

**229. The Constitution of Complex Metallic Salts. Part XII.  
Bridged Compounds containing Two Different Metallic Atoms.**

By FREDERICK G. MANN and DONALD PURDIE.

The bridged cadmium mercury compound  $[(Pr_3^aP)_2CdHgI_4]$ , in which each metallic complex has the tetrahedral configuration, can readily be prepared by the interaction of (a)  $[(Pr_3P)_2CdI_2]$  and mercuric iodide, (b)  $[(Pr_3P)_2(CdI_2)_2]$  and  $[(Pr_3P)_2(HgI_2)]$ . The second method of preparation indicates that the parent bridged dicadmium and dimercury compounds must exist in solution partly as the free radicals  $Pr_3P \rightarrow CdI_2$  and  $Pr_3P \rightarrow HgI_2$  respectively. Bridged cadmium mercury compounds having mixed halogen and mixed phosphine arsine residues, such as  $[(Pr_3P)_2CdHgBr_2I_2]$  and  $[(Pr_3P)(Pr_3As)CdHgI_4]$ , have also been isolated. The bridged palladium mercury compound  $[(Pr_3As)_2PdHgBr_4]$ , containing a uniplanar and a tetrahedral metallic complex, has been prepared. The properties of these compounds are discussed.

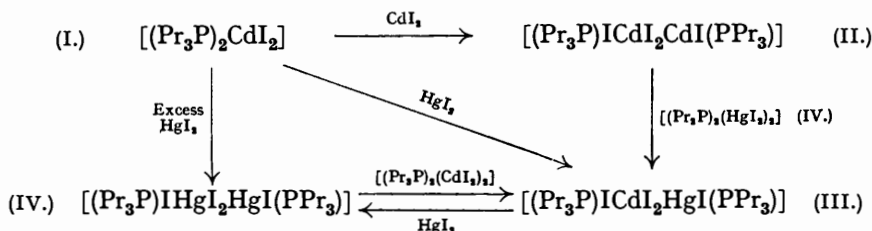
In the preceding paper it was shown that tertiary phosphines and arsines react readily with cadmium and mercuric halides to give "bridged" derivatives containing two metallic atoms per molecule, and that when, *e.g.*, di-iodobis(tri-*n*-propylphosphine)cadmium (I) is boiled in alcoholic solution with 1 mol. of cadmium iodide, the bridged di-iodobis(tri-propylphosphine)- $\mu$ -di-iododicadmium (II) is readily formed. In both these compounds each 4-covalent cadmium complex has the tetrahedral configuration, and moreover, the compound (II) possesses a centre of symmetry since it has the *trans*-symmetric\* structure. It was of interest therefore to investigate whether similar bridged compounds could be prepared having two different metallic atoms in the molecule. It has been found that in certain cases such compounds can be readily obtained. For instance, when the unbridged cadmium compound (I) is similarly treated with 1 mol. of mercuric iodide, the highly crystalline di-iodobis(tri-propylphosphine)- $\mu$ -di-iodocadmium-mercury (III) is readily formed. The same compound can also be prepared by boiling the bridged dicadmium compound (II) with 1 equiv. of di-iodobis(tri-propylphosphine)- $\mu$ -di-iododimercury (IV); in these circumstances there is an exchange of metallic atoms, with the sole formation of the cadmium mercury compound (III). Since the *trans*-symmetric structures of both the compounds (II) and (IV) are known beyond reasonable doubt, their interaction to give (III) indicates that they must dissociate to a certain extent in hot alcoholic solution

to give the free radicals  $\begin{array}{c} Pr_3P \\ \diagdown \\ Cd \\ \diagup \\ I \end{array}$  and  $\begin{array}{c} Pr_3P \\ \diagdown \\ Hg \\ \diagup \\ I \end{array}$  respectively; as the mixed solution

cools, these unlike radicals unite in pairs to give the cadmium mercury derivative (III), since the last is less soluble than either of the parent compounds (II) and (IV). Given this solubility factor, the formation of the compound (III) is not unexpected, in view of the close chemical relations between the two metals and the fact that the 4-covalent compounds of both metals have the tetrahedral configuration. The term "free radical" can be correctly applied to both the above groups, since in each group the metallic atom has two electrons less than in its normal 4-covalent complexes, and the groups show therefore some of the normal properties of free radicals, *e.g.*, ready reassociation in pairs.

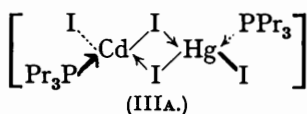
\* The term "*trans*-symmetric" is used here (as in previous papers) to indicate the relative positions of the unbridged phosphine (or arsine) residues and the unbridged halogen atoms (*cf.* Chatt and Mann, *J.*, 1939, 1622).

It is noteworthy, however, that when the unbridged cadmium compound (I) is boiled in alcoholic solution with an excess of mercuric iodide, bridging occurs but

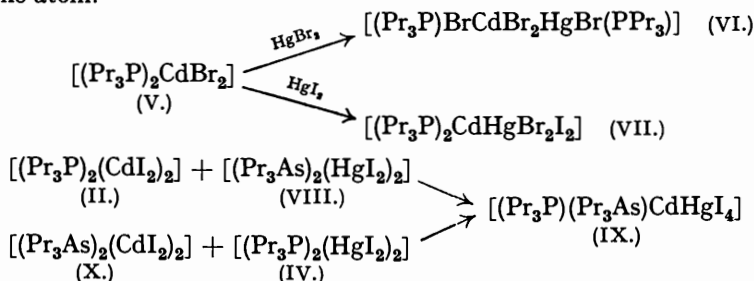


the cadmium is entirely replaced by mercury, with the formation of di-iodobis(tri-propylphosphine)- $\mu$ -di-iododimercury (IV); the latter compound is also formed when the bridged cadmium mercury compound (III) is similarly treated with an excess of mercuric iodide. The formation of the dimercury compound (IV) in these circumstances, although favoured by the excess of mercury iodide, is probably due primarily to the greater co-ordinating power of the mercuric atom compared with that of the cadmium atom.

It is highly probable that the cadmium mercury compound (III) has the *trans*-symmetric structure (III A)\* similar to that of all bridged 4-covalent compounds whose structure has been determined by X-ray analysis. Crystallographic analysis of the compound (III) has not been carried out owing to inherent difficulties: it should be noted that in any case the centre of symmetry present in all previous bridged compounds is now destroyed in (III A) by the presence of the mixed metals.



It has also been possible to prepare bridged cadmium mercury compounds containing two different halogens and also containing both a co-ordinated phosphine and a co-ordinated arsine residue. Thus when dibromobis(tri-propylphosphine)cadmium (V) was boiled in alcoholic solution with 1 mol. of mercuric bromide, the *dibromobis(tri-propylphosphine)- $\mu$ -dibromocadmium-mercury* (VI) was formed; when, however, 1 equiv. of mercuric iodide was used, the *dibromodi-iodocadmium-mercury* compound (VII) was formed. It is impossible to assign a systematic name or a structure to this compound, as it is not known whether the bridging halogen atoms are both bromine or both iodine atoms; it is unlikely for reasons of stability and symmetry that they consist of one bromine and one iodine atom.

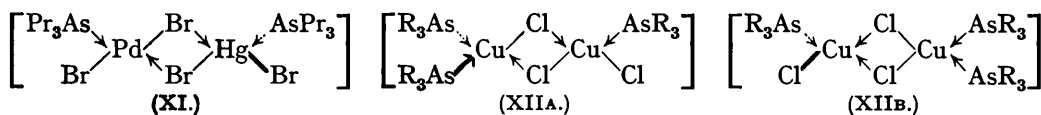


To prepare a bridged compound having both a phosphine and an arsine residue, equimolecular quantities of di-iodobis(propylphosphine)- $\mu$ -di-iododicadmium (II) and di-iodobis(propylarsine)- $\mu$ -di-iododimercury (VIII) were boiled in alcoholic solution; the *di-iodo(propylphosphine)(propylarsine)- $\mu$ -di-iodocadmium-mercury* (IX) was readily obtained. The same compound (IX) was similarly prepared by the interaction of bridged propylarsinecadmium iodide (X) and the bridged propylphosphinemercury iodide (IV). Here again, it is impossible to give a precise structure to the compound (IX), as it is not known which metallic atom is co-ordinated to the phosphine residue and which to the arsine residue.

\* In these structural formulæ, bonds in normal type are in the plane of the paper, whilst those in heavy type project above, and those in dotted type project below, this plane.

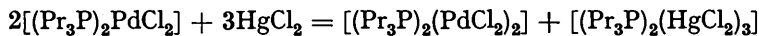
In view of the ease with which the bis(phosphine)cadmium-mercury compound (III) and the phosphine-arsine compound (IX) were prepared, it is noteworthy that all attempts to prepare a bis(arsine)cadmium-mercury compound,  $[(\text{Pr}_3\text{As})\text{ICdI}_2\text{HgI}(\text{Pr}_3\text{As})]$ , failed. This failure is the more remarkable because the potential parent compounds  $[(\text{Pr}_3\text{As})_2(\text{CdI}_2)_2]$  and  $[(\text{Pr}_3\text{As})_2(\text{HgI}_2)_2]$  are isomorphous. It is possible, however, that the required compound is in this case *more* soluble than one or both of the parent compounds and hence would not be formed from the free radicals to which they give rise in solution.

Attempts have also been made to prepare a bridged compound containing two different metals, one of which should have a planar, and the other a tetrahedral, distribution of its valencies. For this purpose palladium and mercury compounds were investigated, as previous work in this series has shown that their bridged derivatives are readily formed and have in both cases the *trans*-symmetric structure in the crystalline state, and that moreover the 4-covalent palladium complex is planar and the mercuric complex is tetrahedral. A compound of the required type was finally obtained by boiling equivalent quantities of dibromobis(tri-*n*-propylarsine)palladium and mercury bromide in alcoholic solution, whereby orange crystals of *dibromobis(tripropylarsine)-μ-dibromopalladium-mercury* (XI) were obtained. This compound is stable in the solid state and can be readily recrystallised from alcohol. Cryoscopic molecular-weight determinations showed considerable dissociation in both benzene and ethylene dibromide; the compound slowly decomposes in benzene, but can be recovered unchanged from the ethylene dibromide solution. If in this compound the arsine residues are (as usual) linked to different metallic atoms (XI), it will follow that the palladium and mercury atoms, the bridged bromine atoms, and the unbridged bromine and arsenic atoms linked to the palladium are all in the plane of the paper, whilst the unbridged bromine and arsenic atoms linked to the mercury atoms must be respectively above and below this plane. The compound thus possesses molecular



dissymmetry. The general type of molecule (as distinct from the nature and linkage of the constituent groups) is similar to that of the two isomeric compounds of formula  $[(\text{PhMe}_2\text{As})_3\text{Cu}_2\text{Cl}_3]$  isolated by Mellor, Burrows, and Morris (*Nature*, 1938, **141**, 414), in which each form has a tetrahedral 4-covalent cuprous and a planar 4-covalent cupric complex bridged though chlorine atoms (XII A and B).

The formation of a bridged mixed-metal compound such as (XI) must be dependent to a certain extent on the valency lengths and the intervalency angles of each of the constituent 4-covalent metallic complexes. It is also dependent to a surprising extent on the nature of the specific groups linked to the two metals. For instance, the compound (XI) was the only bridged palladium mercury compound that could be isolated, although the preparation of several others was attempted. The results obtained in these experiments showed remarkable variation. Thus, in striking contrast to the previous experiment, no reaction occurred in hot alcoholic solution between the unbridged  $[(\text{Bu}_3\text{P})_2\text{PdI}_2]$  and mercuric iodide. When, however, equimolecular quantities of the unbridged  $[(\text{Pr}_3\text{P})_2\text{PdCl}_2]$  and mercuric chloride were similarly treated, the bridged dipalladium compound  $[(\text{Pr}_3\text{P})_2(\text{PdCl}_2)_2]$  and the bis(propylphosphine)tris(mercuric chloride)  $[(\text{Pr}_3\text{P})_2(\text{HgCl}_2)_3]$  were isolated, so that in spite of the relative amounts of reactants present, the reaction was evidently



Further, when equimolecular quantities of the unbridged  $[(\text{Et}_3\text{P})_2\text{PdCl}_2]$  and mercuric chloride were employed, the bridged dipalladium compound  $[(\text{Et}_3\text{P})_2(\text{PdCl}_2)_2]$  and the bis(ethylphosphine)tetrakis(mercuric chloride)  $[(\text{Et}_2\text{P})_2(\text{HgCl}_2)_4]$  were obtained, so the reaction was now



Finally, when the two bridged butylphosphinepalladium iodide and butylphosphinemercury iodide compounds were used, the mercury was completely evicted from the complex, with the formation of the unbridged palladium compound :



It is clear from these results that the specific nature of the palladium and mercury atoms themselves determines to only a limited extent the formation of the mixed bridged compounds. Furthermore, it should be noted that no bridged palladium cadmium compounds could be prepared; this is also surprising, in view of the ease with which mercury and cadmium can be exchanged in their bridged derivatives.

The interaction of mercuric iodide with various members of the tetrakis{iodotrialkylphosphine(or arsine)copper} series and the corresponding argentous series,  $[\text{R}_3\text{P}(\text{As}), \text{CuI}]_4$  and  $[\text{R}_3\text{P}(\text{As}), \text{AgI}]_4$  (Mann, Purdie, and Wells, J., 1936, 1503) has been studied in the hope of preparing bridged cuprous mercuric or argentous mercuric compounds such as (XIII) or (XIV).



Such compounds would be closely similar to those of Mellor, Burrows, and Morris (*loc. cit.*), but would differ in that all the metallic complexes present (cuprous, argentous, and mercuric) would have the tetrahedral configurations. Various derivatives of mercury were obtained, but the desired compounds could not be prepared.

#### EXPERIMENTAL.

The solvent used for recrystallisation is named in parentheses after the substance concerned. The solubility of the mixed cadmium mercury derivatives in organic solvents was in each case lower than that of the corresponding dicadmium or dimercury compounds: the tetrabromocadmium-mercury compounds were also less soluble than the corresponding tetraiodo-cadmium-mercury compounds.

*Preparation of Di-iodobis(tri-n-propylphosphine)-μ-di-iodocadmium-mercury* (III).—(a) Solutions of  $[(\text{Pr}_3\text{P})_2\text{CdI}_2]$  (I; 1.15 g., 1 mol.) and mercuric iodide (0.76 g., 1 mol.) in hot alcohol (10 and 20 c.c.) were mixed; the solution became yellow and then colourless, and crystals of the *cadmium-mercury compound* (III) began to separate. After 3 hours these were collected (1.8 g.), and obtained as fine white needles (alcohol), m. p. 141° (Found: C, 18.6; H, 3.7; I, 44.3.  $\text{C}_{18}\text{H}_{42}\text{I}_4\text{P}_2\text{CdHg}$  requires C, 18.9; H, 3.9; I, 44.5%). The compound is slightly soluble in alcohol, readily soluble in acetone. The mother-liquor in the original preparation contained solely a small amount of the same material.

(b) Solutions of the tetraiodocadmium compound (II; 0.52 g., 1 mol.) and the tetraiododimercury compound (IV; 0.61 g., 1 mol.) in hot alcohol (15 and 35 c.c.) were mixed, and on cooling the cadmium-mercury compound (III) (0.9 g.) separated, m. p. 141° (alcohol) unchanged when mixed with the product from the above experiment.

When solutions of  $[(\text{Pr}_3\text{P})_2\text{CdI}_2]$  (I; 3.4 g., 1 mol.) and mercuric iodide (4.4 g., 2 mols.) in hot alcohol (25 and 75 c.c.) were mixed, the mixture became yellow and deposited pale yellow crystals, which gave white needles from alcohol, m. p. 112–113° identified as the tetraiododimercury compound (IV).

When acetone solutions of the cadmium mercury compound (III; 1.14 g., 1 mol.) and of α'-dipyridyl (0.156 g., 1 mol.) were mixed, a white precipitate of di-iododipyridylcadmium,  $[\text{dipyCdI}_2]$ , rapidly separated in almost theoretical yield; the filtrate appeared to contain a mixture of  $[(\text{Pr}_3\text{P})_2(\text{HgI}_2)_2]$  and  $[(\text{Pr}_3\text{P})_3(\text{HgI}_2)_2]$ . This result is undoubtedly determined by the lower solubility of  $[\text{dipyCdI}_2]$  than of  $[\text{dipyHgI}_2]$ .

*Di-iodobis(tri-n-butylphosphine)-μ-di-iodocadmium-mercury* (as III).—Similarly prepared from equimolecular quantities of  $[(\text{Bu}_3\text{P})_2(\text{CdI}_2)_2]$  and  $[(\text{Bu}_3\text{P})_2(\text{HgI}_2)_2]$ , this *compound* was obtained as white leaflets, m. p. 140–141° (alcohol) (Found: C, 23.6; H, 4.5; Hg, 16.1.  $\text{C}_{24}\text{H}_{64}\text{I}_4\text{P}_2\text{CdHg}$  requires C, 23.5; H, 4.4; Hg, 16.4%).

*Di-iodotri-n-propylphosphinetri-n-amyolphosphine-μ-di-iodocadmium-mercury* (as III).—This compound, isomeric with the above, was prepared by the interaction of  $[(\text{Pr}_3\text{P})_2(\text{CdI}_2)_2]$  and  $[(\text{Am}_3\text{P})_2(\text{HgI}_2)_2]$  in cold benzene solution; the residue obtained by spontaneous evaporation of

the solvent gave, after rapid crystallisation from alcohol, white crystals, m. p. 91—93° (Found : C, 23.1; H, 4.4.  $C_{24}H_{54}I_4P_2CdHg$  requires C, 23.5; H, 4.4%).

*Dibromobis(tri-propylphosphine)-μ-dibromocadmium-mercury* (VI).—Similarly prepared by mixing solutions of  $[(Pr_3P)_2CdBr_2]$  (V; 1.97 g., 1 mol.) and mercuric bromide (1.20 g., 1 mol.) in hot alcohol (25 and 25 c.c.), this was formed as an immediate white precipitate, which became crystalline when the mixture was boiled. The compound (VI) was obtained as white crystals (acetone), m. p. 179°, almost insoluble in hot alcohol and benzene, readily soluble in acetone (Found : C, 22.6; H, 4.5; Br, 33.8.  $C_{18}H_{42}Br_4P_2CdHg$  requires C, 22.7; H, 4.4; Br, 33.5%). Cadmium and mercury were detected in the mother-liquors obtained in the halogen estimation. The same compound was obtained when alcoholic solutions of equimolecular quantities of  $[(Pr_3P)_3(CdBr_2)_2]$  and  $[(Pr_3P)_3(HgBr_2)]$  were mixed.

*Dibromodi-iodobis(propylphosphine)cadmium-mercury* (VII).—Similarly obtained from  $[(Pr_3P)_2CdBr_2]$  (V; 1.50 g., 1 mol.) and mercuric iodide (1.15 g., 1 mol.) in hot alcohol (15 and 25 c.c.), the compound (VII) separated on cooling in white needles (2.5 g.); m. p. 138° (acetone), moderately soluble in hot alcohol and benzene, readily soluble in acetone (Found : C, 20.6; H, 4.1.  $C_{18}H_{42}Br_2I_2P_2CdHg$  requires C, 20.6; H, 4.0%).

*Di-iodotripropylphosphinetripropylarsine-μ-di-iodocadmium-mercury* (IX).—(a) Solutions of  $[(Pr_3P)_2(CdI_2)_2]$  (II; 0.53 g., 1 mol.) and  $[(Pr_3As)_2(HgI_2)_2]$  (VIII; 0.66 g., 1 mol.) in hot alcohol were mixed, and on cooling gave white crystals of the compound (IX), m. p. 121—123° with slight softening at 115° (Found : C, 18.2; H, 3.9.  $C_{18}H_{42}I_4AsPCdHg$  requires C, 18.2; H, 3.6%).

(b) Precisely similar results were obtained by the interaction of  $[(Pr_3As)_2(CdI_2)_2]$  (X; 0.57 g., 1 mol.) and  $[(Pr_3P)_2(HgI_2)_2]$  (IV; 0.61 g., 1 mol.).

All attempts to prepare the mixed compound of formula  $[(Pr_3As)ICdI_2HgI(AsPr_3)]$  by the action of the bridged cadmium compound  $[(Pr_3As)_2(CdI_2)_2]$  on mercuric iodide or on  $[(Pr_3As)_2(HgI_2)_2]$  failed.

*Dibromobis(tri-n-propylarsine)-μ-dibromopalladium-mercury* (XI).—When solutions of  $[(Pr_3As)_2PdBr_2]$  (1.34 g., 1 mol.) and mercuric bromide (0.72 g., 1 mol.) in hot alcohol (20 and 25 c.c.) were mixed, no colour change occurred, but after several hours orange crystals of the compound (XI) separated; these had m. p. 89—90° (alcohol) (Found : C, 20.9; H, 4.2; M, cryoscopic in 1.850% benzene solution, 676; in 0.829% ethylene dibromide solution, 510; in 2.071% solution, 566; in 3.019% solution, 579.  $C_{18}H_{42}Br_4As_2HgPd$  requires C, 20.9; H, 4.1%; M, 1031). The compound is readily soluble in alcohol, ether, and acetone, but when warmed in benzene solution it dissociates into its original constituents, mercuric bromide being precipitated.

When alcoholic solutions of  $[(Pr_3P)_2PdCl_2]$  (0.50 g., 1 mol.) and mercuric chloride (0.27 g., 1 mol.) were mixed and set aside, fine colourless crystals of  $[(Pr_3P)_2(HgCl_2)_2]$ , m. p. 114° (benzene), separated, and the filtrate later deposited orange crystals of  $[(Pr_3P)_2(PdCl_2)_2]$ , m. p. 187° (alcohol); each compound was identified by analysis or mixed m. p. determination with an authentic sample.

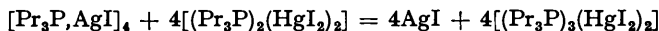
When alcoholic solutions of  $[(Et_3P)_2PdCl_2]$  (0.41 g., 1 mol.) and mercuric chloride (0.27 g., 1 mol.) were similarly treated, colourless crystals of  $[(Et_3P)_2(HgCl_2)_2]$ , m. p. 162—164°, were first obtained, and later orange crystals of  $[(Et_3P)_2(PdCl_2)_2]$ , m. p. 230°, each compound being identified as above.

When alcoholic solutions of  $[(Bu_3P)_2(PdI_2)_2]$  (0.56 g., 1 mol.) and  $[(Bu_3P)_2(HgI_2)_2]$  (0.66 g., 1 mol.) were similarly treated, the dark brown colour of the mixed solution faded at once to a deep orange colour, and on slow evaporation orange crystals of  $[(Bu_3P)_2PdI_2]$  (0.6 g.), m. p. 63—64° (alcohol), were obtained, and free mercuric iodide was also isolated.

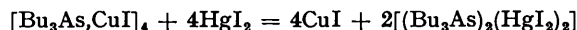
In an attempt to prepare a compound of type (XIV), tri-*n*-propylphosphine (3.6 g., 3 mols.) was added to silver iodide (1.76 g., 1 mol.) and mercuric iodide (3.40 g., 1 mol.) dissolved together in excess of aqueous potassium iodide solution. Vigorous shaking rapidly gave a white precipitate, which when collected, washed, drained, and rapidly recrystallised from alcohol gave white needles of *di-iodobis(tri-propylphosphine)mercury*,  $[(Pr_3P)_2HgI_2]$ , (5 g.) m. p. 117—119° (Found : C, 26.4; H, 5.25; I, 32.8.  $C_{18}H_{42}I_2P_2Hg$  requires C, 27.9; H, 5.4; I, 32.7%). The compound is unstable, and liberates propylphosphine slowly on standing, rapidly on heating in organic solvents. Further recrystallisation therefore gives a product having a m. p. over a wider range.

When solutions of tetrakis(iodopropylphosphine)silver,  $[Pr_3P, AgI]_4$  (0.79 g., 1 mol.), and the bridged mercury compound  $[(Pr_3P)_2(HgI_2)_2]$  (2.46 g., 4 mols.), each in acetone (25 c.c.), were mixed, silver iodide (0.41 g.) was at once precipitated, and the filtrate gave on evaporation

solely tris(propylphosphine)bis(mercury iodide),  $[(\text{Pr}_3\text{P})_3(\text{HgI}_2)_2]$ , m. p. 124—125°. The reaction is therefore



When hot alcoholic solutions of tetrakis(iodobutylarsine-copper),  $[\text{Bu}_3\text{As,CuI}]_4$ , and of the bridged mercury compound  $[(\text{Bu}_3\text{As})_2(\text{HgI}_2)_2]$  were mixed, no reaction could be detected. When however solutions of the cuprous compound (1.75 g., 1 mol.) and of mercuric iodide (1.82 g., 4 mols.) in hot alcohol (25 c.c. and 50 c.c.) were mixed, cuprous iodide (0.7 g.) was precipitated, and the solution gave solely  $[(\text{Bu}_3\text{As})_2(\text{HgI}_2)_2]$ , m. p. 55—56° (alcohol). The reaction is therefore



When only 2 mols. of mercuric iodide were employed in this reaction, the cuprous iodide was again almost entirely precipitated, but the excess of phosphine then gave  $[(\text{Bu}_3\text{As})_3(\text{HgI}_2)_2]$  in addition to the above mercuric derivative.

THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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