Table 8. *Geometry in the hydrogen bonds*

Donor (D)-H	Acceptor (A)	Distance $D\cdots A$	Distance $H\cdots A$	Angle D-H$\cdots A$
O(5)-H(15)	O(6) $-x$ $2-y$ $1-z$	2·764 (6) Å	1·95 (7) Å	158 (6)°
O(6)-H(16)	O(5) x y $1+z$	2·785 (6)	2·21 (7)	140 (6)

carboxyl group moiety in the ester when compared with free acids in general. These findings are corroborated by other analyses of esters as Table 7 shows.

The hydrogen-bonding system in the *meso*-tartaric acid ester is very similar to that found in the racemic acid dihydrate (Parry, 1951) and the triclinic modifications of *meso*-tartaric acid (Bootsma & Schoone, 1967). Each hydroxyl group takes part in two hydrogen bonds, as shown in Fig. 4. One hydroxyl group is connected to a hydroxyl group of an antipode molecule [O(5)–H(15)···O′(6)] and the other one with a hydroxyl group of a molecule of the same configuration shifted one period along the c axis [O(6)–H(16)···O″(5)] (Table 8).

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The Crystal and Molecular Structure of Diiodobis(triphenylphosphine)palladium(II)

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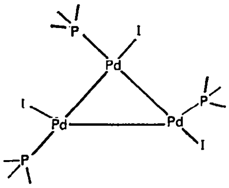
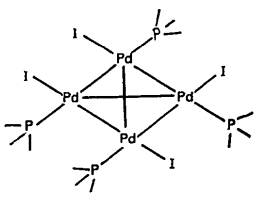
The compound crystallizes in the form of monoclinic yellow needles; $a=11{\cdot}922$, $b=20{\cdot}432$, $c=8{\cdot}35$ Å, $\beta=95{\cdot}18°$, space group $P2_1/c$. The palladium atom is on an inversion centre which is the centre of an octahedron formed by the atoms of iodine, phosphorus and the hydrogen on a β carbon of a phenyl ring.

Introduction

Schmid & Weber (1971) have pointed out the interest of the X-ray structure analysis of a compound for which the chemical analysis of carbon, iodine and hydrogen had suggested the formula $[(C_6H_5)_3PPdI]_n$, in which n was unknown but greater than 2, and probably equal to 3 or 4, where the molecules were linked together by metal–metal bonds. The structures were supposed to be of the form:





Usually, palladium(II) with a d^8 configuration forms quadratic complexes with 4 ligands. This is the case for *n* equals three, but other forms where no metal-metal bond exists have been reported (Bailey & Mason, 1968).

Crystal data

Diiodobis(triphenylphosphine)palladium(II) crystallizes in the form of yellow needles with two molecules of the solvent, dichloromethane: $[(C_6H_5)_3P]_2PdI_2.2CH_2Cl_2$.

The lattice constants, space group and density are given in Table 1(*a*); these values are compared with those from the two crystalline forms of diiodobis(dimethylphenylphosphine)palladium(II) (Bailey & Mason, 1968) in Table 1(*b*).

Experimental

The intensities of 3818 unique reflexions were measured using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) with a graphite monochromator on an automatic four-circle Philips PW 1100 diffractometer. Each reflexion was scanned in 20 sec at a speed of 0·05° $\sec^{-1}$; the background was measured at the beginning and end of the peak scan each time for 2 sec. Each hour the intensity and location of 3 reference reflexions were measured, these did not show any significant variation during the measurement. The background value used was set equal to $\frac{2}{3}(B_1+B_2+B_{\sin\theta})$, where $B_{\sin\theta}$ is the average background value taken as a function of sin θ. Out of the 3818 reflexions, 1102 were unobserved, a reflexion being considered as unobserved when $I_0 \le 2{\cdot}5 * \sigma(I_0)$, where $\sigma = \sqrt{N+B_1+B_2}$, N = peak count and B_1, B_2 are the background counts. The appropriate background value and the Lorentz and polarization corrections were computed for each reflexion by our data reduction program; the data were not corrected for absorption.

Table 1. *Crystallographic data*

(*a*) Crystal data for the title compound.
Diiodobis(triphenylphosphine)palladium(II)
$[(C_6H_5)_3P]_2Pd\ I_2.2CH_2Cl_2$
Molecular weight 1054·66

Monoclinic, $a = 11{\cdot}922$ (5) Å	Space group $P2_1/c$
$b = 20{\cdot}432$ (15)	$Z = 2$
$c = 8{\cdot}35$ (2)	$F(000) = 1024$
$\alpha = \gamma = 90°$	
$\beta = 95{\cdot}18$ (6)°	
Volume 2019·00 Å^3	

$D_{calc} = 1{\cdot}74$, $D_{meas} = 1{\cdot}67$ g cm^{-3} (by flotation in a $KI.H_2O$ solution).

Structure analysis

From examination of a three-dimensional Patterson synthesis it appeared that the palladium atom occupied a special position of the space group. We fixed the palladium atom with the coordinates (0,0,0). The coordinates of the iodine and phosphorus atoms were also obtained from the Patterson map. After two cycles of least-squares refinement with these atoms, we computed a difference-Fourier synthesis which showed the carbon atoms of the three independent phenyl rings of the molecule. Three strong peaks, which did not belong to the molecule, remained; later they were identified as a molecule of the solvent, dichloromethane.

The refinement of the parameters was carried out with the full-matrix least-squares program of the X-ray 70 system. From the beginning of the refinement only the 2716 observed reflexions were used. The values of the atomic form factors were those from Hanson, Herman, Lea & Skillman (1964). The Hughes weighting scheme was used: $\sigma = 3{\cdot}36$ for $F_{obs} < 11{\cdot}7$ and $\sigma = 0{\cdot}051 * F_{obs}$ for $F_{obs} \ge 11{\cdot}7$. The quantity minimized is $\sum w(F_o - kF_c)^2$, where $w = 1/\sigma^2$ and k is a scale factor.

In the initial stages of the refinement isotropic temperature factors were used, later an anisotropic tem-

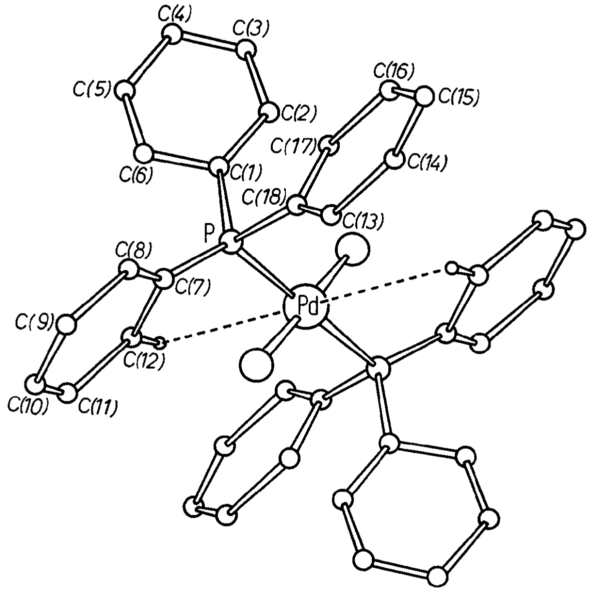


Fig. 1. Molecular geometry of the molecule.

Table 1 (*cont.*)

(*b*) Comparison between the different crystallographic data.

	Space group	Z	a	b	c	β	D_m	D_c
Diiodobis(tri-φ-phos)Pd (This work)	$P2_1/c$	2	11·898 Å	20·452 Å	8·332 Å	95·244°	1·58 g cm^{-3}	1·53 g cm^{-3}
Diiodobis(di-me-φ-phos) Pd (Bailey & Mason, 1968)								
Form 1: red isomer	$P2_12_12_1$	4	8·79	13·06	17·82		2·06	2·067
Form 2: yellow isomer	$P2_1/c$	2	10·20	10·71	10·23	111·7	2·03	2·035

perature factor was introduced for all the 24 atoms. The temperature factor is of the form $T=\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. The refinement was stopped when the parameter shifts were less than than 0·10 of the estimated standard deviation: at this stage the R value was 0·064 and the weighted R_w value 0·081. The quantity $\sqrt{\sum w(F_o-F_c)^2/(NO-M)}$ is equal to 0·98. The R value is defined as:

$$R=\frac{\sum(|F_o|-|F_c|)}{\sum|F_o|},$$

and

$$R_w=\frac{\sum w(|F_o|-|F_c|)}{\sum w|F_o|},$$

NO is the total number of reflexions and M is the number of variable parameters. The atomic positional and vibrational parameters are given in Table 2, intra-

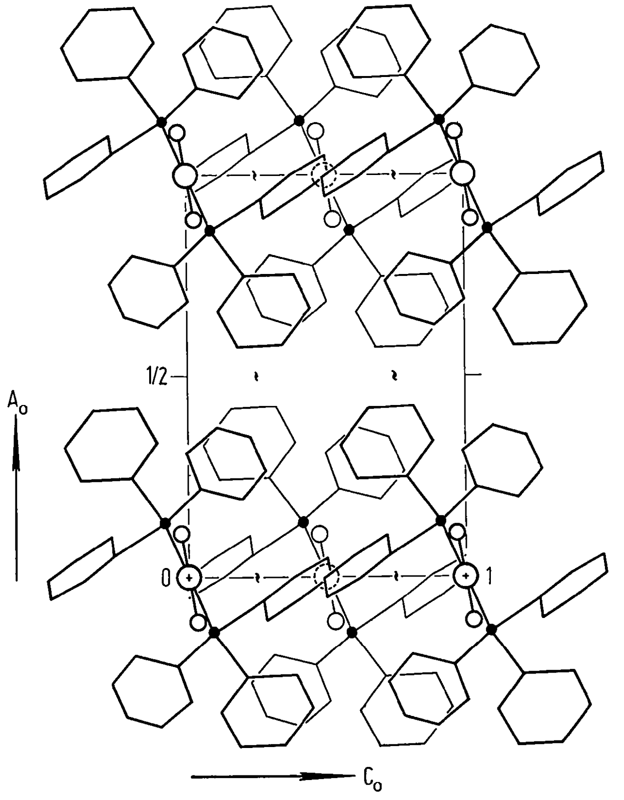


Fig. 2. Packing of the molecules in the unit cell.

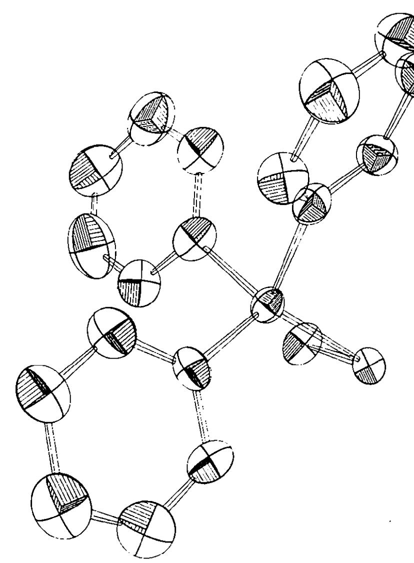


Fig. 3. Thermal ellipsoids of the asymmetric part of the molecule of $[(C_6H_5)_3P]_2PdI_2$.

Table 2. *Atomic positional* ($\times 10^4$) *and vibrational parameters with estimated standard deviations in parentheses*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0·0	0·0	0·0	2·64 (4)	1·91 (3)	2·93 (4)	0·00 (5)	0·75 (4)	0·25 (4)
I	1086·3 (5)	1082·4 (2)	−310·2 (7)	4·54 (3)	2·73 (3)	5·23 (6)	0·53 (19)	1·57 (2)	0·29 (19)
P	1381·2 (14)	−621·1 (8)	−898·4 (19)	2·50 (9)	2·11 (8)	2·70 (9)	0·2 (5)	0·6 (6)	−0·03 (4)
C(1)	2506 (7)	−210 (4)	−2068 (9)	4·2 (4)	2·7 (3)	4·2 (4)	−0·2 (11)	1·2 (3)	0·4 (3)
C(2)	3384 (8)	+96 (4)	−1117 (11)	4·1 (4)	3·6 (3)	5·4 (4)	0·3 (3)	0·6 (3)	0·3 (3)
C(3)	4244 (9)	+438 (7)	−1825 (17)	5·2 (5)	5·6 (6)	10·2 (9)	1·1 (1·3)	−0·6 (5)	−1·0 (1·0)
C(4)	4233 (10)	+472 (6)	−3413 (15)	6·5 (6)	5·1 (6)	6·8 (5)	1·4 (1·0)	2·2 (8)	−0·6 (8)
C(5)	3303 (10)	+164 (6)	−4468 (14)	5·6 (4)	6·6 (3)	6·1 (3)	−0·6 (3)	2·4 (3)	−1·4 (3)
C(6)	2470 (8)	−182 (4)	−3798 (11)	5·2 (4)	3·8 (4)	5·1 (4)	0·4 (3)	1·8 (3)	0·4 (8)
C(7)	770 (5)	−1170 (3)	−2675 (8)	2·7 (3)	2·9 (3)	3·1 (3)	−0·3 (1·7)	0·9 (3)	−0·2 (1)
C(8)	1044 (7)	−1823 (4)	−2804 (10)	4·4 (3)	2·5 (3)	4·0 (4)	−0·1 (3)	0·6 (3)	−0·2 (3)
C(9)	509 (8)	−2206 (5)	−4027 (12)	5·1 (4)	3·3 (4)	5·5 (4)	−0·1 (3)	−0·1 (6)	−0·5 (4)
C(10)	−289 (8)	−1917 (5)	−5116 (10)	4·9 (4)	5·0 (4)	3·9 (4)	−0·7 (3)	0·2 (3)	−0·7 (3)
C(11)	−519 (7)	−1267 (4)	−5019 (9)	4·0 (4)	4·5 (5)	3·1 (4)	0·2 (3)	−0·5 (3)	−0·1 (3)
C(12)	−32 (6)	−877 (4)	−3783 (8)	3·5 (3)	3·6 (3)	2·9 (3)	0·5 (2)	0·1 (2)	0·1 (3)
C(13)	2234 (6)	−1126 (3)	406 (8)	2·5 (3)	3·0 (3)	3·2 (3)	0·0 (2)	−0·8 (2)	0·3 (2)
C(14)	1965 (7)	−1165 (4)	1963 (9)	3·8 (3)	3·8 (3)	3·2 (3)	0·4 (3)	0·2 (3)	0·1 (2)
C(15)	2629 (10)	−1497 (5)	3105 (13)	5·9 (4)	3·9 (4)	5·1 (5)	0·3 (3)	−0·5 (4)	0·0 (2)
C(16)	3488 (8)	−1838 (5)	2755 (12)	5·0 (3)	3·2 (3)	6·3 (4)	0·7 (3)	−0·2 (4)	−1·2 (3)
C(17)	3729 (7)	−1840 (5)	1034 (11)	4·3 (4)	4·0 (4)	4·8 (4)	−0·1 (5)	−0·6 (3)	−0·7 (3)
C(18)	3115 (7)	−1470 (4)	−51 (11)	3·8 (3)	4·2 (4)	4·0 (4)	0·1 (2)	−0·1 (3)	−0·1 (4)
Cl(1)	4483 (4)	1485 (3)	2705 (6)	10·1 (1·1)					
Cl(2)	3134 (4)	2685 (3)	2872 (7)	10·6 (1·2)					
C(19)	3224 (16)	1805 (11)	3127 (21)	9·2 (7)					

Table 3. *Interatomic bond distances and angles*

(*a*) Interatomic distances with standard deviations in parentheses.

Pd–P	2·331 (2) Å
Pd–I	2·587 (1)
P–C(1)	1·828 (8)
P–C(7)	1·826 (7)
P–C(13)	1·855 (8)
C(1)–C(2)	1·40 (1)
C(2)–C(3)	1·41 (2)
C(3)–C(4)	1·32 (2)
C(4)–C(5)	1·49 (2)
C(5)–C(6)	1·38 (2)
C(6)–C(1)	1·44 (1)
Mean	1·40
Cl(2)–Cl(2)	2·941 (8) Å
Cl(1)–C(19)	1·70 (2)
Cl(2)–C(19)	1·81 (2)
C(7)—C(8)	1·38 (1)
C(8)—C(9)	1·39 (1)
C(9)—C(10)	1·38 (1)
C(10)–C(11)	1·36 (1)
C(11)–C(12)	1·39 (1)
C(12)–C(7)	1·40 (1)
Mean	1·38
C(13)–C(14)	1·37 (1) Å
C(14)–C(15)	1·36 (1)
C(15)–C(16)	1·29 (1)
C(16)–C(17)	1·49 (2)
C(17)–C(18)	1·34 (2)
C(18)–C(13)	1·35 (1)
Mean	1·36

(*b*) Interatomic angles with estimated standard deviations in parentheses.

I——Pd–P	87·1 (1)°
C(7)—P—Pd	111·7 (2)
C(13)–P—Pd	113·4 (2)
C(1)—P—Pd	119·6 (3)
C(1)—P—C(7)	103·0 (3)
C(1)—P—C(13)	100·2 (3)
C(7)—P—C(13)	107·5 (3)
C(2)-C(1)-C(6)	120·1°
C(1)-C(2)-C(3)	121·1
C(2)-C(3)-C(4)	120·1
C(3)-C(4)-C(5)	120·5
C(4)-C(5)-C(6)	120·1
C(5)-C(6)-C(1)	118·0
Mean	120·0
C(8)—C(7)—C(12)	120·9°
C(7)—C(8)—C(9)	120·4
C(8)—C(9)—C(10)	118·7
C(9)—C(10)-C(11)	120·5
C(10)-C(11)-C(12)	122·2
C(11)-C(12)-C(7)	117·2
Mean	120·0
C(14)-C(13)-C(18)	119·6°
C(13)-C(14)-C(15)	121·4
C(14)-C(15)-C(16)	122·2
C(15)-C(16)-C(17)	116·4
C(16)-C(17)-C(18)	120·5
C(17)-C(18)-C(13)	119·6
Mean	120·0
Cl(1)-C(19)-Cl(2)	113·7°

For the C–C–C angles in the phenyl rings the average standard deviation is ± 1·0°.

Table 4. *Anisotropic thermal ellipsoids for* $[(C_6H_5)_3P]_2PdI_2$

		R.M.S.D	Direction cosines		
Pd	*x*	0·153	0·0	0·0	1·000
	y	0·178	0·836	0·548	0·0
	z	0·198	−0·548	0·836	0·0
I	*x*	0·180	0·254	−0·006	0·967
	y	0·215	−0·786	0·582	0·210
	z	0·277	−0·564	−0·813	0·143
P	*x*	0·160	0·591	−0·267	0·761
	y	0·173	−0·581	0·514	0·631
	z	0·192	−0·560	−0·815	0·149
C(1)	*x*	0·175	−0·298	0·358	0·885
	y	0·214	0·705	−0·542	0·457
	z	0·251	−0·644	−0·760	0·091
C(2)	*x*	0·214	0·289	0·127	0·949
	y	0·233	−0·955	−0·029	0·295
	z	0·261	0·065	−0·992	0·113
C(3)	*x*	0·237	0·843	0·149	0·518
	y	0·285	−0·433	−0·384	0·815
	z	0·375	−0·320	0·911	0·259
C(4)	*x*	0·228	0·619	−0·208	0·758
	y	0·258	−0·437	0·710	0·552
	z	0·331	−0·653	−0·673	0·348
C(5)	*x*	0·217	−0·721	0·661	−0·207
	y	0·270	−0·530	−0·335	0·779
	z	0·331	0·446	0·671	0·592
C(6)	*x*	0·223	−0·175	0·409	0·896
	y	0·227	0·734	−0·552	0·396
	z	0·265	−0·656	−0·726	0·204
C(7)	*x*	0·166	−0·850	0·503	0·158
	y	0·191	−0·112	−0·466	0·878
	z	0·215	0·515	0·728	0·453
C(8)	*x*	0·189	−0·066	−0·121	0·990
	y	0·222	−0·330	0·939	0·093
	z	0·227	0·942	0·321	0·102
C(9)	*x*	0·213	−0·125	−0·238	0·963
	y	0·244	0·764	0·595	0·247
	z	0·269	−0·633	0·767	0·108
C(10)	*x*	0·216	−0·325	−0·834	0·446
	y	0·249	−0·761	0·511	0·399
	z	0·263	0·561	0·209	0·801
C(11)	*x*	0·185	0·472	0·882	0·019
	y	0·234	0·602	−0·338	0·724
	z	0·245	−0·644	0·330	0·690
C(12)	*x*	0·185	0·272	0·940	0·206
	y	0·200	0·676	−0·339	0·654
	z	0·221	−0·685	0·038	0·728
C(13)	*x*	0·162	0·732	0·651	0·204
	y	0·196	−0·238	−0·036	0·971
	z	0·220	0·639	−0·759	0·129
C(14)	*x*	0·181	0·665	−0·736	0·127
	y	0·214	0·160	0·307	0·938
	z	0·238	−0·730	−0·603	0·322
C(15)	*x*	0·229	0·147	0·108	0·983
	y	0·251	−0·260	−0·955	0·144
	z	0·267	−0·954	0·277	0·112
C(16)	*x*	0·184	0·226	−0·255	0·940
	y	0·246	−0·870	−0·486	0·077
	z	0·300	−0·438	0·836	0·332
C(17)	*x*	0·214	0·584	0·689	0·429
	y	0·229	−0·532	−0·073	0·843
	z	0·264	0·613	−0·721	0·324
C(18)	*x*	0·211	−0·725	−0·687	−0·043
	y	0·229	0·238	−0·309	0·921
	z	0·238	−0·646	0·658	0·388

molecular distances and angles are given in Table 3. Parameters of the anisotropic thermal ellipsoids are given in Table 4. Table 5 lists observed and calculated structure factors.

Discussion

The idea of a chain of *n* molecules of type $[(C_6H_5)_3PIPd]_n$ linked to each other by metal–metal bonds had to be rejected in the initial stages of the structure analysis. The palladium atom is on an inversion centre around which the triphenylphosphine groups and the atoms of iodine are located. Because of this inversion centre the atoms of palladium, iodine and phosphorus all lie in the same plane, so that a fourfold coordination around the central atom results. The molecular geometry is shown in Fig. 1, the packing of the molecules in Fig. 2. Thermal ellipsoid are shown in Fig. 3. The bond lengths Pd–I: 2·587 Å; Pd–P: 2·331 Å, and the angle I–Pd–P: 87·1° suggest a nearly quadratic configuration. A comparison between the bond lengths Pd–I and Pd–P and the angle I–Pd–P obtained by Bailey & Mason and those obtained in this work show that they are in good agreement.

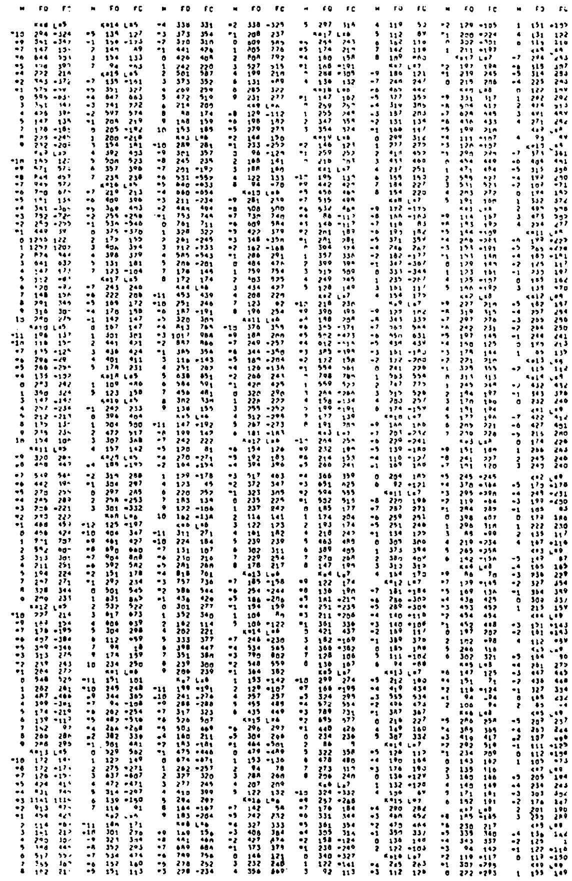
	Bailey & Mason (1968)		
	Red isomer	Yellow isomer	This work
Pd–I(1)	2·638 Å	Pd–I 2·592 Å	Pd–I 2·587 Å
Pd–I(2)	2·619		
Pd–P(1)	2·326	Pd–P 2·333	Pd–P 2·331
Pd–P(2)	2·333		
I(1)–Pd–P(1)	90·2°	I–Pd–P 87·6°	I–Pd–P 87·1°
I(1)–Pd–P(2)	88·9		
I(2)–Pd–P(1)	89·8		
I(2)–Pd–P(2)	90·1		

The mean Pd–P–C angle (114·9°) is greater than the regular tetrahedral value (109·5°), and this was also found by Bailey & Mason (115·2°). The enlarged angles are probably due to repulsion between the different phenyl rings.

Bailey & Mason pointed out in the structure analysis of the two isomers of diiodobis(dimethylphenyl-

Table 5. *Observed and calculated structure factors for* $[(C_6H_5)_3P)_2PdI_2$

Table 5 (*cont.*)



phosphine)palladium(II) that the octahedral coordination sites of the palladium atom were occupied by hydrogen atoms. The same symmetry could be argued for this structure. The β hydrogen atom H(12) occupies the octahedral coordination site of the palladium atom; this suggests an interaction between the hydrogen atom and the palladium atom so that the positions of these two atoms may be somewhat closer to each other. The distance from the palladium atom to the calculated position of the hydrogen atom H(12) [from C(12)] is 3·18 Å, which is comparable to the value found by Bailey & Mason for their yellow isomer (3·28 Å). The angles P–C(7)–C(8) (124·7°) and P–C(7)–C(12) (114·4°) differ from 120°, P–C(7)–C(10) (175·1°) differs from 180° in the sense that the hydrogen atom, H(12), is nearer to the metal. Owing to the fact that only one hydrogen atom can occupy this site, one should observe no bending of the other phenyl rings in the direction of the metal; this is confirmed by the values of the angles P–C(1)–C(2) (119·7°), P–C(1)–C(6) (120·2°), P–C(1)–C(4) (176·8°) and P–C(13)–C(14) (121·0°), P–C(13)–C(18) (119·4°), P–C(13)–V(16) (177·5°). The fixation of the hydrogen atom H(12) in the octahedral coordination site of the palladium stabilizes the position of the carbon atom C(12) and the carbon atoms C(7), C(8), C(9), C(10) and C(11) of that phenyl ring. Therefore the bond lengths between these atoms do not differ very much from each other and are in very good agreement with the values usually found: they do not show such large variation as the C–C bond lengths in the other phenyl rings.

It should be pointed out that in the chemical formula, as it appears from the crystal structure, the percentages of carbon, iodine and hydrogen are identical with those initially proposed, and that 2 molecules of solvent have also to be taken into account.

All the programs which have been used in these calculations were part of the X-RAY 70 system, in a version from the Max Planck Institut für Eiweiss- und Lederforschung, München, modified to run on the IBM 370/145 (150 Kbytes) computer of our Institute.

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