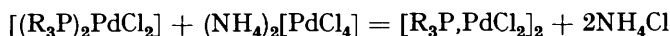


**202.** *The Constitution of Complex Metallic Salts. Part IV. The Constitution of Certain Bridged Dipalladium Derivatives. A Novel Type of Tautomerism.*

By FREDERICK G. MANN and DONALD PURDIE.

IN Part III (J., 1935, 1549) we described the preparation and properties of a number of homologous non-ionic four-covalent derivatives of palladium. These compounds were formed by the union of two molecules of aliphatic sulphides, phosphines, and arsines with palladous chloride, and the three series had the general formulæ  $[(R_2S)_2PdCl_2]$ ,  $[(R_3P)_2PdCl_2]$ , and  $[(R_3As)_2PdCl_2]$  respectively: all members showed a marked negative parachor anomaly. It has now been found that these phosphine and arsine compounds, when boiled in alcoholic solution with ammonium palladochloride, give rise to a new series of complex non-ionic palladium derivatives, whose empirical formula corresponds to one molecule of the phosphine or arsine and one of palladium dichloride:



The same arsine compounds can also be obtained by heating the original dichlorobisarsine-palladium\* compounds in a high vacuum, whereupon 1 equiv. of the free arsine distils, leaving a residue of the new compound:



The dichlorobisphosphinepalladium compounds, similarly treated, distil almost unchanged, and only a small residue is left.

A preliminary investigation revealed the following fundamental properties of the new compounds:

(1) They are markedly darker in colour, and have in general higher m. p.'s than the parent compounds; e.g., the original dichloro-bisphosphine- and -bisarsine-palladium compounds are yellow and orange, while the new phosphine and arsine compounds are orange-red and deep red respectively. The m. p.'s of the new phosphine and arsine compounds fall steadily as the homologous series is ascended, in which respect they resemble the parent compounds.

(2) Their molecular weight in all solvents is twice that required for the simplest empirical formula, and therefore the complete molecule is as shown above. This was expected, since clearly a compound of formula  $[R_3P, PdCl_2]$  would contain a 3-covalent palladium atom and presumably be very unsaturated.

(3) All the new compounds (except the very high-melting trimethylarsine compound) have sharp m. p.'s and are crystallographically homogeneous, and a mixture of isomeric forms is thus never obtained in the solid state. Moreover, corresponding members of the phosphine and arsine series are strictly isomorphous; certain chemical differences which the phosphine and arsine series show must therefore be due to a difference in stability and not to one in structure. All but the lowest members possess considerable thermal stability, and can be kept in the molten condition for long periods without decomposition.

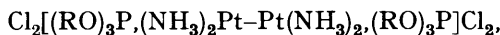
(4) The formation of these compounds is not dependent upon the chlorine atoms, since similar compounds having iodide, nitrite, and thiocyanate radicals, of type  $[R_3P, PdX_2]_2$ , have been obtained.

Although these phosphine and arsine compounds are new, similar compounds of platinum and palladium dichloride with carbon monoxide, phosphorus trichloride, and the alkyl phosphites have been known for many years. Schützenberger and his collaborators (*Bull. Soc. chim.*, 1870, 14, 483; 1872, 17, 482, 18, 101, 148) showed that platinum dichloride combined with carbon monoxide to give compounds of empirical formulæ  $CO, PtCl_2$  and  $2CO, PtCl_2$ , and with phosphorus trichloride to give similar compounds  $PCl_3, PtCl_2$  and  $2PCl_3, PtCl_2$ . The latter compounds reacted with aliphatic alcohols to give phosphite ester

\* In order to systematise the nomenclature, non-ionic compounds of this type are now termed "dichlorobisphosphine(or arsine)palladium" instead of "bisphosphine(or arsine)palladium dichloride" as in Part III.

derivatives,  $(RO)_3P, PtCl_2$  and  $2(RO)_3P, PtCl_2$ . Later, Fink (*Compt. rend.*, 1892, **115**, 176; 1898, **126**, 646) prepared precisely similar derivatives of carbon monoxide, phosphorus trichloride, and the alkyl phosphites with palladium dichloride.

The phosphite ester derivatives  $(RO)_3P, PdCl_2$  and  $(RO)_3P, PtCl_2$  are clearly of the same general type as the present phosphine and arsine compounds, and must also have the double formula, e.g.,  $[(RO)_3P, PdCl_2]_2$ . Fink showed that these palladium compounds reacted with ammonia to give ionic compounds of formula  $[(RO)_3P, (NH_3)_2PdCl]Cl$ , and this reaction would therefore indicate that the two ester molecules are joined to different palladium atoms in the original compound. Rosenheim and his co-workers (*Z. anorg. Chem.*, 1903, **37**, 394; 1905, **43**, 35) reinvestigated the corresponding platinum compounds in detail, and showed by molecular-weight determinations that the two series of alkyl phosphite compounds had the molecular formulæ  $[(RO)_3P, PtCl_2]_2$  and  $[2(RO)_3P, PtCl_2]$ . The former, when treated with aniline, *p*-toluidine, or pyridine, gave *cis*- and *trans*-forms of, e.g.,  $[(RO)_3P, PhNH_2, PtCl_2]$ , thus again indicating that in the original compound the ester molecules are joined to different platinum atoms. It was further shown that the compound  $[(RO)_3P, PtCl_2]_2$  added on ammonia to give a product which was expected to have the constitution  $[(RO)_3P, (NH_3)_2PtCl]Cl$ : since, however, both chlorine atoms appeared to be ionic, Rosenheim claimed that this compound must have the constitution

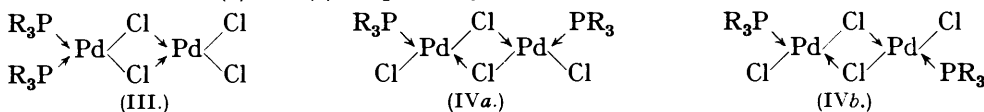


and that therefore the original compound must also have possessed a Pt-Pt link. Later, Herty and Davies (*J. Amer. Chem. Soc.*, 1908, **30**, 1084) showed that the ammonia addition compound had only one ionised chlorine atom, and it follows that there is no evidence for the unlikely Pt-Pt linkage. Werner and Pfeiffer ("Anorganische Chemie," 5th Ed., pp. 56, 170) suggested that the chlorine atoms bridged the metallic atoms in these compounds, and that the ester derivatives theoretically could have the isomeric formulæ (I) and (II).

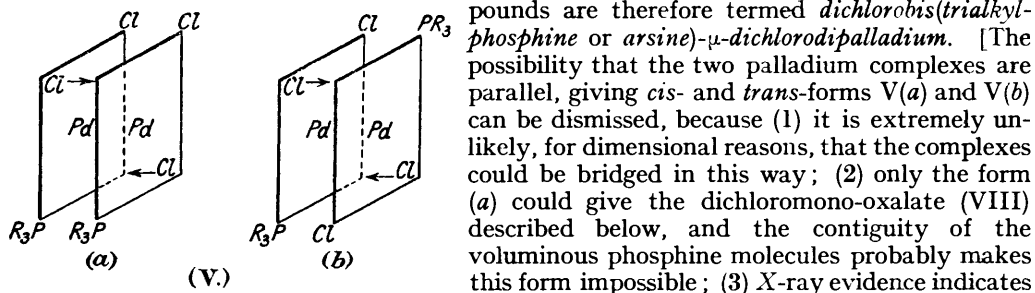


Similar formulæ in modern notation for monoethyldibromogold were put forward by Burawoy and Gibson (*J.*, 1934, 860; 1935, 219), who pointed out that compounds of type (II) could also exist as *cis-trans*-isomerides.

It is clear that, in the tertiary phosphine and arsine compounds now studied, the metallic atoms must also be linked through bridged chlorine atoms, and, if the two uniplanar palladium complexes thus formed are themselves in the same plane, the compounds can theoretically exist in either the unsymmetrical (III) or the symmetrical form (IV), the latter having *cis*- and *trans*-forms, (a) and (b), respectively.



Upon Werner's system of nomenclature for bridged metallic derivatives, these compounds are therefore termed *dichlorobis(trialkylphosphine or arsine)-μ-dichlorodipalladium*.



[The possibility that the two palladium complexes are parallel, giving *cis*- and *trans*-forms V(a) and V(b) can be dismissed, because (1) it is extremely unlikely, for dimensional reasons, that the complexes could be bridged in this way; (2) only the form (a) could give the dichloromono-oxalate (VIII) described below, and the contiguity of the voluminous phosphine molecules probably makes this form impossible; (3) X-ray evidence indicates

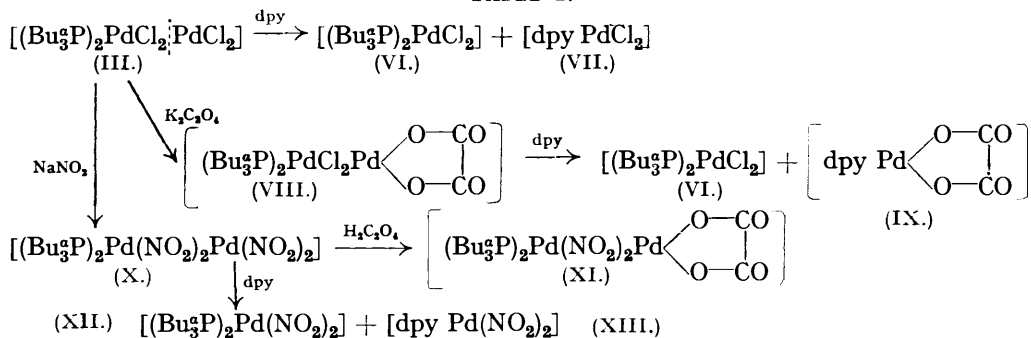
that the trimethylarsine member has a long, wide, flat molecule, which prohibits formulæ of type (V) and strongly supports those of type (III) and (IV).]

The constitution of the only form of these compounds which exists in the crystalline state is still undecided : a complete X-ray analysis (the only method available) is extremely difficult owing to the complexity of the crystals. The remarkable fact is now established, however, that in organic solvents an equilibrium mixture of the isomerides (III) and (IV) exists, since decisive reactions for each form can be obtained : a novel and unexpected type of tautomerism is thus revealed. In view of the rapid interconversion of the compounds (III) and (IV), it is probable that the latter form exists in solution as both the *cis*- and the *trans*-forms, (a) and (b), although in the equilibrium mixture, on grounds of comparative stability, (b) probably preponderates considerably over (a). This tautomerism explains why, in the case of the arsine compounds, the same substance can be obtained by two such different methods, for it would otherwise have been expected that the interaction of the dichlorobisarsinepalladium  $[(R_3As)_2PdCl_2]$ , and ammonium palladochloride would by simple addition give a compound of type (III), whilst the thermal dissociation of the bisarsine compound would give rise momentarily to the radical  $[(R_3As)PdCl_2]$ , which would at once unite in pairs to give a compound of type (IV). Moreover, although the parent dichlorobisphosphine(or arsine)palladium compounds have undoubtedly the *trans*-configuration, it has been shown by Mann, Crowfoot, Gattiker, and Wooster (J., 1935, 1642) that the interconversion *cis*  $\rightleftharpoons$  *trans* occurs readily in the 4-covalent palladium series, and hence the action of ammonium palladochloride on the parent compounds in solution might give rise either to the bridged compound (III) or to (IV), although the phosphine (and arsine) groups have the *cis*-positions in (III) and the *trans*-positions (relative to the chlorine) in (IV).

The *n*-butyl phosphine and arsine members (in particular) have been used for a detailed investigation of the reactions of these compounds, and the evidence for the unsymmetrical form (III) can first be summarised :

(1) The phosphine compound (III) (Table I) on treatment with one equivalent of  $\alpha\alpha'$ -dipyridyl in cold alcoholic solution gives rise to the original dichlorobisphosphinepalladium (VI) and also *dichlorodipyridylpalladium* (VII) : the dipyridyl clearly splits the compound (III) across the dotted line as shown, thus providing strong evidence for the unsymmetrical formula. The arsine compound corresponding to (III) gives precisely the same reaction.

TABLE I.

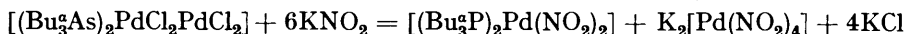


(2) The phosphine compound (III), when warmed in aqueous alcoholic suspension with potassium oxalate, gives a *dichloromono-oxalato*-derivative (VIII). This reaction would appear to necessitate the presence of two unbridged chlorine atoms attached in the *cis*-position to one palladium atom in the tetrachloro-molecule (III), and strong evidence that the dichloro-oxalate has the constitution (VIII) is given by the action of  $\alpha\alpha'$ -dipyridyl, which splits the molecule into the dichlorobisphosphinepalladium (VI) and *oxalato-dipyridylpalladium* (IX). It should, however, be noted that the dipole moment of the dichloro-oxalate (see p. 879) can be satisfactorily explained only on the assumption that the oxalate radical replaces the two *bridged* chlorine atoms.

It is noteworthy that the arsine compound corresponding to (III) gave no reaction with potassium oxalate under similar conditions.

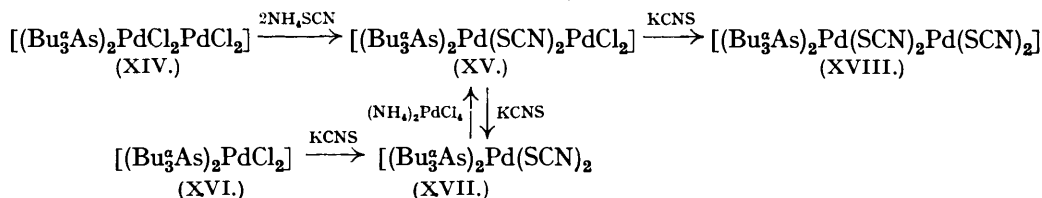
(3) The phosphine compound (III) reacts with sodium nitrite to give the corresponding bridged *tetranitrito*-compound (X). The latter in turn reacts readily with oxalic acid in cold alcoholic solution to give the *dinitritomono-oxalato*-compound (XI), and also with  $\alpha'$ -dipyridyl to give the *dinitrito*-compound (XII) and *dinitritodipyridylpalladium* (XIII). These reactions show clearly that the tetranitrite (X) must also have the unsymmetrical formula.

When the arsine compound corresponding to (III) is treated with potassium nitrite, the bridged tetranitrite is not obtained, the compound splitting at once into the *dinitrobis-butylarsinepalladium* and potassium palladonitrite, again indicating the unsymmetrical form (III) :



(4) The *arsine* compound (XIV) (Table II), corresponding to the phosphine compound (III), reacts with 2 equivs. of ammonium thiocyanate to give the bridged *dithiocyanato*-

TABLE II.

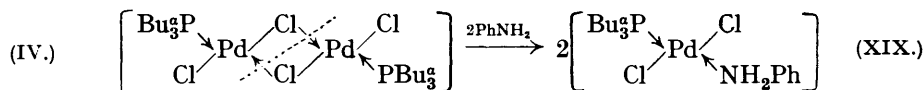


*dichloro*-compound (XV). The fact that the thiocyanate and not the chlorine radicals bridge the metallic atoms in (XV) is shown by the conversion of the dichlorobisarsinepalladium (XVI) into the *dithiocyanato*-compound (XVII), which readily condenses with 1 equiv. of ammonium palladochloride to give (XV). When now the compound (XV) is treated with an excess of potassium thiocyanate, part is converted into the bridged *tetra-thiocyanato*-compound (XVIII) and part appears to undergo direct fission to the unbridged dithiocyanate (XVII). It is probable that the compound (XVIII) is a definite intermediate in this reaction, and alone by fission gives (XVII), but the production of the latter in either case is a strong argument for the unsymmetrical formula (XIV).

A precisely similar series of reactions is obtained with the phosphine derivatives, with the exception that the tetrathiocyanate corresponding to (XVIII) is so stable that no fission to the phosphine dithiocyanate corresponding to (XVII) occurs.

The evidence for the symmetrical formula (IV) for these phosphine and arsine compounds can be summarised :

(1) The phosphine compounds in cold alcoholic solution react immediately with 2 equivs. of aniline, *p*-toluidine, or pyridine, the deep colour fading to the characteristic colour of the unbridged dichloro-compounds : evaporation at room temperature then gives the pure *dichloromonophosphinemonoaminopalladium* compound (XIX) in theoretical yield.

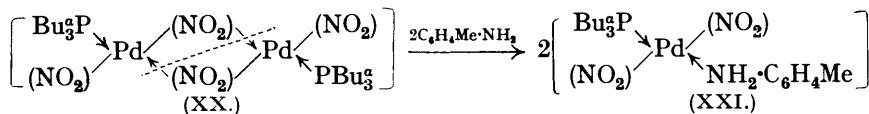


The constitution of these unbridged compounds (XIX), which show normal molecular weights in solution, is beyond doubt, and the reaction therefore consists of a simple splitting of (IV) by the two molecules of the amine along the dotted line as shown : it is therefore conclusive evidence for this symmetrical formula (IV).

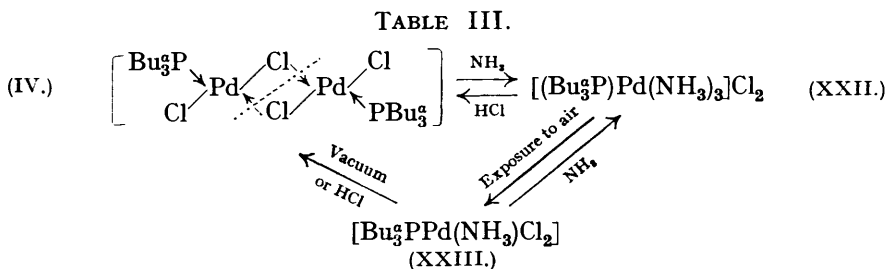
Precisely similar reactions are given by the corresponding arsine compounds.

(2) The bridged tetranitrito-derivative (XX) in cold alcoholic solution reacts with *p*-toluidine to give solely the *dinitrito*-compound (XXI), the molecule being thus split across the dotted line as before. Since the tetranitrite (XX) is identical with (X) (Table I)

it thus shows decisive reactions in alcoholic solution for both the unsymmetrical and the symmetrical form.



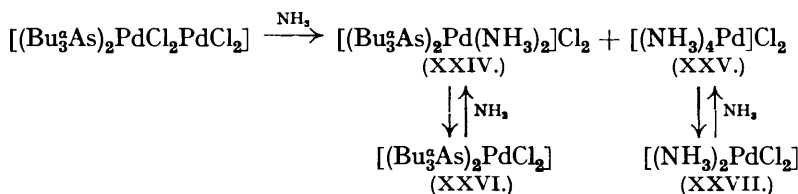
(3) Ammonia gives similar but rather more complicated results. When the phosphine compound (IV) (Table III) in cold benzene solution is treated with an excess of ammonia, the molecule is split as before, but now the co-ordinated chlorine atoms are also replaced by ammonia, giving the ionic *triammino-n-butylphosphinepalladium dichloride* (XXII): this



reaction is readily reversed by acids. The compound (XXII) is unstable, and on exposure to air, or on warming with acetone, rapidly loses ammonia to give the more stable non-ionic *dichloromonoammino-n-butylphosphinepalladium* \* (XXIII), a change which is also easily reversible. The compound (XXIII) is also, however, unstable, and loses its remaining ammonia when placed in a vacuum, or on standing in cold benzene solution, or immediately on treatment with acids, regenerating the original bridged derivative (IV). These reactions are thus very strong evidence for the symmetrical formula (IV).

The action of ammonia on the arsine compound isomorphous with (IV) gives evidence, on the contrary, for the unsymmetrical formula corresponding to (III), for this compound in cold benzene solution reacts with ammonia to give a white, amorphous, water-soluble, ionised product, which is apparently a mixture of the unstable diamminobisarsinepalladium dichloride (XXIV) (Table IV) and tetramminopalladium dichloride (XXV). When this

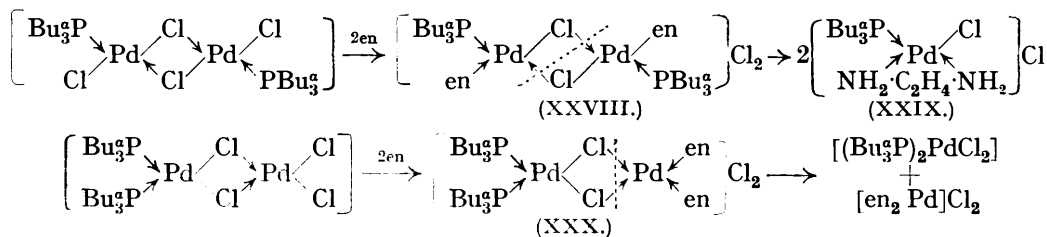
TABLE IV.



mixed product is warmed with acetone, the compound (XXIV) loses ammonia and passes into solution as the yellow non-ionic dichlorobisarsinepalladium (XXVI), which crystallises out in the pure condition: this reaction is reversible. The insoluble residue from the acetone extraction is the compound (XXV), which can also be readily converted (by a reversible reaction) into the yellow non-ionic dichlorodiamminopalladium (XXVII).

\* In a preliminary note on these compounds (*Chem. and Ind.*, 1935, 54, 814) this derivative (XXIII) was erroneously stated to be isomeric with (IV). The error arose partly because the compound lost ammonia so readily on heating that the usual tests for nitrogen and for ammonia gave negative results, and partly because the analytical values obtained for C, H, Cl, and Pd agreed closely with those required by (IV): the molecular weight obtained for (XXIII) could not, however, be explained by isomerism with (IV).

(4) Ethylenediamine reacts with the butylphosphine tetrachloro-compound in cold alcoholic solution, giving a pale yellow derivative having ionised chlorine. This compound may have the constitution (XXVIII), the unbridged chlorine atoms of the symmetrical tetrachloro-compound having apparently been replaced by ethylenediamine molecules, each co-ordinating by one amino-group alone.\* This compound is unstable, and when



heated with *cyclohexane*, acetone, etc., appears to split as shown across the dotted line, the ethylenediamine molecules becoming chelated, with the formation of two molecules of the water-soluble ionic *monochloro-n-butylphosphine-ethylenediaminopalladium chloride* (XXIX). The latter, when treated with hydrochloric acid, readily loses its ethylenediamine and re-forms the original tetrachloro-compound, thus again providing strong evidence for the symmetrical formula.

When, however, the initial reaction is carried out in benzene solution, the isomeric intermediate compound (XXX) is apparently formed, either from the unsymmetrical form of the tetrachloride as shown, or (less probably) by interconversion from (XXVIII). The compound (XXX) is very unstable (as would be expected from the neighbouring positions of the ethylenediamine molecules) and breaks down spontaneously along the vertical line as shown, giving the dichlorobisbutylphosphinepalladium and bisethylenediaminopalladium dichloride.

When similar experiments are performed with the butylarsine tetrachloro-compound, an intermediate compound similar to (XXX) is apparently formed both in alcoholic and in benzene solution, and in both cases rapidly decomposes, giving the dichlorobisarsinepalladium and bisethylenediaminopalladium dichloride.

Further evidence for the tautomerism of these compounds is furnished by their dipole moments, which have been determined by Mr. A. E. Finn, working under Prof. Sidgwick's direction. Mr. Finn reports: "The dipole moments of the *n*-butylphosphine tetrachloro-compound and of its arsenic analogue were found to be 2.34 and 2.52 Debye units respectively in benzene solution at 25°. For the interpretation of these results, it must be borne in mind that the dichlorobisethylphosphinepalladium [(Et<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>], and its arsine analogue (Mann and Purdie, *loc. cit.*) have moments of 1.05 and 1.04D respectively, both compounds having undoubtedly the *trans*-configuration. Jensen (*Z. anorg. Chem.*, 1935, 225, 97) has measured the moments of many alkylsulphideplatinum compounds, and finds that the *trans*(α)- and the *cis*(β)-forms of dichlorobisdiethylsulphideplatinum have moments

\* It is possible that the ethylenediamine replaces the two bridged chlorine atoms, and that the compounds (XXVIII) and (XXX) have the constitution (XXVIIIa) and (XXXa) respectively. Fission of the molecule across the dotted lines under the influence of solvents would then give the same products



as those described above. Linkage of two metallic atoms by an ethylenediamine molecule is, however, very rare, owing to the strong tendency of the diamine molecule to form a chelate grouping with one metallic atom alone. On the other hand, it is noteworthy that while the tetrachloro-phosphine and -arsine compounds react with *one* molecule of *aa'*-dipyridyl, they will not react with less than *two* molecules of ethylenediamine, a striking difference in behaviour which may be due to the steric inability of the dipyridyl to bridge the palladium atoms [as in (XXVIIIa) and (XXXb)]: consequently, one molecule splits the unsymmetrical bridged complex directly, as shown on p. 875.



and the dinitro-oxalate (XI), show low molecular weights in ethylene dibromide and particularly in bromoform solution. The reason for this apparent dissociation is still obscure. No fundamental change in the character of the compounds can occur in these solvents, for the solutions have the same colour as those in non-dissociating solvents; moreover, the bridged compounds can be recovered unchanged from solution by evaporation. The cause of these abnormal molecular weights may, however, invalidate any interpretation of the dipole moment of the dichloro-oxalate, although these moments were determined in benzene solution.

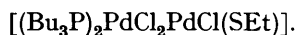
The parachors of four of the new tetrachloro-compounds have been determined: the results are parallel to those of the parent dichlorobisphosphine (and arsine) palladium compounds (Mann and Purdie, *loc. cit.*) in that the parachors show a marked negative anomaly, and that the apparent parachor of the constituent palladium atoms falls steadily as the homologous series is ascended. The table records the parachor of each constituent palladium atom in the molecule: if, however, the four-membered bridged ring in the molecule is assumed to have the normal parachor ( $-9.5$  units) of four-membered rings in purely organic molecules, then the parachors of each palladium atom should be further reduced by 5 units.

*Parachors of Bridged Palladium Derivatives.*

[(R <sub>3</sub> P)PdCl <sub>2</sub> ] <sub>2</sub> .				[(R <sub>3</sub> As) <sub>2</sub> PdCl <sub>2</sub> ] <sub>2</sub> .					
Compound.	M. p.	[P], obs.	Σ[P].*	Parachor of 1 Pd atom.	Compound.	M. p.	[P], obs.	Σ[P].*	Parachor of 1 Pd atom.
R = <i>n</i> -Bu	145°	1376	1336	20	R = <i>n</i> -Bu	128°	1395	1364	15
<i>n</i> -Am	127	1589	1573	8	<i>n</i> -Am	108	1622	1601	10

\* Σ[P] represents the sum of the parachors of all the elements except the two metallic atoms.

When the butylphosphine tetrachloro-compound in cold alcoholic solution is treated with 1 equiv. of ethylthiol, one chlorine atom is replaced by the ethylthio-radical, giving *monochloromono(ethylthio)bis(butylphosphine)-μ-dichlorodipalladium*,



Only one form of this compound has been obtained in the solid state: but it will be clear that it should exist in the unsymmetrical form (given in the above formula) and also in *cis*- and *trans*-modifications of the symmetrical form, corresponding to (III) and to (IVa) and (IVb) respectively, and its constitution is now being fully investigated.

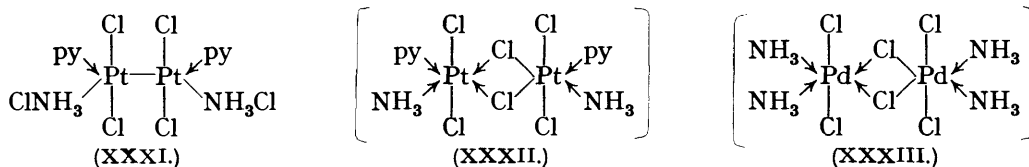
It is noteworthy that bridged tetrachloropalladium derivatives of the aliphatic sulphides are difficult to prepare, and the lower members appear to be extremely unstable. When alcoholic solutions of the lower dichlorobisalkylsulphidepalladium compounds and ammonium palladochloride were boiled together, considerable reduction to metallic palladium occurred, and the required bridged derivatives could not be isolated, but the higher members, *e.g.*, the *n*-octyl sulphide derivative, could be readily prepared. Attempts to prepare the corresponding bridged platinum compounds of the phosphines and arsines also failed, chiefly because the metallic platinochlorides are almost insoluble in aqueous alcohol, and considerable reduction to platinum occurred when, *e.g.*, dichlorobistri-*n*-butylphosphineplatinum, [(Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>], was boiled with an aqueous-alcoholic solution of potassium platinochloride. Attempts to prepare mixed platinum-palladium compounds, such as [(Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>PdCl<sub>2</sub>], by boiling alcoholic solutions of the former platinum derivative and of ammonium palladochloride, also failed, considerable reduction again occurring. It is possible that differences in the dimensions of the two metallic complexes prevent this mixed bridging.

The tautomerism shown by the above dipalladium derivatives is undoubtedly due to the comparatively weak co-ordinating power of the palladium atoms, the phosphine and arsine molecules and the acid radicals being thus abnormally labile: this factor also explains why, in 4-covalent palladium compounds of type [a<sub>2</sub>Pd b<sub>2</sub>], only the more stable *trans*-isomeride can usually be isolated. The corresponding bridged diplatinum compounds would be of great interest, as it is probable that in such compounds the more stable co-ordination



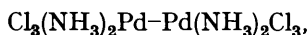
of the phosphine or arsine molecules to the platinum atoms would partially or completely inhibit tautomerism parallel to that shown by the palladium compounds.

The investigation of the above bridged phosphine and arsine compounds throws new light upon the true constitution of a number of complex platinum and palladium derivatives to which apparently abnormal compositions have been ascribed in the past. It is noteworthy that all these compounds possess deep colours, and in the majority the metal appears to show a co-ordination number of five. If, however, these compounds are formulated as bridged-halogen derivatives, their apparent abnormality at once disappears. For instance, Jörgensen (*J. pr. Chem.*, 1886, **33**, 489) described a reddish-brown monoammino-monoethylaminoplatinum tribromide,  $\text{NH}_3\text{etn PtBr}_3$  (where  $\text{etn} = \text{EtNH}_2$ ); and Drew, Pinkard, Wardlaw, and Cox (*J.*, 1932, 1013) described the analogous dark-red pyridine compound,  $\text{NH}_3\text{py PtCl}_3$ , which they obtained by exposing a mixture of  $[\text{NH}_3\text{py PtCl}_2]$  and hydrochloric acid to the oxidising action of the air, and to which they allotted the



formula (XXXI). It is, however, extremely unlikely that this compound could possess two platinum atoms, each of co-ordination number five, directly linked in this way, or that two of the chlorine atoms can have even an electrovalent attachment to the co-ordinated ammonia molecules. It is clear that actually a portion of the original platinum compound has undergone oxidation to the non-ionic platinic derivative  $[\text{NH}_3\text{py PtCl}_4]$ , and that two chlorine atoms of this compound have co-ordinated to the platinum atom of the unchanged material, giving the bridged derivative (XXXII). Great interest attaches to a compound of this type because it possesses two platinum atoms each showing a co-ordination number of six, the first (or left-hand) atom *being a platinous\* and the second a platinic atom*, each atom being presumably at the centre of the usual 6 co-ordination octahedron. The platinous atom, being co-ordinated by two covalent and four co-ordinate links, will give a non-ionic complex: the (right-hand) platinic atom, being co-ordinated by four covalent and two co-ordinate links, will give a similar complex, and the complete molecule will therefore be non-ionic as shown. A precisely similar formulation can be applied to Jörgensen's compound.

Drew, Pinkard, Preston, and Wardlaw (*J.*, 1932, 1898) obtained a similar compound,  $(\text{NH}_3)_2\text{PdCl}_3$ , as black crystals by the combined action of hydrochloric acid and hydrogen peroxide on  $[(\text{NH}_3)_2\text{PdCl}_2]$ , ascribed to it the unlikely constitution

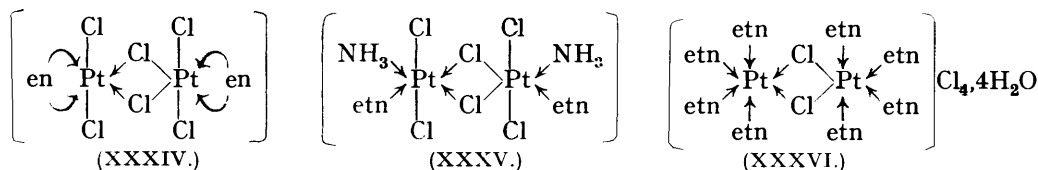


and suggested that its black colour was due to the Pd-Pd linkage. Here again, there is little doubt that oxidation has given the non-ionic palladic complex  $[(\text{NH}_3)_2\text{PdCl}_4]$ , which was then co-ordinated through two bridged chlorine atoms to the original palladous derivative, giving thus the compound (XXXIII) which similarly possesses palladous and palladic atoms each showing a co-ordination number of six. Tschugaeff and Tscherniaeff (*Z. anorg. Chem.*, 1929, **182**, 159) described a similar compound of composition  $(\text{NH}_3)_2\text{Pd}(\text{OH})\text{Cl}_2$ , which also formed black needles, and to which a precisely parallel constitution to (XXXIII) can clearly be applied. Since the only effective difference in condition between the two metallic atoms in this class of compound is that one possesses two electrons less than the

\* Several previous examples of bivalent platinum and palladium showing a co-ordination number of six have been described, e.g., the stable bis(triaminopropane)platinous di-iodide,  $[\{\text{C}_3\text{H}_7(\text{NH}_2)_3\}_2\text{Pt}]\text{I}_2$ , and its palladium analogue (Mann, *J.*, 1928, 892; 1929, 656); the two stable isomeric acetonitrile derivatives,  $[(\text{NH}_3)_4(\text{Me}\cdot\text{CN})_2\text{Pt}]\text{Cl}_2$ , and the corresponding picrates (Tschugaeff and Lebedinski, *Compt. rend.*, 1915, **161**, 563); the compound  $[(\text{NH}_2\text{OH})_4\text{Pt}(\text{OH})_2]$ , in which the hydroxyl groups are not ionised, the compound being a very weak base unaffected by carbon dioxide (Werner-Pfeiffer, *op. cit.*, p. 180); the unstable compound  $[(\text{NH}_3)_6\text{Pt}]\text{I}_2$  (Peters, *Z. anorg. Chem.*, 1912, **77**, 137).

other, resonance between the two atomic states will occur very readily, and it is probably this resonance which is mainly responsible for the dark colour the compounds possess.

The correctness of the bridged-chlorine formulæ of type (XXXII) and (XXXIII) for the above compounds receives strong confirmation from Drew and Tress's discovery (J., 1935, 1246) that the red compound  $\text{en PtCl}_3$  can be made *either* by the gentle oxidation of  $[\text{en PtCl}_2]$  *or* by grinding together a moist mixture of  $[\text{en PtCl}_2]$  and  $[\text{en PtCl}_4]$  : clearly,



therefore, the latter compound must have co-ordinated through bridged-chlorine atoms to the former platinum derivative to give a compound of constitution (XXXIV). Drew and Head (J., 1934, 224) showed similarly that  $[(\text{NH}_3)_2 \text{etn PtCl}_2]$  and  $[(\text{NH}_3)_2 \text{etn PtCl}_4]$  combined to give a compound of empirical formula  $\text{NH}_3 \text{etn PtCl}_3$ , which evidently has the constitution (XXXV).

A final important example of this type of bridged complex salt is the deep red compound which Wolfram (Diss., Königsberg, 1900) obtained by the action of hydrochloric acid and hydrogen peroxide on tetrakisethylaminoplatinous dichloride,  $[\text{etn}_4\text{Pt}]_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , and which Reihlen and Flohr (*Ber.*, 1934, 67, 2010) and also Drew and Tress (J., 1935, 1244) showed to have the empirical formula  $\text{etn}_4\text{PtCl}_3 \cdot 2\text{H}_2\text{O}$ . The former authors prepared this compound also by the interaction of aqueous solutions of the colourless  $[\text{etn}_4\text{Pt}]_2\text{Cl}_2$  and the yellow  $[\text{etn}_4\text{PtCl}_2]_2\text{Cl}_2$ : they considered it to be a special lattice compound which behaved as a double salt of type  $[\text{etn}_4\text{Pt}]_2\text{Cl}_2 \cdot [\text{etn}_4\text{PtCl}_2]_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ , since it gave a pale yellow aqueous solution, which in turn gave normal reactions for both components. Drew and Tress found that the red hydrate gave a yellow anhydrous derivative, which rapidly reabsorbed water on exposure to the air. They also showed that only two-thirds of the chlorine in the red salt was ionised in solution (which would be expected if it dissociated into its components), and that potassium thiocyanate converted it into a compound of empirical formula  $\text{etn}_4\text{PtCl}(\text{CNS})_2$ , and potassium bromide similarly into  $\text{etn}_4\text{PtBr}_3 \cdot 2\text{H}_2\text{O}$ . They concluded therefore (a) that Wolfram's red salt had the formula  $[\text{etn}_4\text{PtCl}]_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , being a derivative of tervalent platinum of co-ordination number five, (b) that it was intertransformable into a dimeric form of constitution  $[\text{Cl etn}_4\text{Pt}-\text{Pt etn}_4\text{Cl}]_2\text{Cl}_4$ , containing quadrivalent platinum, and (c) that in solution it gave the ions  $[\text{etn}_4\text{Pt}]^{2+}$ ,  $[\text{etn}_4\text{PtCl}_2]^{2+}$ , and  $4\text{Cl}^-$ . It is now clear, however, that when  $[\text{etn}_4\text{Pt}]_2\text{Cl}_2$  and  $[\text{etn}_4\text{PtCl}_2]_2\text{Cl}_2$  are mixed in solution, no reaction other than simple ionisation occurs, and the colour thus remains pale yellow. The separation of the red salt (which evidently exists only in the solid state) is due to the complex platinum ion in concentrated solution co-ordinating through its two chlorine atoms with the platinum ion, and separating immediately as the hydrated tetrachloride (XXXVI). Here again the compound consists of a platinumous and a platinumic atom each showing a co-ordination number of six, and each when linked in this way showing an external valency of two: hence the formation of the tetrachloride. On dissolution in water, the bridged linkages break, and the original two complex platinum ions and the simple chlorine ions are again formed. The work of Drew and Tress shows that the bridged chlorine atoms can be replaced by bromine, but not replaced stably by thiocyanate radicals, since even the dichloro-tetrathiocyanate decomposed in hot water. The formula (XXXVI) accounts for all the properties described by the earlier workers.

The failure to elucidate the constitution of these bridged platinum compounds has been due chiefly to their insolubility in most liquids, and occasionally to their instability. The palladium derivatives of the organic phosphines and arsines, on the other hand, are freely soluble in organic liquids and possess great stability, and it is primarily these physical properties that have rendered possible the first detailed investigation of the structure of these bridged metallic derivatives.

## EXPERIMENTAL.

The dipole and the crystallographic data were supplied by Mr. A. E. Finn (Dyson Perrins Laboratory, University of Oxford) and by Mr. A. F. Wells (Crystallography Laboratory, University of Cambridge) respectively and are gratefully acknowledged.

The names of the solvents used for recrystallisation are given in parenthesis immediately after the name of the substance concerned. All molecular weights recorded were measured cryoscopically, except those marked †, which were ebullioscopic. The parachors were determined in the same apparatus as that already described (Mann and Purdie, *loc. cit.*), the symbols having the same significance.

*Dichlorobis(trialkylphosphine)-μ-dichlorodipalladium*, (III) and (IV).—All members form orange-red crystals. The general method of preparation is best shown by that of the *ethyl* compound, the preparation of the other members being precisely similar except that smaller quantities of alcohol and a shorter period of heating are required for the higher members. A solution of ammonium palladochloride (2.8 g.) in warm water (20 c.c.) was diluted with alcohol (40 c.c.) and then added to a solution of dichlorobistriethylphosphinepalladium (4.0 g., 1 mol.) in hot alcohol (150 c.c.). The mixture was boiled under reflux for 1½ hours, a trace of palladium being then removed by filtration: on cooling, the ethyl compound crystallised. It was separated and washed with water; yield 5.3 g.; m. p. 230° (alcohol) (Found: C, 24.2; H, 5.1; Pd, 36.0. C<sub>12</sub>H<sub>30</sub>Cl<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 24.3; H, 5.1; Pd, 36.1%).

The *n-propyl* compound (alcohol, then acetone), m. p. 189° (Found: C, 32.3; H, 5.9; Pd, 31.5. C<sub>18</sub>H<sub>42</sub>Cl<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 32.0; H, 6.3; Pd, 31.6%).

The *n-butyl* compound (alcohol), m. p. 145° (Found: C, 37.8; H, 6.8; Cl, 18.8; Pd, 28.2; *M*, in 1.617% benzene solution, 756; in 3.462%, 763; in 0.588% ethylene dibromide solution, 805; in 2.051%, 828; in 2.370% alcohol † solution, 779; in 4.948%, † 862; in 3.855% acetone † solution, 1030. C<sub>24</sub>H<sub>54</sub>Cl<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 37.9; H, 7.2; Cl, 18.6; Pd, 28.1%; *M*, 760; *t*, 156°; *d*, 1.269;  $\gamma$  (dynes/cm.), 27.92;  $[P]$ , 1376;  $[P]_{Pd} = 20$ .

The crystals belong to the monoclinic system and show a very simple development, being flat plates tabular on  $a\{100\}$  with prisms  $\{110\}$  or compact crystals with the same forms:  $a : b : c = 1.62 : 1 : 1.10$ ,  $\beta' = 74\frac{1}{2}^\circ$ . The crystals have high negative birefringence and a large optic axial angle. There is marked pleochroism:  $\alpha$  pale yellow,  $\beta = b$ , lemon yellow, and  $\gamma$  (19° from the *c* axis in the obtuse angle  $\beta$  113½°) deep orange. Referred to the above axes, the structural unit cell has  $a' = 20.5$ ,  $b = 12.7$ ,  $c = 14.0$  A., and  $\beta' = 74\frac{1}{2}^\circ$ , and is body-centred. The alternative *c*-face-centred cell has  $a = 21.5$ ,  $b = 12.7$ ,  $c = 14.0$  A.,  $\beta = 113\frac{1}{2}^\circ$ . Referred to these new axes, the indices of the faces become  $a(100)$  and  $m(11\bar{1})$ . Oscillation photographs about these axes and a Weissenberg photograph about the *b* axis showed the halvings characteristic of the space-groups *Cc* or *C2/c*. Since the crystals show no pyroelectricity when tested in liquid air, the latter is the more probable. The observed density, 1.43 (floatation), indicates that there are 4 molecules in the unit cell, and these will be situated either on diad axes or at symmetry centres. Further work is required to distinguish between these possibilities.

*Dipole measurement on the n-butyl compound in benzene at 25°.*

$f_2$ .	$d^{25^\circ}$ .	$\epsilon^{25^\circ}$ .	$n_{25^\circ}^2$ .	$P_2$ .	$R_{P_2}$ .
0.0000	0.8738	2.2727	2.2580	—	—
0.003437	0.8848	2.3053	2.2647	301.1	188.5
0.004123	0.8870	2.3121	2.2659	301.3	186.8
0.004742	0.8888	2.3171	2.2671	299.5	188.0
0.006075	0.8929	2.3307	2.2693	302.3	186.8

$\infty P_2$ , 301.0 c.c.;  $R_{P_2}$ , 187.5 c.c.;  $\infty P_2 - R_{P_2} = 113.5$  c.c.;  $\mu = 2.34$  D. The symbols have their usual significance.

A solution of the above butyl tetrachloro-compound (2.0 g.) and ammonium iodide (1.5 g., 4 mols.) in alcohol (50 c.c.) was boiled for 30 minutes; on cooling, deep red crystals of *di-iodobis(tri-n-butylphosphine)-μ-di-iododipalladium* separated, m. p. 136° (acetone) (Found: C, 25.9; H, 5.1. C<sub>24</sub>H<sub>54</sub>I<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 25.6; H, 4.85%).

The *n-amyl* compound (alcohol), m. p. 127° (Found: C, 42.6; H, 7.6; Cl, 16.8; Pd, 25.1; *M*, in 1.709% benzene solution, 825; in 2.367% †, 848. C<sub>30</sub>H<sub>66</sub>Cl<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 42.7; H, 7.9; Cl, 16.8; Pd, 25.3%; *M*, 844): *t*, 144°, 156°; *d*, 1.199, 1.190;  $\gamma$ , 26.00, 25.28;  $[P]$ , 1589, 1590; mean, 1589.  $[P]_{Pd} = 8$ .

The higher members of the above homologous series are sparingly soluble in cold alcohol and cyclohexane, moderately soluble in acetone, and freely soluble in benzene and chloroform;

solubility in organic liquids increases as the series is ascended, this increase being greatest between the methyl, ethyl, and *n*-propyl members.

*Dichlorobis(trialkylarsine)-μ-dichlorodipalladium* (as III and IV).—All members formed deep (garnet) red crystals; the general method of preparation was precisely similar to that of the phosphine analogues.

The *methyl* compound (alcohol), decomp. 252—260° without melting (Found : C, 12.5; H, 2.8; Pd, 35.7.  $C_6H_{18}Cl_4As_2Pd_2$  requires C, 12.1; H, 3.05; Pd, 35.85%), forms small needles of nearly square cross-section, showing straight extinction along the needle. There is high birefringence and marked pleochroism : pale yellow for vibrations along the needle and orange-red at right angles to the needle axis. The *X*-ray photographs and the optical properties of the crystals when viewed in the direction of the needle axis suggest that they may be twinned. The spacing along the needle axis is 7.22 Å.

The methyl compound is sparingly soluble in boiling water, the ethyl homologue is slightly soluble, and the higher members insoluble in hot water.

The *ethyl* compound (acetone) m. p. 212° (slight decomp.) (Found : C, 21.2; H, 4.2.  $C_{12}H_{30}Cl_4As_2Pd_2$  requires C, 21.2; H, 4.4%). This compound was also prepared by heating dichlorobistriethylarsinepalladium at  $3 \times 10^{-3}$  mm. pressure; at 195—200° decomposition occurred, with evolution of triethylarsine and solidification of the product. The latter when recrystallised from acetone gave the above pure ethyl derivative.

The *n-propyl* compound (alcohol), m. p. 160° (Found : C, 28.1; H, 5.55.  $C_{18}H_{42}Cl_4As_2Pd_2$  requires C, 28.3; H, 5.5%).

The *n-butyl* compound (alcohol), m. p. 128° (Found : C, 34.1; H, 6.5; Pd, 24.9; *M*, in 1.693% benzene solution, 818; in 4.898%, 844; in 0.664% bromoform solution, 803; in 1.444%, 832; in 0.975% ethylene dibromide solution, 833; in 1.629%, 829.  $C_{24}H_{54}Cl_4As_2Pd_2$  requires C, 34.0; H, 6.4; Pd, 25.2%, *M*, 847; *t*, 145°, 157°; *d*, 1.412, 1.398;  $\gamma$ , 29.07, 28.14; [*P*], 1394, 1396; mean, 1395; [*P*]<sub>Pd</sub> = 15.

This compound was also prepared by heating dichlorobistri-*n*-butylarsinepalladium at  $3 \times 10^{-3}$  mm. : the molten material lost tri-*n*-butylarsine at 195—210°, and then solidified on cooling, the crude product when recrystallised from alcohol giving the above pure butyl derivative.

Crystals of this butyl compound are completely isomorphous with those of its phosphorus analogue, there being no appreciable difference in cell size or crystal habit. Density (floatation) 1.58, giving 4 molecules in the unit cell.

*Dipole measurement on the n-butyl compound in benzene at 25°.*

$f_d$	$d^{25^\circ}$	$\epsilon^{25^\circ}$	$n_{25^\circ}^3$	$P_2$	$E_{P_2}$
0.0000	0.8738	2.2727	2.2580	—	—
0.003226	0.8870	2.3077	2.2647	323.8	193.0
0.003890	0.8896	2.3146	2.2670	322.4	196.2
0.005660	0.8965	2.3340	2.2692	323.9	191.4
0.005771	0.8970	2.3351	2.2696	323.3	191.5

$$\infty P_2, 323.4 \text{ c.c.}; E_{P_2}, 192.0 \text{ c.c.}; \infty P_2 - E_{P_2} = 131.4 \text{ c.c.}; \mu = 2.52 \text{ D.}$$

The *n-amyl* compound (alcohol), m. p. 108° (Found : C, 38.9; H, 7.1.  $C_{30}H_{66}Cl_4As_2Pd_2$  requires C, 38.6; H, 7.1%); *t*, 145°, 157°; *d*, 1.304, 1.294;  $\gamma$ , 26.57, 25.75; [*P*] 1622, 1622; [*P*]<sub>Pd</sub> = 10.

The solubility of the members of this homologous arsine series in various organic liquids is closely similar to that of the analogous phosphine compounds.

*Action of αα'-Dipyridyl.*—(1) *On the phosphine compounds.* A solution of dipyridyl (0.21 g.) in cold alcohol (20 c.c.) was rapidly added to a solution of the *n*-butylphosphine tetrachloro-compound (III) (1.00 g., 1 mol.) in alcohol (100 c.c.) at 25°. The deep orange-red colour immediately changed to pale yellow, and on cooling, a small crop of yellow needles of *dichlorodipyridylpalladium* (VII) separated. The mixture was taken to dryness in a desiccator and the residue extracted with hot alcohol. The insoluble residue was the dipyridyl compound (Found : C, 36.2; H, 2.55; Pd, 31.8.  $C_{16}H_8N_2Cl_2Pd$  requires C, 36.0; H, 2.4; Pd, 32.0%), and the alcoholic extract on evaporation gave pure dichlorobis(*n*-butylphosphine)palladium, yellow crystals, m. p. 65—66°, unchanged when mixed with an authentic specimen.

The identity of the dichlorodipyridylpalladium was confirmed by a direct preparation, a solution of αα'-dipyridyl (0.5 g.) in alcohol (30 c.c.) being added to one of ammonium palladichloride (0.9 g., 1 mol.) in warm water (10 c.c.), diluted with alcohol (50 c.c.) before the addition.

An immediate buff precipitate separated, and changed rapidly on stirring into honey-yellow needles identical in appearance with those obtained above; after the mixture had been warmed gently on a water-bath for 30 minutes and then cooled, the crystals were separated, washed with water, alcohol, and ether, and dried (Found: C, 36.1; H, 2.5; Pd, 31.7%). The dipyriddy compound is unchanged when heated to 300°; it is very slightly soluble in boiling water, alcohol, and acetone, and is best recrystallised in small quantities from a mixture of dioxan (4 vols.) and water (1 vol.), in which solvent, however, reduction occurs after several minutes' heating.

(2) *On the arsine compounds.* Precisely similar results were obtained when a solution of dipyriddy (0.18 g.) in alcohol was added to a solution of the *n*-butylarsine tetrachloro-compound (as III) (1.00 g., 1 mol.) in alcohol (100 c.c.) at 25°; the colour of the solution at once became pale yellow, but the precipitation of dichlorodipyriddy palladium started within a few seconds and was soon complete. The filtrate, similarly treated, gave pure dichlorobis-(*n*-butylarsine)-palladium, m. p. 52—54°, unchanged on admixture with an authentic sample.

*Oxalatobis-(n-butylphosphine)-μ-dichlorodipalladium* (VIII).—The finely-powdered tetrachloro-compound (III) (8 g.), suspended in a solution of potassium oxalate (20 g.) in water (120 c.c.) and alcohol (15 c.c.), was heated on a water-bath with occasional shaking until conversion into the brown oxalate was complete (6—7 hours). The product was cooled, and the oxalate separated, washed with water, dried, and recrystallised from benzene. The *dichloromono-oxalate* was obtained as pale yellowish-brown crystals, which, placed in a bath at 180°, had m. p. 185—186° (decomp.); slow heating gave a lower m. p. The oxalate can be recrystallised also from alcohol or acetone, but is then usually contaminated with a trace of finely-divided palladium (Found: C, 40.1; H, 7.0; Pd, 27.5; *M*, in 0.554% benzene solution, 767; in 5.350%, † 803; in 1.658% ethylene dibromide solution, 482; in 2.915%, 476; in 1.272% bromoform solution, 396. C<sub>24</sub>H<sub>54</sub>O<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 40.2; H, 7.0; Pd, 27.5%; *M*, 776).

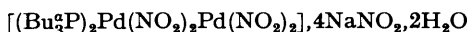
*Dipole measurement on the dichloro-oxalate in benzene at 25°.*

$f_2$ .	$d^{25}$ .	$\epsilon^{25}$ .	$n_{25}^2$ .	$P_2$ .	$\Sigma P_2$ .
0.0000	0.8737	2.2727	2.2580	—	—
0.001642	0.8787	2.3041	2.2604	452.4	191.6
0.002279	0.8808	2.3167	2.2617	452.7	191.5
0.002744	0.8823	2.3257	2.2622	452.1	189.5
0.002974	0.8829	2.3296	2.2626	450.9	191.1

$$\infty P_2, 452.0 \text{ c.c.}; \Sigma P_2, 191.4 \text{ c.c.}; \infty P_2 - \Sigma P_2 = 260.6 \text{ c.c.}; \mu = 3.55 \text{ D.}$$

*Action of αα'-dipyriddy.* Solutions of the oxalate (VIII) (1.500 g.) and dipyriddy (0.302 g.) in acetone (45 c.c. and 20 c.c. respectively) were mixed, a buff-coloured precipitate slowly forming. After 24 hours, this precipitate was separated, and the solution evaporated to dryness in a desiccator. The residue was extracted with boiling acetone, a further crop of the insoluble buff-coloured precipitate remaining; the acetone solution on cooling deposited the dichlorobisphosphine (VI), as yellow crystals, m. p. 65—66°, unchanged by admixture with an authentic sample. The buff precipitate was pure *oxalatodipyriddy palladium*, (IX), which on heating decomposes without melting (Found: C, 40.9; H, 2.6; Pd, 30.3. C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub>Pd requires C, 41.05; H, 2.3; Pd, 30.4%).

*Dinitritobis-(n-butylphosphine)-μ-dinitritodipalladium* (X).—The finely-powdered chloro-compound (III) (6.0 g.) was shaken with saturated aqueous sodium nitrite solution (30 c.c.) with occasional warming until conversion into the pale yellow product was complete (2—3 days). This product was filtered off and dried, and proved to be an unstable hydrated *addition compound* of the above compound (X) and sodium nitrite, of composition



(Found: C, 26.1; H, 5.5; N, 9.5; Pd, 19.25; NaNO<sub>2</sub>, 23.8. C<sub>24</sub>H<sub>58</sub>O<sub>18</sub>N<sub>8</sub>Na<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 25.9; H, 5.3; N, 10.1; Pd, 19.2; NaNO<sub>2</sub>, 24.7%). This product, when shaken with water, dissociated, giving (X): the latter, when added to saturated sodium nitrite solution, re-formed the addition product. The *tetranitrito*-compound (X), obtained as above, was separated, dried, recrystallised from cyclohexane, and thus obtained as yellow crystals, m. p. 138° (slight decomp.) (Found: C, 35.6; H, 6.7; N, 6.75; Pd, 26.5; *M* in 0.849% benzene solution, 1010; in 2.842%, 1100; in 5.000%, 1110; in 0.489% ethylene dibromide solution, 855; in 0.917%, 858; in 1.970%, 883; in 0.381% bromoform solution, 930; in 0.970%, 1020; in 1.789%, 1060. C<sub>24</sub>H<sub>54</sub>O<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 35.9; H, 6.8; N, 7.0; Pd, 26.6%; *M*, 802). The tetranitrite is insoluble in water, but readily soluble in alcohol; it is rapidly converted by hydrochloric

acid into the original tetrachloro-compound (III), and by concentrated sodium nitrite solution on boiling into the dinitrobisphosphinepalladium (XII).

*Action of oxalic acid on the tetranitrite (X).* When cold alcoholic solutions of the butylphosphine tetranitrite compound (X) (4.00 g.) and of oxalic acid (0.64 g., 1 mol.) were mixed, bright yellow crystals were rapidly precipitated. These were separated, and when recrystallised from alcohol or acetone gave *oxalatobis-(n-butylphosphine)-μ-dinitritodipalladium* (XI) as yellow needles which, when placed in a bath at 185° and then heated, darkened at 192—195° and melted 201—204° (decomp.) (Found: C, 39.0; H, 6.8; N, 3.3; Pd, 26.6; *M*, in 0.455% ethylene dibromide solution, 710; in 0.575%, 709; in 0.522% bromoform solution, 723; in 1.490%, 722.  $C_{26}H_{54}O_8N_2P_2Pd_2$  requires C, 39.2; H, 6.8; N, 3.5; Pd, 26.75%; *M*, 798).

*Action of dipyridyl.* Solutions of the tetranitrite (X) (1.500 g.) and  $\alpha\alpha'$ -dipyridyl (0.292 g.) in alcohol (20 c.c. and 10 c.c. respectively) were mixed, a fine yellow crystalline precipitate rapidly separating. Evaporation to dryness in a desiccator gave the yellow compound mixed with white crystals. Extraction with a small quantity of hot alcohol left the insoluble yellow crystals of *dinitritodipyridylpalladium* (XIII), which on heating decomposes without melting (Found: N, 15.6; Pd, 29.7.  $C_{10}H_8O_4N_4Pd$  requires N, 15.8; Pd, 30.1%), while the filtrate on cooling deposited white crystals of *dinitritobis(butylphosphine)palladium* (XII), m. p. 140° (Found: C, 47.6; H, 8.7; N, 4.65.  $C_{24}H_{54}O_4N_2P_2Pd$  requires C, 47.75; H, 9.0; N, 4.6%).

*Dinitritobis(tri-n-butylarsine)palladium.*—A mixture of the finely-powdered butylarsine tetrachloro-compound (XIV) (5 g.) and saturated aqueous sodium nitrite solution (20 c.c.) was shaken for 1 hour, and then gently warmed until the reaction was complete and the deep red particles of the tetrachloro-compound entirely replaced by yellow crystals. The latter were separated, washed with water, and recrystallised from methyl alcohol, the above *dinitrito-compound* being thus obtained as pale yellow prisms, m. p. 96° (Found: C, 42.0; H, 7.7; Pd, 15.6.  $C_{24}H_{54}O_4N_2As_2Pd$  requires C, 41.7; H, 7.9; Pd, 15.4%). No compound analogous to the phosphine derivative (X) could be detected in the reaction product.

*Thiocyanate Derivatives.*—The arsenic compounds are described first, in accordance with Table II.

*Dichlorobis-(n-butylarsine)-μ-dithiocyanatodipalladium* (XV). (1) The butylarsine tetrachloro-compound (XIV) (2.00 g.) and pure ammonium thiocyanate (0.36 g., 2 mols.) were boiled together in alcoholic solution for 5 minutes. On cooling, orange crystals of the above *compound* (XV) separated, and when recrystallised from alcoholic acetone had m. p. 101° (Found: C, 34.9; H, 6.1; N, 3.3; Pd, 23.7.  $C_{26}H_{54}N_2Cl_2S_2As_2Pd$  requires C, 35.0; H, 6.0; N, 3.1; Pd, 23.9%).

(2) Hot alcoholic solutions of dichlorobis-*n*-butylarsinepalladium (XVI) and of excess potassium thiocyanate were mixed, potassium chloride being immediately precipitated. The latter was separated, and the filtrate on cooling gave yellowish-orange crystals of *dithiocyanatobis-(n-butylarsine)palladium* (XVII), which after recrystallisation from alcohol had m. p. 75° (Found: C, 43.6; H, 7.4; Pd, 15.0.  $C_{26}H_{54}N_2S_2As_2Pd$  requires C, 43.6; H, 7.6; Pd, 14.9%). This thiocyanate (2.00 g.) and ammonium palladochloride (0.79 g., 1 mol.) were boiled together in alcoholic solution for 1 hour. On cooling, an oil separated and slowly solidified; the solid product when twice recrystallised from alcoholic acetone gave the dithiocyanato-dichloride (XV), m. p. 101°, unchanged by admixture with that obtained by method (1).

*Dithiocyanatobis-(n-butylarsine)-μ-dithiocyanatodipalladium* (XVIII). Cold alcoholic solutions of the dithiocyanato-dichloride (XV) and of potassium thiocyanate were mixed, potassium chloride being at once precipitated. Water was added drop by drop with stirring to the clear filtrate, and fractional precipitation of the palladium compounds thus obtained. The first fraction, recrystallised from alcohol, gave orange crystals of the dithiocyanate (XVII), m. p. 74—75°, unchanged by admixture with a sample prepared as above; the second fraction, twice crystallised from alcohol, gave orange crystals of the above *tetrathiocyanato-compound* (XVIII), m. p. 111° (Found: C, 35.7; H, 5.9; N, 5.7; S, 13.8.  $C_{28}H_{54}N_2S_2As_2Pd_2$  requires C, 35.8; H, 5.8; N, 6.0; S, 13.7%).

The identity of the tetrathiocyanate (XVIII) was further confirmed by treating the dichloride (XVI) (2.50 g.) in alcoholic solution with ammonium palladothiocyanate,  $(NH_4)_2[Pd(SCN)_4]$ , (1 mol.), prepared by adding pure ammonium thiocyanate (1.13 g., 4 mols.) to ammonium palladochloride (1.07 g., 1 mol.) in alcoholic solution. After the mixed solutions had been boiled for 20 minutes and then cooled, orange crystals separated; these, when four times recrystallised from acetone, had m. p. 109—110°, unchanged by admixture with (XVIII). It is clear that in this reaction the dithiocyanate (XVII) must have first been formed and then converted into the tetrathiocyanate (XVIII).

The above series of reactions was repeated with corresponding *n*-propyl derivatives :

*Dichlorobis*-(*n*-propylarsine)- $\mu$ -dithiocyanatodipalladium (as XV). (1) The propylarsine tetrachloro-compound (as XIV) (2 g.) was boiled in alcoholic solution with ammonium thiocyanate (0.80 g., 2 mols.) for 10 minutes. The orange crystals of the required compound (as XV) which separated on cooling were recrystallised from alcoholic acetone, and had m. p. 151° (Found : C, 29.4; H, 5.05; N, 3.3; S, 8.1; Pd, 26.1.  $C_{20}H_{42}N_2Cl_2S_2As_2Pd_2$  requires C, 29.7; H, 5.2; N, 3.5; S, 7.9; Pd, 26.4%).

(2) Dichlorobis-*n*-propylarsinepalladium (as XVI) (3 g.) was warmed with a 20% alcoholic potassium thiocyanate solution (10 c.c.) until the colour changed to a clear yellow. The mixture was filtered and cooled, and the crystals separated, washed with water, drained, and four times recrystallised from alcohol. The dithiocyanatobis-(*n*-propylarsine)palladium (as XVII) was obtained as golden-yellow crystals, m. p. 90—91.5° (Found : C, 38.1; H, 7.0; N, 4.7.  $C_{20}H_{42}N_2S_2P_2Pd$  requires C, 38.0; H, 6.7; N, 4.4%).

When an alcoholic solution of this dithiocyanate (1.50 g.) and of ammonium palladochloride (0.68 g., 1 mol.) was boiled for 1 hour and then cooled, orange crystals of the above dithiocyanato-dichloride (as XV) separated; these when recrystallised from alcoholic acetone had m. p. 151°, unchanged on admixture with a specimen prepared by method (1).

*Dithiocyanatobis*-(*n*-propylarsine)- $\mu$ -dithiocyanatodipalladium (as XVIII). The above dithiocyanato-dichloride (as XV) was treated in cold alcoholic solution with an excess of potassium thiocyanate. Water was then added with stirring and the mixed product fractionally precipitated as before. This first fraction, recrystallised from alcohol, gave the arsine analogue of (XVII), m. p. 90—91°; the second fraction, recrystallised from alcoholic acetone, gave orange crystals of the tetrathiocyanato-compound (as XVIII), m. p. 142° (Found : C, 31.1; H, 5.3; N, 6.3.  $C_{22}H_{42}N_4S_4As_2Pd_2$  requires C, 30.9; H, 5.0; N, 6.6%).

*Dichlorobis*-(*n*-butylphosphine)- $\mu$ -dithiocyanatodipalladium (as XV).—This compound was prepared by two methods as before.

(1) The butylphosphine tetrachloro-compound (as XIV) (2 g.) was boiled for 20 minutes in alcoholic solution with ammonium thiocyanate (0.80 g., 2 mols.); the orange crystals of the dithiocyanato-dichloride (as XV) which separated on cooling were recrystallised from alcoholic acetone; m. p. 142° (Found : C, 38.6; H, 6.6; N, 3.7; S, 8.1.  $C_{26}H_{54}N_2Cl_2S_2P_2Pd_2$  requires C, 38.8; H, 6.8; N, 3.5; S, 7.95%).

(2) Mixed alcoholic solutions of dichlorobisbutylphosphinepalladium (as XVI) and of excess potassium thiocyanate were boiled for a few minutes, filtered to remove potassium chloride, and cooled. White crystals of dithiocyanatobis-(*n*-butylphosphine)palladium (as XVII) separated, m. p. 112° after crystallisation from alcohol (Found : C, 49.65; H, 8.5; N, 4.4.  $C_{28}H_{54}N_2S_2P_2Pd$  requires C, 49.8; H, 8.7; N, 4.5%).

This dithiocyanate (1.00 g.) and ammonium palladochloride (0.45 g., 1 mol.) were boiled together in alcoholic solution. Cooling gave crystals of the above dithiocyanato-dichloride, m. p. 142° after crystallisation from alcoholic acetone, unchanged when mixed with a specimen obtained by method (1).

*Dithiocyanatobis*-(*n*-butylphosphine)- $\mu$ -dithiocyanatodipalladium (as XVIII).—The above dithiocyanato-dichloride (as XV) (2.00 g.) and pure ammonium thiocyanate (0.38 g., 2 mols.) were boiled together in alcoholic solution. On cooling, orange crystals of the tetrathiocyanato-compound (as XVIII) separated, and after recrystallisation from alcohol had m. p. 165° (Found : C, 39.5; H, 6.2; N, 6.8; Pd, 24.7.  $C_{28}H_{54}N_4S_4P_2Pd_2$  requires C, 39.5; H, 6.4; N, 6.6; Pd, 25.1%).

The same compound was obtained when the dithiocyanato-dichloride was similarly treated with an excess of either ammonium or potassium thiocyanate, rupture of the molecule to give the unbridged dithiocyanate (as XVII) apparently never occurring.

*Action of Monoamines on the Phosphine and Arsine Compounds.*—(1) *Aniline*. Solutions of the butylphosphine tetrachloro-compound (IV, 1.50 g.) and aniline (0.36 c.c., 2 mols.) in alcohol (100 c.c. and 10 c.c. respectively) were mixed at 20°, the orange-red colour of the phosphine compound immediately changing to pale yellow. The alcohol was removed in a desiccator, and a homogeneous yellow residue, m. p. 65—67°, was obtained. Recrystallisation from light petroleum (b. p. 40—50°) gave yellow crystals of dichloromonoanilinomono-*n*-butylphosphinepalladium (XIX), m. p. 68° (Found : C, 45.5; H, 7.2; N, 3.1.  $C_{18}H_{34}NCl_2PPd$  requires C, 45.7; H, 7.25; N, 3.0%).

(2) *p*-Toluidine. (a) Cold benzene solutions of the butylphosphine tetrachloro-compound (IV, 2.00 g.) and of *p*-toluidine (0.563 g., 2 mols.) were mixed, the orange-red colour again changing immediately to yellow. The benzene was removed in a desiccator, and the homogeneous

product recrystallised as in (1). *Dichloromono-p-toluidinomonon-butylphosphinepalladium* (as XIX) was obtained as yellow crystals, m. p. 75° (Found : C, 46.4; H, 7.6; N, 2.9; M, in 1.502% benzene solution, 496; in 3.014%, 496.  $C_{19}H_{36}NCl_2PPd$  requires C, 46.8; H, 7.5; N, 2.9%; M, 487).

(b) Cold ethereal solutions of the butylarsine tetrachloro-compound (as IV) (2.00 g.) and of *p*-toluidine (0.505 g., 2 mols.) were mixed, the deep red colour of the arsine compound changing immediately to pale orange. The homogeneous crystalline residue, obtained and recrystallised as before, gave the *arsine* analogue of the preceding compound, orange crystals, m. p. 87° (Found : C, 42.9; H, 6.5; N, 2.6; M, in 1.750% benzene solution, 533; in 3.468%, 541.  $C_{19}H_{36}NCl_2AsPd$  requires C, 42.95; H, 6.8; N, 2.6%; M, 531).

(c) Cold alcoholic solutions of the butylphosphine tetranitrite compound (XX, 2.00 g.) and of *p*-toluidine (0.54 g., 2 mols.) were mixed and evaporated in a desiccator. The residual yellow oil on exposure to air rapidly solidified to a homogeneous product, which on recrystallisation from *cyclohexane* gave *dinitritomonon-p-toluidinon-butylphosphinepalladium* (XXI), pale yellow crystals, m. p. 86–88° (partial decomp.) [Found : C, 45.1; H, 7.1; N, 8.1; M, in 1.680% benzene solution, 509; in 3.258% (almost saturated), 550.  $C_{19}H_{24}O_4N_3PPd$  requires C, 44.9; H, 7.15; N, 8.3%; M, 508].

*Action of Ammonia.*—(1) *On the butylphosphine tetrachloro-compound* (IV) (see Table III). A slow stream of dry ammonia was passed over a weighed porcelain boat containing the finely-powdered tetrachloro-compound (IV, 2.000 g.) : the latter was rapidly converted into a white crystalline derivative, a constant increase in weight of 0.356 g. being ultimately obtained. Although an addition of 4 mols. of ammonia to each palladium atom in (IV) requires an increase of 0.358 g., the constitution of this very unstable product is difficult to decide : the white colour, however, indicates a rupture of the bridged complexes, and the compound may be a 6-co-ordination derivative of bivalent palladium of formula  $[(Bu_3P)PdCl(NH_3)_4]Cl$ . This compound when placed in a vacuum or even on exposure to air rapidly lost 1 equiv. of ammonia, giving the white *triammino-n-butylphosphinepalladium dichloride* (XXII). Since it was difficult to stop the dissociation sharply at this stage, the triammino-compound was also prepared by blowing dry ammonia through a solution of the tetrachloro-compound (IV) (5 g.) in cold benzene (120 c.c.); the orange colour rapidly faded, the triammino-compound then being precipitated. The latter was separated, washed with ammoniacal light petroleum (b. p. 40–50°), and finally dried quickly on the filter by a stream of air containing ammonia (Found : C, 32.3; H, 8.1; Pd, 24.0.  $C_{12}H_{36}N_3Cl_2PPd$  requires C, 33.4; H, 8.4; Pd, 24.8%). In spite of these precautions, further slight loss of ammonia occurred, the compound developing a faint yellow surface tint owing to the formation of the compound (XXIII).

The triammino-compound (XXII) is itself very unstable, and on treatment with concentrated hydrochloric acid loses all its ammonia, at once reverting to the original tetrachloro-compound (IV). When it is exposed to air, only 2 mols. of ammonia are lost; the same reaction occurs rapidly when it is boiled with acetone, and the clear solution on cooling deposits yellow crystals of *dichloromonammino-n-butylphosphinepalladium* (XXIII), which, recrystallised from alcohol or from *cyclohexane*–light petroleum, has m. p. 71° (Found : C, 36.6; H, 7.3; N, 3.2; Cl, 18.2; Pd, 26.9; M, in 1.681% benzene solution, 373; in 4.709%, 390; in 0.329% bromoform solution, 396; in 0.994%, 397.  $C_{12}H_{30}NCl_2PPd$  requires C, 36.3; H, 7.6; N, 3.5; Cl, 17.9; Pd, 26.9%; M, 397).

The monoammino-compound (XXIII) on treatment with ammonia in benzene solution reverts to the triammino-compound (XXII). On treatment with concentrated hydrochloric acid, it loses ammonia and at once gives the original tetrachloro-compound (IV); the same reaction occurs, but more slowly, when the monoammino-compound is exposed in a vacuum, or when its benzene solution is allowed to stand for several days at room temperature.

(2) *On the butylarsine tetrachloro-compound* (see Table IV). This compound, when finely powdered and treated exhaustively with dry ammonia, underwent complete decomposition, the free arsine being liberated. It was therefore treated with dry ammonia in a boat as before until a homogeneous friable white powder was obtained, and the reaction was then stopped before liberation of free arsine began. This white product was too unstable for detailed investigation. When treated with dry acetone, it lost ammonia, deposited a white powder, and gave a yellow solution. The white powder was separated, quickly dried, and proved to be tetrammino-palladium dichloride (XXV) (Found : H, 4.9; C, nil; Pd, 44.2. Calc. for  $H_{12}N_4Cl_2Pd$  : H, 4.9; Pd, 43.4%); the high Pd value is due to the instability of this compound, the identity of which was confirmed by treatment with concentrated hydrochloric acid, which at once gave the yellow dichlorodiamminopalladium (XXVII). The yellow solution on evaporation gave dichlorobis-



*n*-butylarsinepalladium (XXVI), which when recrystallised from alcohol had m. p. 54°, unchanged by admixture with an authentic sample.

Precisely similar results were obtained when ammonia was blown into a solution of the butylarsine tetrachloro-compound in cold benzene; the solution deposited a white precipitate and rapidly became colourless. The precipitate, extracted with acetone, gave the tetrammino-compound (XXV) and the bisbutylarsine derivative (XXVI) as before.

*Action of Ethylenediamine.*—(1) *On the butylphosphine tetrachloro-compound.* (a) A 1% alcoholic solution of ethylenediamine hydrate (40.8 c.c., 2 mols.) was added to a solution of the tetrachloro-compound (2 g.) in cold alcohol (100 c.c.), the colour of the solution immediately becoming pale yellow. Evaporation in a vacuum at room temperature gave a homogeneous yellow oil which subsequently crystallised. This yellow compound proved too unstable for purification, but is apparently the *bis*-(*n*-butylphosphine)*bis*(ethylenediamino)- $\mu$ -dichlorodipalladium dichloride (XXVIII) (Found: N, 5.7; Pd, 24.4.  $C_{28}H_{70}N_4Cl_4P_2Pd_2$  requires N, 6.4; Pd, 24.25%). It is soluble in alcohol, but insoluble in water: its aqueous alcoholic solution gives an immediate and copious precipitate with alcoholic silver nitrate solution. Boiling with cyclohexane converted it into white insoluble crystals of *monochloro-n*-butylphosphine-ethylenediaminopalladium monochloride (XXIX). The latter is freely soluble in water, the solution giving an immediate precipitate with silver nitrate; boiling with water decomposed the compound, and recrystallisation was not achieved (Found: C, 38.5; H, 8.1; N, 6.2; Pd, 24.2.  $C_{14}H_{32}N_2Cl_2PPd$  requires C, 38.2; H, 8.0; N, 6.4; Pd, 24.25%). Hydrochloric acid, added to its aqueous solution, gave a yellow precipitate of the original tetrachloro-compound, which after recrystallisation from alcohol had m. p. 144–145°, unchanged when mixed with an authentic sample.

(b) A solution of ethylenediamine hydrate (0.41 g., 2 mols.) in benzene (5 c.c.) and absolute alcohol (10 c.c.) was added to a solution of the tetrachloro-compound (2 g.) in benzene (20 c.c.). The colour slowly faded and white crystals of bis(ethylenediamino)palladium dichloride began to form. These were separated [Found: N, 18.85; Pd, 35.2 (ignition). Calc. for  $C_4H_{16}N_2Cl_2Pd$ : N, 18.8; Pd, 35.8%] and the filtrate evaporated at room temperature; the solid residue on recrystallisation from alcohol gave dichlorobisbutylphosphinepalladium, m. p. 64–65°, unchanged when mixed with an authentic sample.

(2) *On the butylarsine tetrachloro-compound.* When absolute alcoholic solutions of the tetrachloro-compound and of ethylenediamine hydrate (2 mols.) were mixed, an intermediate compound of type (XXX) was undoubtedly formed, but steadily decomposed during the evaporation at room temperature, the white crystals of bis(ethylenediamino)palladium dichloride being continuously precipitated, while the dichlorobisarsine-compound formed the final residue. In benzene solution, this decomposition is much more rapid. Thus a solution of ethylenediamine hydrate (0.74 g., 2 mols.) in benzene (10 c.c.) and absolute alcohol (10 c.c.) was added to one of the butylarsine tetrachloro-compound (4 g.) in benzene (25 c.c.). The colour of the solution faded and a white precipitate of bis(ethylenediamino)palladium dichloride rapidly formed. The residue obtained by evaporating the filtrate gave dichlorobisbutylarsinepalladium, m. p. 54° after recrystallisation from alcohol. It is noteworthy that when either the butylphosphine or -arsine tetrachloro-compound in alcoholic solution was treated with only one molecular equivalent of ethylenediamine, much of the tetrachloro-compound was recovered unchanged, and therefore a reaction similar to that given by  $\alpha\alpha'$ -dipyridyl apparently does not occur.

*Monochloromonoethylthiobis*-(*n*-butylphosphine)- $\mu$ -dichlorodipalladium.—Cold solutions of the butylphosphine tetrachloro-compound (2 g.) and of ethylthiol (0.24 c.c., 1.2 mols.) in alcohol (150 and 25 c.c. respectively) were mixed: the colour of the solution faded to a pale yellow and fine yellow crystals separated in a few minutes. These were collected and recrystallised from alcohol, the above compound being obtained as yellow needles, m. p. 151° (Found: C, 39.9; H, 7.5; Cl, 13.4; S, 4.05; *M*, in 1.065% ethylene dibromide solution, 896; in 2.040% 974.  $C_{22}H_{59}Cl_2SP_2Pd_2$  requires C, 39.7; H, 7.6; Cl, 13.55; S, 4.1%; *M*, 785). It is noteworthy that the palladium and mercury bismercaptides (Mann and Purdie, *loc. cit.*) showed an association in solution which similarly increased with increasing concentration.

*Dichlorobis*-(*n*-octylsulphide)- $\mu$ -dichlorodipalladium.—When an aqueous solution of ammonium palladochloride was shaken with pure di-*n*-octyl sulphide (2 mols.) for 3 hours, the dichloro-compound [ $\{(C_8H_{17})_2S\}_2PdCl_2$ ] which separated could not be recrystallised, as its m. p. was below room temperature. It was therefore dissolved in a little alcohol, and shaken with an aqueous solution of  $(NH_4)_2[PdCl_4]$  (1 mol.) at 40° for a further 3 hours. The brown solid product which had separated was collected, washed with water, dried, and twice recrystallised from petrol, the above tetrachloro-compound being obtained as pale brown crystals, m. p. 61° (Found: C, 44.1; H, 8.0; Pd, 24.3.  $C_{32}H_{88}Cl_4S_2Pd_2$  requires C, 44.0; H, 7.9; Pd, 24.5%). This com-

pound, warmed in ethereal solution with 1 equiv. of dioctyl sulphide, regenerated the above dichlorobisocetylsulphidepalladium.

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