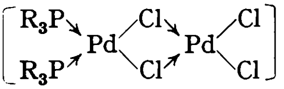
340. *The Constitution of Complex Metallic Salts. Part X. Further Evidence for the Structure of Bridged Dipalladium Derivatives.*

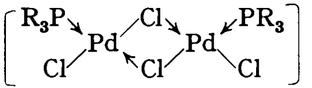
By Joseph Chatt and Frederick G. Mann.

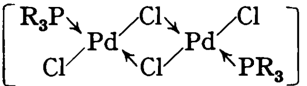
Bridged compounds of the type dichlorobis(trialkyl-phosphine or -arsine)-μ-dichlorodipalladium can theoretically exist in one unsymmetric and two symmetric forms : (I), (IIA), and (IIB). Physical evidence showed that in solution they exist as a tautomeric mixture either of (IIA) and (IIB) or of all three forms : chemical evidence indicated that all three forms were present. The compounds exist in the crystalline condition as only one form, proved by *X*-ray analysis to be (IIB). Attempts have now been made to isolate bridged compounds which would contain *cis*-chelated disulphide or diarsine molecules and must therefore have the unsymmetric structure (I). Several unbridged palladium compounds containing such chelated molecules have been prepared, but none reacted further with palladous chloride to give the required bridged derivatives. In view of these results, the reactions originally cited by Mann and Purdie as evidence for the existence of the unsymmetric form of the bridged dipalladium derivatives have now been investigated in greater detail. They prove to be less simple than originally appeared and do not afford evidence for this unsymmetric form. It is concluded that the tautomerism indicated by dipole measurements is limited to that between the *cis*- and *trans*-symmetric forms (IIA and IIB) of the dipalladium compounds.

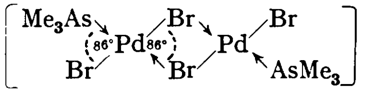
The compound $[C_2H_4(AsPhBu)_2PdCl_2]$, which contains two similar asymmetric 4-covalent arsenic atoms, has been obtained in two forms, α m. p. 172—174°, β m. p. 185—186°: one of these forms must be the *meso* and the other the externally compensated isomeride. This is the first recorded example of such isomerism in complex metallic compounds.

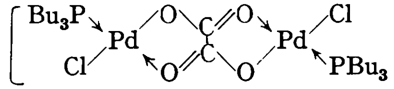
THE bridged derivatives of the trialkyl-phosphines and -arsines with palladous halides, of general formula $[R_3P(As),PdX_2]_2$, can theoretically exist in three isomeric forms, *viz.*, the unsymmetric form (I), and the *cis*- and *trans*-symmetric forms (IIA and IIB). Physical evidence (from dipole-moment determinations) indicated that these bridged compounds in organic solvents exist as a tautomeric mixture either of the two symmetric forms (IIA) and (IIB), or of all three forms; chemical evidence, however, indicated that all three forms are present, since these compounds in organic solvents gave certain reactions that could be simply explained only as due to the presence of the unsymmetric form (I), and other reactions that were similarly explained as due to the symmetric forms (IIA) and (IIB) (Mann and Purdie, J., 1936, 873). The compounds in the crystalline state, however, exist in only one form, which has been shown by *X*-ray analysis in the trimethylarsinepalladous chloride and bromide compounds to be the *trans*-symmetric form (III) (Mann and Wells, J., 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169).


(I.)


(IIA.)


(IIB.)

(III.)



(IV.)

One reaction cited by Mann and Purdie (*loc. cit.*) in support of the presence of the unsymmetric form (I) was that dichlorobis(tributylphosphine)-μ-dichlorodipalladium, when treated with one equivalent of αα′-dipyridyl, appeared to undergo a "vertical splitting" (equation A), since it gave dichlorobistributylphosphinepalladium and dichlorodipyridylpalladium.

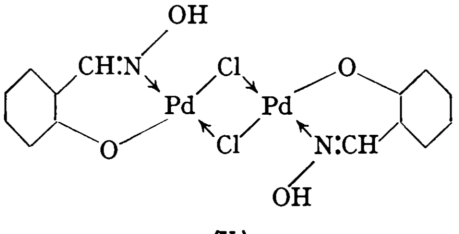
$$[(\mathrm{Bu_3P})_2\mathrm{PdCl_2}\vdots\mathrm{PdCl_2}] + \mathrm{dpy} = [(\mathrm{Bu_3P})_2\mathrm{PdCl_2}] + [\mathrm{dpy\ PdCl_2}] \qquad \text{(A)}$$

It was later shown that this reaction is less simple than indicated, since the corresponding dichloro-oxalate, which has been shown by *X*-ray analysis to have the *trans*-symmetric structure (IV) (Chatt, Mann, and Wells, J., 1938, 2086), gives a similar reaction:

$$[(\mathrm{Bu_3P})\mathrm{ClPdC_2O_4PdCl}(\mathrm{PBu_3})] + \mathrm{dpy} = [(\mathrm{Bu_3P})_2\mathrm{PdCl_2}] + [\mathrm{dpy\ PdC_2O_4}].$$

We have therefore attempted to obtain decisive evidence for the existence of the unsymmetric form (I) by the preparation of a bridged compound which could have only this structure. Clearly, if the two phosphine or arsine molecules were replaced by a suitable chelated molecule, having two atoms united by co-ordinate links in the *cis*-position to one palladium atom, the resulting bridged molecule must necessarily be of type (I).

It should first be noted that the use of chelate groups as such does not prevent the formation of these bridged compounds: several such compounds have been recorded, but in all cases the chelated organic molecule was linked to the metal by *one covalent and one* *co-ordinate link*, and thus allowed the symmetric structure of type (IIA) and (IIB). Examples are bis(salicylaldoxime)-μ-dichlorodipalladium (V) (Cox, Pinkard, Wardlaw, and Webster, J., 1935, 459) and bis-(4 : 4′-dicarbethoxy-3 : 3′ : 5 : 5′-tetramethylpyromethene)-μ-dichlorodipalladium (VI) (Porter, J., 1938, 368).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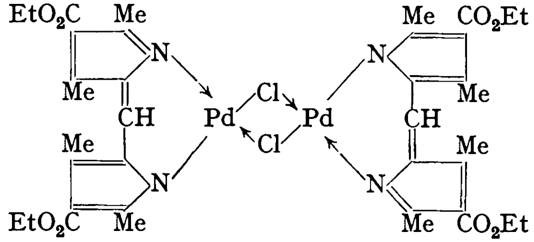
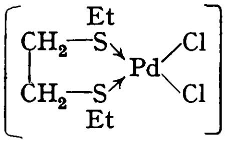
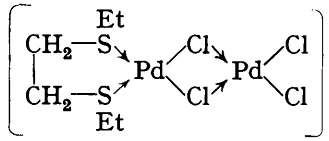

(VI.)

The first example investigated of a compound having a chelated di-co-ordinate group was ethylene-αβ-bis(ethylsulphide)dichloropalladium (VII). This compound is readily prepared and extremely stable : if it were capable of forming a bridged compound, the latter must have the unsymmetric structure (VIII) of type (I). When, however, the

(VII.)



(VIII.)

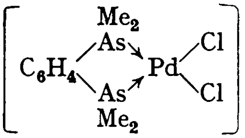
unbridged compound (VII) was boiled in alcoholic solution with ammonium palladochloride (the standard method for preparing bridged compounds), no reaction occurred and the compound (VII) was recovered unchanged. It was known, however, that in the dialkyl sulphide series $[(R_2S)_2PdCl_2]$ (Mann and Purdie, *loc. cit.*) formation of the bridged compounds is shown by the higher members, *e.g.*, the *n*-octyl, but not by the lower (methyl and ethyl) members. The *ethylene-αβ-bis-*(n-*octylsulphide*)*dichloropalladium*,

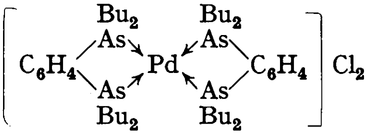
$$[C_2H_4(S{\cdot}C_8H_{17})_2PdCl_2],$$

analogous to (VII), was therefore prepared, but it also failed to form a bridged compound of type (VIII).

Previous work had shown, however, that the bridged palladium compounds are formed much more readily from tertiary phosphines and arsines than from dialkyl sulphides. The palladium derivatives of the ditertiary arsines previously described (Chatt and Mann, this vol., p. 610) were therefore investigated. These diarsines have the arsenic atoms separated by only two carbon atoms, and they also give stable 5-membered rings by co-ordination with palladium, the arsenic atoms necessarily occupying the *cis*-position around the metallic atom.

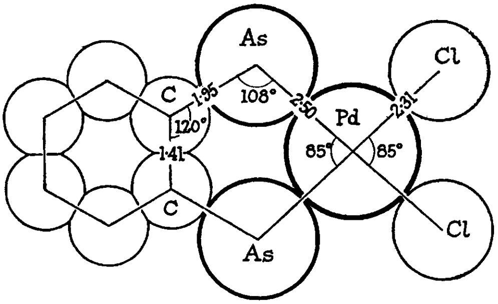
When equimolecular quantities of ammonium palladochloride (in aqueous solution) and *o*-phenylenebis(dimethylarsine), $C_6H_4(AsMe_2)_2$, were vigorously shaken together, the only product was the ionic *di-*o*-phenylenebis*(*dimethylarsine*)*palladium palladochloride*, $[(C_6H_4As_2Me_4)_2Pd][PdCl_4]$. This compound possessed great stability, but when boiled with alcohol and hydrochloric acid gave the non-ionic o-*phenylenebis*(*dimethylarsine*)-*dichloropalladium* (IX); all attempts, however, to convert this into a bridged derivative,

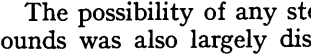
(IX.)



(X.)

$[(C_6H_4As_2Me_4)PdCl_2PdCl_2]$, failed. Similar experiments were then made with *o*-phenylenebis(di-*n*-butylarsine). The chief product was the very stable *di-*o*-phenylenebis*(*dibutylarsine*)*palladium dichloride* (X), which was converted by the further action of ammonium palladochloride into *o-phenylenebis(dibutylarsine)dichloropalladium* (as IX). The latter compound also failed, however, to give bridged dipalladium compounds.

The remarkable stability of compounds of type (IX) and (X), and particularly the rapid and preferential formation of the complex ion as in (X), show that the structure of these diarsines must enable them to form very stable chelate rings with the palladium atom. A diagram of the compound (IX), with the four alkyl groups omitted for simplicity, is shown in the figure. In the construction of this diagram the only valency angles adopted primarily were those of 120° between the ring valencies of the aromatic carbon atoms: the rest of the diagram was then drawn by using solely the interatomic "half-bond lengths" of Pauling and Huggins (*Z. Krist.*, 1934, **87**, 205). It will be seen that the C–As–Pd valencies subtend an angle of 108°, *i.e.*, almost exactly the natural angle for the tetrahedral co-ordinated arsenic atom. Moreover, the As–Pd–As angle (85°) is almost identical with the As–Pd–Br and the Br–Pd–Br angles (86°) in the bridged trimethylarsine compound (III), and with the Cl–Pd–Cl angle (87°) in the chains of bridged $PdCl_2$ units in crystalline palladium chloride (XI) (Wells, *Z. Krist.*, 1938, **100**, 189). These are probably the decisive factors determining the high stability of the ring systems in the compounds (IX) and (X); at the same time, however, it is clear that the chlorine atoms in the figure are sterically in an almost ideal position to form a bridged ring with another $PdCl_2$ residue. The apparent non-existence of such a bridged compound must be regarded as strong evidence against the existence of stable unsymmetric compounds of type (I).

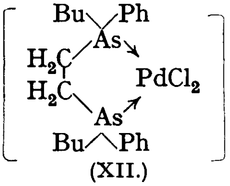


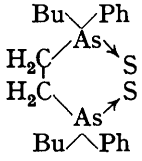


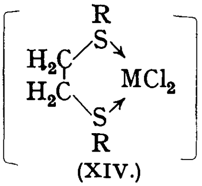
(XI.)

The possibility of any steric difficulty preventing the formation of such bridged compounds was also largely discounted by the fact that *bis(phenyldi-*n*-butylarsine)dichloropalladium*, $[(PhAsBu_2)_2PdCl_2]$, readily gave the bridged *derivative* $[(PhAsBu_2)PdCl_2]_2$, and *bis(triphenylphosphine)dichloropalladium*, $[(Ph_3P)_2PdCl_2]$, also gave the bridged *derivative* $[(Ph_3P)PdCl_2]_2$. These are the first bridged compounds to be described in which aryl groups are attached to the phosphorus or arsenic atoms: the bridging process is clearly, therefore, not inhibited by the size or nature of the groups attached to such atoms, provided such groups allow the formation of the stable symmetric forms (IIA and IIB) of the bridged product.

In case the failure to bridge the above chelated diarsine compounds was possibly due to the presence of the *o*-phenylene group, similar experiments were performed upon diarsines in which the arsenic atoms were linked by the $-CH_2{\cdot}CH_2-$ group (Chatt and Mann, *loc. cit.*). Ethylene-αβ-bis(diphenylarsine) readily gave *ethylene-αβ-bis(diphenylarsine)-dichloropalladium*, $[C_2H_4(AsPh_2)_2PdCl_2]$, but no bridged derivative of the latter could be obtained. Ethylene-αβ-bis(phenylbutylarsine) similarly gave *ethylene-αβ-bis(phenylbutylarsine)dichloropalladium* (XII). This yellow crystalline compound was isolated in two isomeric forms, α m. p. 172—174°, β m. p. 185—186°; mixed m. p. 137—150°. Since the compound contains two similar asymmetric 4-covalent arsenic atoms, one of these forms must be the *meso* and the other the externally compensated form, and they are therefore similar to the two forms of ethylenebis(phenylbutylarsine sulphide) (XIII) (Chatt and Mann, *loc. cit.*). They differ markedly from the bis-sulphide isomers, however, in that no interconversion could be detected: each form remained unchanged when kept for 1½ hours in a molten condition just above its m. p., and also when boiled in alcoholic solution for 2 hours. This greater stability probably arises from the fact that in the palladium compounds


(XII.)


(XIII.)


(XIV.)

the asymmetric arsenic atoms form part of the chelated ring and thus cannot readily undergo a change of configuration : in the sulphide compounds the arsenic atoms are not part of a ring system and change of configuration (*i.e.*, interconversion) occurs readily under the above conditions. It is noteworthy that this is the first example of such isomerism in co-ordinated metallic derivatives; Bennett, Mosses, and Statham (J., 1930, 1668) prepared several similar disulphide compounds of type (XIV) where M = Pd and Hg, but failed to detect the presence of both internally and externally compensated forms. Neither form of the diarsine compound (XII) would, however, give a bridged derivative when treated with ammonium palladochloride.

A similar ditertiary arsine containing only alkyl groups has now been synthesised by the interaction of ethylene dibromide, *n*-butyldichloroarsine and aqueous sodium hydroxide to give *ethylene-αβ-bis(butylarsonic acid)*, $C_2H_4\{AsBuO(OH)\}_2$. This on reduction with sulphur dioxide and hydrochloric acid gave *ethylene-αβ-bis(butylchloroarsine)*, $C_2H_4(AsBuCl)_2$, which by a Grignard reaction then gave *ethylene-αβ-bis(di-*n*-butylarsine)*, $C_2H_4(AsBu_2)_2$. The latter reacted readily with ammonium palladochloride to give *ethylene-αβ-bis(dibutylarsine)-dichloropalladium* (as XII), but this would not undergo further reaction with the palladochloride to give a bridged dipalladium derivative.

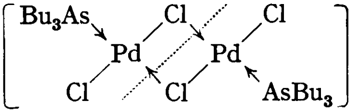
This repeated failure to isolate a compound which must necessarily have the unsymmetric bridged sturcture (I) raised doubt as to whether compounds possessing this structure are sufficiently stable to exist either in solution or in the solid state. We have therefore re-investigated in considerably greater detail the remainder of the reactions originally cited by Mann and Purdie (*loc. cit.*) as evidence for the unsymmetric form (I). In each case, however, these reactions prove to be less simple than originally appeared, and consequently we now consider that they do not afford evidence for the existence of the unsymmetric form in solution. These reactions can be summarised as follows :

(1) Mann and Purdie showed that when powdered dichlorobis(tri-*n*-butylarsine)-μ-dichlorodipalladium (XV) was freely treated with gaseous ammonia, a vigorous reaction ensued with production of heat, decomposition of the tetrachloro-compound, and evolution of free tributylarsine. When, however, the tetrachloro-compound (XV), either powdered or in cold benzene solution, was treated with a limited quantity of gaseous ammonia, two ionic compounds, diamminobis(tributylarsine)palladium dichloride (XVI) and tetramminopalladium dichloride (XVII), were formed (equation B) : these were both unstable and readily lost ammonia to give the non-ionic derivatives (XVIII) and (XIX), a process that could readily be reversed.

$$\begin{tikzcd}
\underset{\text{(XV.)}}{[(\mathrm{Bu_3As})_2\mathrm{PdCl_2PdCl_2}]} \arrow[r, "\mathrm{NH_3}"] & \underset{\text{(XVI.)}}{[(\mathrm{Bu_3As})_2\mathrm{Pd(NH_3)_2}]\mathrm{Cl_2}} \arrow[d, shift right] & + & \underset{\text{(XVII.)}}{[(\mathrm{NH_3})_4\mathrm{PdCl_2}]} \arrow[d, shift right] & \text{(B)} \\
 & \underset{\text{(XVIII.)}}{[(\mathrm{Bu_3As})_2\mathrm{PdCl_2}]} \arrow[u, shift right, "\mathrm{NH_3}"'] & & \underset{\text{(XIX.)}}{[(\mathrm{NH_3})_2\mathrm{PdCl_2}]} \arrow[u, shift right, "\mathrm{NH_3}"'] &
\end{tikzcd}$$

The ready formation of the compounds (XVI) and (XVIII) apparently showed that the bridged compound (XV) also had two arsine molecules joined to *one* palladium atom and hence had the unsymmetric structure (as I).

We now find that when the tetrachloro-compound (XV) in cold benzene or ethereal solution is treated quantitatively with only *two* molecules of ammonia in alcoholic solution, it acts in the symmetric form (XVB), undergoing fission as shown in equation C, with the sole formation of *dichloromonoamminotributylarsinepalladium* (XX). This compound is unstable, however; when its solution in organic solvents is kept at room temperature, ammonia is slowly lost and the original tetrachloro-compound is regenerated, and when the solution is boiled, the same reaction occurs more readily, but at the same time much of the dichloro-compound decomposes to form the compounds (XVIII) and (XIX) (equation D). Finally, when its cold solution is treated with excess of alcoholic ammonia, the colourless ionic compounds (XVI) and (XVII) are precipitated. It is clear, therefore, that the unstable dichloro-compound (XX) is the first product of the action of ammonia on the tetrachloro-compound, and that the latter is acting as the symmetric form (as IIA or IIB), in spite of the later formation of compounds such as (XVI) and (XVIII).



(XVB.)

$$\xrightarrow{2NH_3} 2[(Bu_3As)NH_3PdCl_2] \qquad (C)$$

(XX.)

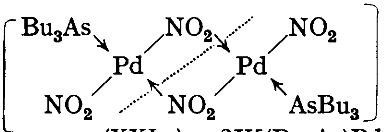
$$2[(Bu_3As)(NH_3)PdCl_2] = [(Bu_3As)_2PdCl_2] + [(NH_3)_2PdCl_2] \qquad (D)$$

(2) Mann and Purdie showed that the butylphosphinetetrachloro-compound, when treated with excess of aqueous potassium nitrite solution, gave the corresponding bridged tetranitro-compound (equation E); when the butylarsinetetrachloro-compound was used, however, the corresponding tetranitro-compound (XXI) was apparently so unstable that it immediately underwent " vertical splitting " with the production of dinitrobis(tributylarsine)-palladium (XXII) and potassium palladonitrite, these compounds being the sole products isolated. Here again the production of the compound (XXII) appeared to be strong evidence for the unsymmetric structure of the parent bridged tetrachloro-compound.

$$[(Bu_3P)_2PdCl_2PdCl_2] + 4KNO_2 = [(Bu_3P)_2Pd(NO_2)_2Pd(NO_2)_2] + 4KCl \qquad (E)$$

$$[(Bu_3As)_2PdCl_2PdCl_2] \xrightarrow{4KNO_2} \underset{\text{(XXI.)}}{[(Bu_3As)_2Pd(NO_2)_2 \vdots Pd(NO_2)_2]} \xrightarrow{2KNO_2} \underset{\text{(XXII.)}}{[(Bu_3As)_2Pd(NO_2)_2]} + K_2[Pd(NO_2)_4]$$

Now, if the bridged tetranitro-compound (XXI) had actually had the symmetric structure (XXIB), the first action of the excess of potassium nitrite would undoubtedly be to give a " diagonal splitting " (similar to that in equation C), with the production of the ionic potassium butylarsinetrinitropalladium (XXIII). Compounds of this type, having a univalent anion containing 4-covalent palladium or platinum, are so unstable that very few (if any) have ever been isolated : the compound (XXIII) would therefore almost certainly have broken down under the above conditions to give one molecule of $[(Bu_3As)_2Pd(NO_2)_2]$ and one of $K_2[Pd(NO_2)_4]$ (reaction F). This instability of the ionic compound (XXIII) has now been confirmed by its attempted preparation. When an aqueous solution of potassium palladonitrite was vigorously shaken with 1 mol. of free butylarsine, half the palladium separated as $[(Bu_3As)_2Pd(NO_2)_2]$ and half remained as unchanged $K_2[Pd(NO_2)_4]$. Hence the ionic monopotassium salt (XXIII) was either not formed, or, if formed, rapidly decomposed as shown in reaction (F). It follows that the dinitro-compound (XXII) and potassium palladonitrite would be the products of the interaction of potassium nitrite and the bridged tetranitrite (XXI), irrespective of whether the compound (XXI) (and hence the parent tetrachloro-compound) had the unsymmetric or the symmetric structure.



(XXIB.)

$$\xrightarrow{2KNO_2} \underset{\text{(XXIII.)}}{2K[(Bu_3As)Pd(NO_2)_3]} \longrightarrow [(Bu_3As)_2Pd(NO_2)_2] + K_2[Pd(NO_2)_4] \qquad (F)$$

The instability of compounds such as (XXIII) has already been demonstrated by Mann (J., 1930, 1746), who showed similarly that when potassium platinochloride was treated with 1 equiv. of methyl ethyl sulphide, the only products were $[(MeEtS)_2PtCl_2]$ and unchanged $K_2[PtCl_4]$, both apparently resulting from the decomposition of the $K[(MeEtS)PtCl_3]$ which would first be formed.

(3) The remaining reaction cited by Mann and Purdie in support of the unsymmetric structure is closely parallel to the preceding one. When the bridged butylarsine-tetrathiocyanate was treated with an excess of aqueous potassium thiocyanate, it also underwent an apparent " vertical splitting " :

$$[(Bu_3As)_2Pd(SCN)_2 \vdots Pd(SCN)_2] + 2KSCN = [(Bu_3As)_2Pd(SCN)_2] + K_2[Pd(SCN)_4] \quad (G)$$

Here again, however, if the bridged tetrathiocyanate had had the symmetric structure, it would have given a " diagonal splitting " similar to that shown in reaction (F) and with the production of the ionic $K[(Bu_3As)Pd(SCN)_3]$; the latter would have been unstable and would have decomposed with the formation of the same final products as those shown in equation (G) :

$$2K[(Bu_3As)Pd(SCN)_3] = 2[Bu_3As)_2Pd(SCN)_2] + K_2[Pd(SCN)_4]$$

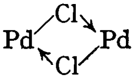
To confirm this, potassium palladothiocyanate in aqueous solution was vigorously shaken with 1 equiv. of tributylarsine. The ionic monopotassium derivative which must apparently be the first product of the reaction at once decomposed, forming the unbridged dithiocyanate and the original potassium palladothiocyanate :

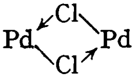
$$2K_2[Pd(SCN)_4] + 2Bu_3As \longrightarrow 2K[(Bu_3As)Pd(SCN)_3]$$
$$\longrightarrow 2[(Bu_3As)_2Pd(SCN)_2] + K_2[Pd(SCN)_4]$$

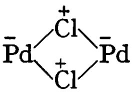
The decomposition of the monopotassium salt is not due to the comparative insolubility of $[(Bu_3As)_2Pd(SCN)_2]$ in water, for the experiment was repeated in alcohol and the same results obtained, although the two final products were both soluble in the original solution.

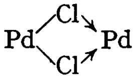
There would, therefore, appear to be very little evidence now for the existence of the unsymmetric form (I) in organic solvents, although possibly a minute quantity may exist in equilibrium with the two symmetric forms. The high value of the dipole moments of the bridged tetrachlorides and the dichloro-oxalate cited by Mann and Purdie (*loc. cit.*) must be due primarily to the presence of a tautomeric mixture of the *cis*- and the *trans*-symmetric forms alone. This tautomerism is to be expected in view of the facile interconversion of *cis*- and *trans*-forms known to occur in 4-covalent palladium compounds (Mann, Crowfoot, Gattiker, and Wooster, J., 1935, 1642).

It should be noted that there is one essential difference between the bridged ring system present in the symmetric forms (IIA and IIB) and that present in the unsymmetric form (I). The ring system in the forms (IIA and IIB) can be represented as (XXIV), or alternatively


(XXIV.)


(XXV.)


(XXVI.)


(XXVII.)

the covalent and co-ordinate links can be interchanged about the chlorine atoms as in (XXV), the unbridged groups being omitted for simplicity in each formulation. If, however, the co-ordinate link is represented as a charged covalent link as in (XXVI), it will be seen that the ring systems (XXIV) and (XXV) are essentially the same and there is no fundamental difference between the inter-atomic linkages. These considerations are in accordance with the experimental facts; for instance, Mann and Wells (this vol., p. 702) found that both the compounds $[(Me_3As)ClPdCl_2PdCl(Me_3As)]$ and $[(Me_3As)BrPdBr_2PdBr(Me_3As)]$ had the *trans*-symmetric structure, and that in each compound the halogen–palladium distance was constant around the ring. This equivalence of the linkages around the ring (XXVI) will clearly have the effect of stabilising the ring system considerably. In the ring system (XXVII) present in the unsymmetric form (I), however, the positions of the covalent and co-ordinate links are fixed and cannot be similarly interchanged; the ring-system as such is thus less symmetric and more unstable than that in (XXVI), and in addition the molecule will have a high dipole moment.

The results obtained in the study of these bridged di-palladium compounds now throw considerable light on the probable mechanism of their formation, which is usually carried out by treating, *e.g.*, the unbridged dichloride with ammonium palladochloride in boiling aqueous-alcoholic solution, the course of the overall reaction being indicated as

$$[(R_3P)_2PdCl_2] + (NH_4)_2[PdCl_4] = [(R_3P)_2Pd_2Cl_4] + 2NH_4Cl \qquad (H)$$

The ready progress of this reaction probably depends primarily on two factors : (i) the comparatively loose co-ordination of the phosphine or arsine molecules to the palladium atoms (as proved by the ready conversion of *cis* $\rightleftharpoons$ *trans*-isomerides); (ii) the consequent formation of an unstable salt which contains a univalent anion and decomposes under these conditions to give the bridged derivative. Thus, in general terms, if X is a univalent acid radical and M a univalent cation, the reaction proceeds first by the palladium atoms sharing the available phosphine or arsine molecules to form the unstable salt (XXVIII), which

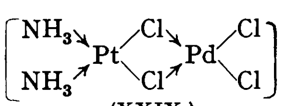
$$[(R_3P)_2PdX_2] + M_2[PdX_4] \rightleftharpoons \underset{\text{(XXVIII.)}}{2M[(R_3P)PdX_3]} \rightleftharpoons [(R_3P)_2Pd_2X_4] + 2MX \qquad (I)$$

then in the boiling solution decomposes to give the corresponding bridged dipalladium compound, which thus will have the symmetric structure. In the nitrite and thiocyanate reactions described under (2) and (3) respectively, it is clear that the general reaction (I) has been completely reversed, the bridged compound under the influence of a considerable excess of aqueous MX having reverted through the salt (XXVIII) to the original unbridged compound. This reversal can be effected even by ammonium salts : the yield of the bridged butylphospinetetrachloro-compound in reaction (H) is greatly reduced if the ammonium palladochloride solution is first diluted with ammonium chloride.

One compound is known, however, which may have the unsymmetric bridged structure. Chattaway and Drew (J., 1938, 198) have shown that *cis*(or β)-dichlorodiamminoplatinum $[(NH_3)_2PtCl_2]$ gives with potassium palladochloride a reaction which they formulate as

$$[Pt(NH_3)_2]Cl_2 + K_2[PdCl_4] \rightleftharpoons [Pt(NH_3)_2]PdCl_4 + 2KCl.$$

It is significant that the *trans*(or α)-compound does not give a similar reaction. Now the α- and the β-form of $[(NH_3)_2PtCl_2]$ differ from *cis*- and *trans*-forms of similar non-ionic palladous compounds in possessing considerable stability and in showing very little (if any) direct interconversion. Therefore, if the product of the above reaction is a bridged compound, it necessarily follows that only the *cis*-$[(NH_3)_2PtCl_2]$ could give such a compound, and that the latter must have the unsymmetrical structure (XXIX). The fact that several other *cis*-platinous compounds failed to give similar products does not invalidate the bridged structure (XXIX). Many bridged compounds containing two different metals (*e.g.*, mercury–cadmium, and mercury–palladium) have been prepared in these laboratories and will be described in a later communication; their formation, however, appears to be affected not only by the metals present but also very markedly by the groups linked to these metals. The elucidation of the structure of Chattaway and Drew's compound will be of great interest therefore.



(XXIX.)

EXPERIMENTAL.

To determine whether an unbridged palladium compound would form a bridged derivative, the former in alcoholic solution was boiled with an equimolecular quantity of ammonium palladochloride dissolved in a minimum of water. In these circumstances, if bridging occurred the reaction was rapid, and even after prolonged boiling only a trace of metallic palladium was deposited; if, however, bridging failed to occur, considerable reduction of the palladochloride and consequent deposition of palladium soon took place. When negative results were obtained, the unchanged palladium compound was always recovered. The bridging of suitable compounds will occur in acetone solution, but less readily than in alcohol; in acetone, however, very little reduction takes place even if bridging fails.

Experiments with Disulphides.—(1) Solutions of ethylenebis(ethylsulphide)dichloropalladium (VII; 1 g.) in a minimum of boiling alcohol and of ammonium palladochloride (0·86 g., 1 mol.) in water (10 c.c.) diluted with alcohol (10 c.c.) were mixed and boiled under reflux for 45 mins. Considerable reduction to palladium occurred, and the filtered solution on cooling deposited the unchanged dichloro-compound (VII), m. p. 180°.

(2) *n*-Octylthiol (5·6 g., 2 mols.) and ethylene dibromide (3·6 g., 1·7 c.c.; 1 mol.) were added in turn to the product obtained by the interaction of sodium (0·9 g.; 2 atoms) and hot alcohol (50 c.c.). The mixture was boiled under reflux for 2 hours, and filtered hot; the chilled filtrate deposited colourless waxy plates of *ethylenebis*(n-*octylsulphide*) which, when recrystallised from alcohol, had m. p. 29° (Found : S, 20·05. $C_{18}H_{38}S_2$ requires S, 20·1%).

Solutions of this disulphide (2 g.) in alcohol (100 c.c.) and of ammonium palladochloride (1·8 g.; 1 mol.) in water (20 c.c.) diluted with alcohol (40 c.c.) were mixed and vigorously shaken. The pale orange *ethylenebis*(n-*octylsulphide*)*dichloropalladium* (as VII) which separated was collected, washed with alcohol and water, and recrystallised from acetone; on being heated, the crystals darkened at *ca.* 270°, and melted with effervescence at *ca.* 280° (Found : Pd, 21·6. $C_{18}H_{38}Cl_2S_2Pd$ requires Pd, 21·3%). When this compound was boiled with ammonium palladochloride in aqueous alcohol, similar results to those with the ethyl analogue were obtained. Experiments in boiling acetone enabled more concentrated solutions to be used, but bridging did not occur.

Experiments with Diarsines.—(1) o-*Phenylenebis*(*dimethylarsine*) *derivatives.* Solutions of the arsine (2 g.; 2 mols.) in alcohol (10 c.c.) and of the palladochloride (1 g.) in water (10 c.c.) diluted with alcohol (20 c.c.) were mixed and boiled for 5 minutes. The clear yellow solution so obtained was then evaporated to dryness on a water-bath. The residue was very soluble in water and methyl and ethyl alcohols, but insoluble in nearly all other organic liquids. Recrystallised from water, it separated as a very pale yellow (almost colourless) hydrate; this, however, spontaneously lost water on exposure to the atmosphere for even 15 minutes and gave the anhydrous deep yellow *di*-o-*phenylenebis*(*dimethylarsine*)*palladium dichloride* (as X) (Found : C, 32·3; H, 4·4. $C_{20}H_{32}Cl_2As_4Pd$ requires C, 32·1; H, 4·3%).

Solutions of the diarsine (2 g.) and ammonium palladochloride (1 g.) in aqueous alcohol as before were boiled together to give a solution of the above ionic dichloride (as X), and a mixture of concentrated hydrochloric acid (12 c.c.) and alcohol (80 c.c.), and then more ammonium palladochloride (1 g.), were added in turn. *Di*-o-*phenylenebis*(*dimethylarsine*)*palladium palladochloride*, $[(C_6H_4As_2Me_4)_2Pd][PdCl_4]$, was immediately precipitated as minute, deep red crystals; more hydrochloric acid (6 c.c.) in alcohol (20 c.c.) was added to convert these insoluble crystals into the dichloro-compound (IX) and the boiling was continued for 1 hour. Most of the red crystals were still unchanged, however, so the solution was filtered hot; the residue of the red palladochloride was washed and dried (Found : C, 26·05; H, 3·7. $C_{20}H_{32}Cl_4As_4Pd_2$ requires C, 25·9; H, 3·5%). The solution on cooling deposited o-*phenylenebis*(*dimethylarsine*)*dichloropalladium* (IX) as greenish-yellow crystals, which were recrystallised rapidly from dilute methyl alcohol (1 : 1 by vol.) (charcoal); the crystals were unaffected by heating to 300° (Found : C, 25·7; H, 3·5. $C_{10}H_{16}Cl_2As_2Pd$ requires C, 25·9; H, 3·5%). Further supplies of this compound were obtained by boiling the red palladochloride again with alcoholic hydrochloric acid, but the yield was low.

When mixed aqueous-alcoholic solutions of the dichloro-compound (IX) and ammonium palladochloride were boiled, rapid reduction of the latter to metallic palladium occurred. In order to avoid this, and to work in more concentrated solution, solutions of the dichloro-compound (0·5 g.) in acetone (120 c.c.) and water (30 c.c.) and of the palladochloride (0·33 g.; 1 mol.) in acetone (30 c.c.) and water (30 c.c.) were mixed and boiled under reflux for 2 hours. No reduction occurred, and on cooling, the unchanged dichloro-compound (0·25 g.) separated.

(2) o-*Phenylenebis*(*di*-n-*butylarsine*) *derivatives.* The metallic derivatives of this diarsine were more readily prepared and more soluble in organic solvents than those of the previous diarsine; they were therefore examined in considerable detail.

The direct action of the diarsine on ammonium palladochloride always gave the ionic dichloride (X). For instance, a solution of the diarsine (2 g.) in alcohol (15 c.c.) was slowly added with vigorous shaking to one of ammonium palladochloride (1·4 g.; 1 mol.) in water (20 c.c.). After 5 mins.' shaking, water (50 c.c.) was added and the agitation continued for 30 mins. The precipitate was then collected, and washed with a very small quantity of alcohol and water. This pale yellow solid was freely soluble in warm methyl and ethyl alcohol but insoluble in benzene, *cyclo*hexane, and ethyl carbonate. It was recrystallised from benzene containing 10% of alcohol, colourless crystals of the *tetrahydrate* of *di*-o-*phenylenebis*(*dibutylarsine*)*palladium* *dichloride* (X) being obtained (Found: C, 45·0; H, 7·7; H_2O, 6·15. $C_{44}H_{80}Cl_2As_4Pd,4H_2O$ requires C, 45·6; H, 7·7; $4H_2O$, 6·2%). This hydrate when exposed to sulphuric acid in a vacuum for several days gave the deep yellow anhydrous compound, but the latter on exposure to the air for even 1—2 minutes reverted to the colourless hydrate; hence the latter is always obtained when the material is recrystallised and collected on a filter. This intense avidity for water is in marked contrast to the readiness with which the hydrated methyl analogue loses water on exposure to air.

o-*Phenylenebis*(*di*-n-*butylarsine*)*dichloropalladium* (as IX) was made by the united action of hydrochloric acid and of ammonium palladochloride on the previous compound. A solution of the palladochloride (1·3 g.) in water (12 c.c.) and alcohol (24 c.c.) was divided into two equal portions. A solution of the diarsine (2 g.) in alcohol (6 c.c.) was added to one portion, and the mixture boiled to give a solution of the ionic dichloride (X). Concentrated hydrochloric acid (2 c.c.) and the second portion of the palladochloride solution were added in turn, giving an immediate reddish-brown precipitate of the complex palladochloride $[\{C_6H_4(AsBu_2)_2\}_2Pd][PdCl_4]$. More hydrochloric acid (10 c.c.) and alcohol (80 c.c.) were added, and the boiling continued; the colour of the solution rapidly faded as the brown palladochloride was completely converted into the required dichloro-compound, which separated as yellow crystals when the solution was filtered and cooled; these crystals, when recrystallised from alcohol, had m. p. 273—275° (Found: C, 41·7; H, 6·1. $C_{22}H_{40}Cl_2As_2Pd$ requires C, 41·8; H, 6·4%). This compound is very soluble in chloroform, slightly soluble in hot alcohol and acetone, and insoluble in benzene.

The complete conversion of the insoluble palladochloride into the dichloro-compound under the influence of hydrochloric acid is in marked contrast to the behaviour of the analogous methyl derivative, which even after prolonged heating in these conditions gave only slight conversion to the dichlorodiarsinepalladium.

When solutions of *o*-phenylenebis(dibutylarsine)dichloropalladium (1 g.) in boiling alcohol (200 c.c.) and ammonium palladochloride (0·5 g.) in water (6 c.c.) and alcohol (12 c.c.) were mixed and boiled, reduction and precipitation of palladium occurred within 2—3 mins. After 10 mins., the solution was mixed with animal charcoal to withhold the palladium, and then filtered; unchanged dichloro-compound (0·8 g.) separated on cooling. Similar experiments were carried out in boiling dilute acetone; after 1 hour's boiling no reduction had occurred, but the solution, when filtered and cooled, gave the unchanged dichloro-compound.

For comparison with this diarsine, *phenyldi*-n-*butylarsine* was prepared by the interaction of phenyldichloroarsine (20 g., 12 c.c.) in ether (70 c.c.) and a Grignard reagent prepared from magnesium (6·5 g.; 3 atoms) under ether (70 c.c.) and *n*-butyl bromide (36·8 g., 29 c.c.; 3 mols.) in ether (70 c.c.). The product was hydrolysed in the usual way with ammonium chloride (36 g.) dissolved in water (200 c.c.), and the arsine obtained as a colourless liquid, b. p. 158—161°/21 mm. (Found: C, 63·3; H, 8·6. $C_{14}H_{23}As$ requires C, 63·1; H, 8·7%). Yield 14·5 g.

When solutions of the arsine (5 g., 2 mols.) in alcohol (20 c.c.) and of ammonium palladochloride (2·7 g.) in water (50 c.c.) were vigorously shaken, a red oil separated, and ultimately solidified when water (50 c.c.) was added and ice-cooling applied. This crude solid was recrystallised from alcohol, strong cooling affording orange crystals of *bis*(*phenyldi*-n-*butylarsine*)*dichloropalladium*, m. p. 47° (Found: Cl, 9·8. $C_{28}H_{46}Cl_2As_2Pd$ requires Cl, 10·0%).

When the solutions of the last compound (2 g.) in alcohol (50 c.c.) and of ammonium palladochloride (0·95 g.; 1 mol.) in water (7 c.c.) and alcohol (14 c.c.) were mixed and boiled, bridging rapidly occurred, and after 10 mins.' boiling the solution, when filtered and cooled, deposited bright red crystals of *dichlorobis*(*phenyldi*-n-*butylarsine*)-*μ*-*dichlorodipalladium*; these, when twice recrystallised from alcohol, had m. p. 166° (Found: C, 37·8; H, 5·0. $C_{28}H_{46}Cl_4As_2Pd_2$ requires C, 37·8 ; H, 5·3%). The same compound was also obtained in a series of experiments in which aqueous alcohol and aqueous acetone were used in turn as solvents with 1 hour's boiling, and in which the concentration of ammonium palladochloride was approximately the same as in the experiments with the diarsines. It is clear, therefore, that the physical conditions used in the diarsine experiments were suitable for successful bridging, and that the failure was due solely to the nature of the compounds employed.

To show that aromatic groups do not inhibit bridging, solutions of triphenylphosphine (1 g.) in hot alcohol (10 c.c.) and of ammonium palladochloride (0·55 g.) in hot water (5 c.c.) and alcohol (10 c.c.) were mixed and shaken. A yellow solid was immediately precipitated. Water (50 c.c.) was added, and after further shaking, the *bis*(*triphenylphosphine*)*dichloropalladium* was collected, dried, and recrystallised from toluene, from which it separated in bright yellow crystals, which when rapidly heated decomposed at *ca.* 250—270° (Found: Pd, 15·1. $C_{36}H_{30}Cl_2P_2Pd$ requires Pd, 15·2%). The solubility of this compound in various solvents is much lower than that of similar compounds having alkyl groups : it is almost insoluble in hot alcohol and acetone.

Bridging occurred readily with this compound, although its low solubility made manipulation difficult. For instance, solutions of the dichloro-compound (0·5 g.) in a boiling mixture of chloroform (100 c.c.) and alcohol (150 c.c.) and of ammonium palladochloride (0·4 g.) in water (40 c.c.) and alcohol (50 c.c.) were mixed and boiled under reflux for 1 hour, during which fine deep red crystals were deposited. These were collected, and a second crop obtained by spontaneous evaporation of the filtrate. These crystals of *dichlorobis(triphenylphosphine)-μ-dichlorodipalladium* were insoluble in all solvents tried; they were therefore washed with hot chloroform, alcohol, and water, but a trace of metallic palladium could not be eliminated (Found : Pd, 25·1. $C_{36}H_{30}Cl_4P_2Pd_2$ requires Pd, 24·2%). On strong heating, the crystals slowly decomposed.

(3) *Ethylene-αβ-bis(diphenylarsine).* When solutions of this diarsine (2 g.) and ammonium palladochloride (1·2 g.; 1 mol.) in aqueous alcohol were boiled as before, a yellow solid rapidly separated; after 1—2 mins.' boiling, this was collected, washed, dried, and recrystallised from ethylene dibromide. *Ethylene-αβ-bis(diphenylarsine)dichloropalladium* was obtained as yellow crystals, which on heating melted with decomposition at a high temperature (Found : C, 46·7; H, 3·7. $C_{26}H_{24}Cl_2As_2Pd$ requires C, 47·0; H, 3·65%); it is sparingly soluble in alcohol and acetone, freely soluble in chloroform.

When solutions of this compound in alcoholic chloroform and of ammonium palladochloride in aqueous alcohol were boiled, reduction to palladium rapidly occurred, and the filtered solution on cooling gave the unchanged dichloro-compound. Similar attempts to form the bridged compound in acetone also failed.

(4) *Ethylene-αβ-bis(phenylbutylarsine).* When this diarsine was treated directly with an aqueous solution of ammonium palladochloride, a dark, sticky, impure product was obtained. A cleaner product, consisting of the α- and the β-form of the dichloropalladium compound, was obtained when *cyclo*hexane solutions of the diarsine were used. A mixture of *cyclo*hexane (75 c.c.) and a solution of ammonium palladochloride (8·7 g.) in water (400 c.c.) was vigorously shaken whilst a solution of the diarsine (13·6 g.) in *cyclo*hexane (75 c.c.) was slowly added. The greenish-yellow sticky solid which separated during 1 hour's shaking was collected, washed with water, and dried; a small sample obtained crystalline by cooling its alcoholic solution for 2—3 days was used to seed the main portion, which was then recrystallised from alcohol (charcoal). A mixture, m. p. 135—145°, of the α- and the β-form of *ethylene-αβ-bis(phenylbutylarsine)dichloropalladium* was thus obtained as pale yellow crystals (Found : C, 42·7; H, 5·25; *M*, ebullioscopic in 2·59% acetone, 600; in 4·05% acetone, 621. $C_{22}H_{32}Cl_2As_2Pd$ requires C, 42·3; H, 5·2%; *M*, 624). The alcoholic mother-liquor contained a very soluble by-product, probably $[(C_2H_4As_2Bu_2Ph_2)_2Pd]Cl_2$; this was obtained solid by evaporation, but subsequently gave a sticky product from all those solvents in which it was only moderately soluble.

The separation of the two forms proved very tedious and could be performed satisfactorily only by using small quantities at each operation. A solution of the above mixed α- and β-forms (0·5 g.) in hot alcohol (30 c.c.) was cooled to 25° and kept at this temperature with scratching until no further crystallisation occurred. The mixture was filtered, the filtrate transferred to a dust-free flask, warmed until any crystals which had subsequently appeared were just dissolved, and then set aside until crystallisation at room temperature was complete. Two types of crystals were deposited; these were collected and separated by hand. Type I, m. p. *ca.* 155—165°, rectangular crystals, consisted of crude α-form; type II, m. p. *ca.* 134—140°, consisted of stellate groups each having a nucleus of the α-form with radiating needles of the β-form. These needles were broken off mechanically, and had m. p. *ca.* 160—170°; mixed m. p. with type I crystals, 134—140°.

By repetitions of this process, 0·5 g. of type I crystals was finally obtained, and after four recrystallisations from alcohol gave the pure α-form, m. p. 172—174° (Found : Pd, 17·1; *M*, ebullioscopic in 1·23% acetone solution, 591; in 2·88% solution, 618. $C_{22}H_{22}Cl_2As_2Pd$ requires Pd, 17·1%; *M*, 624).

The crystals which had separated as the original alcoholic solution cooled to 25° were ultimately found to be the best source of the pure β-form, since this crop, although small, contained a higher proportion of the β-form than did the larger crop which separated below 25°. This small crop was therefore dissolved in alcohol to give a saturated solution at 25° and set aside as before for spontaneous crystallisation at room temperature. Crystals of type II, having however only a very small nucleus of the α-form, slowly separated, and on repeated recrystallisation ultimately gave the pure β-*form*, m. p. 185—186° (Found : Pd, 17·25%; *M*, ebullioscopic in 1·18% acetone solution, 647; in 2·22% solution, 636). A mixture of approximately equal quantities of the two pure forms melted at 137—150°. It should be emphasised that the difference in solubility of the two forms in alcohol is so small, and crystallisation of each form is initiated so readily by chance nuclei, that the isolation of the two forms by fractional crystallisation is not practicable unless in addition a considerable separation is made by hand : even so, the process is exceedingly tedious.

It is remarkable that no interconversion of the two forms was observed on heating in the molten condition just above their m. p.'s, or on prolonged boiling in alcoholic solution. For instance, the pure α-form was heated at 180° for $1\frac{1}{2}$ hours, and the molten material then allowed to cool and solidify; it melted almost unchanged at 170—173°. Also, a solution of the α-form (0·088 g.) in alcohol (9 c.c.) was boiled under reflux for 2 hours, and on cooling deposited the pure α-crystals, m. p. 172—174°. Similarly, the pure β-form, maintained molten at 189° for $1\frac{1}{2}$ hours, when allowed to cool and solidify, melted at 181—183°; an alcoholic solution, boiled for 2 hours, on cooling deposited the unchanged β-form, m. p. 185—186°.

All attempts to prepare bridged compounds from these forms failed.

(5) *Ethylene-*αβ*-bis(di-*n*-butylarsine).* *n*-Butyldichloroarsine (100 g.; 2 mols.), prepared by the method of Quick and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 805), and a solution of sodium hydroxide (79 g.; 8 mols.) in water (190 c.c.) were boiled under reflux with stirring until marked foaming ceased; the mixture was allowed to cool slightly, ethylene dibromide (46·3 g.; 1 mol.) added, and the boiling continued for 3 hours. More dibromide (20 g.) was added, and after 3 hours' further boiling the solution was cooled, a foul-smelling, oily by-product extracted with ether, and the aqueous layer made just acid to Congo-red with concentrated hydrochloric acid. The white precipitate (14 g.) was collected, washed with water, twice recrystallised from aqueous alcohol (1 : 1 by vol.) and finally from water; *ethylene-*αβ*-bis(arsonic acid)* was thus obtained as colourless crystals, m. p. 201—202° (decomp.), almost insoluble in cold water or alcohol (Found : C, 33·3; H, 6·6. $C_{10}H_{24}O_4As_2$ requires C, 33·5; H, 6·8%).

Solutions of the crude bis(arsonic acid) (26 g.) in dilute hydrochloric acid (50 c.c., 1 : 1 by vol.) and of potassium iodide (0·75 g.) in water (5 c.c.) were mixed, and sulphur dioxide passed in for 3 hours. The oily chloro-arsine was extracted with chloroform and dried (sodium sulphate), the chloroform removed by distillation, and the residue fractionally distilled at greatly reduced pressure. *Ethylene-*αβ*-bis(butylchloroarsine)* was thus obtained as an odourless, pale yellow liquid, b. p. 160—165°/0·05 mm. (Found : C, 33·0; H, 6·3. $C_{10}H_{22}Cl_2As_2$ requires C, 33·05; H, 6·1%).

The ditertiary arsine was prepared by the interaction in a hydrogen atmosphere of the chloro-arsine (12·5 g.) in benzene (50 c.c.) and a Grignard reagent prepared from magnesium (3 g.; 3·5 atoms) and *n*-butyl bromide (16·5 g.; 3·6 mols.) in ether (60 c.c.), the mixture throughout being vigorously stirred with ice-cooling. The solution was then boiled under reflux for 30 mins., strongly cooled, and hydrolysed with a solution of ammonium chloride (26 g.) in water (150 c.c.), the current of hydrogen being maintained throughout. The ethereal layer was separated and dried, the ether removed, and the residue fractionally distilled under reduced pressure. *Ethylene-*αβ*-bis(dibutylarsine)* was thus obtained as a colourless liquid, b. p. 161—162°/0·04 mm., very readily oxidised on exposure to air (Found : C, 53·65; H, 9·85. $C_{18}H_{40}As_2$ requires C, 53·2; H, 9·9%).

When a solution of the diarsine (2·8 g.) in alcohol (20 c.c.) was slowly added with shaking to one of ammonium palladochloride (2·0 g.; 1 mol.) in water (20 c.c.) and alcohol (40 c.c.), a fine reddish precipitate, presumably of $[(C_2H_4As_2Bu_4)_2Pd][PdCl_4]$, first separated but rapidly redissolved, and ultimately the yellow *ethylene-*αβ*-bis(dibutylarsine)dichloropalladium* (as XII) separated. After 2 hours, this was collected, thrice recrystallised from alcohol, and obtained as yellow crystals, m. p. 221° (without decomp.) (2 g.) (Found : Pd, 18·4; *M*, ebullioscopic in 0·997% acetone solution, 634; in 4·04%, 625; cryoscopic in 0·818% bromoform solution, 1997. $C_{18}H_{40}Cl_2As_2Pd$ requires Pd, 18·3%; *M*, 584. The high association in bromoform is noteworthy). This compound differs from all the previous similar palladium derivatives of ditertiary arsines, except that of $C_2H_4(AsPhBu)_2$, in its high solubility in hot alcohol, in which it resembles the corresponding derivatives of the simple trialkylarsines; it differs from the latter, however, in its pale yellow colour (compared with the deep orange of the trialkyl derivatives) and its very low solubility in benzene.

When solutions of this palladium compound (1 g.) in alcohol (30 c.c.) and of ammonium palladochloride (0·5 g.; 1 mol.) in water (5 c.c.) were mixed and boiled under reflux for 30 mins., much metallic palladium was deposited. The solution was mixed with charcoal and filtered, and the filtrate on cooling deposited the unchanged diarsine compound (0·97 g.), m. p. after recrystallisation, 220—221°, mixed m. p. 220—221°. A similar experiment in hot acetone solution gave no reduction to palladium, but the results were otherwise identical. No indication of a bridged compound could be detected in either experiment.

Action of Ammonia on Dichlorobis(tributylarsine)-μ-dichlorodipalladium (XVB).—An alcoholic solution of ammonia (1·57 g./l.) was prepared. The dry powdered tetrachloro-compound (XVB; 3·8 g.) was shaken with insufficient ether (40 c.c.) to dissolve it, and to the saturated solution and solid, alcoholic ammonia (100 c.c. containing 0·157 g. = 2·05 mols.) was slowly added with shaking; the suspended tetrachloro-compound rapidly dissolved, and the colour of the solution changed from red to orange. The greater part of the solvent was then allowed to evaporate spontaneously, and the orange compound which separated was collected, washed with water, dried, and then very rapidly recrystallised from *cyclo*hexane (charcoal). *Dichloromonoamminotributylarsinepalladium* (XX) separated as orange crystals, m. p. 73—74° (decomp.) (Found: N, 3·0; Pd, 23·7; *M*, cryoscopic in 1·11% ethylene dibromide solution, 460; in 1·89% solution, 468. $C_{12}H_{30}NCl_2AsPd$ requires N, 3·2; Pd, 24·2%; *M*, 441). The same reaction occurs in benzene solution, but the more rapid evaporation of the ethereal alcohol is advantageous in view of the unstable nature of the product.

When orange solutions of (XX) in cold *cyclo*hexane were exposed to the air for 2—3 days, the colour slowly deepened to red, and ultimately the original tetrachloro-compound (XVB) was deposited. When a solution of (XX; 0·5 g.) in *cyclo*hexane (10 c.c.) was boiled under reflux, it immediately became cloudy owing to deposition of $[(NH_3)_2PdCl_2]$ and slowly lost ammonia; after 12 hours the yellow $[(NH_3)_2PdCl_2]$ was collected, and when washed with hot *cyclo*hexane and dried, was pure (Found: N, 13·2. Calc. for $H_6N_2Cl_2Pd$: N, 13·2%). The original filtrate on cooling deposited red crystals of the tetrachloro-compound (XVB), which were collected and recrystallised; m. p. 128—129°, alone and when mixed with an authentic sample. The original filtrate was finally evaporated to dryness, and the orange residue of $[(Bu_3As)_2PdCl_2]$ after recrystallisation from alcohol had m. p. 52—53°, alone and mixed.

When a *cyclo*hexane or benzene solution of (XX) was treated with an excess of alcoholic ammonia, the colour faded to a very pale yellow, and a white mixture of $[(Bu_3As)_2Pd(NH_3)_2]Cl_2$ and $[(NH_3)_4Pd]Cl_2$ was deposited.

Interaction of Tributylarsine and Potassium Palladonitrite.—Solutions of potassium palladonitrite (1·05 g.) in water (40 c.c.) and of tributylarsine (0·7 g.; 1 mol.) in alcohol (7 c.c.) were vigorously shaken together, an immediate evolution of heat and deposition of $[(Bu_3As)_2Pd(NO_2)_2]$ occurring. After 1 hour's shaking, the product was collected, washed with water, and dried. Yield, 0·95 g. (calc.: 0·98 g.). The dinitrite, recrystallised from alcohol, had m. p. 97—98°, unchanged by admixture with an authentic sample.

Interaction of Tributylarsine and Potassium Palladothiocyanate.—Solutions of $K_2[Pd(SCN)_4]$ (1·2 g.) in water (30 c.c.) and of tributylarsine (0·7 g.) in alcohol (7 c.c.) were similarly mixed and shaken. After 1 hour, the product was collected, washed with water, and dried: yield, 1·05 g. This product, m. p. 66—73°, consisted of $[(Bu_3As)_2Pd(SCN)_2]$ containing a small quantity of the tetrathiocyanate, $[(Bu_3As)_2Pd_2(SCN)_4]$. Fractional crystallisation from alcohol gave first the latter compound, m. p. 112—113° (0·08 g.), and finally the unbridged dithiocyanate, m. p. 74—75°, alone or mixed with an authentic sample. The intermediate product $K[(Bu_3As)Pd(SCN)_3]$ had thus decomposed in both the directions shown in equation I, but mainly to give the unbridged derivative.

The experiment was repeated under the following conditions in order to retain all the reactants in solution. Chilled solutions of $K_2[Pd(SCN)_4]$ (2·8 g.) in water (2·5 c.c.) and alcohol (50 c.c.) and of tributylarsine (1·65 g., 1 mol.) in alcohol (16 c.c.) were slowly mixed with shaking; the colour faded considerably but no precipitation occurred. The solution was allowed to evaporate spontaneously and finally taken to dryness in a desiccator. White crusts of potassium thiocyanate and red needles of $K_2[Pd(SCN)_4]$ were extracted with water, and the dried residue weighed 2·35 g. (theoretical for $[(Bu_3As)_2Pd(SCN)_2]$, 2·4 g.). This residue, as before, consisted of the unbridged dithiocyanate with a trace of the tetrathiocyanate.

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THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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