390. *Bridged Complexes of Palladium*(II) *containing Chelate Ligands.*

By Stanley E. Livingstone.

Bridged complexes of Pd^{II} containing chelate ligands are described. The polynuclear character of a number of these compounds has been demonstrated by molecular-weight determinations in the polar solvent, nitrobenzene; in addition, their covalent nature is established by their non-conductance in solution. The chelate ligands containing thiol groups react readily with Pd^{II}, forming complexes having sulphur bridges. These compounds display less tendency to react with other ligands than halogeno-bridged complexes.

Several bridged complexes of palladium with the chelate group, *o*-(methylthio)benzoic acid, have been described in earlier papers.[1] The chelate groups, *o*-(benzylthio)benzoic acid and *o*-(octadecylthio)benzoic acid, also form bridged compounds with palladium. Treatment of potassium bromopalladite with the respective palladium inner complex in aqueous-acetone solution yields the bromo-bridged compounds, which are insoluble in water, alcohol, and acetone, but sparingly soluble in nitrobenzene, in which they are undissociated.

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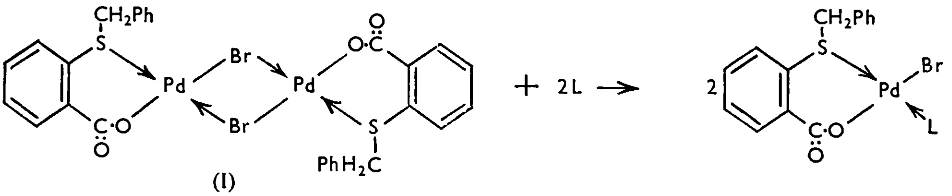
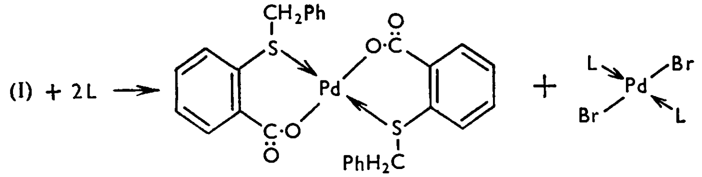
[1] Livingstone and Plowman, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 188; 1951, **85**, 116.

Attempts were made to split the bridge in di-[*o*-(benzylthio)benzoato]-μμ′-dibromodipalladium (I) by treating the compound with a monodentate ligand (L) to produce a palladium complex containing one molecule of chelate and one of ligand as in the reaction:


(I)

Mann and Purdie[2] were able to split the bridged complex, dichlorodi(tri-*n*-butylphosphine)-μμ′-dichlorodipalladium in this way, using aniline. When treated with two mols. of methyldiphenylarsine and *p*-toluidine in acetone, the bromo-bridged complex (I) dissolves to golden and red solutions, respectively, from which bis-[*o*-(benzylthio)benzoato]-palladium can be isolated. Accordingly, it appears that the principal reaction which occurs is:



Bridged compounds were obtained with a number of other chelated compounds, *viz.*, *o*-methylthiobenzenethiol, 3-dimethylarsinopropane-1-thiol, 3-ethylthiopropane-1-thiol, and *o*-aminobenzenethiol. The palladium inner complexes of these thiols have been previously described.[3] The bridged complexes are readily precipitated from aqueous acetone solution when either a solution of the palladium inner complex or the chelate itself is treated with excess of K_2PdX_4 solution ($X = Cl, Br, NO_2, SCN$). All the bridged compounds prepared in this investigation are listed in Table 1.

TABLE 1. *Palladium bridged complexes containing chelate groups.*

Chelating compound	Compound	Bridging atoms	Non-bridging group
$PhCH_2{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$	I	Br	$-CO_2-$
$C_{17}H_{35}{\cdot}CH_2{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$	II	Br	$-CO_2-$
$Me_2As{\cdot}[CH_2]_3{\cdot}SH$	III	S	$-Cl$
,,	IV	S	$-Br$
,,	V	S	$-NO_2$
,,	VI	S	$-SCN$
,,	VII	S	$-C_2O_4-$
$MeS{\cdot}C_6H_4{\cdot}SH$	VIII	S	$-Cl$
,,	IX	S	$-Br$
,,	X	S	$-NO_2$
,,	XI	S	$-SCN$
$EtS{\cdot}[CH_2]_2{\cdot}SH$	XII	S	$-Cl$
,,	XIII	S	$-Br$
,,	XIV	S	$-NO_2$
,,	XV	S	$-SCN$
$H_2N{\cdot}C_6H_4{\cdot}SH$	XVI	S	$-Br$

Cryoscopic determinations in nitrobenzene of the molecular weights of compounds (III), (IV), (V), (XII), (XIII), and (XIV) are in agreement with the values expected for a bridged formulation. The molecular conductivities of the bridged complexes in nitrobenzene and acetone are 0·1—0·3 mho and 1—5 mho, respectively. The values for the molecular conductivity of uni-univalent electrolytes in these solvents are of the order of 25—30 mho and 110—180 mho respectively.

It is assumed that the thiolo-compounds are bridged through the sulphur atoms. The reasons for assuming that these compounds have the configuration (*a*) rather than (*b*)—as shown for the 3-dimethylarsinopropane-1-thiolo-complexes—is as follows: First, the colours of the bridged complexes of 3-dimethylarsinopropane-1-thiol and 3-ethylthiopropane-1-thiol are lighter than would be expected if they contained halogen bridges. The

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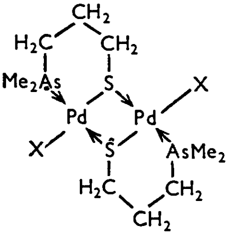
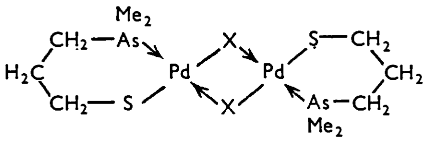
[2] Mann and Purdie, *J.*, 1936, 873.
[3] Livingstone, *J.*, 1956, 437.

bromo-bridged complexes of *o*-(methylthio)benzoic acid,[1] *o*-(benzylthio)benzoic acid, and *o*-(octadecylthio)benzoic acid are orange-brown, whereas the bromo-complexes of the above-mentioned thiols are yellowish-orange. Also, chloro-bridged palladium complexes containing trialkylphosphines are red, but the corresponding ethylthio-bridged complexes are yellow.[4] Secondly, the compounds (III) and (XII) react differently from the bromo-bridged complex (I) when treated with certain ligands. If an acetone solution of the chloro-compound of 3-dimethylarsinopropane-1-thiol (III) is refluxed for an hour with an excess of ethanethiol, then concentrated and cooled, the original compound (III) can be recovered unchanged. A similar result is obtained when using methyldiphenylarsine. Both these ligands react readily with di-[(*o*-benzylthio)benzoato]-μμ′-dibromodipalladium (I). It has been found[4, 5, 6] that chloro-bridged compounds of trialkylphosphines react with ethanethiol forming μμ′-bisethylthio-complexes, which are unaffected by *p*-toluidine. The chloro-complex of 3-ethylthiopropane-1-thiol (XII), when treated in hot benzene solution with excess of *p*-toluidine, is unaffected and can be recovered on concentration and cooling of the solution.



(a)



(b)

If the sulphur atoms form bridges in the oxalato-compound (VII), the latter must be polymeric; this would explain its low solubility compared with that of the other complexes of 3-dimethylarsinopropane-1-thiol. When an attempt was made to prepare a similar oxalato-complex with the ligand 3-ethylthiopropane-1-thiol, reduction to metallic palladium occurred.

Using similar procedures to those used in the preparation of the complexes already described, unsuccessful attempts were made to prepare bridged palladium complexes with the following chelating compounds: (i) Anthranilic acid, (ii) *o*-aminophenol, (iii) *o*-carboxyphenyldimethylarsine, (iv) 3-amino-2-naphthoic acid, (v) glycine, (vi) (methylthio)-acetic acid. The failure of these ligands to form bridged compounds could be attributed, in some cases, to the insolubility of the palladium inner complex. However, this does not account for the lack of bridged formation with (iii) and (v) since the palladium inner complexes of these ligands are soluble in aqueous acetone. The readiness of ligands containing a thiol group to form binuclear complexes appears to be due to the especial stability of a thiolo-bridge compared to halogeno-, nitro-, and thiocyanato-bridges.

The reaction between potassium bromopalladite and bis-(3-dimethylarsinopropane-1-thiolo)palladium reaches equilibrium very quickly even in dilute solution. When aqueous acetone solutions (5 × 10⁻⁴M-concentration) of potassium bromopalladite and the palladium complex are mixed, the optical density of the solution, a few seconds after mixing, at 360 and 410 mμ, is almost identical with that of a 2·5 × 10⁻⁴M-solution of the bridged complex (IV) at the same wavelengths. No alteration occurs even after two days.

EXPERIMENTAL

The palladium complexes used in the preparation of the bridged compounds described below have been reported in a previous paper.[3]

Bis-[o-(*benzylthio*)*benzoato*]-μμ′-*dibromodipalladium* (I).—Bis-[*o*-(benzylthio)benzoato]-palladium (6 g.) was dissolved in hot 50% aqueous acetone (1·5 l.) and poured into a boiling

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[4] Chatt and Mann, *J.*, 1938, 1949.
[5] Chatt, Mann, and Wells, *J.*, 1938, 2086.
[6] Chatt and Hart, *J.*, 1953, 2363.

solution containing potassium bromopalladite (6·5 g.) and sodium bromide (4·5 g.) in 50% aqueous acetone (400 ml.). After 90 min. at the b. p. crystallization commenced. After another 30 min. on the hot plate, the mixture was filtered, and the product washed with boiling aqueous acetone, then boiling water, and finally hot acetone, affording deep orange prisms (7·3 g.) of the *compound* (I), m. p. 201° (decomp.) (Found: C, 39·3; H, 2·7; Pd, 24·8; Br, 18·0. $C_{28}H_{22}O_4Br_2S_2Pd_2$ requires C, 39·1; H, 2·6; Pd, 24·8; Br, 18·6%). The molecular conductance (Λ_{4000}) in nitrobenzene is 0·4 mho cm.$^{-2}$ at 25°.

Di-[o-(octadecylthio)benzoato]-μμ'-dibromodipalladium (II).—By an essentially similar method, bis-[*o*-(octadecylthio)benzoato]palladium (1·5 g.) afforded the bridged *complex* as orange-brown crystals; these were filtered off from the hot mother-liquor, and then boiled with acetone to dissolve the small amount of the contaminating original inner complex; yield 1·1 g., m. p. 174° (decomp.) (Found: C, 50·8; H, 6·9; Pd, 18·0; Br, 13·5. $C_{50}H_{82}O_4Br_2S_2Pd_2$ requires C, 50·7; H, 7·0; Pd, 18·0; Br, 13·5%). The molecular conductance (Λ_{2500}) in nitrobenzene is 0·5 mho cm.$^{-2}$ at 25°.

Dichlorodi-(3-dimethylarsinopropane-1-μ-thiolo)dipalladium (III).—Potassium chloropalladite (2·54 g.), dissolved in water (40 ml.), was added to a suspension of 3-dimethylarsinopropane-1-thiol (1·4 g.) in 1 equiv. of 0·5N-sodium hydroxide. Yellow crystals of the inner complex were at first precipitated, but dissolved on further addition of potassium chloropalladite. After 2 days, the crystalline precipitate (2·3 g.) was filtered off, and washed with water, then acetone. The *complex* darkens on heating to 250° and decomposes, but does not melt (Found: C, 18·8; H, 3·7; Cl, 11·1; Pd, 33·2%; *M*, cryoscopically in nitrobenzene, 645 in 0·28%, 615 in 0·32%, and 640 in 0·21% solution. $C_{10}H_{24}S_2As_2Pd_2$ requires C, 18·7; H, 3·8; Cl, 11·0; Pd, 33·2%; *M*, 642). It had $\Lambda_{1000} = 0·3$ mho cm.$^{-2}$ in nitrobenzene at 25°.

Dibromodi-(3-dimethylarsinopropane-1-μ-thiolo)dipalladium (IV).—By a method similar to that used for (I), bis-(3-dimethylarsinopropane-1-thiolo)palladium (0·45 g.) afforded a red precipitate which dissolved when the mixture was stirred; after half the reagent had been added, the colour changed from red to yellow and crystals commenced to form. After cooling, the orange-yellow prisms of the *compound* (0·71 g.) were filtered off, washed with aqueous acetone, and dried. The crystals are insoluble in water and aqueous acetone, but soluble in acetone, chloroform, and nitrobenzene; they can be recrystallized from glacial acetic acid. When heated above 200° they become red but do not melt (Found: C, 16·6; H, 3·2; Br, 22·2; Pd, 29·4%; *M*, cryoscopically in 0·26% nitrobenzene solution, 740. $C_{10}H_{24}Br_2S_2As_2Pd_2$ requires C, 16·4; H, 3·3; Br, 21·9; Pd, 29·2%; *M*, 731): Λ_{1000} in nitrobenzene $= 0·1$ mho cm.$^{-2}$ at 25°.

Dinitrodi-(3-dimethylarsinopropane-1-μ-thiolo)dipalladium (V).—Di-(3-dimethylarsinopropane-1-thiolo)palladium (0·4 g.) and potassium nitrite (0·3 g.) were dissolved in 50% acetone (40 ml.), and an aqueous acetone solution of potassium nitropalladite (0·6 g.) was added slowly at the b. p. After a few minutes crystals were deposited. The pale yellow needles (0·52 g.) were washed with water and dried. The *compound* is moderately soluble in acetone, chloroform, and nitrobenzene (Found: C, 18·1; H, 3·5; N, 4·2; Pd, 32·0%; *M*, cryoscopically in 0·14% nitrobenzene solution, 700. $C_{10}H_{24}O_4N_2S_2As_2Pd_2$ requires C, 18·1; H, 3·6; N, 4·2; Pd, 32·1%, *M*, 663).

Dithiocyanatobis-(3-dimethylarsinopropane-1-μ-thiolo)dipalladium (VI).—Potassium thiocyanatopalladite (0·5 g.), bis-(3-dimethylarsinopropane-1-thiolo)palladium (0·3 g.), and potassium thiocyanate under similar conditions to those described for (I), rapidly (5 min.) formed yellowish-brown crystals (0·43 g.) of the *complex* (VI); these were filtered off and washed with water and a small amount of acetone, in which they are soluble (Found: C, 20·8; H, 3·4; N, 4·1. $C_{12}H_{24}N_2S_4As_2Pd_2$ requires C, 20·9; H, 3·5; N, 4·1%).

Oxalatodi-(3-dimethylarsinopropane-1-μ-thiolo)dipalladium (VII).—Potassium oxalato palladite tetrahydrate (0·32 g.) and bis-(3-dimethylarsinopropane-1-thiolo)palladium (0·4 g.), treated as in the general method, gave a solution which at first went blood-red, then, on completion of the addition, became orange. On cooling, orange-coloured plates separated. These (0·33 g.) were washed with water, then acetone, and dried, and had m. p. 180° (decomp.). The *compound* is only sparingly soluble in chloroform and nitrobenzene (Found: C, 21·8; H, 3·5; Pd, 32·0. $C_{12}H_{24}O_4S_2As_2Pd_2$ requires C, 21·8; H, 3·7; Pd, 32·4%).

Dichlorodi-(o-methylthiobenzene-μ-thiolo)dipalladium (VIII).—Bis-*o*-methylthiobenzenethiolopalladium (0·4 g.), by the general method, afforded vermilion crystals (0·47 g.), which were washed with hot water, then hot acetone. The *compound* is insoluble in water and organic solvents (Found: C, 28·1; H, 2·4; Cl, 11·8; Pd, 35·3. $C_{14}H_{14}Cl_2S_4Pd_2$ requires C, 28·3; H, 2·4; Cl, 11·9; Pd, 35·9%).

Dibromodi-(o*-methylthiobenzene-*μ*-thiolo*)*dipalladium* (IX).—Di-(*o*-methylthiobenzenethiolo)-palladium (0·4 g.) and potassium bromopalladite (0·5 g.) rapidly afforded scarlet crystals (0·62 g.), which were washed with hot water and acetone. The *compound* is insoluble in organic solvents (Found : C, 24·8; H, 2·2; Pd, 30·9. $C_{14}H_{14}Br_2S_4Pd_2$ requires C, 24·6; H, 2·1; Pd, 31·2%).

Dinitrodi-(o*-methylthiobenzene-*μ*-thiolo*)*dipalladium* (X).—Potassium nitropalladite (0·33 g.), di-(*o*-methylthiobenzenethiolo)palladium (0·27 g.), and potassium nitrite (0·15 g.), under the usual conditions, gave yellowish-orange crystals of the *compound* (X) (0·26 g.), which, when heated, darken at about 200° and slowly decompose without melting (Found : C, 28·1; H, 2·4; Pd, 34·0. $C_{14}H_{14}O_4N_2S_4Pd_2$ requires C, 27·3; H, 2·3; Pd, 34·6%).

Dithiocyanatodi-(o*-methylthiobenzene-*μ*-thiolo*)*dipalladium* (XI).—Similarly, from potassium thiocyanatopalladite, the *dithiocyanato-complex* was prepared as salmon-pink crystals, which were filtered off, and washed with water, then acetone; it is insoluble in acetone, chloroform, and nitrobenzene, and decomposes but does not melt below 200° (Found : C, 29·8; H, 2·2; N, 4·4; Pd, 33·6. $C_{16}H_{14}N_2S_6Pd_2$ requires C, 30·0; H, 2·2; N, 4·4; Pd, 33·3%).

Dichlorodi-(3*-ethylthiopropane-*1*-*μ*-thiolo*)*dipalladium* (XII).—3-Ethylthiopropane-1-thiol (2·4 g.), treated as in the preparation of (III), gave the *complex*, which recrystallized from acetone in yellowish-orange crystals (3·9 g.), m. p. 230° (Found : C, 21·7; H, 3·9; Cl, 12·7; Pd, 38·5%; *M*, cryoscopically in 0·29% nitrobenzene solution, 585. $C_{10}H_{22}Cl_2S_4Pd_2$ requires C, 21·7; H, 4·0; Cl, 12·8; Pd, 38·5%; *M*, 555). Solutions of the complex in acetone and nitrobenzene at 25° had $\Lambda_{1000} = 5$ and 0·3 mho cm.$^{-2}$, respectively.

Dibromodi-(3*-ethylthiopropane-*1*-*μ*-thiolo*)*dipalladium* (XIII).—Use of potassium bromopalladite (3·0 g.) and sodium bromide (1·0 g.) with 0·70 g. of the thiol as in the preceding preparation gave an immediate precipitation of a reddish-brown material, which, on boiling, became crystalline. This was collected, extracted with boiling acetone (300 ml.), and the extract concentrated to 100 ml. and cooled, yielding yellowish-orange needles (0·33 g.) of the *complex* (XIII) which is soluble in acetone, nitrobenzene, and chloroform and slightly soluble in benzene; m. p. 193° (Found : C, 18·7; H, 3·4; Br, 24·9; Pd, 33·1%; *M*, cryoscopically in 0·27% nitrobenzene solution, 640. $C_{10}H_{22}Br_2S_4Pd_2$ requires C, 18·7; H, 3·4; Br, 24·8; Pd, 33·1%; *M*, 644). Molecular conductance (Λ_{1000}) at 25° : in acetone, 1 mho cm.$^{-2}$; in nitrobenzene, 0·1 mho cm.$^{-2}$.

Dinitrodi-(3*-ethylthiopropane-*1*-*μ*-thiolo*)*dipalladium* (XIV).—Use of 3-ethylthiopropane-1-thiol (0·52 g.), potassium nitropalladite (1·43 g.), and potassium nitrite (0·5 g.) similarly gave a yellowish-orange precipitate which, recrystallized from acetone, afforded yellow crystals of the *complex* (XIV) (0·23 g.), m. p. 154°. This is more soluble in acetone, nitrobenzene, and chloroform than the corresponding chloro- and bromo-complexes (Found : C, 21·2; H, 3·5; N, 4·6; Pd, 37·0; *M*, cryoscopically in 0·30% nitrobenzene solution, 625. $C_{10}H_{22}O_4N_2S_4Pd_2$ requires C, 20·9; H, 3·8; N, 4·9; Pd, 37·1%; *M*, 576). Molecular conductance (Λ_{1000}) at 25° : in acetone, 1 mho cm.$^{-2}$; in nitrobenzene, 0·1 mho cm.$^{-2}$.

Dithiocyanatodi-(3*-ethylthiopropane-*1*-*μ*-thiolo*)*dipalladium* (XV).—Potassium thiocyanatopalladite (2·1 g.), and 3-ethylthiopropane-1-thiol (0·58 g.) under the same conditions gave a precipitate which ultimately became crystalline, repeated extraction with boiling acetone and concentration yielding bright yellow prisms of the pure *complex* (XV) (0·45 g.), only sparingly soluble in nitrobenzene and acetone; m. p. 197° (Found : C, 23·8; H, 3·5; N, 4·6; Pd, 35·6. $C_{12}H_{22}N_2S_6Pd_2$ requires C, 24·0; H, 3·7; N, 4·7; Pd, 35·6%). Molecular conductance (Λ_{1000}) at 25° : in acetone, 1·5 mho cm.$^{-2}$; in nitrobenzene, 0·1 mho cm.$^{-2}$.

Dibromodi-(o*-aminobenzene-*μ*-thiolo*)*dipalladium* (XVI).—By the method used for (I) di-(*o*-aminobenzenethiolo)palladium (0·75 g.) was refluxed in 70% acetone (120 ml.) containing sodium bromide (3 g.) and potassium bromopalladite. The original fine buff crystals were converted into dark amber crystals of the solvated *complex* (XVI), which was filtered off and washed well with hot water and acetone; yield, 1·27 g. (Found : C, 25·1; H, 2·3; N, 4·2; Br, 23·7; Pd, 32·5. $C_{12}H_{12}N_2Br_2S_2Pd_2,\frac{1}{2}C_3H_6O$ requires C, 24·9; H, 2·3; N, 4·3; Br, 24·5; Pd, 32·8%). The compound is sparingly soluble in nitrobenzene; when heated in a closed tube to decomposition, it evolves a gas which condenses to a colourless liquid. Unsolvated compounds do not give this result. In nitrobenzene at 25° : $\Lambda_{1000} = 0·1$ mho cm.$^{-2}$.

Reaction of (I) *with Methyldiphenylarsine.*—The bridged complex (I) (1·06 g.) was boiled under reflux with acetone (500 ml.), and to it was slowly added (2 hr.) methyldiphenylarsine (0·6 g., 2 mol.) in acetone (50 ml.). The compound (I) dissolved to a golden solution, which was evaporated to 20 ml., and addition of ether precipitated pale yellow needles of di-[*o*-(benzylthio)benzoato]palladium (0·16 g.), m. p. 170° (lit.[3], m. p. 169°) (Found : Pd, 18·0. Calc. for

$C_{28}H_{22}O_4S_2Pd$: Pd, 18·0%). The filtrate was evaporated to dryness, and the product recrystallized from alcohol to give yellowish-brown crystals (0·24 g.) (Found : C, 41·9; H, 3·7; Br, 18·4; Pd, 15·0. $C_{26}H_{26}Br_2As_2Pd$ requires C, 41·4; H, 3·5; Br, 21·2; Pd, 14·1%). Hence the substance was probably *dibromobis(methyldiphenylarsine)palladium*, contaminated with di-[*o*-(benzylthio)benzoato]palladium.

Reaction of (I) *with* p-*Toluidine.*—To (I) (0·9 g.) in acetone (70 ml.), *p*-toluidine (0·23 g., 2 mol.) was added. The mixture was heated to reflux, and the undissolved (I) (0·14 g.) filtered off. The deep red filtrate was concentrated to 5 ml.; pale yellow crystals (0·12 g.) of di-[*o*-(benzylthio)benzoato]palladium were deposited, m. p. 169° (Found : Pd, 18·2%). No pure compound was isolated from the filtrate.

Reaction of (III) *with Ethanethiol.*—To (III) (0·45 g.) in acetone (100 ml.), was added ethanethiol (0·2 g.), and the solution refluxed for 1 hr.; concentration to 10 ml. and cooling afforded yellow crystals of (III) (Found : C, 18·8; H, 3·6; Cl, 10·7. Calc. for $C_{10}H_{24}Cl_2S_2As_2Pd_2$: C, 18·7; H, 3·8; Cl,11·0%).

Non-reaction of (III) *with Methyldiphenylarsine.*—To (III) (0·43 g.), in boiling acetone (100 ml.), methyldiphenylarsine (0·36 g., 2·4 mol.) was added, and the solution refluxed for 30 min.; concentration to 40 ml. afforded yellow crystals of unchanged (III) (Found : Pd, 33·2. Calc. for $C_{10}H_{24}Cl_2S_2As_2Pd_2$: Pd, 33·2%).

Non-reaction of (XII) *with* p-*Toluidine.*—*p*-Toluidine (0·7 g.) was added to (XII) (1 g.), dissolved in hot benzene (250 ml.); the solution was kept at the b. p. for 15 min., and on cooling, deposited yellowish-orange crystals of unchanged (XII), m. p. 230° (Found : Pd, 38·3%).

Spectrophotometric Measurements.—Measurements of the optical density of solutions were made with a Hilger " Uvispec " spectrophotometer, 0·5-cm. quartz cells being used. The optical densities of 5×10^{-4}M-solutions of di-(3-dimethylarsinopropane-1-thiolo)palladium and potassium bromopalladite in 66% acetone–water containing sodium bromide (2×10^{-3}M) were measured at 360 and 410 mμ. The solutions were mixed in the ratio of 1 : 1 and the measurement was taken 30 sec. after mixing and remained unchanged after 2 days. The optical density of the bridged complex (IV) ($2·5 \times 10^{-4}$M-solution in 66% acetone–water) was also measured. The optical densities are given below :

	360 mμ	410 mμ		360 mμ	410 mμ
$Pd(C_5H_{12}SAs)_2$	0·50	0·10	$Pd(C_5H_{12}SAs)_2 + K_2PdBr_4$	1·20	0·38
K_2PdBr_4	0·48	0·52	$(C_5H_{11}SAs)_2Pd_2Br_2$	1·15	0·35

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