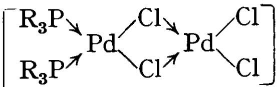
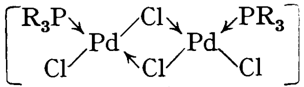
366. *The Constitution of Complex Metallic Salts. Part VIII. The Bridged Thio-derivatives of Palladous Halides with Tertiary Phosphines.*

By Joseph Chatt and Frederick G. Mann.

The properties and reactions of the mono- and bis-ethylthiol compounds, $[(Bu_3P)_2Pd_2Cl_3(SEt)]$ and $[(Bu_3P)_2Pd_2Cl_2(SEt)_2]$, are discussed, and evidence is adduced to show that in these compounds the EtS groups act as the " bridging " groups linking the palladium atoms. In organic solvents the first compound undergoes an equilibrium conversion into the second and the tetrachloride, $[(Bu_3P)_2Pd_2Cl_4]$: hence the bridging groups in the ring share the mobility of the unbridged groups. The properties of similar thiocyanate and *o*-phenylenedithiol compounds are also discussed.

It has been shown (Mann and Purdie, J., 1936, 873; Mann and Wells, this vol. p. 702) that the 4-covalent compounds of palladous halides with tertiary phosphines and arsines, $[(R_3P)_2PdCl_2]$ and $[(R_3As)_2PdCl_2]$, readily react with ammonium palladochloride to give " bridged " compounds, *e.g.*, $[(R_3P)PdCl_2]_2$, which should theoretically exist in three isomeric forms, *viz.*, the unsymmetrical form (I) and the *cis*- and the *trans*-symmetric form (II) and (III) respectively. These compounds exist in the crystalline state in only one isomeric form, which in the trimethylarsine series was shown by *X*-ray analysis to have the *trans*-symmetric structure (as III); solutions of these compounds in organic solvents, however, gave reactions of all three isomeric forms, which are therefore present apparently in tautomeric equilibrium. The presence of this equilibrium was further indicated by dipole measurements. These properties were not dependent on the halogen groups, because analogous compounds having nitrito- and thiocyanato-radicals possessed similar properties.


(I.)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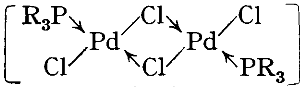

(III.)

The formation of this equilibrium on dissolution in organic solvents, and its complete suppression on crystallisation, clearly entail a very facile intramolecular wandering of both the phosphine (or arsine) molecules and the terminal unbridged halogen atoms. Certain organic thiol and dithiol derivatives of these bridged dipalladium compounds have now been investigated, to obtain further insight into the establishment of the above equilibrium, and in particular, to determine whether the " bridging " acid radicals are firmly held in the central ring or whether they also can migrate about the molecule.

When dichlorobis(tri-*n*-butylphosphine)-μ-dichlorodipalladium (as in I—III) in cold alcoholic solution is treated with 1 mol. of ethylthiol, the corresponding trichloro-monoethylthiol compound (IV) is formed (Mann and Purdie, *loc. cit.*); when, however, even a large excess of ethylthiol is used, only the *dichloro-bisethylthiol* compound (V) is formed, and the two remaining chloro-groups cannot be expelled under these conditions. It was originally thought that the ethylthiol radicals would first displace the unbridged chloro-groups in the above reaction, but further evidence now shows that the sulphur atom in the SEt radical has such strongly co-ordinating properties that this radical always bridges the palladium atoms (as in IV and V) and cannot apparently occupy the terminal unbridged positions in these compounds; hence the bisethylthiol derivative (V) is unaffected by further application of the free thiol. [Clearly, each of the compounds (IV) and (V), irrespective of the identity of the bridging radicals, could theoretically exist in the three isomeric forms illustrated by (I)—(III) : the difference between these forms does not affect the points discussed below, particularly the nature of the central ring, and therefore the *trans*-symmetric form (as III) has been adopted throughout.]

The positions of the SEt radicals in the compound (V) are shown by the following considerations. It is known (Mann and Purdie, *loc. cit.*) that dichlorobis(butylphosphine)-μ-dichlorodipalladium (VI) when treated in solution with αα'-dipyridyl reacts as if it existed in form (I) and gives two compounds, $[(Bu_3P)_2PdCl_2]$ and $[dpy\ PdCl_2]$ (Equation A);

when similarly treated with *p*-toluidine, however, it reacts in form (III) and gives solely $[(Bu_3P)(C_6H_4Me{\cdot}NH_2)PdCl_2]$ (Equation B). The bisethylthiol compound (V), however, is

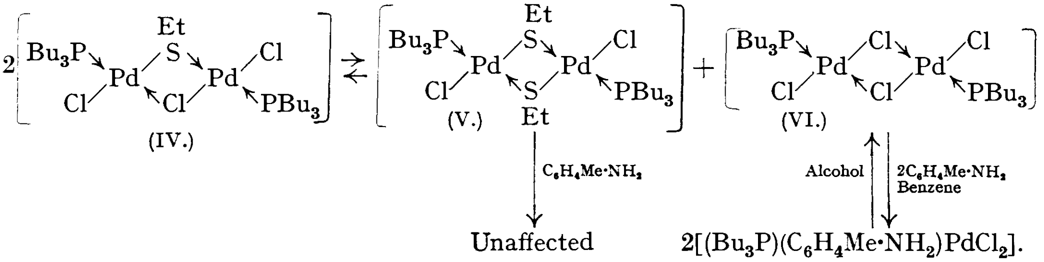
$$\text{A.}\quad [(Bu_3P)_2PdCl_2PdCl_2] + \text{dpy} = [(Bu_3P)_2PdCl_2] + [\text{dpy } PdCl_2]$$

$$\text{B.}\quad [(Bu_3P)ClPdCl_2PdCl(Bu_3P)] + 2C_6H_4Me{\cdot}NH_2 = 2[(Bu_3P)(C_6H_4Me{\cdot}NH_2)PdCl_2]$$

unaffected by either reagent, and clearly cannot possess this bridged $PdCl_2Pd$ ring; hence the SEt radicals are the bridging groups and form the central ring. By analogy, the monoethylthiol compound (IV) has a similar constitution.

In spite of the great stability of the $Pd(SEt)_2Pd$ ring, compared with that of the $PdCl_2Pd$ ring, the SEt radicals are found to be capable of ready migration. This is shown by the remarkable behaviour of the monoethylthiol compound (IV) which in organic solvents undergoes partial conversion into the bisethylthiol compound (V) and the tetrachloro-compound (VI), an equilibrium mixture of the three compounds being thus established (Equation C).

C.



The following physical and chemical evidence places the existence of this equilibrium beyond doubt: (1) The ethylthiol compounds (IV) and (V) are bright canary-yellow in colour, but the tetrachloro-compound (VI) is deep orange-red. When the monothiol compound (IV) is dissolved in benzene, the solution is yellow, and the equilibrium point must lie far over on the left in Equation C. On warming, however, the colour becomes distinctly orange, due to the equilibrium point shifting to the right, and cooling reverses this effect. Similar changes occur in alcoholic solution.

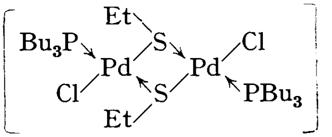
(2) When cold alcoholic solutions of equimolecular quantities of (V) and (VI) are mixed, the orange colour of (VI) slowly fades, and in a few minutes the pure monothiol compound (IV) crystallises. A similar reaction occurs in cold concentrated benzene solution.

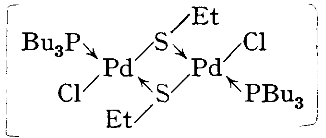
(3) Of the three compounds forming the above equilibrium, only (VI) will react directly with αα′-dipyridyl and with *p*-toluidine. Consequently, if dipyridyl is added to a cold benzene solution of (IV), the equilibrium moves to the right, and the tetrachloro-compound (VI) so formed reacts normally with the amine according to Equation A, and an equivalent quantity of the bisethylthiol compound (V) is liberated: all the three palladium compounds thus formed have been isolated from the reaction product. Similarly, if *p*-toluidine is added to a benzene solution of the monothiol compound (IV), the equilibrium is again shifted, and the tetrachloro-compound so formed reacts with the amine according to Equation B, with liberation of the bisthiol compound (V). The course of this reaction depends largely on the solvent and is reversed in, *e.g.*, methyl and ethyl alcohol: when cold alcoholic solutions of (V) and of 2 equivs. of $[(Bu_3P)(C_6H_4Me{\cdot}NH_2)PdCl_2]$ are mixed, the latter regenerates free *p*-toluidine and the tetrachloro-compound (VI), which then reacts with the bisthiol compound (V), shifting the equilibrium C to the left, and the monothiol compound (IV) crystallises, free *p*-toluidine being present in the mother-liquor.

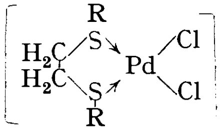
The important deduction from these experiments is that, in these bridged dipalladium derivatives, a particular compound may exist in organic solvents, not only as a tautomeric mixture of its three isomeric forms, but also as an equilibrium mixture with two other similar but distinct compounds. Moreover, the great mobility of the unbridged phosphine and halogen groups is clearly shared also by the bridging radicals, even if the bridging is of comparatively great stability.

Several attempts have been made to prepare the unbridged bisethylthiol compound $[(Bu_3P)_2Pd(SEt)_2]$. When a cold alcoholic solution of dichlorobisbutylphosphinepalladium, $[(Bu_3P)_2PdCl_2]$, was treated with either 1 or 2 mols. of ethylthiol, the yellow colour of the solution changed to orange, but on spontaneous evaporation only the unchanged dichloro-compound remained. When the cold alcoholic solution was treated with 1 mol. of potassium ethyl sulphide, and the precipitated potassium chloride removed, spontaneous evaporation gave a heavy red oil, from which, after a few weeks' standing, the bridged bisethylthiol compound (V) crystallised. The formation of this compound, which clearly involves the eviction of part of the butylphosphine, testifies strongly to the stability of the bridged $—S(Et)\rightarrow$ linkage. When the alcoholic solution of the original unbridged dichloro-compound was treated with 2 mols. of potassium ethyl sulphide, only the red oil was obtained, and it is possible that the compound $[(Bu_3P)_2Pd(SEt)_2]$ is liquid at room temperature.

It should be noted that the bridged bisethylthiol compound (V) can theoretically exhibit a further type of isomerism, in addition to the three forms similar to (I)—(III). The tetrahedral disposition of the co-ordinated sulphur atoms will enable the two ethyl groups to occupy either the *cis* (VA) or the *trans* (VB) position relative to the four-membered PdS_2Pd ring, and each of the forms corresponding to (I)—(III) can theoretically show this geometric isomerism. Dr. R. C. Evans has, however, kindly examined several samples of the compound (V) crystallographically, and reports that the anorthic crystals are homogeneous, no evidence of a second form being detectable. A similar type of isomerism was sought by Bennett, Mosses, and Statham (J., 1930, 1668), who prepared several compounds of type (VII) but failed to detect *cis-trans*-isomerism (*i.e.*, no separation into the *meso*- and the racemic form could be effected).


(VA.)

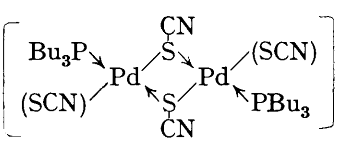

(VB.)


(VII.)

The stability of the bridged ring in the bisethylthiol compound (V) affords a very interesting comparison with that of the ring in dithiocyanatobis(tri-*n*-butylphosphine)-μ-dithiocyanatodipalladium (VIII) (Mann and Purdie, *loc. cit.*) which, incidentally, also gives no indication of the *cis-trans*-isomerism discussed above. The atoms in the two rings are identical, but in the thiocyanato-compound it would be expected that the dipole on the CN group, by attracting electrons from the sulphur atom, would necessarily weaken the electron-donor properties of this atom and thus also weaken its co-ordinating (and therefore bridging) properties. This was found to be the case. The ring in the tetrathiocyanato-compound (VIII) is sufficiently stable to be unaffected by *p*-toluidine, but not sufficiently strong to withstand the greater "splitting action" of dipyridyl, which breaks the molecule down into $[(Bu_3P)_2Pd(SCN)_2]$ and *dithiocyanatodipyridylpalladium*, [dpy Pd$(SCN)_2$]. The tetrathiocyanate occupies therefore an intermediate position between the tetrachloride (VI), which is split by both these reagents, and the dichlorobisethylthiol compound (V), which is not split by either. Free butylphosphine splits the tetrathiocyanate into 2 mols. of $[(Bu_3P)_2Pd(SCN)_2]$: this was expected, in view of the vigorous co-ordinating properties of the tertiary phosphine molecule. The behaviour of the dichloro-dithiocyanato-compound,

$$[Cl(Bu_3P)Pd(SCN)_2Pd(Bu_3P)Cl],$$

towards these reagents is now being investigated : preliminary experiments indicate a complex series of reactions.


(VIII.)

The results obtained with ethylthiol throw considerable light on those obtained earlier with 4-chloro-*o*-phenylenedithiol * (IX), which was originally employed because with its

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* The nuclear chlorine in this molecule has no significance regarding its use for the above purpose. The compound (IX) was used because it was more accessible than the unsubstituted dithiol.

aid it was hoped to replace the unbridged terminal chloro-groups in the butylphosphine tetrachloro-compound of form (I), and so obtain the derivative (X). The only

(IX.)

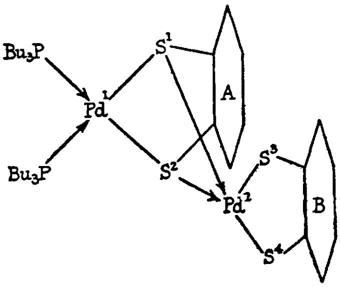
$[(Bu_3P)_2PdCl_2Pd{:}S_2C_6H_3Cl]$ (X.)

$[(Bu_3P)_2Pd(S_2C_6H_3Cl)Pd{:}S_2C_6H_3Cl]$

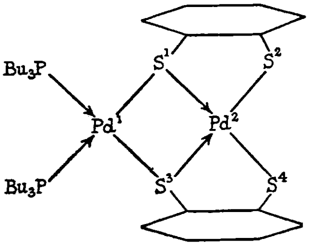
(XI.)

crystalline product isolated from the interaction of the tetrachloro-compound with the dithiol (IX) was, however, the deep red crystalline 4-*chloro*-o-*phenylenedithiolbis*-(*tri*-n-*butylphosphine*)-μ-4-*chloro*-o-*phenylenedithioldipalladium* (XI). This compound is of great stability: for instance, when dichlorobis(butylphosphine)palladium, $[(Bu_3P)_2PdCl_2]$, was treated with only 1 mol. of the dithiol (IX), some of the unbridged 4-*chloro*-o-*phenylenedithiolbis*(*butylphosphine*)*palladium*, $[(Bu_3P)Pd{:}S_2C_6H_3Cl]$ was formed, but the chief product was the bridged compound (XI), free butylphosphine having been evicted during its preparation. So vigorous is the bridging action of the dithiol molecule that, had the compound (X) been isolated, there is little doubt that the dithiol residue would have bridged the palladium atoms and the chloro-groups would have been unbridged: the existence of such a molecule would therefore have been no guide to its constitution.

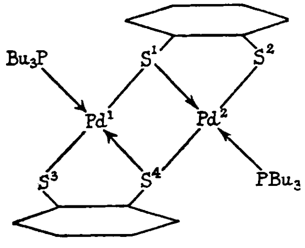
The theoretical possibilities of isomerism of the bridged bis(dithiol) compound (XI) are of interest. It is clear that two isomerides corresponding to the unsymmetrical structure (I), *i.e.*, having 2 phosphine molecules co-ordinated to one palladium atom, should exist: these are shown in (XIA) and (XIB), where the aromatic nuclear chlorine atoms are omitted for simplicity. In (XIA), if the atom Pd^1 and the phosphorus and sulphur atoms attached to it are in the plane of the paper, then to preserve the tetrahedral disposition of these co-ordinated sulphur atoms S^1 and S^2, the benzene nucleus A must be behind the plane of the paper, and the Pd^2 atom and the dithiol residue B must be in front. In (XIB), unlike (XIA), the atom Pd^1 is linked to the sulphur atoms S^1 and S^3 of two different dithiol residues: in (XIB), if the phosphorus atoms and the atoms Pd^1, Pd^2, S^1, S^2, S^3, and S^4 are in the plane of the paper, the molecule must be folded across the axes S^1–S^2 and S^3–S^4, so that the benzene rings lie above or below the plane of the paper.



(XIA.)



(XIB.)



(XIC.)

A third form (XIC), corresponding to the symmetrical form (III) and having the phosphine residues linked to different palladium atoms, should also exist. Here again, if the phosphorus atoms and the palladium and sulphur atoms are all in the plane of the paper, the molecule must also be folded across the axes S^1–S^2 and S^3–S^4, with the benzene rings above or below this plane. In view of the possible existence of these three forms and the further possibilities of isomerism arising from (*a*) the *cis-trans* positions of the benzene ring about the S–S planes, and (*b*) the position of the nuclear chlorine atoms relative to the rest of the molecule, it is remarkable that the compound has been isolated in only one form in the solid state, having m. p. 114° without decomposition. It is probable that this form (as in the methylarsine series) is the isomeride of greatest symmetry, *i.e.*, form (XIC) with the benzene rings severally above and below the plane of the paper.

EXPERIMENTAL.

The preparation of the monoethylthiol compound (IV) has already been described (Mann and Purdie, *loc. cit.*, p. 889).

Dichlorobis(*tri*-n-*butylphosphine*)-*μ-bisethylthioldipalladium* (V).—Cold solutions of the tetrachloro-compound (VI; 4 g.) and of ethylthiol (1·2 c.c.; 3 mols.) in alcohol (300 and 50 c.c., respectively) were mixed. The solution, which rapidly became deep yellow, was concentrated in a desiccator until large crystals had formed. These were collected and recrystallised from alcohol, the *compound* (V) separating as deep yellow crystals, m. p. 115—116° (Found: C, 41·2; H, 8·1; Cl, 8·8; S, 7·3; Pd, 25·8; *M*, ebullioscopic in 0·858% ethylene dibromide solution, 829. $C_{28}H_{64}Cl_2S_2P_2Pd_2$ requires C, 41·4; H, 8·0; Cl, 8·7; S, 7·9; Pd, 26·3%; *M*, 811). This compound is moderately soluble in cold alcohol, and very soluble in benzene; the monoethylthiol compound (IV) is only feebly soluble in both solvents.

(1) *Action of αα′-dipyridyl.* Cold solutions of the bisethylthiol compound (1 g.) and dipyridyl (0·192 g.; 1 mol.) in cold benzene (25 c.c. and 10 c.c.) were mixed. No apparent change occurred, so the solution was evaporated to dryness in a vacuum. Crystallisation of the residue from a small quantity of warm alcohol gave the pure unchanged bisethylthiol compound, and unchanged dipyridyl was isolated from the alcoholic extract.

(2) *Action of* p-*toluidine.* A similar experiment was performed with the bisethylthiol compound (1 g.) and *p*-toluidine (0·264 g.; 2 mols.) dissolved in alcohol (50 c.c. and 10 c.c. respectively). The yellow crystals which separated as the solution evaporated to small bulk proved to be the unchanged bisthiol compound, and the amine was recovered unchanged from the mother-liquor.

(3) *Action of ethylthiol.* Cold alcoholic solutions of the bisthiol compound were treated severally with 1 and with 2 mols. of ethylthiol. Spontaneous evaporation in each case gave yellow crystals which on recrystallisation from alcohol proved to be the unchanged bisthiol compound.

The Trichloromonoethylthiol Compound (IV).—(1) *Formation by interaction of* (V) *and* (VI). Equal quantities (0·5 g.) of the compounds (V) and (VI) were dissolved separately in a minimum of cold alcohol, and the solutions mixed. The orange-red colour rapidly faded, and yellow crystals of the pure monothiol compound (IV) separated, the reaction being complete within 10 minutes. Yield 0·75 g.

The reaction was repeated in cold benzene, in which both (V) and (VI) are far more soluble. The colour again rapidly faded, but yellow crystals of (IV) separated only on scratching.

(2) *Action of dipyridyl.* Solutions of the monoethylthiol compound (2 g.) and dipyridyl (0·40 g.; 1 mol.) in benzene (60 c.c. and 20 c.c. respectively) were mixed at 60°, a slight change in colour occurring. On standing overnight, fine acicular crystals of [dpy $PdCl_2$], insoluble in benzene, had separated and were collected (Found: Pd, 31·5. Calc. for $C_{10}H_8N_2Cl_2Pd$: Pd, 32·0%). The solution was allowed to evaporate spontaneously to about one-third of its volume, and the yellow crystals of the bisethylthiol compound (V) which had formed were removed and recrystallised from alcohol; m. p., alone and mixed with authentic sample, 115°. The original mother-liquor, allowed to evaporate to dryness, deposited further yellow crystals, which proved on repeated recrystallisation from alcohol to be $[(Bu_3P)_2PdCl_2]$, m. p., both alone and mixed, 65—66°. These final mother-liquors, taken to dryness again and extracted with dilute hydrochloric acid, yielded the unchanged excess dipyridyl, m. p., alone and mixed, 69—70°.

(3) *Action of* p-*toluidine.* A solution of *p*-toluidine (0·55 g.; 2 mols.) in cold benzene (20 c.c.) was added to a suspension of the powdered monoethylthiol compound (2 g.) in benzene (100 c.c.); the thiol compound rapidly dissolved, and in a few minutes a red colour developed in the solution. Spontaneous evaporation gave a viscous oil which, taken up in hot *cyclo*hexane, deposited the bisethylthiol compound on cooling (m. p., alone and mixed, 113°). The *cyclo*hexane mother-liquor on spontaneous evaporation left an orange oil which on seeding gave a crystalline mass of impure dichlorobutylphosphine-*p*-toluidinepalladium

$$[(Bu_3P)(C_6H_4Me{\cdot}NH_2)PdCl_2].$$

This was taken up in cold methyl alcohol, and the solution after standing was filtered to remove a trace of insoluble material; on evaporation it gave orange yellow crystals. These were extracted with warm petrol, and the filtrate then gave the pure unbridged dichloro-compound, m. p., alone and mixed, 79—80°. The excess of *p*-toluidine was recovered from the methyl alcohol.

This action was reversed in alcohol. Cold solutions of dichlorobutylphosphine-*p*-toluidine-palladium (1 g.; 2 mols.) and the bisethylthiol compound (0·85 g.; 1 mol.), each in alcohol (50 c.c.), were mixed. Deposition of yellow crystals of the monoethylthiol compound rapidly occurred, and continued for about 1 hour; m. p., alone and mixed, 150—151°. Free *p*-toluidine was identified in the mother-liquor.

Dithiocyanatobis(butylphosphine)-μ-dithiocyanatodipalladium (VIII).—(1) *Action of dipyridyl.* Cold benzene solutions of the tetrathiocyanate (1 g.) and dipyridyl (0·43 g.; 2 mols.) were mixed. No change in colour was apparent, but a fine crystalline precipitate began to separate within a few minutes. After standing overnight, this precipitated *dithiocyanatodipyridyl-palladium* was collected, washed with benzene and acetone, and dried (Found: N, 14·8; Pd, 28·0. $C_{12}H_8N_4S_2Pd$ requires N, 14·8; Pd, 28·2%). The mother-liquor on evaporation gave $[(Bu_3P)_2Pd(SCN)_2]$, which, when recrystallised from alcohol, had m. p. 112—113°, alone and mixed with an authentic sample.

(2) *Action of* p-*toluidine.* A similar experiment was performed with benzene solutions of the tetrathiocyanate (1 g.) and *p*-toluidine (0·25 g.; 2 mols.). No change was apparent on mixing, and spontaneous evaporation gave a yellow solid smelling strongly of the base. This solid was extracted with cold alcohol, and the residue recrystallised from hot alcohol containing dioxan. The unchanged tetrathiocyanate was thus recovered, m. p. 170—171°, alone and mixed.

(3) *Action of tributylphosphine.* When cold benzene solutions of the tetrathiocyanate (2 g.) and butylphosphine (1·1 g.; 2 mols.) were mixed, an immediate reaction occurred and the solution became pale yellow. Spontaneous evaporation gave only greenish-white crystals of $[(Bu_3P)_2Pd(SCN)_2]$ which, when recrystallised from alcohol, had m. p. 111—113°, alone and mixed.

4-*Chloro*-o-*phenylenedithiolbis(tributylphosphine)-μ-4-chloro*-o-*phenylenedithioldipalladium* (XI).—Solutions of the tetrachloro-compound (VI; 2 g.) and of 4-chloro-*o*-phenylenedithiol (IX; 0·9 g., 2 mols.) in cold alcohol (150 and 10 c.c. respectively) were mixed; a deep red colour immediately developed, and red crystals slowly separated. After spontaneous evaporation of the solution to small bulk, these crystals of the *compound* (XI) were collected and recrystallised from alcohol; m. p. 114° (Found: C, 44·6; H, 6·2; Cl, 7·4; S, 12·6; Pd, 21·9. $C_{36}H_{60}Cl_2S_4P_2Pd_2$ requires C, 44·7; H, 6·3; Cl, 7·35; S, 13·2; Pd, 21·7%. Sulphur was estimated in the filtrate from the palladium analysis and hence the result was slightly low). Yield, 1·5 g.

4-*Chloro*-o-*phenylenedithiolbis(tributylphosphine)palladium.*—Cold solutions of $[(Bu_3P)_2PdCl_2]$ (1 g.) and the dithiol (IX; 0·25 g., 1·25 mols.) in alcohol (50 and 10 c.c. respectively) were similarly mixed, with the immediate formation of the red colour. On spontaneous evaporation to small bulk, the bis(dithiol) compound (XI) separated, and a marked odour of butylphosphine was detected. The red crystals of (XI) were collected, and the mother-liquor on further evaporation deposited buff-coloured crystals of the above *monodithiol* compound; these when recrystallised from alcohol had m. p. 116° (Found: C, 52·0; H, 8·3. $C_{30}H_{57}ClS_2P_2Pd$ requires C, 52·5; H, 8·4%).

The authors are greatly indebted to the Department of Scientific and Industrial Research for a grant, to Messrs. The Mond Nickel Company, Ltd., for a loan of palladium, and to Sir Gilbert Morgan and Dr. R. E. D. Clark for gifts of dipyridyl and 4-chloro-*o*-phenylenedithiol respectively.

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[*Received, September* 19*th*, 1938.]