

**450.** *The Preparation of Chloro-bridged Complexes of Palladium(II) containing Uncharged Monodentate Ligands having Nitrogen, Phosphorus, Arsenic, Antimony, Sulphur, Selenium, and Tellurium as Donor Atoms.*

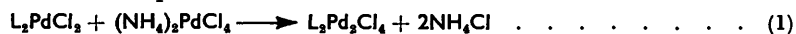
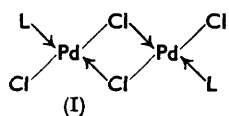
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A series of chloro-bridged complex compounds of the type  $[L_2Pd_2Cl_4]$  (I) has been prepared. These contain amines, tertiary organic phosphines, arsines, or stibines, or dialkyl sulphides, selenides, or tellurides as the ligands L.

The amine complexes are somewhat anomalous, but the remainder form two well-graded series, according to the positions of the donor atoms of L in the Periodic Table. Generally the bridged complexes are less stable than their platinous analogues, but the selenide bridged complexes ( $L = R_2Se$ ) are more stable.

A SERIES of chloro-bridged complexes of the type  $[L_2Pd_2Cl_4]$  (I) was necessary to our studies<sup>1</sup> of the inductive and mesomeric effects of a series of uncharged ligands L, and here we describe their preparation and properties. In formula (I), L is an uncharged ligand of the type amine, tertiary organic phosphine, arsine, or stibine, dialkyl sulphide, selenide, or telluride.

Many binuclear complexes of palladium(II), containing tertiary phosphines and arsines as the ligand L, have been described<sup>2</sup> and their *trans*-symmetrical structures (I) are well established.<sup>3</sup> The most general method of preparation, developed by Mann and his co-workers, consists of boiling under reflux an aqueous-alcoholic solution of equimolecular proportions of the simple complex  $L_2PdCl_2$  and ammonium chloropalladite. This reaction is complete in 0.5–1.5 hr. and can be written :

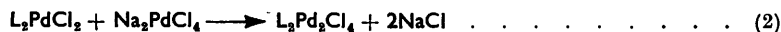


<sup>1</sup> Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

<sup>2</sup> Mann, *Ann. Reports*, 1938, **35**, 148; Gmelin, "Handbuch der anorganischen Chemie. Palladium." System no. 65, pp. 422–432, Verlag Chemie, Berlin, 1942.

<sup>3</sup> Mann and Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169.

It is readily applicable to the preparation of the bridged complexes of tertiary phosphines and arsines, but not to the less stable bridged complexes, such as we have now prepared (see Table 1). These are better prepared by a simple modification using sodium chloropalladite, instead of the ammonium salt, in ethanol or acetone at room temperature. The reaction then requires a few hours to a few days for completion, but it appears to have universal application, except to bridged complexes (I) in which L is an olefin or an amine. The reaction is carried out at a temperature consistent with the stability of the product, and may occur according to equation (2) or (3), depending on the starting materials available:



The ease with which the chloro-bridged complexes of palladium(II) are obtained is in marked contrast to the more difficult preparation of the analogous platinum(II) complexes where a variety of methods is used to prepare the complete series.<sup>4</sup> The bridged complexes prepared in this research are listed in the Table, together with their methods of preparation. A few known phosphine and arsine members of the series are included there for comparison.

*Preparation of Amine Chloro-bridged Complexes (I; L = amine).*—This was difficult. Only di-*n*-pentylamine and piperidine of the amines tried gave products of the correct composition; and the piperidine complex is probably a polymer, being obtained as a light brown insoluble precipitate by the reaction of equimolecular proportions of [piperidine<sub>2</sub>PdCl<sub>2</sub>] or of piperidine itself with sodium chloropalladite in alcohol. Its insolubility is in marked contrast to the solubility of its platinum analogue which is known to be dimeric. It therefore seems improbable that the palladium complex is a binuclear

*Halogen-bridged complexes of palladium(II).*

Complex	Method *	M. p.	Colour
{PiperidinePdCl <sub>2</sub> } <sub>2</sub> †	A and B	178—180° (decomp.)	Brown
{NH( <i>n</i> -C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> } <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	178—181.5 (decomp.)	Ochre
(PEt <sub>3</sub> ) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub>	A and B	230	Orange
(PPr <sub>3</sub> ) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub>	A	189—191	Orange
(PBu <sup>n</sup> Ph) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	193—193.5	Reddish-orange
(PPh <sub>3</sub> ) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub>	A and B	Decomp. ca. 250—270	Brownish-orange
{P(MeO) <sub>3</sub> } <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> §	B	114—115	Yellowish-orange
{P(PhO) <sub>3</sub> } <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	168—171	Yellowish-orange
(AsPr <sup>n</sup> ) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub>	B	159—160	Dark orange
(SbEt <sub>3</sub> ) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	87—88 (decomp.)	Dark red
(Et <sub>2</sub> S) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	A and B	143—144.5	Tan
(Pr <sup>n</sup> S) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	80—81	Tan
(Et <sub>2</sub> Se) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	A and B	148.5—150	Reddish-brown
(Pr <sup>n</sup> Se) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	86.5—87	Reddish-brown
(Et <sub>2</sub> Te) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	A and B	110—125 (decomp.)	Dark reddish-brown
(Pr <sup>n</sup> Te) <sub>2</sub> Pd <sub>2</sub> Cl <sub>4</sub> †	B	131.5—132 (decomp.)	Dark reddish-brown
(PPr <sup>n</sup> ) <sub>2</sub> Pd <sub>2</sub> Br <sub>4</sub> †	B	178—179	Dark red
(PPr <sup>n</sup> ) <sub>2</sub> Pd <sub>2</sub> I <sub>4</sub> †	B	202—203	Purple-black

\* A, prepared by reaction 2; B, prepared by reaction 3. † New compounds. ‡ Prepared by Ardell, "Palladiumsalts föreningar med alkylsulfider," Akad. Afhandl. Lund, 1896, p. 9 and formulated as the "double salt" [Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>]PdCl<sub>2</sub>. § Prepared by Fink (*Compt. rend.*, 1892, **115**, 176) but not characterised.

complex of the usual type. Nevertheless, when it is treated with triphenylphosphine it gives some *trans*-[Ph<sub>3</sub>P,piperidinePdCl<sub>2</sub>] identical with the compound prepared from [(Ph<sub>3</sub>P)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>] and piperidine. The di-*n*-pentylamine complex, similarly prepared, was soluble in some organic solvents and its molecular weight and composition indicated the formula [{NH(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>}<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>] in solution.

Attempts to obtain [(4-*n*-pentylpyridine)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>] by methods A and B led to the recovery of the simple complex, [(4-*n*-pentylpyridine)<sub>2</sub>PdCl<sub>2</sub>]. The following methods also failed: (a) boiling an acetone solution of pentylpyridine (1 mol.) and sodium chloropalladite (1 mol.) under reflux for 3 hr.; (b) fusion of [(4-*n*-pentylpyridine)<sub>2</sub>PdCl<sub>2</sub>] with

<sup>4</sup> Chatt and Venanzi, *J.*, 1955, 2787.

powdered palladous chloride; (c) heating the simple pentylpyridine complex above its melting point under a high vacuum for 2 hr.<sup>5</sup> In all cases the unchanged mononuclear complex was recovered. This failure to prepare  $[(4-n\text{-pentylpyridine})_2\text{Pd}_2\text{Cl}_4]$  is somewhat puzzling. In the platinumous series, amine compounds of this type are prepared by the spontaneous decomposition of the mixed olefin complex, *trans*-[olefin,amPtCl<sub>2</sub>] (where am = amine), in a solvent where the bridged complex  $[\text{am}_2\text{Pt}_2\text{Cl}_4]$  is insoluble.<sup>4</sup> Attempts to use this route in the palladous series were frustrated by the impossibility of obtaining complexes of the type [olefin,amPdCl<sub>2</sub>]. Two methods were tried and many attempts were made to apply them. In the first a solution of  $[(\text{cyclohexene})_2\text{Pd}_2\text{Cl}_4]$ <sup>6</sup> in methylene chloride was treated at  $-70^\circ$  with a cold solution of *p*-toluidine in methylene chloride, but the solution blackened immediately after the first addition. Attempts to prepare  $[\text{C}_2\text{H}_4\text{,amPdCl}_2]$ , via  $\text{K}[\text{C}_2\text{H}_4\text{PdCl}_3]$  in analogous manner to the platinum complex,<sup>7</sup> in water and in the presence of hydrochloric and of perchloric acid respectively led to instantaneous evolution of ethylene.

*Properties of the Chloro-bridged Complexes of Palladium(II).*—These complexes are beautifully crystalline and usually deeper in colour and more soluble in organic solvents than their platinumous analogues.<sup>4</sup> They show well-graded properties according to the Groups of donor atoms P, As, and Sb, and S, Se, and Te contained in them. The stabilities decrease and the colours become more intense on ascending each Group. The stabilities of the complexes lie roughly in the order of donor atoms  $\text{P} > \text{As} \sim \text{S} > \text{Se} > \text{Te} > \text{Sb}$ . The crystalline triethylstibine complex is very unstable in moist air, becoming semiliquid and liberating the stibine. Stored in a desiccator it decomposes in 2–3 days. It is also to be noted that the melting points of the arsine complexes are lower than those of their phosphine analogues, yet those of the selenide complexes are higher than those of their sulphide analogues. Generally the chloro-bridged complexes of palladium(II) are rather less stable than those of platinum, with the notable exception of the dialkyl selenide complexes which are considerably more stable.

In the platinumous series of chloro-bridged complexes of the type  $[\text{L}_2\text{Pt}_2\text{Cl}_4]$  the selenide complexes ( $\text{L} = \text{Et}_2\text{Se}$ ) are very unstable, so that the stabilities of the complexes are in order of ligands  $\text{L}$ ,  $\text{R}_2\text{S} \gg \text{R}_2\text{Se} < \text{R}_2\text{Te}$ .<sup>1</sup> In the palladous series the stabilities of the selenide complexes are truly intermediate, so that the sequence is  $\text{R}_2\text{S} > \text{R}_2\text{Se} > \text{R}_2\text{Te}$ . This difference in the sequence of stabilities may depend on the relative sizes of the orbitals used in forming the co-ordinate  $\sigma$ -bonds. It may be that those of selenium are comparable with those of palladium and those of tellurium with platinum and the strengths of the Se–Pd and Te–Pt bonds may be enhanced by this. This could account for the irregular order of stabilities observed in the platinumous series and its absence in the analogous palladous series. It is remarkable that the irregularity in the platinumous series also extends to the colours of the complexes, e.g.,  $[(\text{Et}_2\text{S})_2\text{Pt}_2\text{Cl}_4]$  is bright yellow whereas the selenium and tellurium analogues are both a dull brownish-orange.<sup>4</sup> In the palladous series the corresponding compounds grade uniformly from a light tan colour (S) through reddish-brown (Se) to a dark reddish-brown (Te) (see Table).

#### EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

The known mononuclear complexes  $[\text{L}_2\text{PdCl}_2]$  used in the preparations described below, except those whose preparations are given, were prepared by adding two equivalents of the ligand L to an alcoholic solution of sodium chloropalladite tetrahydrate.

*Bis(diethyl telluride)dichloropalladium*,  $[(\text{Et}_2\text{Te})_2\text{PdCl}_2]$ .—Ammonium chloropalladite (3.2 g.) in water (20 c.c.) was treated with diethyl telluride (3.8 g.) in a nitrogen atmosphere. After a few minutes' shaking a dark orange precipitate was formed. This was filtered off, washed with water, ethanol, and ether, and dried. Recrystallised three times from methanol, the

<sup>5</sup> Cf. Mann and Purdie, *J.*, 1936, 873.

<sup>6</sup> Kharasch, Seyler, and Mayo, *J. Amer. Chem. Soc.*, 1938, 60, 882.

<sup>7</sup> Chatt, *J.*, 1949, 3340.

product was obtained as deep reddish-orange plates, m. p. 98.5—99° (28%) (Found: C, 17.7; H, 3.7.  $C_8H_{20}Cl_2PdTe_2$  requires C, 17.5; H, 3.7%).

The simple complexes of amines,  $[am_2PdCl_2]$ , were prepared by treating the palladite in aqueous solution with an excess of the amine until a colourless solution of the salt  $[Pd am_2]Cl_2$  had been formed, and decomposing this salt by concentrated hydrochloric acid. The orange solid, which separated, was filtered off, dried, and recrystallised from a suitable solvent. In this way were prepared dipiperidinedichloropalladium,  $[(C_5H_{11}N)_2PdCl_2]$ , orange needles (from methanol), decomp. 175—189° (yield 52%) (Found: C, 34.7; H, 6.25; N, 8.4. Calc. for  $C_{10}H_{22}N_2Cl_2Pd$ : C, 34.5; H, 6.4; N, 8.05%), and bis-4-n-pentylpyridinedichloropalladium,  $[(C_{10}H_{15}N)_2PdCl_2]$ , orange leaflets (from methanol), m. p. 145° (sinters at 143.5°) (56%) (Found: C, 50.2; H, 6.4; N, 5.9.  $C_{20}H_{30}N_2Cl_2Pd$  requires C, 50.45; H, 6.35; N, 5.9%). The two amine complexes are non-electrolytes in nitrobenzene solution.

*Preparation of the Chloro-bridged Complexes by Method A.—Reaction between [(piperidine)<sub>2</sub>PdCl<sub>2</sub>] and sodium chloropalladite.* Dipiperidinedichloropalladium (1 g.) in ethanol (100 c.c.) and chloroform (50 c.c.) was treated with sodium chloropalladite tetrahydrate (0.7 g.) in ethanol and left at room temperature for 3 days. A brown solid formed was filtered off and dried *in vacuo*. It decomposed at ~180° and was insoluble in all solvents tried except pyridine, from which it could not be recovered. A sample was washed in water, ethanol, and chloroform and then dried. It is probably slightly impure  $[piperidinePdCl_2]_x$  (Found: C, 24.1; H, 4.6; N, 5.4. Calc. for  $C_8H_{11}NCl_2Pd$ : C, 22.85; H, 4.2; N, 5.3%).

*Reaction of [piperidinePdCl<sub>2</sub>]<sub>x</sub> with triphenylphosphine.* A suspension of the above brown solid (0.5 g.) in a solution of triphenylphosphine (0.5 g.) in acetone (50 c.c.) was shaken until the brown solid had disappeared, leaving a greenish-yellow solid (not investigated) and an orange solution. The solution was evaporated to dryness at 15 mm. and the yellow residue recrystallised from light petroleum (b. p. 80—100°). The yellowish-orange product was  $[PPh_3, piperidinePdCl_2]$ , and decomposed at 160—172° alone and mixed with an authentic specimen.

*Bis(triethylphosphine)dichloro- $\mu\mu'$ -dichlorodipalladium, [(PEt<sub>3</sub>)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>].* Hydrated sodium chloropalladite (2.1 g.) and  $[(PEt_3)_2PdCl_2]$  (2.9 g.) in ethanol (180 c.c.) were boiled under reflux for 45 min., then evaporated to dryness at 15 mm. and the solid residue was washed with water, dried, and recrystallised from ethanol (yield 81%). Its tri-*n*-propyl analogue was prepared similarly in 60% yield.

*Bis(triphenylphosphine)dichloro- $\mu\mu'$ -dichlorodipalladium, [(PPh<sub>3</sub>)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>].*  $[(PPh_3)_2PdCl_2]$  (1.5 g.) in chloroform (200 c.c.) and sodium chloropalladite hydrate (1.5 g.) in ethanol (50 c.c.) were mixed and boiled under reflux for 1 hr. The solid deposited was removed, washed with water, then with ethanol, then chloroform, dried, and precipitated with light petroleum (b. p. 40—60°) from a large volume of hot chloroform and so was obtained in reddish-orange needles which decompose gradually at >250° (yield 98%) (Found: C, 49.1; H, 3.5. Calc. for  $C_{38}H_{30}Cl_4P_2Pd_2$ : C, 49.2; H, 3.4%).

*Bis(diethyl sulphide)dichloro- $\mu\mu'$ -dichlorodipalladium, [(Et<sub>2</sub>S)<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub>].*  $[(Et_2S)_2PdCl_2]$  (1 g.) and hydrated sodium chloropalladite (0.8 g.) were dissolved in ethanol (75 c.c.), and the solution kept for 24 hr. The mixture was then taken to dryness at 15 mm. and the residual solid washed with water, dried, and recrystallised from chloroform and light petroleum (yield 27%) (Found: C, 18.2; H, 3.8; S, 11.7. Calc. for  $C_8H_{20}Cl_4S_2Pd_2$ : C, 17.9; H, 3.8; S, 12.0%). Similarly prepared were bis(diethyl selenide)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Et_2Se)_2Pd_2Cl_4]$  (recrystallised from ethyl methyl ketone; yield 25%) (Found: C, 15.7; H, 3.25.  $C_8H_{20}Cl_4Pd_2Se_2$  requires C, 15.3; H, 3.2%), and bis(diethyl telluride)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Et_2Te)_2Pd_2Cl_4]$  (recrystallised from methanol; yield 23%) (Found: C, 13.5; H, 2.8.  $C_8H_{20}Cl_4Pd_2Te_2$  requires C, 13.2; H, 2.8%).

*Preparation of the Chloro-bridged Complexes by Method B.—Reaction between piperidine and sodium chloropalladite.* Piperidine (1.5 c.c.) was added to a solution of the sodium salt (5 g.) in ethanol (100 c.c.) and kept for several days. The brown solid formed was removed and dried (3.5 g.). Soluble material was extracted from it with boiling acetone, and the insoluble product washed with water and ethanol, and then dried (1.8 g.) (Found: C, 23.1; H, 4.1; N, 5.5%). It is identical with the  $[piperidinePdCl_2]_x$  prepared by method A.

*Bis(di-n-pentylamine)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[\{NH(C_5H_{11})_2\}_2Pd_2Cl_4]$ .* Di-*n*-pentylamine (0.14 c.c.) and the hydrated sodium salt (2 g.) in ethanol (50 c.c.) were left for 3 days. The red solution was filtered from a grey solid and taken to dryness at 15 mm. in the cold. The

reddish-brown residue was recrystallised three times from ethyl acetate (yield approx. 45%) (Found: C, 36.1; H, 6.7; N, 4.1%; *M*, ebullioscopic in 0.8% benzene solution, 582, 587.  $C_{20}H_{46}N_2Cl_4Pd_2$  requires C, 35.9; H, 6.9; N, 4.2%; *M*, 669). It is a non-electrolyte in nitrobenzene and decomposes in boiling solvents.

*Bis*(triethylphosphine)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(PEt_3)_2Pd_2Cl_4]$ . The sodium salt (6 g.) in ethanol (100 c.c.) was treated under nitrogen with triethylphosphine (1.94 g.). The solution was filtered after 24 hr. from some whitish residue and taken to dryness at 15 mm. The residual product (68%) was treated in the same way as that prepared by method A. Its tri-*n*-propylarsine analogue was prepared similarly.

*Bis*(di-*n*-butylphenylphosphine)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(PBu^u_2Ph)_2Pd_2Cl_4]$ . Di-*n*-butylphenylphosphine (5.6 g.) was added, under nitrogen, to a solution of the sodium salt (9.3 g.) in acetone (150 c.c.), and the mixture set aside for 3 days, filtered, and taken to dryness at 15 mm. The residual product was recrystallised three times from propan-1-ol (yield 30%) (Found: C, 42.0; H, 5.8.  $C_{28}H_{46}Cl_4P_2Pd_2$  requires C, 42.1; H, 5.8%).

*Bis*(triphenylphosphine)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(PPh_3)_2Pd_2Cl_4]$ . The sodium salt (4 g.) in ethanol (50 c.c.) and triphenylphosphine (3 g.) in chloroform (200 c.c.) were mixed and boiled under reflux for 2 hr. The resulting yellow solid quickly redissolved, and a reddish solid was precipitated. This was identical with the product obtained by method A, and was purified in the same way (yield 73%).

*Bis*(trimethyl phosphite)dichloro- $\mu\mu'$ -dichlorodipalladium,  $\{[P(OMe)_3]_2Pd_2Cl_4\}$ . This was prepared in acetone solution analogously to the triethylphosphine compound (no nitrogen atmosphere necessary) and recrystallised from toluene by precipitation with light petroleum (b. p. 60–80°) in 30% yield (Found: C, 12.2; H, 3.1%; *M*, ebullioscopic in 0.6% benzene solution, 571. Calc. for  $C_6H_{18}O_6Cl_4P_2Pd_2$ : C, 11.95; H, 3.0%; *M*, 603). It is a non-electrolyte in nitrobenzene.

*Bis*(triphenyl phosphite)dichloro- $\mu\mu'$ -dichlorodipalladium,  $\{[P(OPh)_3]_2Pd_2Cl_4\}$ , was prepared analogously to the trimethyl phosphite complex. It was recrystallised from benzene (yield 42%) (Found: C, 44.2; H, 3.2%; *M*, ebullioscopic in 0.4% benzene solution, 771.  $C_{36}H_{30}O_6Cl_4P_2Pd_2$  requires C, 44.3; H, 3.1%; *M*, 986). It is a non-electrolyte in nitrobenzene.

*Bis*(triethylstibine)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(SbEt_3)_2Pd_2Cl_4]$ . Triethylstibine (1.1 g.) in acetone (20 c.c.) was gradually added to a stirred solution of the sodium salt (1.6 g.) in acetone (30 c.c.) at –70° under nitrogen. The mixture was then allowed to warm to room temperature and a solid began to separate. Evaporation at 15 mm. in the cold under nitrogen yielded a reddish residue. It was dissolved in warm ethyl methyl ketone, the solution cooled, and the product reprecipitated as a dark-red powder in very poor yield by addition of light petroleum (b. p. 60–80°) (Found: C, 17.7; H, 3.6. Calc. for  $C_{12}H_{30}Cl_4Pd_2Sb_2$ : C, 18.6; H, 3.9%). The analyst reported that the substance gained weight during weighing).

*Bis*(diethyl sulphide)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Et_2S)_2Pd_2Cl_4]$ . Diethyl sulphide (1.6 g.) was added to a solution of the sodium tetrachloropalladate (5.2 g.) in ethanol (100 c.c.) and the mixture was kept for 3 days. The solid product was removed, washed with water, and then ethanol, and dried. A further small quantity was obtained from the mother-liquor. It was recrystallised from chloroform by precipitation with light petroleum (b. p. 60–80°) (yield 38%) (Found: C, 18.05; H, 3.8%). It was identical with the product obtained by method A.

Similarly prepared were: *bis*(di-*n*-propyl sulphide)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Pr^u_2S)_2Pd_2Cl_4]$  (recrystallised from carbon tetrachloride; yield 26%) (Found: C, 24.5; H, 4.7%; *M*, ebullioscopic in 1.4% chloroform solution, 604.  $C_{12}H_{28}Cl_4S_2Pd_2$  requires C, 24.4; H, 4.8%; *M*, 592); *bis*(diethyl selenide)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Et_2Se)_2Pd_2Cl_4]$  (recrystallised from ethyl methyl ketone; yield 28%) identical with the product obtained by method A (Found: C, 15.8; H, 3.3%); *bis*(diethyl telluride)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Et_2Te)_2Pd_2Cl_4]$  (recrystallised from methanol; yield 70%), identical with the product obtained by method A (Found: C, 13.3; H, 2.9%); *bis*(di-*n*-propyl telluride)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Pr^u_2Te)_2Pd_2Cl_4]$  (recrystallised from methanol; yield 30%) (Found: C, 18.3; H, 3.55.  $C_{12}H_{28}Cl_4Pd_2Te_2$  requires C, 18.4; H, 3.6%), and *bis*(di-*n*-propyl selenide)dichloro- $\mu\mu'$ -dichlorodipalladium,  $[(Pr^u_2Se)_2Pd_2Cl_4]$ . In the last case no precipitate of the binuclear complex was formed during the reaction. After evaporation of the solvent at 15 mm. the brown residual product was recrystallised from carbon tetrachloride (yield 45%) (Found: C, 21.0; H, 4.1%; *M*, ebullioscopic in 1.0% chloroform solution, 660.  $C_{12}H_{28}Cl_4Pd_2Se_2$  requires C, 21.0; H, 4.1%; *M*, 686).

*Bis(tri-n-propylphosphine)dibromo- $\mu\mu'$ -dibromodipalladium*,  $[(PPr^{\text{n}})_3)_2Pd_2Br_4]$ .—Lithium bromide (12 g.) and sodium tetrachloropalladite hydrate (10 g.) were dissolved in ethanol, and tri-*n*-propylphosphine (4.4 g.) added to this solution under nitrogen. The mixture was then boiled under reflux for 4 hr. The resultant solution was taken to dryness at 15 mm. and the residual *product* recrystallised from acetone (Found: C, 25.55; H, 4.9%; *M*, ebullioscopic in 1% benzene solution, 767.  $C_{18}H_{42}Br_4P_2Pd_2$  requires C, 25.3; H, 5.0%; *M*, 853). In a similar experiment in which acetone was used as solvent and the solution was not boiled but instead was kept at room temperature for 24 hr., a mixture of  $(PPr^{\text{n}})_3)_2PdBr_2$  and  $(PPr^{\text{n}})_3)_2Pd_2Br_4$  resulted. This was separated by extracting the former from the latter with light petroleum (b. p. 80–100°).

*Bis(tri-n-propylphosphine)di-iodo- $\mu\mu'$ -di-iododipalladium*,  $[(PPr^{\text{n}})_3)_2Pd_2I_4]$ .—Lithium iodide (18 g.) in acetone (100 c.c.) and hydrated sodium tetrachloropalladite (10 g.) in acetone (100 c.c.) were mixed, and tri-*n*-propylphosphine (4.3 g.) added under nitrogen. After 18 hr. the solution was taken to dryness at 15 mm. and the residual product was washed with methanol and dried. It was a mixture of  $[(PPr^{\text{n}})_3)_2PdI_2]$  and  $[(PPr^{\text{n}})_3)_2Pd_2I_4]$ . The former was extracted with light petroleum (b. p. 80–100°), and the residue, recrystallised from chloroform, yielded iodine-like crystals (3.5 g.) of the desired *product* (Found: C, 20.9; H, 4.05.  $C_{18}H_{42}I_4P_2Pd_2$  requires C, 20.8; H, 4.1%).

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