCl_3,PtCl_2]_2$.

structure $>O \rightarrow O$. In the palladium compounds described above, it is clear that 6-membered rings can be formed, since dinitrobis(tributylphosphine)-μ-dinitrodipalladium (XI) has been prepared (Mann and Purdie, *loc. cit.*). The ***dinitrite-dichloride*** derivative of trimethylarsine, $[\mathrm{Me_3As,Pd(NO_2)Cl}]_2$, has therefore been prepared and is under investigation. This compound was obtained by the action of ammonium palladochloride on *dinitrobis(trimethylarsine)palladium*, $[(\mathrm{Me_3As})_2\mathrm{Pd(NO_2)_2}]$, and it is probable therefore that in this compound the nitro-groups (and not the chlorine radicals) bridge the palladium atoms, with the production of a 6-membered ring.

Since the unsymmetrical and the *cis*-symmetrical forms (I and II) of the tetrachloride and tetrabromide compounds have not been detected in the solid state, we have, in collaboration with Dr. D. Purdie, investigated the phosphine and arsine derivatives of certain other metallic halides, particularly those of the mercuric halides. Preliminary experiments show that such isomerism does apparently occur in the crystalline state in such compounds. Thus di-iodobis(tri-*n*-propylphosphine)-μ-di-iododimercury, $[\mathrm{Pr}^{\alpha}_3\mathrm{P,HgI_2}]_2$, has been isolated in two forms of correct molecular weight: one white and of m. p. 114°, and the second yellow and convertible into the white form on heating. The apparent isomerism of these mercury derivatives is now being investigated in detail.

EXPERIMENTAL.

Chemical Data.

Dichlorobis(trimethylarsine)palladium, $[(\mathrm{Me_3As})_2\mathrm{PdCl_2}]$.—The preparation of this compound, from which almost all the subsequent compounds are derived, is considerably improved by the following method, which is speedy and avoids the troublesome isolation of trimethylarsine. A Grignard reagent was prepared by the action of methyl iodide (34 c.c., 78 g.) dissolved in ether (50 c.c.) upon magnesium (13 g., 4·5 atoms per 1 mol. $\mathrm{AsCl_3}$) covered with ether (150 c.c.) in a flask fitted with a reflux condenser, mechanical stirrer, and a gas inlet tube; hydrogen was passed into the flask, and directly the reaction started, the mixture was cooled in ice-water to allow rapid addition of the methyl iodide without undue boiling of the ether. The mixture was then vigorously stirred, and the stirring and ice-cooling (in the atmosphere of hydrogen) continued until the final preparation of the arsine was complete. A solution of arsenic trichloride (10 c.c., 22 g.) in ether (50 c.c.) was next added, and when the reaction was complete, hydrolysis was performed by the addition of ammonium chloride (50 g.) dissolved in cold freshly-boiled water (250 c.c.). The condenser was then replaced by a syphon-shaped tube, through which the solution was transferred by the pressure of hydrogen into a separating-funnel. The ethereal layer was separated, filtered if necessary, and at once shaken vigorously with increasing quantities of an aqueous solution of ammonium palladochloride. When about 16 g. of the latter had been added, a copious separation of the bright yellow dichloro-compound occurred; an excess of palladochloride must be avoided, otherwise the dichloro-compound becomes contaminated with the reddish-brown bridged tetrachloro-compound. (It is advisable, therefore, to withhold a few c.c. of the ethereal solution, which can then if necessary be added to the final product to decompose any brown tetrachloro-compound and thus restore the yellow colour of the dichloro-compound.) The dichloro-compound should be collected without delay, washed with water and dried, and can be used without further purification for the following preparations. Yield, *ca.* 21 g.

Dibromobis(trimethylarsine)palladium.—Solutions of the above dichloro-compound (5 g.) in boiling alcohol (200 c.c.) and of ammonium bromide (7 g., 6 mols.) in water (15 c.c.) were mixed, and boiled for 1 hour, the colour of the mixture changing rapidly to orange. On cooling, the *dibromo*-compound separated as orange needles, which, after recrystallisation from alcohol, had m. p. 229° (Found: C, 14·3; H, 3·5. $\mathrm{C_6H_{18}Br_2As_2Pd}$ requires C, 14·2; H, 3·6%). The compound was also prepared by the action of trimethylarsine (2 mols.) upon an aqueous solution of ammonium palladobromide.

Dichlorobis(trimethylarsine)-μ-dichlorodipalladium (III).—The preparation of this compound, and its purification by recrystallisation from alcohol, have already been described (Mann and Purdie, *loc. cit.*). It can also be recrystallised from dioxan, acetic acid, and ethylene dichloride. Prolonged boiling with dioxan causes reduction, with separation of palladium. Hence, for recrystallisation sufficient dioxan must be taken to give a clear solution rapidly on boiling; the solution can then be allowed to cool spontaneously, since reduction does not occur below the b. p. of dioxan. The well-formed crystals so obtained contain small quantities of dioxan, which is slowly lost in a vacuum without change of the crystal form. For instance, three different samples, after being in a vacuum for 24 hours, gave (i) C, 13·2; H, 2·9; (ii) C, 13·9; H, 3·2; (iii) Pd, 35·3 (Calc. for $C_6H_{18}Cl_4As_2Pd_2$: C, 12·1; H, 3·05; Pd, 35·85%). Rapid crystallisation from dioxan gave minute needles which readily lost all traces of the solvent in a vacuum and thus were soon obtained analytically pure.

Dibromobis(trimethylarsine)-μ-dibromodipalladium.—Hot solutions of dibromobis(trimethylarsine)palladium (2 g.) in alcohol (150 c.c.) and of ammonium palladobromide (1·8 g., 1 mol.) in water (15 c.c.) were mixed, and boiled under reflux for 30 minutes. The solution when filtered and cooled deposited the above *tetrabromide* in fine reddish-brown needles; after recrystallisation from alcohol, these decomposed at 258—260° with previous darkening but without melting (Found: C, 9·5; H, 2·5; Pd, 27·3. $C_6H_{18}Br_4As_2Pd_2$ requires C, 9·3; H, 2·3; Pd, 27·6%). Larger needles were obtained from dioxan, but these (like those of the above tetrachloride) contained traces of dioxan which were slowly lost in a vacuum: three different samples after 24 hours in a vacuum gave (i) C, 10·8; H, 2·3; (ii) C, 12·2; H, 2·9; (iii) Pd, 26·4.

Dichlorobis(trimethylarsine)-μ-dibromodipalladium (V).—This was prepared as the above tetrabromide, but from dibromobis(trimethylarsine)palladium (2 g.) and ammonium palladochloride (1·1 g., 1 mol.). The alcoholic solution on slow cooling deposited tetragonal needles of the *dichloride-dibromide*: these when recrystallised from alcohol, darkened on heating at 230° and by 248° had decomposed with the formation of a palladium mirror (Found: C, 10·5; H, 2·5; Pd; 31·0. $C_6H_{18}Cl_2Br_2As_2Pd_2$ requires C, 10·5; H, 2·6; Pd, 31·2%). The mother-liquor on long standing deposited compact monoclinic crystals (IV and V); these were collected, but were contaminated by a small proportion of the rhombic needles which started to separate during the filtration (Found, for the mixture: C, 10·5; H, 2·6%).

Dithiocyanatobis(trimethylarsine)palladium.—The finely-powdered dichloro-compound was added to excess of a cold concentrated aqueous solution of potassium thiocyanate. The mixture on shaking became at first brown, and later gave a copious precipitate of the yellow dithiocyanate. After 2 hours' shaking, the product was collected, washed with water, and twice recrystallised from alcohol; the *dithiocyanate* was thus obtained in deep yellow crystals, m. p. 124° (Found: C, 20·7; H, 3·9; N, 6·1. $C_8H_{18}N_2S_2As_2Pd$ requires C, 20·75; H, 3·9; N, 6·05%); when molten, it is deep red, and its hot concentrated alcoholic solution is also red, but deposits the yellow form unchanged on cooling.

Dichlorobis(trimethylarsine)-μ-dithiocyanatodipalladium (VI).—This was prepared by the usual method, hot alcoholic and aqueous solutions of the above dithiocyanate and of ammonium palladochloride (1 mol.) respectively being mixed and heated. The rapid change in colour indicated ready formation of the bridged complex, and after 5 minutes' heating, the solution was allowed to cool. The crystals which separated were dissolved in acetone, and the hot solution diluted with alcohol; the *dichloride-dithiocyanate* separated as minute dark orange crystals, m. p. 192—193° (decomp.) (Found: C, 15·4; H, 2·8; N, 4·5. $C_8H_{18}N_2Cl_2S_2As_2Pd_2$ requires C, 15·0; H, 2·8; N, 4·4%).

The *dibromide-dithiocyanate* was similarly prepared from ammonium palladobromide, and after recrystallisation from acetone was obtained as orange-red crystals, m. p. 189—190° (decomp.) (Found: C, 13·2; H, 2·45; N, 3·8. $C_8H_{18}N_2Br_2S_2As_2Pd_2$ requires C, 13·2; H, 2·7; N, 3·8%).

Dinitrobis(trimethylarsine)palladium.—The finely powdered dichloro-compound was shaken with excess of a cold concentrated aqueous solution of sodium nitrite for 2 hours, by which time the yellow dichloro-compound had been entirely replaced by the almost white *dinitro*-compound; this was collected, washed with water, and recrystallised from alcohol–acetone, being obtained as very pale lemon-coloured crystals, m. p. 234° (decomp.) (Found: N, 6·3; Pd, 24·0. $C_6H_{18}O_4N_2As_2Pd$ requires N, 6·4; Pd, 24·3%).

Dichlorobis(trimethylarsine)-μ-dinitrodipalladium.—A hot solution of ammonium palladochloride (1·3 g.) in water (4 c.c.) and alcohol (20 c.c.) was added to a boiling solution of the foregoing compound (2 g., 1 mol.) in alcohol (100 c.c.), and the mixture, the colour of which changed rapidly to reddish-orange, was at once allowed to cool spontaneously. After 24 hours, a fine, microcrystalline, buff-coloured deposit was separated, and the filtrate set aside for a further 48 hours. Fine, pale orange crystals of the *dinitro-dichloride* slowly developed: these, when collected, washed with water, and dried, had m. p. 186—188° (decomp. with preliminary softening) (Found: C, 11·8; H, 3·3; N, 4·4. $C_6H_{18}O_4N_2Cl_2As_2Pd_2$ requires C, 11·7; H, 2·9; N, 4·5%).

In the above preparation the mixed solution must not be boiled, otherwise the nitro-groups are evicted with the formation of $[(Me_3As)_2PdCl_2]$. A similar experiment in which ammonium palladobromide was used, with 30 minutes' boiling, gave chiefly $[(Me_3As)_2PdBr_2]$.

The tetranitrite, $[(Me_3As)Pd(NO_2)_2]_2$, appears to be very unstable. When a suspension of the powdered tetrachloride in concentrated aqueous potassium nitrite was gently warmed for a few seconds, reaction occurred with splitting of the bridged linkage and formation of $[(Me_3As)_2Pd(NO_2)_2]$ and ammonium palladonitrite.

Trimethylphosphine.—This compound is so reactive that it cannot be prepared by the usual methods. We are indebted to Dr. D. Purdie for the following method of isolating the phosphine as the silver iodide derivative, $[Me_3P \rightarrow AsI]_4$ (Mann, Wells, and Purdie, J., 1937, 1828), from which the phosphine can be regenerated when required. An ethereal solution of methylmagnesium iodide was prepared from magnesium (24 g., 6 atoms per 1 mol. PCl_3), methyl iodide (60·5 c.c., 138 g.), and ether (300 c.c.) in a 3-necked flask with ground glass connexions for a reflux condenser, inlet-tube for hydrogen, and mechanical stirrer. The product was strongly cooled, and a solution of phosphorus trichloride (14 c.c., 22·5 g.) in ether (50 c.c.) slowly added with vigorous stirring. The flask was then kept at room temperature for 30 minutes, and the solution (without hydrolysis) distilled directly from an oil-bath, the temperature of which was finally taken to 200° until no further distillate was obtained. The stream of hydrogen was continued throughout the preparation until this distillation was complete. The ethereal distillate was then without delay shaken with a solution of silver iodide in aqueous potassium iodide solution. The white solid was filtered, washed, and well pressed in drying paper. This silver iodide derivative is too unstable to be recrystallised: when dry, it can be kept indefinitely in a sealed tube. To regenerate the trimethylphosphine, the silver derivative was heated gently in one arm of an inverted U-tube, the other arm being immersed in a freezing mixture. The silver derivative dissociated, and the pure phosphine collected in the cold arm; it was used at once, otherwise at room temperature the silver iodide reabsorbed it, becoming white again.

Dichlorobis(trimethylphosphine)palladium.—Prepared in the usual way, and recrystallised from alcohol, this was obtained as pale yellow crystals, m. p. 282° (decomp.) (Found: C, 21·7; H, 5·2. $C_6H_{18}Cl_2P_2Pd$ requires C, 21·8; H, 5·45%).

Dichlorobis(trimethylphosphine)-µ-dichlorodipalladium.—This compound was prepared in the usual way by the action of ammonium palladochloride upon the foregoing compound in alcoholic solution, from which it separated as beautiful, well-formed, red crystals, m. p. 285° (decomp.) with preliminary darkening and shrinking (Found: C, 14·0; H, 3·7; Pd, 42·0. $C_6H_{18}Cl_4P_2Pd_2$ requires C, 14·2; H, 3·55; Pd, 42·1%).

Crystallographic Data.

In view of the voluminous nature of the observations and evidence obtained (in particular) in the complete analysis of the tetrabromide, only the essential points in this evidence are given below: the full detailed evidence will be published elsewhere.

Dichlorobis(trimethylarsine)-µ-dichlorodipalladium (III) *and Dibromobis(trimethylarsine)-µ-dibromodipalladium.*—The tetrachloride crystallises from alcohol and from dioxan as isomorphous tetragonal prisms {110} showing high negative birefringence and pleochroism, the light transmitted being pale yellow for vibrations along the needle axis and orange-red perpendicular to that axis. The crystals are not pyroelectric. The cell dimensions of the crystals from dioxan are about 1·5% greater than those of the crystals from alcohol: from dioxan, $a = 16{\cdot}25$; $c = 7{\cdot}31$ A.; from alcohol, $a = 16{\cdot}0$; $c = 7{\cdot}22$ A. Oscillation and Weissenberg photographs show that the space group is $I4$, $I\bar{4}$ or $I4/m$.

The tetrabromide crystallises from dioxan as tetragonal prisms isomorphous with those of the tetrachloride and with cell dimensions $a = 16{\cdot}6$; $c = 7{\cdot}48$ A. The approximate density was determined by flotation (2·5 g./c.c.): that calculated for 4 molecules of $[Me_3As,PdBr_2]_2$ per unit cell is 2·48 g./c.c. Crystals of the tetrabromide from alcohol, however, are not tetragonal, and on account of their poor quality they were not further examined. The spacing along the needle axis of these crystals from alcohol is 7·41 A., and it is clear that their structure is only a distortion of that of the tetragonal crystals from dioxan. From X-ray photographs of the three isomorphous tetragonal crystals (tetrachloride from alcohol and dioxan, and tetrabromide from dioxan) it is obvious that their structures differ only in detail.

The optical properties and cell dimensions suggested that this structure was built up of planar molecules lying in planes parallel to (001), and an F^2 projection on the ac plane confirmed the planar nature of the molecules. Whichever of the three possible space-groups is chosen, the planar molecule must possess a diad axis of symmetry perpendicular to the plane of the molecule. This implies that the molecules in the crystal must have the *trans*-symmetrical structure (III; or with Br for Cl). The space group *I*4/*m* was finally adopted, in which the molecular symmetry is 2/*m*. The plane of symmetry merely raises the symmetry of the Me_3As group. The mutual orientation of the molecules in planes at $z = 0$ and $z = \frac{1}{2}$ was first found by trial and error methods, and finally determined (together with the configuration of the molecule itself) from a section at $z = 0$ of the three-dimensional electron-density distribution. The structure may therefore be represented as in Fig. 1. In the tetrabromide the molecules lie with their Pd–Pd axes inclined at 1·5° to the *a* axes. The configuration of the tetrabromide molecule was finally determined as that shown in Fig. 2.

A notable feature of the structure of the tetrachloride and tetrabromide is the existence of approximately cylindrical tunnels parallel to the *c* axis. The diameter of these tunnels is about that of the dioxan molecule if this molecule is assumed to be an oblate spheroid of effective radius 3·45 A. (Fig. 1). In the crystals of the tetrachloride from alcohol these tunnels are empty, but when the crystals are grown from dioxan they are filled—either partly or completely—by molecules of the solvent. Since the axis of the holes is a four-fold axis of symmetry, it is to be concluded that the dioxan molecules are rotating in the crystal.

If a configuration for the molecule of the tetrachloride analogous to that of the tetrabromide is assumed (allowing for the difference in size between Br and Cl), the high-order intensities may be used to determine the inclination of the molecule to the axes in the crystals from alcohol and from dioxan. Good agreement is obtained with the molecules inclined at 2° to the axes in the crystals from alcohol, and parallel to the axes in the crystals from dioxan. In all cases the positions of the carbon atoms were determined by considerations of packing. The agreement between calculated and observed structure factors for the tetrachloride and tetrabromide from dioxan is shown in the table for a number of reflexions. Intensities were estimated visually on Weissenberg photographs, the intensity scale being adjusted to make the values of *F*′, obs., and *F*, calc., comparable for low orders, where $F' = [I_{\text{obs.}} \sin 2\theta/(1 + \cos^2 2\theta)]^{\frac{1}{2}}$. The values of *F*, calc., are those for the following parameters:

Tetrabromide.

		x.	*y*.	*z*.
Pd	8(*h*)	0·608	0·003	0
As	8(*h*)	0·715	0·109	0
Br^1	8(*h*)	0·497	0·101	0
Br^2	8(*h*)	0·717	− 0·094	0
C	16(*i*)	0·783	0·100	0·212
	8(*h*)	0·669	0·219	0

Tetrachloride.

	x.	*y*.	*z*.
Pd	0·604	0	0
As	0·716	0·106	0
Cl^1	0·500	0·097	0
Cl^2	0·708	− 0·096	0
C	0·785	0·100	0·217
	0·669	0·218	0

Br^1 and Cl^1 represent halogen atoms linked each to two palladium atoms, Br^2 and Cl^2 those linked to only one palladium atom.

(Space-group nomenclature: International Tables.)

Tetrachloride from dioxan.

hkl.	*F*′, obs.	*F*, calc.	*hkl.*	*F*′, obs.	*F*, calc.
200	14	+13	501	5	− 9
400	<4	− 1	701	15	+19
600	8	− 7	901	<7	+ 3
800	22	+27	*11*01	9	+16
*10*00	56	+52			
			002	67	+73
101	11	+13	004	57	+64
301	20	+22	006	28	+48

Tetrabromide from dioxan.

hkl.	*F*′, obs.	*F*, calc.	*hkl.*	*F*′, obs.	*F*, calc.
200	26	+18	110	53	−57
400	<4	0	220	3	+ 2
600	16	−16	330	17	+16
800	33	+44	440	63	−73
*10*00	59	+67	550	73	+80
			660	26	−23
101	11	+16	770	<6	+ 2
301	15	+15	880	15	+19
501	33	−33	990	41	−50
701	18	+12	*1010*0	38	+46
901	<7	− 2			
*11*01	19	+25			

Dichlorobis(trimethylarsine)-μ-dibromodipalladium (V).—Three different crystalline forms of this compound were examined.

(i) *The first main crop of needles from alcohol.* These were very similar in appearance to the tetragonal needles of the tetrachloride and tetrabromide, and showed the same pleochroism. The crystals were very imperfect and easily split along the needle axis. They are apparently monoclinic, and the fact that the spacing along the needle axis is 7·34 A., together with the pleochroism, suggests that their structure is, like that of the tetrabromide crystals from alcohol, closely related to the tetragonal structure already described.

(ii) *Monoclinic crystals which separated from the alcoholic mother-liquor on standing.* Compact monoclinic crystals, with the forms {001} and {110}, sometimes elongated along the *c* axis. Cell dimensions are $a = 12{\cdot}1$, $b = 10{\cdot}6$, $c = 6{\cdot}83$ A., $\beta = 72°$. For a density of 2·70 the unit cell contains 2 molecules of $[Me_3As,PdClBr]_2$. The halvings were $0k0$ for k odd and $h0l$ for h odd; the space-group is therefore $P\ 2_1/a$. Since there are only 2 molecules of the bridged complex in the unit cell, these molecules must be centro-symmetrical. Hence the configuration of the molecule must be (IV) or (V).

(iii) *Rhombic needles which separated with the monoclinic crystals* (ii) *above.* These needles {110} have the cell dimensions: $a = 23{\cdot}4$, $b = 12{\cdot}7$, $c = 11{\cdot}4$. For a density of 2·67, the cell contains 8 molecules of $[Me_3As,PdClBr]_2$. The space group is *P ccn*: in this space group the 8 molecules could occupy two 4-fold positions with point symmetry $\bar{1}$, two sets of 4-fold positions with symmetry 2, or an 8-fold position without symmetry. It is therefore impossible to draw any conclusions with regard to the symmetry of the molecules in these crystals.

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