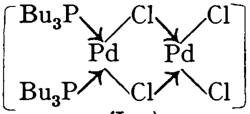
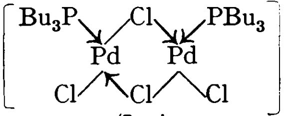
396. *The Constitution of Complex Metallic Salts. Part IX. The Oxalate Radical as a "Bridging Group" between Metallic Atoms. The Structure and Reactions of Dichlorobistri-*n*-butylphosphine-μ-oxalato-dipalladium.*

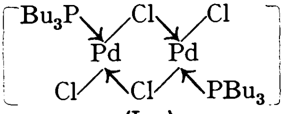
By JOSEPH CHATT, FREDERICK G. MANN, and ALEXANDER F. WELLS.

The palladium atoms in the dichloro-oxalate compound $[(Bu_3P)_2Pd_2Cl_2C_2O_4]$, prepared by the action of potassium oxalate on the tetrachloride $[(Bu_3P)_2Pd_2Cl_4]$, have previously been considered to be bridged by the chlorine atoms, the oxalate radical occupying the unbridged position, *i.e.*, $[(Bu_3P)_2PdCl_2PdC_2O_4]$. In this case the Pd–Pd distance should be *ca.* 3·4 A. If, on the other hand, the palladium atoms were bridged by the oxalate radical, as in $[(Bu_3P(Cl)PdC_2O_4Pd(Cl)PBu_3]$, this distance should be *ca.* 5·3 A. By *X*-ray analysis the Pd–Pd distance has been determined as 5·48 A., and hence in compounds of this type the oxalate radical does bridge the metallic atoms. The chemical reactions of the dichloro-oxalate are described, and discussed on the basis of this constitution.

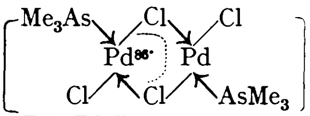
A CONSIDERABLE volume of evidence has been adduced by Mann and Purdie (J., 1936, 873) to show that dichlorobistri-*n*-butylphosphine-μ-dichlorodipalladium, $[(Bu_3P)_2Pd_2Cl_4]$, although existing in only one crystalline form, gives in organic solvents a tautomeric mixture of the unsymmetrical (I A) and the *cis*- and *trans*-symmetrical (I B and I C) isomerides. A crystallographic examination of the corresponding trimethylarsinepalladium chloride and bromide compounds, $[(Me_3As)_2Pd_2X_4]$, then showed that these compounds in the solid state have the *trans*-symmetric structure (II), and the interatomic distances and the intervalency angles were determined in detail (Mann and Wells, this vol., p. 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169).

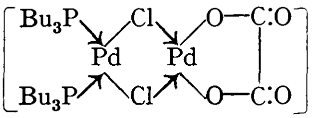

(I A.)


(I B.)


(I C.)

One point cited by Mann and Purdie in favour of the unsymmetrical structure (I A) of the butylphosphinetetrachloro-compound was that it reacted with potassium oxalate to give a dichloro-oxalate, $[(Bu_3P)_2Pd_2Cl_2C_2O_4]$. Now, in complex salts, the oxalate radical had always apparently occupied the *cis*-position by the normal operation of two covalent links, and had indeed been proved to do so in oxalatodiamminopalladium, $[(NH_3)_2PdC_2O_4]$ (Mann, Crowfoot, Gattiker, and Wooster, J., 1935, 1642). Hence it appeared that in the dichloro-oxalate this radical must be similarly attached, and that the compound must therefore have the unsymmetrical structure (III). This conclusion received apparently strong confirmation by the action of αα′-dipyridyl, which split the dichloro-oxalate thus:

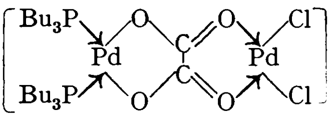
(II.)

Pd—Pd distance = 3·4 A.

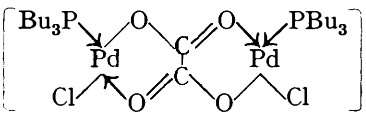

(III.)

$$[(Bu_3P)_2PdCl_2 \vdots PdC_2O_4] + dpy = [(Bu_3P)_2PdCl_2] + [dpy\ PdC_2O_4] \qquad (1)$$

The dinitrito-oxalate $[(Bu_3P)_2Pd_2(NO_2)_2C_2O_4]$ was similarly prepared from the tetranitrite, and was split by dipyridyl into $[(Bu_3P)_2Pd(NO_2)_2]$ and $[dpy\ PdC_2O_4]$, and hence appeared to have the analogous structure $[(Bu_3P)_2Pd(NO_2)_2PdC_2O_4]$.

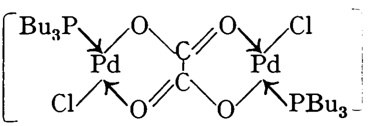
The dipole moment of the dichloro-oxalate in benzene solution was found by Finn, however, to be 3·55 D., whereas the structure (III) should have a value of about 12—14 D. Hence, Finn suggested that in this compound the oxalate group bridged the palladium atoms, and thus that a tautomeric mixture of three forms (IV A, B, and C) again existed in organic solvents. A similar bridging action of the oxalate radical had been ascribed, without experimental evidence, by Weinland ("Komplex-Verbindungen," 1924, 2nd Edtn., p. 410) to the compounds $Pb_2C_2O_4(ClO_4)_2,3H_2O$ (V) and $Pb_2C_2O_4(NO_3)_2,2H_2O$,

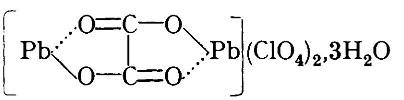
(IV A.)



(IV B.)

but otherwise the suggestion that one oxalate radical could link two metallic atoms by the operation of four co-valencies was novel.

(IV c.)





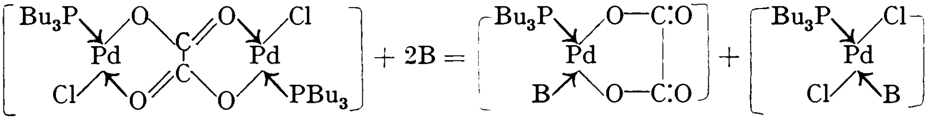
(V.)

Finn's formulation allows resonance to occur around the oxalate rings of the symmetric forms (IVB and c) of the dichloro-oxalate, and the stability of these two forms should thus be increased.

We have therefore obtained further physical and chemical evidence for the structure of the dichloro-oxalate. The physical evidence—by *X*-ray crystal analysis—proves that Finn's formulation is correct: the new chemical evidence, although less decisive, also supports this formulation.

It is known from the dimensions of the molecule of the methylarsinetetrachloro-compound (II) that the palladium atoms bridged by two chlorine atoms are *ca.* 3·4 A. apart, and there is no reason to suppose that the replacement of the arsine by phosphine molecules would sensibly affect this distance. If, however, an oxalate radical bridged the two palladium atoms (as in IV A—C), an inter-palladium distance of *ca.* 5·3 A. would be expected. An *X*-ray examination of the monoclinic crystals of the dichloro-oxalate shows that the Pd—Pd distance is *ca.* 5·48 A., and these metallic atoms must therefore be linked through the oxalate radical and not through two chlorine atoms. Moreover, since there are two molecules per cell in the crystal, and the space-group is probably $P2_1/c$ (see later), the molecules will have a centre of symmetry and thus possess the constitution (IV C).

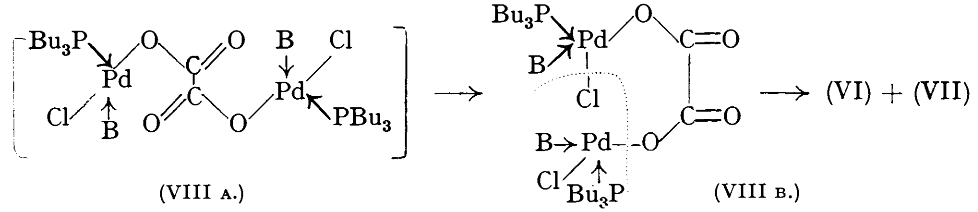
On the chemical side it is noteworthy that the dichloro-oxalate, when treated with 2 mols. of *p*-toluidine at room temperature, breaks down to furnish 1 mol. of *oxalato*-n-*butylphosphine*-p-*toluidinepalladium* (VI) and one of dichloro-butylphosphine-*p*-toluidine-palladium (VII) [Equation (2), in which B represents one mol. of the organic base]. This reaction is extremely difficult to interpret on the basis of formula (III). It is, however,



(2)

(IV C.) (VI.) (VII.)

readily explained on the basis of formula (IV C), since the base would probably first break two links of the oxalate radical, giving the unstable complex (VIII A): free rotation about the C–C link of the oxalate radical is now possible, and the complex (VIII A) can thus assume the form (VIII B).* The strong tendency of the oxalate radical to adopt the very stable *cis*-chelating position on to one metallic atom now causes splitting of the molecule



(VIII A.) (VIII B.)

(as shown by the dotted line) and the consequent formation of the oxalato- and the dichloro-compound, (VI) and (VII). It may be objected that the very ready interchange of groups—both bridged and unbridged—in these dipalladium compounds (cf. Chatt

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* In considering the mechanism of such reactions, the ready interconversion of *cis–trans*-isomerides of 4-covalent palladium, when no chelate group is involved, must always be borne in mind (Mann, Crowfoot, Gattiker, and Wooster, *loc. cit.*).

and Mann, this vol., p. **1949**) renders any precise formulation of the mechanism of their reactions meaningless. It must be borne in mind, however, that this interchange of groups, in spite of its ready occurrence, must be severely controlled by specific factors. This is clearly shown by the fact that the butylphosphinetetrachloro-compound (I, A—C), similarly treated with *p*-toluidine, reacts as in equation (3), a very soluble compound being the sole product; if, however, the constituent groups were entirely free for mutual

$$[Bu_3P(Cl)PdCl_2Pd(Cl)PBu_3] + 2B = 2[Bu_3P(B)PdCl_2] \quad . \; . \; . \quad (3)$$

rearrangement, the dichlorobisphosphinepalladium, $[(Bu_3P)_2PdCl_2]$, and the dichlorobis-*p*-toluidinepalladium, $[B_2PdCl_2]$, would preferentially be produced, since the latter is almost insoluble in the usual organic solvents (Gutbier, *Ber.*, 1905, **38**, 2110).

When the dichloro-oxalate is treated with 2 mols. of ethylthiol, oxalic acid is split off and dichlorobisbutylphosphine-μ-bisethylthioldipalladium is formed (4). In view of the vigorous

$$[Bu_3P(Cl)PdC_2O_4Pd(Cl)PBu_3] + 2EtSH = [Bu_3P(Cl)Pd(SEt)_2Pd(Cl)PBu_3] + (COOH)_2 \; . \; (4)$$

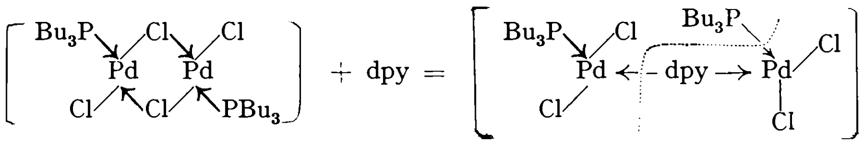
bridging properties of the EtS radical (Chatt and Mann, *loc. cit.*) and the several reactions previously investigated in which the bridging groups have been shown to be preferentially displaced by other radicals, this action of the ethylthiol is not unexpected. An intermediate phase probably occurs here also, in which two covalent bonds joining the oxalate radical to the palladium atoms are severed by the thiol residues, followed by complete ejection of oxalic acid and the formation of the very stable bisethylthiol derivative.

It is clear, however, from the above results that the action of αα′-dipyridyl on bridged dipalladium compounds cannot be the simple "vertical splitting" shown in equation (1). It is probable that the action of dipyridyl on the tetrachloride, hitherto formulated in accordance with equation (5), consists actually of the fission of the ring in the symmetric

$$[(Bu_3P)_2PdCl_2 \vdots PdCl_2] + dpy = [(Bu_3P)_2PdCl_2] + [dpy\ PdCl_2] \quad . \; . \quad (5)$$

form (I B or I C) by the co-ordination of the dipyridyl, producing the complex (IX): the strong *cis*-co-ordinating properties of the dipyridyl then cause the fission indicated by the

(I c.)



(IX.)

dotted line, with formation of the two dichloro-compounds shown in equation (5). The action of dipyridyl, irrespective of its mechanism, can no longer, however, be cited as evidence of unsymmetrical structures such as (I A) and (III). It should be emphasised, however, that nevertheless there still remains a considerable volume of other evidence in support of the existence of the unsymmetric form of bridged dipalladium compounds in solution (Mann and Purdie, *loc. cit.*).

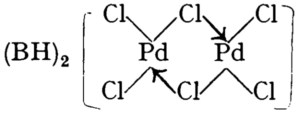
We have attempted to prepare the dichloro-oxalate (IV) by the interaction of *oxalatobis-*n-*butylphosphinepalladium*, $[(Bu_3P)_2PdC_2O_4]$, and ammonium palladochloride. The final product was, however, the tetrachloro-compound (I). The reaction consists first in a simple double decomposition forming the butylphosphinedichloro-compound and ammonium palladodichloro-oxalate, followed by the interaction of these two compounds to give the bridged tetrachloro-compound and ammonium oxalate:

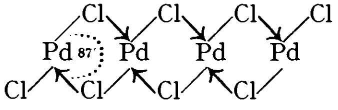
$$[(Bu_3P)_2PdC_2O_4] + (NH_4)_2[PdCl_4] = [(Bu_3P)_2PdCl_2] + (NH_4)_2[PdCl_2C_2O_4]$$
$$[(Bu_3P)_2PdCl_2] + (NH_4)_2[PdCl_2C_2O_4] = [(Bu_3P)_2Pd_2Cl_4] + (NH_4)_2C_2O_4$$

This mechanism is confirmed by (i) the isolation of $[(Bu_3P)_2PdCl_2]$ when the reaction was arrested before completion, and (ii) by the production of small quantities of dichlorodiamminopalladium, $[(NH_3)_2PdCl_2]$, and oxalic acid by the decomposition of a portion of the ammonium palladodichloro-oxalate. When calcium palladochloride was used, the butylphosphinetetrachloro-compound was formed very readily, owing to the insolubility of the calcium oxalate.

All the bridged palladium compounds discussed in the present series of investigations have consisted of neutral non-ionic molecules. It is clear, however, that a bridged palladium structure may possibly occur in an anion or a cation. For instance, Gutbier and Fellner (*Z. anorg. Chem.*, 1916, **95**, 169) have described a number of salts of amine hydrochlorides with palladous dichloride, to which they assigned the general formula $B,H[PdCl_3]$. It is very unlikely that the anion in these compounds contains 3-covalent palladium. It is almost certain that these compounds have the " double " formula $(BH)_2[Pd_2Cl_6]$ and

(X.)





(XI.)

the structure (X), in which the anion contains two palladium atoms, bridged through chlorine atoms. This bridged formulation is strongly supported by the structure of palladium dichloride, which has been shown by one of us (Wells, *Z. Krist.*, 1938, **100**, 189) to consist of long chains of palladium atoms bridged through chlorine atoms as in (XI) : here it is probably the deficiency of electrons on the terminal palladium atoms that causes the production of the chains of indefinite length proceeding throughout the crystals. In Gutbier and Fellner's compounds this deficiency of electrons does not occur, and the chain is thus limited to two palladium atoms. It is noteworthy that the intervalency angle between palladium and two adjacent chlorine atoms in the 4-membered ring of palladium chloride is 87° : the analogous angle in the bridged trimethylarsine compound (II) is 86°, and the identity of the two types of ring is thus strongly confirmed. The structure of the compounds (X) is now being investigated.

EXPERIMENTAL.

Crystallographic Data.

The dichloro-oxalate, $[(Bu_3P)_2Pd_2Cl_2C_2O_4]$, forms yellow monoclinic crystals, usually flat plates (010) elongated along the *c* axis. The crystals are pleochroic, the light transmitted varying from pale to deep yellow. Oscillation and Weissenberg photographs (Cu-K_α) gave the following cell dimensions : $a = 9{\cdot}95$, $b = 23{\cdot}0$, $c = 7{\cdot}98$ A., $\beta = 83°$, all $\pm \frac{1}{2}\%$. The density was not determined since that of $[(Bu_3P)_2Pd_2Cl_4]$ is known to be 1·43 g./c.c. (Mann and Purdie, *loc. cit.*). For 2 molecules of $[(Bu_3P)_2Pd_2Cl_2C_2O_4]$ in the above cell the calculated density is 1·42 g./c.c. The orders $0k0$ are halved and $h0l$ is absent for l odd except for a trace of the reflexion $10\bar{1}$. This reflexion was observed both on a [010] Weissenberg photograph and on an oscillation photograph about [001] taken with monochromatic Cu-K_α radiation and hence must be regarded as a genuine reflexion. Since, however, it is extremely weak and is the only reflexion $h0l$ with l odd observed, the space group is effectively $P\,2_1/c$. There is no sign of pyroelectricity when the crystals are tested in liquid air.

The placing of 2 molecules in the space group $P\,2_1/c$ would imply that the molecules are centro-symmetrical and would immediately establish the constitution of the molecule as (IV C). Since, however, it may be objected that the presence of $10\bar{1}$ invalidates this argument, the approximate positions of the palladium atoms were established by direct methods involving no assumptions as to the space group. If these atoms are bridged by two chlorine atoms, then the Pd–Pd separation within the molecule will be approximately 3·4 A. ; if by an oxalate group, it will be *ca.* 5·3 A. From the intensities of $hk0$ and $0kl$ reflexions estimated visually on Weissenberg photographs about [001] and [100] respectively, F^2-projections along these axes were made. Since palladium is by far the heaviest atom in the molecule, it is possible to distinguish the Pd–Pd peaks in these projections and to determine the approximate positions of the palladium atoms in the unit cell. It is found that they are at : xyz; $\overline{xyz}$; $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$ with the approximate parameters $x = 1/10$, $y = 1/10$ and $z = 1/8$. The intramolecular Pd–Pd separation calculated from these parameters is 5·48 A., proving conclusively that these metallic atoms are bridged by an oxalate radical (as in IV A—C) and not by two chlorine atoms.

The above arrangement of the palladium atoms, determined without making any assumptions regarding the space group, has the symmetry of $P\,2_1/c$. There are two possible explanations of the presence of the reflexion $10\bar{1}$.

(1) The true space group is $P\,2_1$, with $P\,2_1/c$ as the pseudo-space group. For the molecule (IV c) we should have to assume some slight distortion which destroys the centro-symmetry. The molecule might, however, be (IV A) or (IV B), the pseudo-symmetry being due to the similarity in scattering power of the phosphorus and the chlorine atoms.

(2) The true space group is $P\,2_1/c$, and the reflexion 101 is not a primary reflexion but is due to *X*-rays which have been reflected successively by two planes in the crystal. This phenomenon has been discussed by Renninger (*Z. Physik*, 1937, **106**, 141) and by Brandenberger (*Z. Krist.*, 1937, **97**, 476) and probably explains the presence of the " forbidden " reflexion $10\bar{1}$.

hkl.	f_{Pd}.	$F'_{obs.}$.	*hkl.*	f_{Pd}.	$F'_{obs.}$.	*hkl.*	f_{Pd}.	$F'_{obs.}$.	*hkl.*	f_{Pd}.	$F'_{obs.}$.
100	3·2	50	290	2·2	20	510	0	—	011	2·3	13
200	1·2	7	2100	1·2	7	520	1·2	—	021	2·7	40
300	1·2	—	310	2·2	22	530	0	—	031	0·8	—
400	3·2	27	320	0·4	16	540	3·2	16	041	1·6	—
500	4·0	21	330	3·6	24	550	0	—	051	2·8	—
			340	1·0	21	560	3·2	11	012	2·4	26
110	1·4	30	350	0	5	570	0	—	022	0	—
120	1·0	15	360	1·0	4	580	1·2	—	032	3·8	24
130	2·2	31	370	3·6	14	590	0	—	042	0	—
140	3·6	29	380	0·4	—	5100	4·0	11	052	0	—
150	0	8	390	1·2	12				013	2·2	11
160	2·6	21	3100	1·2	5	020	1·2	64	023	2·7	16
170	2·2	7	410	1·4	5	040	3·2	33	033	0·8	7
180	1·0	—	420	1·0	—	060	3·2	—	043	1·6	5
190	1·4	10	430	2·2	—	080	1·2	—	053	2·8	13
1100	3·2	29	440	2·6	20	0100	4·0	35	014	0	—
210	2·2	40	450	0	—				024	1·2	15
220	0·4	7	460	2·6	5	001	0	—	034	0	—
230	3·6	32	470	2·2	—	002	0	—	044	3·2	18
240	1·0	—	480	1·0	—	003	0	—	054	0	—
250	0	—	490	1·4	7	004	4·0	30	015	2·3	12
260	1·0	—	4100	3·2	22	005	0	—	025	2·7	10
270	3·2	25							035	0·8	—
280	0·4	—							045	1·8	—
									055	2·8	15

In the accompanying table the contributions from the four palladium atoms towards a number of reflexions are compared with the observed structure factors (on an arbitrary scale). Complete agreement, particularly for low orders, is not to be expected since all other atoms have been neglected, but it will be seen that the above palladium parameters account satisfactorily for many of the major intensity differences.

Chemical Data.

Mann and Purdie's preparation of the dichloro-oxalate (IV) (*loc. cit.*) is greatly improved by the following modifications. A solution of potassium oxalate (30 g.) in water (240 c.c.) was added to one of the butylphospbinetetrachloro-compound (I; 12 g.) in boiling alcohol (60 c.c.), and the mixture immediately heated on a water-bath with occasional shaking. The tetrachloro-compound which had been precipitated by the aqueous solution slowly redissolved, and fine crystals of the dichloro-oxalate separated; after 30 minutes' heating, the solution was rapidly cooled in ice. (The time of heating is important, since reduction to metallic palladium begins to occur after about 35 minutes' heating.) The dichloro-oxalate which separated during the cooling was collected, washed with alcohol and water, dried, and recrystallised from benzene (charcoal). Yield, 7 g. Well-formed crystals for *X*-ray investigation were obtained by spontaneous evaporation of a solution in carbon tetrachloride.

Reactions of the Dichloro-oxalate (IV).—(1) *With* p-*toluidine.* Solutions of the dichloro-oxalate (4 g.) and of *p*-toluidine (1·1 g.; 2 mols.) in benzene (80 c.c. and 20 c.c respectively) were mixed, an immediate change of colour occurring. The greenish-yellow solid which slowly separated was collected after 24 hours, and recrystallised from ethyl carbonate, from which it separated at first as a gel, and therefore required continuous stirring during cooling. The *oxalato-*n*-butylphosphine-*p*-toluidinepalladium* was thus obtained as a pale greenish-yellow microcrystalline powder, which decomposed at 177° (Found: C, 50·3; H, 7·4; N, 2·7; Pd, 21·4. $C_{21}H_{36}O_4NPPd$ requires C, 50·0; H, 7·2; N, 2·8; Pd, 21·1%). The benzene filtrate on spontaneous evaporation gave dichlorobutylphosphine-*p*-toluidinepalladium, which after recrystallisation from methyl alcohol had m. p. 78—79°, both alone and when mixed with an authentic specimen.

The identity of the above oxalato-compound was further confirmed by boiling a suspension of it in dilute hydrochloric acid under reflux for 1½ hours, decomposition occurring with the formation of the tetrachloro-compound (I). The latter, when collected, and recrystallised from *cyclo*hexane, had m. p. 145° (alone and mixed). The hydrochloric acid solution gave positive tests for *p*-toluidine and oxalic acid.

There is some evidence that the crystals of the above oxalato-compound can occlude certain organic solvents, presumably in the spaces between the oxalate molecules in the crystal, a phenomenon that was discovered for the inclusion of dioxan molecules in the crystals of $[(Me_3As)_2Pd_2Cl_4]$ and $[(Me_3As)_2Pd_2Br_4]$ (Mann and Wells, *loc. cit.*). For instance, the oxalato-compound which separated from the above benzene solution, when dried and analysed directly, always gave high and variable values for carbon, and low values for palladium (*e.g.*, C, 52·8, 52·4; H, 7·6, 7·2; N, 2·7; Pd, 20·7%), and this discrepancy was even more pronounced after recrystallisation from aqueous alcohol (*e.g.*, C, 48·9, 49·4; H, 8·1, 7·9; N, 2·7; Pd, 20·0%): both samples became analytically pure, however, after recrystallisation from ethyl carbonate. When the original preparation was carried out in acetone, the oxalato-compound separated much more rapidly, particularly on scratching. The first fraction of minute crystals, collected within 3 minutes of mixing the original solutions in acetone, was analytically pure (Found: C, 49·8; H, 7·3; Pd, 20·9%). When, however, the oxalato-compound was collected 24 hours after mixing the acetone solutions, larger crystals were obtained, and these retained acetone after drying in a vacuum for several hours (*e.g.*, C, 52·7, 52·9, 52·4; H, 7·5, 7·45, 7·4; N, 2·7; Pd, 17·5%). When a portion of these crystals was boiled with hydrochloric acid as above, and the aqueous solution distilled, the distillate gave strongly positive tests for acetone; when, however a second portion was recrystallised from ethyl carbonate, the analytically pure oxalato-compound was again obtained. Ethyl carbonate is therefore not occluded by the oxalato-compound, either because of the size or shape of the carbonate molecules, or because the oxalate separates as a gel and then gives a microcrystalline powder.

(2) *With ethylthiol.* Ethylthiol (0·22 c.c.; 2·3 mols.) was added to a solution of the dichloro-oxalate (1 g.) in cold alcohol (250 c.c.); the mixed solutions immediately became red, and later faded to yellow. On spontaneous evaporation, a mixture of yellow and white crystals remained. Extraction with cold water removed the white crystals, which were identified as oxalic acid. The residual yellow crystals were dried and recrystallised from alcohol, pure dichlorobisbutylphosphine-μ-bisethylthioldipalladium being obtained, m. p. 116—118° (alone and mixed).

Oxalatobis-n-*butylphosphinepalladium*.—(1) *Preparation.* A solution of $K_2[Pd(C_2O_4)_2],3H_2O$ (5 g.) in warm water (400 c.c.) was cooled with shaking until crystallisation began; butylphosphine (5·7 g.; 2 mols.), dissolved in alcohol (10 c.c.), was immediately added, and the mixture shaken vigorously for 4 hours. The solid product was collected, dried, and extracted with boiling alcohol (100 c.c.). The alcoholic filtrate, when concentrated under reduced pressure, deposited the above *oxalato*-compound. The latter was collected, and recrystallised from *cyclo*hexane (500 c.c.) containing sufficient alcohol (*ca.* 2%) to give a clear hot solution, and so obtained as colourless thread-like crystals, which on heating darkened at 170—175° and melted at 175—180° (decomp.) (Found: C, 51·8; H, 9·15; Pd, 17·9. $C_{26}H_{54}O_4P_2Pd$ requires C, 52·1; H, 9·1; Pd, 17·8%). Yield, 5 g. The oxalate is very soluble in cold alcohol and benzene, but almost insoluble in *cyclo*hexane.

(2) *Action of ammonium palladochloride.* Solutions of the oxalate (1 g.) and of the palladochloride (0·48 g.; 1 mol.) in alcohol (30 c.c.) and water (5 c.c.), respectively, were mixed and boiled under reflux for 30 minutes, during which a small quantity of yellow crystals contaminated by a trace of palladium separated. The yellow crystals were collected from the hot solution, and the filtrate on cooling deposited the red bridged tetrachloro-compound (I), which after recrystallisation from alcohol had m. p. 145—146°, alone and when mixed with an authentic sample. The yellow crystals were recrystallised from much boiling water, and found to be dichlorodiamminopalladium (Found: N, 13·4. Calc. for $H_6N_2Cl_2Pd$: N, 13·2%).

To identify the intermediate compound which must be formed in the above reaction, the experiment was repeated, but the mixed aqueous-alcoholic solutions were heated at 40—50° for 30 minutes instead of being boiled under reflux. The warm filtrate was allowed to cool and was then set aside for 2 days. A small quantity of the bridged tetrachloride was then collected, and the filtrate subsequently deposited the unbridged dichlorobisbutylphosphinepalladium, $[(Bu_3P)_2PdCl_2]$, which after recrystallisation from alcohol had m. p. 65—66° (alone and mixed).

It is clear therefore that the oxalate radical in $[(Bu_3P)_2PdC_2O_4]$ can be readily replaced by the chlorine groups. This was confirmed by mixing warm aqueous-alcoholic solutions of the oxalate and of ammonium chloride, whereupon a yellow colour immediately appeared:

$$[(Bu_3P)_2PdC_2O_4] + 2NH_4Cl \rightleftarrows [(Bu_3P)_2PdCl_2] + (NH_4)_2C_2O_4$$

The colour must be due to $[(Bu_3P)_2PdCl_2]$, which is the only coloured component in the above equilibrium.

The small quantity of $[(NH_3)_2PdCl_2]$ which separated during the reaction (2) above was clearly formed by the decomposition of the ammonium palladodichloro-oxalate. This is shown by the fact that when concentrated solutions of potassium (or ammonium) oxalate and of ammonium palladochloride are mixed, the dichlorodiamminopalladium rapidly separates, and hence potassium (or ammonium) pallado-oxalate cannot be prepared in this way.

$$(COOK)_2 + (NH_4)_2[PdCl_4] \longrightarrow 2KCl + (NH_4)_2[PdCl_2C_2O_4] \longrightarrow [(NH_3)_2PdCl_2] + (COOH)_2$$

(3) *Action of calcium palladochloride.* Solutions of the oxalate (1 g.) and of the palladochloride (0·6 g.; 1 mol.) in alcohol (40 c.c.) and water (2 c.c.), respectively, were mixed and boiled gently under reflux for 30 minutes. A dark sludge was then collected, and the red filtrate on cooling deposited the bridged tetrachloro-compound (I) in good yield (m. p., alone and mixed, 145—146°). The sludge was identified as calcium oxalate containing finely divided palladium.

*Dichlorobis-*p*-toluidinepalladium*, $[(C_6H_4Me{\cdot}NH_2)_2PdCl_2]$.—Gutbier (*loc. cit.*) prepared this compound by heating palladium dichloride with excess of *p*-toluidine hydrochloride until a clear solution was obtained. We have prepared it by the direct interaction of hot solutions of the amine (0·8 g.; 2 mols.) and of ammonium palladochloride (1 g.) in alcohol (40 c.c.) and water (10 c.c.), respectively. An immediate precipitate of fine, pale orange-yellow, acicular crystals of the above dichloro-compound appeared; after 10 minutes' shaking they were collected, washed with water and alcohol, and dried (Found: N, 7·05. Calc. for $C_{14}H_{18}N_2Cl_2Pd$: N, 7·2%). This compound is almost insoluble in boiling alcohol, acetone, and water, and its non-formation during the interaction of the bridged tetrachloro-compound (I) and *p*-toluidine in alcoholic solution (p. 2089) proves that this reaction cannot be a simple double decomposition of the various groups present to form the least soluble product. The dichloro-compound is, however, more soluble in hot dioxan and glycol monoethyl ether acetate, and can be recrystallised from these solvents. It dissolves in, and is reduced by, hot glycol monoethyl ether.

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