Comparison of Stereochemistry in Racemic and Optically Resolved Forms of a Five-co-ordinate Compound. Crystal and Molecular Structures of Dibromotris-(2-phenylisophosphindoline)palladium(II)–Acetone (Orange) and Dibromotris-(2-phenylisophosphindoline)palladium(II) (Red)

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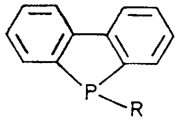
The form of the molecule PdL_3Br_2 (L = 2-phenylisophosphindoline) has been determined by crystal structure analysis of the optically resolved red form (B), and of an orange racemate (A), a 1 :1 solvate with acetone. In both structures the molecule has a modified tetragonal pyramidal arrangement of palladium bonds with one bromine atom at the apex. In both the angle α, between the apical bond and the basal bond, is considerably greater than 90° for the basal bromine and the phosphorus atom *trans* to it. To one of the other phosphorus atoms α is noticeably less than 90° and to the remaining phosphorus atom it is slightly greater than 90°. The form is derived from the tetragonal pyramidal where all α are several degrees greater than 90° by a decrease in α for P(I) and P(III) while α for P(II) and Br(1) is free to increase. This distortion arises from overcrowding of the basal atoms.

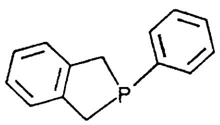
In nearly all respects the molecule (B) differs insignificantly from the same enantiomorph in (A), but the apical bond length to bromine is 2·92 in (B) and 3·02 Å in (A). The large difference can only be attributed to difference of molecular environment. The angle α for the basal bromine is smaller for (A) and this may be a consequence of the bond-lengthening.

Crystals of (A) are monoclinic, space group $P2_1/b$, a = 11·36(2), b = 22·52(4), c = 16·67(3) Å, γ = 95·51(2)°, Z = 4. Crystals of (B) are orthorhombic, space group $P2_12_12_1$, a = 11·63(2), b = 16·36(3), c = 20·48(3) Å, Z = 4. The structures were solved from diffractometer data [(A), Patterson and Fourier, 4989 observed reflections; (B), direct methods, 2822 observed reflections] and refined by least squares to R 0·064 (A) and 0·065 (B).

MOLECULAR environment has often been mentioned as a possible influence on metal stereochemistry but is not easy to investigate directly. The existence of a suitable compound in racemic and optically resolved forms provides an opportunity to do so. Originally the title compounds were considered for structure examination in order to determine whether there was a ligand–ligand interaction of the type found, without known exception, in molecular structures ML_3X_2 (M = Ni, Pd, Pt; X = CN, Br, Cl; L = I).[1,2] The purpose was to replace L by another aromatic ligand since the interaction postulated is between the aromatic parts. The alternative ligand is 2-phenylisophosphindoline (II).



(I)
R = Me or Et



(II)

The compound was prepared by Mann and coworkers[3] who examined the red unsolvated form by X-ray diffraction. Atomic positions were given for the six heavy atoms only. However, in analogous palladium and platinum compounds[2] with L = (I), X = Br, a tetrahedral distortion of the four basal bonds was explained by a steric argument which should apply to the present compound and require the bond angle Br(2)–Pd–P(II) to be several degrees greater than that found. A repetition of the recrystallisation from acetone gave simultaneously two products, a red form (B) and an orange form (A). Form (A) had space group $P2_1/b$, and (B) had unit-cell dimensions very close to those previously reported and space group $P2_12_12_1$. The red form (B) must be optically resolved and it seemed probable that the orange form (A) was the racemate. The unit-cell volume is 6% larger for (A) and, combined with the measured density, is consistent with a molecular weight equal to that of the complex plus a molecule of acetone. Detailed crystal-structure determination by diffractometer methods was made for both compounds to the same degree of accuracy so that a stereochemical comparison could be made.

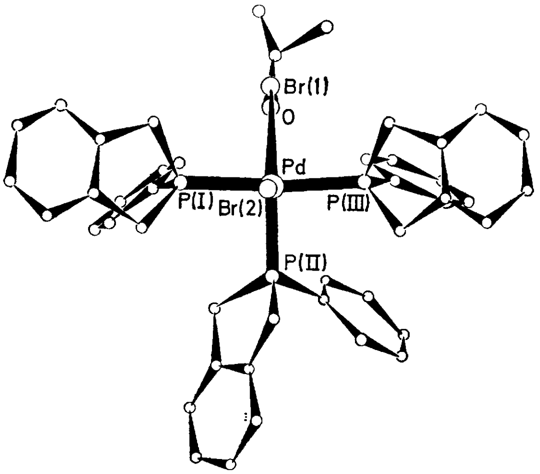


FIGURE 1 The molecules in an asymmetric unit of the structure of the orange form (A) projected on the plane of the three phosphorus atoms

Figures 1 and 2 show the asymmetric units for the

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[1] H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc.* (*A*), 1971, 1803.

[2] K. M. Chui and H. M. Powell, *J.C.S. Dalton*, 1974, 1879.

[3] J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1964, 1803.

two crystals. In both cases the molecule of the metal complex has the same atomic composition and is based on a tetragonal pyramidal arrangement of the palladium bonds with Br(2) at the apex. This apical bond is distinguishable because it is noticeably longer than the other Pd–Br(1) bond. The three Pd–P bonds are in the base. The atom *trans* to Br(1) is P(II) and the ligands are numbered L(I), L(II), L(III) by use of the distinction that angle L(I)–Pd–L(II) < L(I)–Pd–L(III).

The stereochemistry of the palladium atom for both structures is summarised in Table 1. For (B) the previous values are in approximate agreement with the refined distances and angles except for those involving P(II). This atom is now placed considerably below the basal plane of the tetragonal pyramid, angle Br(2)–Pd–P(II) being 99° (previously reported 92°). The Br(1) atom *trans* to it is also well below the basal plane, the angle α between its bond and the apical bond being 105°. P(I) Has α 86° and P(III) α 90·8°. Non-bonded P · · · P and P · · · Br distances required by these angles are given in Table 2. They are in close agreement with the corresponding distances in PdL_3Br_2 [L = (I)]. As shown in ref. 2 the basic cause for distortion of the tetragonal pyramid is that the bond lengths and minimum non-bonded distances require two adjacent Pd–P bonds to be inclined at an angle greater than 90°. A value of 97° was calculated and empirically the lower limit was found to be 93°. The distorted form found when L = (II) is derived from the tetragonal pyramidal where all α are several degrees greater than 90° by a decrease in α for P(I) and P(III) while α for P(II) and Br(1) is free to increase. In this case only one of the two diminished α values is reduced below 90°. In (A) the molecule has a similar form of distortion with Br(1) and P(II) well below the basal plane, P(I) above it, and P(III) nearly in it. In both the red and orange forms a *trans*-effect similar to that in the compounds of ref. 2 is shown by a Pd–P(II) bond shorter by *ca.* 0·03 Å than the other Pd–P bonds.

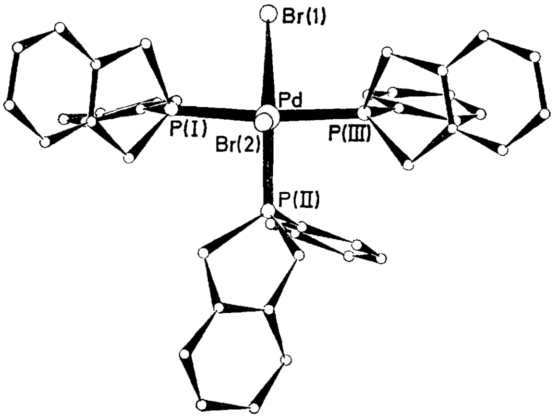

FIGURE 2 The molecule in an asymmetric unit of the structure of the red form (B), projected on the plane of the three phosphorus atoms

TABLE 1

Bond lengths (Å) and angles (°) at the palladium atom, with estimated standard deviations in parentheses. Values from ref. 3 * for the red form (B) are shown in square brackets

(*a*) Bond lengths	(B)		(A)
Pd–P(I)	2·311(5)	[2·28, P(3)]	2·307(3)
Pd–P(II)	2·286(6)	[2·19]	2·273(3)
Pd–P(III)	2·326(5)	[2·30, P(1)]	2·318(3)
Pd–Br(1)	2·544(3)	[2·52]	2·528(2)
Pd–Br(2) (apical)	2·923(3)	[2·93]	3·017(2)
(*b*) Bond angles			
P(I)–Pd–P(II)	95·57(19)	[97, P(3)]	93·00(11)
P(I)–Pd–P(III)	171·34(18)		174·51(12)
P(II)–Pd–P(III)	92·96(19)	[90, P(1)]	92·47(11)
Br(1)–Pd–P(I)	85·98(14)	[88, P(3)]	87·27(9)
Br(1)–Pd–P(II)	155·92(16)		162·19(9)
Br(1)–Pd–P(III)	86·84(13)	[87, P(1)]	87·64(9)
Br(2)–Pd–P(I)	86·37(14)	[84, P(3)]	87·58(9)
Br(2)–Pd–P(II)	99·33(15)	[92]	98·57(9)
Br(2)–Pd–P(III)	90·79(13)	[91, P(1)]	91·21(8)
Br(1)–Pd–Br(2)	104·75(8)	[105]	99·23(5)

* The key to ref. 3 is P(3) = P(I), P(1) = P(III), and P(2) = P(II).

TABLE 2

Non-bonded P · · · P and P · · · Br distances (Å), with values from ref. 3 in brackets

Compound	P(I) · · · P(II)	P(III) · · · P(II)
(B)	3·404 (3·35)	3·344 (3·17)
(A)	3·322	3·315
	P(I) · · · Br(1)	P(III) · · · Br(1)
(B)	3·424 (3·34)	3·351 (3·32)
(A)	3·372	3·358

Comparison of Resolved and Racemic Forms.—Apart from two special cases, the bond lengths and angles show only small differences between the corresponding values for the red and orange forms. One case is the striking difference in the lengths of the apical bonds: 2·92 for (B) and 3·02 Å for (A). The difference (0·1 Å) is 10 × 3σ, and much larger than the probable error. A comparable difference (0·11 Å) found between apical bond lengths in the two compounds PtL_3Br_2,PhBr [L = (I), R = Me or Et] [2] might be attributed to a combination of internal differences of the molecules and intermolecular effects but, in the present case, the complex molecules have the same chemical constitution. One of the structures contains acetone, but the shortest distance between an atom of the acetone molecule and an atom in the apical bond is 6 Å. This is between a carbon atom of a methyl group and Br(2). There is therefore no direct chemical effect such as might arise through co-ordination of the acetone. The ligand L(I) close to the acetone molecule is almost indistinguishable in dimensions and disposition from the corresponding ligand in the unsolvated form so that there is no evidence of an indirect chemical effect which might influence the apical bond length. The observed variation therefore can only be attributed to differences of molecular environment in the two crystals. This includes any environmental effect of the acetone. That there are substantial differences of environment is clear. For example, the relative orientations of the apical bonds (in neighbouring molecules) must be different in the two cases; in the racemate, every molecule is related by a centre of symmetry to another molecule and two apical bonds so related must be antiparallel, though it is not the case that all molecules are related to each other in this way. There are two sets related by a glide plane operation. In the $P2_12_12_1$ structure there is no centre of symmetry and the apical bonds do not form antiparallel pairs, but pairs related by the 2_1 operations. If the bond makes zero angle with the screw axis the two related apical bonds are parallel and if the angle is 90° the related bonds will be antiparallel. The angles between the bond and the three screw axes are 155° 40′, 84° 53′, and 113° 42′. The other case of appreciable difference concerns the angles Br(2)–Pd–Br(1) which differ by 6° whereas other pairs of related valency angles differ by less than 2°. Significantly the atom Br(2) is involved and the effect could be explained by a smaller Br(2) · · · Br(1) repulsion arising for a longer apical bond.

Disposition of the Ligands.—A reference axial system is defined as follows: the apical bond is taken as the Z axis, and two other axes are taken at right angles to each other in the plane perpendicular to the Z axis and containing the palladium atom. The X axis is the intersection of this plane and the plane containing the apical bond and Br(1).

The directions of all the metal bonds may be expressed in terms of the angle θ between the bond and the Z axis and the angle ϕ between the ZX plane and the plane containing the Z axis and the bond. These angles are recorded in the Table 3 which also gives bond lengths (r).

The disposition of the ligands is considered in relation to a reference model. In this, each ligand is imagined to have the plane of symmetry of the phosphindoline ring system coincident with the plane containing the Z axis and the Pd–P bond; the plane of the phenyl ring is imagined to lie in this symmetry plane with the phosphorus–phenyl bond pointing upwards. Any other form of the molecule may be derived by a rotation of the whole ligand about its P–Pd bond through a specific rotation angle (R_1) followed by a rotation of the phenyl ring about its bond to the phosphorus atom through a specific rotation angle (R_2). The rotation angle (R_1) is defined as positive when it appears clockwise to an observer looking from the phosphorus to the palladium atom, and R_2 is defined as positive for a rotation which appears clockwise to an observer looking from the phenyl ring to the phosphorus atom. The angle R_2 is sufficiently defined by a value in the range 0—180°. Table 4 shows values of R_1 and R_2.

TABLE 3

(*a*) Red compound (B)

	P(I)	P(II)	P(III)	Br(1)	Br(2)
r/Å	2·311	2·286	2·326	2·544	2·923
θ	86° 22′	99° 20′	90° 47′	104° 45′	0°
ϕ	84° 54′	180° 1′	273° 4′	0°	0°

(*b*) Orange compound (A)

	P(I)	P(II)	P(III)	Br(1)	Br(2)
r/Å	2·307	2·273	2·318	2·528	3·017
θ	87° 35′	98° 34′	91° 13′	99° 14′	0°
ϕ	86° 49′	180° 0′	272° 12′	0°	0°

TABLE 4

Rotation angles

Compound	L(I)		L(II)		L(III)	
	R_1	R_2	R_1	R_2	R_1	R_2
(B)	171° 24′	18° 29′	155° 20′	81° 5′	185° 37′	159° 20′
(A)	170° 9′	44° 43′	129° 38′	58° 8′	183° 42′	149° 1′

The values of the rotation angles (R_1) of L(I) and L(III) in the two structures are almost identical. There are only small differences (10° and 26°) in the rotation angles (R_2) of the two ligands. L(I) and L(III) are approximately symmetrical to each other about the best plane through the Pd, Br(1), Br(2), and P(II) atoms; this is possible because the difference in angles L(I)–Pd–L(II) and L(III)–Pd–L(II) due to ligand–ligand interaction is small. For ligand L(II) there is greater difference (*ca.* 26°) in rotation angles (R_1) of the two forms. In rotation angles (R_2), there is also 23° difference, but it is of the same order of magnitude as those for L(I) and L(III). In both forms the phenyl rings of L(II) and L(III) are parallel and overlapping, but the overlapping areas differ in the two cases.

The rotation angle (R_1) of L(II) of form (A) would have to be increased by *ca.* 25° clockwise to give an overlap similar to that in form (B). In addition to the change in the rotation angle (R_1), the phenyl ring of the same ligand would have to turn *ca.* 24° clockwise to retain the parallelism of ligand L(II) and L(III).

It is unlikely that the difference in rotation angles (R_1) between the red and orange forms is caused by the acetone molecule. For L(I) and L(III) the angles in the two forms differ by less than 2°. The main difference in R_1 is for L(II) which is the most remote from the acetone. In the orange compound, the shortest distance from solvent molecule to a carbon atom of the complex molecule is the O · · · C(105) distance of 3·53 Å. This comparatively large value rules out any possible interaction other than the normal Van der Waals'. The role of the solvent is space-filling.

Angle of Inclination.—An angle of inclination for these two structures is defined as the angle between the normals to the phenyl rings of L(II) and L(III). It is, as in ref. 1, a measure of the degree of parallelism of the two interacting aromatic systems. The red and orange compounds have nearly equal values (18° 40′ and 17° 0′).

Ligand–Ligand Effect.—In ML_3X_2 [L = (I)], ligand–ligand interaction shows itself in parallelism plane-to-plane of two of the ligands and in angle A always less than B as defined in Table 5. In both the new structures with the alternative ligand, the phenyl groups of L(II) and L(III), defined in the same way, are parallel plane to plane. The difference A–B is negative as required for attractive interaction between L(II) and L(III). The effect is however, very small and of doubtful significance since it refers to one compound only.

TABLE 5

Compound	Stereo-chemistry	A/° L(II)–Pd–L(III)	B/° L(II)–Pd–L(I)	A–B/°
(B)	*c*	92·96	95·57	−2·61
(A)	*c*	92·47	93·00	−0·53

Form of the Ligand.—In the orange compound the parameters of all carbon atoms were refined. The three crystallographically distinguishable ligands L show almost no variation in form. Mean values for the dimensions of the ring systems are given in Figure 3.

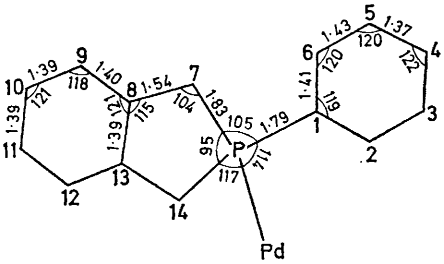

FIGURE 3 Mean bond lengths (Å) and angles (°) of 2-phenylisophosphindoline ligand of the orange compound (A)

The isophosphindoline ring system always has, within the standard deviation, a non-crystallographic plane of symmetry. The bond from phosphorus to the phenyl group lies in this plane. The plane of the phenyl ring is neither parallel nor perpendicular to the symmetry plane of the phosphindoline ring system so the ligand as a whole has no symmetry. The bond lengths in the phosphindoline six-membered ring are all very nearly equal, and the angles observed do not differ significantly from 120°. The bond lengths in the five-membered ring are those of single bonds. Angle C–P–C is 94·7°, and subject to restraints of the ring system.

EXPERIMENTAL

Crystal Preparation.—The brick-red powder form of the compound was dissolved in hot acetone. Orange and ruby red crystals were obtained simultaneously by evaporation of the solvent. The orange crystals (A) contain one acetone molecule for each complex molecule. The red crystals (B) are unsolvated.

Data Collection—Weissenberg photographs were used to determine the space groups and cell dimensions which were refined on the diffractometer. An orange crystal of (A) was mounted about the non-unique *a* axis for data collection on the Hilger and Watts four-circle diffractometer. Intensities in the hkl and $h\bar{k}l$ quadrants with θ ranging from 0—65° were collected with Cu-K_α radiation for 4989 independent reflections with intensity $I > 3\sigma(I)$. Balanced filters were used in the θ range of 0—35°. The monitoring standard reflections were 6,8,0, 4,4,$\bar{4}$, and $\bar{2}$,$\bar{1}\bar{8}$,0. Correction for absorption was made by use of the intensity curves of scattering vectors 4,0,0 and 10,0,0.

A red crystal of (B) was mounted about the *a* axis for data collection on the same diffractometer. Reflections hkl and $\bar{h}\bar{k}l$ were collected up to θ 63° with Cu-K_α radiation. Balanced filters were used in the θ range 0—35°. Reflections 0,0,12, 4,8,0, and 4,2,4 were used as monitors. The intensity curve of the scattering vector $\bar{4}$,0,0 was used for the absorption correction. The two sets of data in the hkl and $\bar{h}\bar{k}l$ quadrants were merged to give 2822 independent reflections of $I > 2\sigma(I)$.

TABLE 6

Atomic co-ordinates for the orange form (A), with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Pd	−0·1066(1)	0·3207(0)	0·5399(1)
Br(2)	0·1185(1)	0·4014(1)	0·5635(1)
Br(1)	−0·0882(1)	0·2505(1)	0·6567(1)
P(I)	−0·0029(3)	0·2589(1)	0·4662(2)
P(III)	−0·2089(3)	0·3789(1)	0·6250(2)
P(II)	−0·1749(3)	0·3645(1)	0·4286(2)
C(101)	−0·0899(11)	0·1999(5)	0·4194(8)
C(102)	−0·0749(13)	0·1840(6)	0·3378(9)
C(103)	−0·1619(14)	0·1417(7)	0·3036(9)
C(104)	−0·2542(16)	0·1147(7)	0·3495(11)
C(105)	−0·2692(16)	0·1321(8)	0·4270(10)
C(106)	−0·1865(12)	0·1735(6)	0·4633(8)
C(107)	0·1125(12)	0·2244(6)	0·5232(8)
C(108)	0·2161(11)	0·2175(6)	0·4619(8)
C(109)	0·3074(12)	0·1813(7)	0·4736(8)
C(110)	0·3876(14)	0·1797(8)	0·4162(11)
C(111)	0·3850(12)	0·2130(8)	0·3450(9)
C(112)	0·2974(12)	0·2488(7)	0·3316(9)
C(113)	0·2114(12)	0·2506(6)	0·3936(7)
C(114)	0·1076(12)	0·2909(6)	0·3900(8)
C(301)	−0·3646(11)	0·3556(5)	0·6376(7)
C(302)	−0·4006(13)	0·2949(6)	0·6283(8)
C(303)	−0·5290(14)	0·2766(8)	0·6370(10)
C(304)	−0·6059(14)	0·3177(8)	0·6549(11)
C(305)	−0·5681(14)	0·3761(8)	0·6613(10)
C(306)	−0·4503(13)	0·3963(7)	0·6549(8)
C(307)	−0·1975(12)	0·4613(6)	0·6081(8)
C(308)	−0·1945(12)	0·4869(5)	0·6921(8)
C(309)	−0·2025(12)	0·5477(6)	0·7049(10)
C(310)	−0·1950(18)	0·5693(8)	0·7841(13)
C(311)	−0·1791(16)	0·5295(9)	0·8461(12)
C(312)	−0·1661(15)	0·4681(7)	0·8337(9)
C(313)	−0·1734(11)	0·4479(5)	0·7541(8)
C(314)	−0·1497(11)	0·3853(5)	0·7277(8)
C(201)	−0·3224(11)	0·3829(5)	0·4349(7)
C(202)	−0·4132(12)	0·3381(7)	0·4457(8)
C(203)	−0·5357(13)	0·3503(9)	0·4536(10)
C(204)	−0·5619(15)	0·4084(9)	0·4427(10)
C(205)	−0·4781(15)	0·4545(8)	0·4277(10)
C(206)	−0·3558(14)	0·4421(7)	0·4245(9)
C(207)	−0·1778(13)	0·3257(5)	0·3317(8)
C(208)	−0·1640(11)	0·3768(5)	0·2702(7)
C(209)	−0·1879(15)	0·3722(6)	0·1909(9)
C(210)	−0·1714(16)	0·4230(7)	0·1433(9)
C(211)	−0·1361(15)	0·4776(7)	0·1739(9)
C(212)	−0·1082(13)	0·4830(6)	0·2555(9)
C(213)	−0·1204(11)	0·4312(5)	0·3046(7)
C(214)	−0·0897(11)	0·4311(5)	0·3926(7)
O(1)	0·4826(13)	0·3803(7)	0·0818(10)
C(1)	0·4914(15)	0·4186(8)	0·1438(11)
C(2)	0·5179(17)	0·4805(8)	0·1763(13)
C(3)	0·4899(15)	0·3835(9)	0·2302(11)

Determination of Structures.—The structure of (A) was determined by Patterson and electron-density synthesis methods. Solution of the sharpened Patterson map gave the positions of the six heavy atoms and hence a first set of phases. Electron-density maps were then computed to show the remaining details of the complex molecule (excluding hydrogen atoms). A 'Ploto' map[4] showed a possible space for an acetone molecule which was then located from a difference-Fourier map of this region phased on all the other atoms of the structure.

TABLE 7

Anisotropic temperature factors ($U_{ij} \times 10^3$) * for the orange form (A), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pd	42(0)	36(0)	34(0)	2(1)	3(1)	18(1)
Br(2)	51(1)	54(1)	58(1)	15(1)	17(1)	2(1)
Br(1)	68(1)	47(1)	36(1)	−10(1)	−8(1)	35(1)
P(I)	43(2)	38(2)	38(2)	0(2)	−2(3)	19(3)
P(III)	41(2)	35(1)	38(2)	7(2)	0(2)	14(2)
P(II)	41(2)	33(1)	37(1)	−3(2)	−8(2)	10(2)
C(101)	46(7)	42(6)	47(7)	−11(11)	−6(11)	21(11)
C(102)	65(9)	40(7)	63(9)	−1(12)	−27(14)	13(12)
C(103)	58(9)	67(9)	65(9)	−23(15)	−2(15)	15(15)
C(104)	79(11)	60(9)	81(11)	−24(16)	−5(18)	−7(16)
C(105)	77(11)	81(11)	56(9)	−11(16)	−6(16)	−24(17)
C(106)	50(8)	56(8)	55(8)	2(13)	3(13)	−15(12)
C(107)	50(8)	59(8)	44(7)	−10(12)	−3(12)	38(12)
C(108)	44(7)	45(7)	53(7)	−14(11)	6(11)	5(11)
C(109)	48(8)	74(9)	59(8)	−13(14)	7(13)	55(14)
C(110)	51(9)	92(12)	77(11)	−4(18)	13(16)	39(16)
C(111)	36(8)	98(11)	63(9)	−29(16)	−0(13)	2(15)
C(112)	38(8)	83(10)	68(9)	−57(16)	13(13)	−13(14)
C(113)	45(7)	57(8)	40(7)	−0(11)	−20(11)	−5(12)
C(114)	51(8)	45(7)	45(7)	−4(11)	11(11)	12(11)
C(201)	42(7)	48(7)	38(6)	−4(10)	−3(10)	2(11)
C(202)	71(9)	58(8)	48(8)	−24(13)	8(13)	−1(13)
C(203)	55(9)	91(11)	70(10)	−25(17)	−0(15)	−46(16)
C(204)	49(9)	98(13)	89(12)	−2(19)	1(17)	−12(18)
C(205)	60(10)	83(11)	72(10)	−24(17)	−30(16)	4(16)
C(206)	64(9)	67(9)	49(8)	8(13)	28(13)	41(15)
C(207)	65(8)	39(7)	47(7)	5(11)	0(12)	5(12)
C(208)	52(7)	39(6)	53(7)	17(11)	8(12)	−2(11)
C(209)	49(8)	48(8)	85(10)	−38(14)	2(14)	19(12)
C(210)	109(15)	58(10)	104(14)	−79(20)	−33(23)	24(19)
C(211)	69(11)	97(13)	96(13)	−102(21)	14(19)	−23(19)
C(212)	82(11)	78(10)	47(8)	38(15)	−20(14)	2(16)
C(213)	45(7)	42(7)	66(8)	16(12)	−8(12)	6(11)
C(214)	50(7)	40(6)	49(7)	2(11)	1(12)	10(11)
C(301)	44(7)	44(6)	34(6)	−7(10)	−7(10)	5(10)
C(302)	51(8)	70(9)	45(7)	−10(12)	−14(12)	23(13)
C(303)	39(8)	110(13)	68(10)	−23(18)	−38(14)	−5(16)
C(304)	62(10)	109(14)	62(10)	−16(18)	−25(16)	71(19)
C(305)	62(10)	96(12)	71(10)	−25(18)	−4(16)	70(18)
C(306)	64(9)	68(9)	56(8)	11(14)	14(14)	50(15)
C(307)	71(9)	35(6)	50(7)	2(11)	−20(13)	20(12)
C(308)	45(7)	43(6)	48(7)	11(11)	6(11)	16(10)
C(309)	89(11)	53(8)	51(8)	11(13)	11(15)	52(15)
C(310)	105(12)	72(10)	43(8)	11(15)	−6(16)	17(17)
C(311)	85(10)	61(9)	46(8)	20(13)	7(14)	−1(15)
C(312)	58(9)	58(8)	63(9)	24(14)	−5(14)	−12(13)
C(313)	50(7)	44(7)	45(7)	5(11)	−16(11)	21(11)
C(314)	43(7)	45(7)	47(7)	5(11)	1(11)	12(10)
O(1)	159(11)	191(11)	195(12)	72(18)	−43(18)	35(18)
C(1)	89(11)	126(11)	143(13)	−37(19)	−7(19)	57(17)
C(2)	133(13)	136(13)	217(15)	−27(22)	19(23)	−6(21)
C(3)	117(12)	179(13)	113(12)	14(20)	52(19)	26(20)

* Temperature factor in the form: $T = \exp -2\pi^2[U_{11}(ha^*)^2 + \cdots + 2U_{12}(ha^*kb^*)]$.

The structure of (B) was determined by the non-centrosymmetric direct method combined with electron-density Fourier synthesis. The process of phase determination was carried out by the trial-and-error tangent formula programme.[5] The origin was fixed by $\phi(2,0,5) = \pi/2$, $\phi(0,1,11) = \pi/2$, and $\phi(1,0,1) = \pi/2$. The enantiomorph was determined by $\phi(0,3,12) = \pi/2$. Eight trials of tangent-formula refinement of phases were carried out by assigning $\pi/4$ or $3\pi/4$ to reflection 0,10,6 and $-\pi/4$, $\pi/4$, $-3\pi/4$ or $3\pi/4$ to 3,2,17. The acceptability of each trial solution was judged by an overall R_T index, defined by $R_T = 100 \times [\Sigma(|E_o| - |E_c|)/\Sigma|E_o|]$. The trial with $\phi(0,10,6) = \pi/4$ and $\phi(3,2,17) = -\pi/4$ which gave the lowest R_T (23·05%) resulted in a solution for the six heavy atoms of the complex molecule. The positions of atoms so found were in turn used to phase the set of F_c for a difference-synthesis which

TABLE 8

Atomic co-ordinates for the red form (B), with estimated standard deviations in parentheses. Values from ref. 3 are in square brackets (see text)

	x/a	y/b	z/c
Pd	0·0948(1)	0·3067(1)	0·1772(1)
	[0·096]	[0·307]	[0·179]
Br(1)	0·1205(2)	0·4462(1)	0·2301(1)
	[0·113]	[0·445]	[0·233]
Br(2)	−0·1026(2)	0·3260(1)	0·0902(1)
	[−0·099]	[0·322]	[0·091]
P(I)	0·2044(4)	0·3578(2)	0·0924(2)
	[0·198]	[0·359]	[0·094]
P(II)	0·1365(4)	0·1724(3)	0·1573(2)
	[0·118]	[0·177]	[0·155]
P(III)	−0·0263(4)	0·2751(3)	0·2640(2)
	[−0·022]	[0·270]	[0·263]
C(101)	0·3573(8)	0·3541(9)	0·1097(5)
C(102)	0·4423(10)	0·3568(14)	0·0617(5)
C(103)	0·5581(9)	0·3562(14)	0·0796(6)
C(104)	0·5891(9)	0·3399(11)	0·1441(7)
C(105)	0·5038(11)	0·3332(18)	0·1918(6)
C(106)	0·3883(10)	0·3409(16)	0·1747(5)
C(107)	0·1838(17)	0·3168(10)	0·0068(6)
C(108)	0·1717(16)	0·3897(6)	−0·0350(5)
C(109)	0·1804(22)	0·3860(7)	−0·1030(5)
C(110)	0·1773(23)	0·4579(9)	−0·1396(4)
C(111)	0·1714(29)	0·5335(7)	−0·1083(5)
C(112)	0·1740(22)	0·5374(6)	−0·0402(5)
C(113)	0·1756(18)	0·4654(7)	−0·0037(4)
C(114)	0·1757(17)	0·4664(11)	0·0707(8)
C(201)	0·2067(12)	0·1212(10)	0·2250(7)
C(202)	0·1462(10)	0·0745(9)	0·2703(8)
C(203)	0·2046(18)	0·0345(11)	0·3205(7)
C(204)	0·3242(17)	0·0394(14)	0·3241(10)
C(205)	0·3832(12)	0·0929(18)	0·2828(13)
C(206)	0·3259(12)	0·1280(13)	0·2297(11)
C(207)	0·0151(20)	0·1088(10)	0·1365(9)
C(208)	0·0630(16)	0·0446(9)	0·0916(8)
C(209)	0·0037(17)	−0·0249(11)	0·0711(10)
C(210)	0·0569(22)	−0·0805(11)	0·0290(13)
C(211)	0·1644(23)	−0·0624(11)	0·0026(10)
C(212)	0·2212(18)	0·0093(13)	0·0205(10)
C(213)	0·1732(17)	0·0605(9)	0·0677(8)
C(214)	0·2264(29)	0·1382(16)	0·0876(9)
C(301)	0·0421(11)	0·2532(9)	0·3413(5)
C(302)	0·1580(11)	0·2738(12)	0·3480(6)
C(303)	0·2157(11)	0·2558(15)	0·4060(8)
C(304)	0·1537(16)	0·2267(18)	0·4596(6)
C(305)	0·0417(17)	0·1984(21)	0·4508(8)
C(306)	−0·0142(13)	0·2115(19)	0·3914(8)
C(307)	−0·1268(13)	0·3598(10)	0·2802(7)
C(308)	−0·2303(11)	0·3164(8)	0·3075(6)
C(309)	−0·3146(13)	0·3544(8)	0·3453(9)
C(310)	−0·4050(13)	0·3083(11)	0·3709(9)
C(311)	−0·4121(13)	0·2249(11)	0·3576(10)
C(312)	−0·3268(13)	0·1866(8)	0·3208(9)
C(313)	−0·2351(11)	0·2323(8)	0·2963(7)
C(314)	−0·1451(18)	0·1944(15)	0·2575(10)

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[4] D. J. Watkin, *Acta Cryst.*, 1972, **A28**, 33.

[5] O. J. R. Hodder, 1970, Trial and Error Tangent Formula Programme, Chemical Crystallography Department, Oxford.

TABLE 9

Anisotropic temperature factors ($\times 10^3$) for the red form (B), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pd	69(1)	61(1)	49(0)	−1(1)	13(1)	−1(1)
Br(1)	95(1)	71(1)	62(1)	−21(2)	10(2)	−10(2)
Br(2)	72(1)	96(1)	75(1)	−6(2)	−12(2)	12(2)
P(I)	81(3)	63(2)	49(2)	2(4)	7(4)	−4(4)
P(II)	92(3)	67(2)	60(2)	11(4)	25(4)	14(4)
P(III)	72(3)	71(2)	56(2)	2(4)	8(4)	−12(4)
C(101)	89(11)	52(8)	57(8)	−17(14)	6(16)	−14(16)
C(102)	83(12)	123(16)	84(12)	75(24)	30(20)	−5(23)
C(103)	82(13)	109(16)	100(13)	−53(24)	51(22)	−13(24)
C(104)	94(12)	79(11)	109(15)	−31(22)	−40(25)	27(22)
C(105)	109(18)	177(25)	95(14)	113(32)	−16(27)	−64(35)
C(106)	88(12)	165(21)	55(9)	1(24)	−10(20)	18(28)
C(107)	112(14)	74(10)	40(7)	33(15)	−2(17)	23(21)
C(108)	84(11)	85(11)	57(9)	19(17)	17(17)	1(20)
C(109)	150(19)	108(15)	51(9)	34(20)	−46(23)	13(29)
C(110)	150(22)	199(28)	53(10)	81(30)	−27(25)	−117(44)
C(111)	228(33)	83(13)	56(10)	32(20)	39(31)	−16(36)
C(112)	149(19)	91(12)	68(11)	52(20)	23(24)	70(27)
C(113)	115(14)	98(14)	70(10)	57(21)	37(21)	34(24)
C(114)	110(14)	70(10)	66(10)	75(17)	11(20)	6(21)
C(201)	90(14)	59(9)	101(15)	34(20)	−84(26)	−12(19)
C(202)	112(14)	60(9)	86(12)	50(18)	5(22)	−8(18)
C(203)	259(32)	93(14)	72(10)	−49(22)	−93(34)	−65(38)
C(204)	161(28)	93(18)	187(34)	−43(41)	−94(56)	85(41)
C(205)	209(41)	144(23)	228(42)	−32(51)	−188(75)	−9(54)
C(206)	138(21)	86(14)	170(25)	32(33)	−129(42)	17(29)
C(207)	199(30)	130(19)	56(11)	24(25)	63(33)	42(42)
C(208)	204(30)	78(12)	67(12)	1(20)	−17(32)	27(33)
C(209)	326(48)	71(13)	105(16)	−10(26)	−178(51)	−20(45)
C(210)	287(67)	128(22)	123(22)	−89(38)	−87(65)	71(67)
C(211)	322(60)	98(20)	81(14)	−19(27)	−36(49)	185(63)
C(212)	328(52)	143(21)	59(12)	−1(28)	85(43)	223(60)
C(213)	238(33)	72(12)	55(11)	33(19)	−17(32)	60(37)
C(214)	199(30)	130(19)	56(11)	24(25)	63(33)	42(42)
C(301)	116(13)	61(9)	62(9)	−10(15)	−53(19)	47(19)
C(302)	107(14)	97(13)	76(11)	2(21)	−44(22)	−26(24)
C(303)	161(23)	133(21)	99(15)	33(30)	−133(33)	35(37)
C(304)	151(23)	213(31)	64(12)	2(33)	34(28)	−110(48)
C(305)	172(28)	213(37)	115(20)	111(50)	11(42)	43(60)
C(306)	107(15)	222(33)	78(12)	123(35)	55(23)	−84(39)
C(307)	66(9)	79(10)	65(9)	−61(17)	18(16)	21(16)
C(308)	83(11)	111(15)	46(8)	19(18)	8(15)	38(22)
C(309)	84(13)	128(17)	82(12)	−43(25)	7(22)	55(26)
C(310)	84(14)	205(29)	91(14)	41(37)	−6(25)	36(43)
C(311)	83(14)	180(24)	80(13)	30(32)	54(25)	−50(36)
C(312)	110(14)	204(26)	73(11)	−61(31)	−9(22)	−171(33)
C(313)	72(11)	108(14)	56(9)	−10(19)	22(17)	−37(21)
C(314)	97(13)	137(17)	95(14)	−43(28)	−6(23)	−89(28)

gave the solution for the rest of the molecule, excluding hydrogen atoms.

Refinement of the Structures.—The structure of (A) was refined anisotropically till R 0·064 with root-mean-square (shift-to-σ) reduced to 0·025. The weighting function was $\sqrt{w} = 1/\{1 + [(|F_o| - P_2)/P_1]^2\}^{\frac{1}{2}}$ with $P_1 = 30{\cdot}4$ and $P_2 = 7{\cdot}2$.

In the anisotropic refinement of structure (B), the carbon atoms of all benzene rings were constrained to regular hexagons with C–C 1·396 Å. The refinement terminated at R 0·065 with root-mean-square (shift-to-σ) $<0{\cdot}02$. The weighting function used was the same as for structure (A), with P_1 32·7, and P_2 9·6. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21052 (80 pp., 1 microfiche).*

Atomic positional and thermal parameters are given in Tables 6—9. In Table 8, all the positional parameters from ref. 3 are added below in square brackets. The coordinates of ref. 3 were converted to the values shown by substitution of an atom at x,y,z by its $\frac{1}{2} - x,\bar{y},\frac{1}{2} + z$ equivalent plus a change of origin to $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

Crystal Data.—(i) *Orange form*, (A). $(C_{14}H_{13}P)_3PdBr_2,(CH_3)_2CO$, $M = 961{\cdot}0$, Monoclinic, $a = 11{\cdot}36 \pm 0{\cdot}02$, $b = 22{\cdot}52 \pm 0{\cdot}04$, $c = 16{\cdot}67 \pm 0{\cdot}03$ Å, $\gamma = 95{\cdot}51 \pm 0{\cdot}02°$, $U = 4245$ Å^3, $D_m = 1{\cdot}50$, $Z = 4$, $D_c = 1{\cdot}50$ g cm^{-3}, $F(000) = 1936$. Space group $P2_1/b$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 74·00 cm^{-1}; t_{op} (optimum thickness) = 0·27 mm. Terminal R 0·064; orange crystal 0·14 × 0·21 × 0·80 mm.

(ii) *Red form*, (B). $(C_{14}H_{13}P)_3PdBr_2$, $M = 902{\cdot}9$, Orthorhombic, $a = 11{\cdot}63 \pm 0{\cdot}02$, $b = 16{\cdot}36 \pm 0{\cdot}03$, $c = 20{\cdot}48 \pm 0{\cdot}03$ Å, $U = 3987$ Å^3, $D_m = 1{\cdot}54$, $Z = 4$, $D_c = 1{\cdot}54$ g cm^{-3}, $F(000) = 1808$. Space group $P2_12_12_1$. μ(Cu-K_α) = 5639 cm^{-1}; $t_{op} = 0{\cdot}35$ mm. Terminal R 0·065; ruby red crystal 0·15 × 0·27 × 0·41 mm.

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