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# *trans*-Iodo(*p*-iodophenyl)bis(triphenylphosphine)palladium(II)

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**Key indicators**

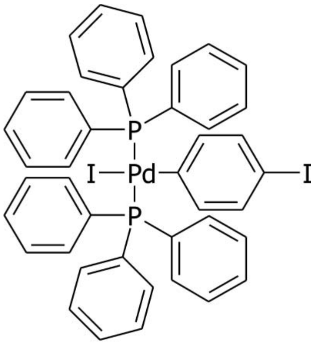
Single-crystal X-ray study
*T* = 100 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.031
*wR* factor = 0.064
Data-to-parameter ratio = 41.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, *trans*-[Pd($C_6H_4I$)I($C_{18}H_{15}P$)$_2$], has been crystallized from dichloromethane. The crystal structure of this complex reveals a slightly distorted square-planar coordination geometry of the Pd atom, which lies on a twofold rotation axis. The P atoms in the triphenylphosphine ligands lie slightly out of the planes of the phenyl rings. The crystal structure is stabilized by short intermolecular I···I contacts, weak C—H···π(arene) hydrogen bonds and π–π stacking interactions.

## Comment

Palladium complexes with phosphine ligands are very often used as catalyst precursors in carbon–carbon bond formation reactions. Such reactions include carbonylation of aryl halides which, depending on the reaction conditions, serve to synthesize carboxylic acids, esters or amides in a one-step process (Mägerlein *et al.*, 2000). Another example is the so-called Heck reaction, which produces functionalized olefins (Herrmann *et al.*, 1995). The key stage in these catalytic processes is the oxidative addition of an aryl halide to a palladium(0) complex and formation of a palladium(II) intermediate containing an X—Pd—Ar fragment (Trzeciak & Ziółkowski, 2005). We report here the synthesis under mild conditions of a palladium(II) complex, (I), which may be considered as such an intermediate state of the palladium catalyst in carbonylation or in the Heck reaction of aryl halides.



**(I)**

Atoms Pd, I1, I2, C1 and C4 lie on a twofold axis (Fig. 1). The Pd atom has a slightly distorted square-planar coordination environment with the phosphine ligands in a *trans* arrangement. The Pd—I1 bond length (Table 1) appears long compared with the expected value of 2.595 Å (Orpen *et al.*, 1989). This is a result of the high *trans* influence of the *p*-iodophenyl group. An almost identical Pd—I distance of 2.7011 (8) Å was found (Flemming *et al.*, 1998) for a similar palladium(II) complex, *trans*-[PdI(Ph)(PPh$_3$)$_2$].

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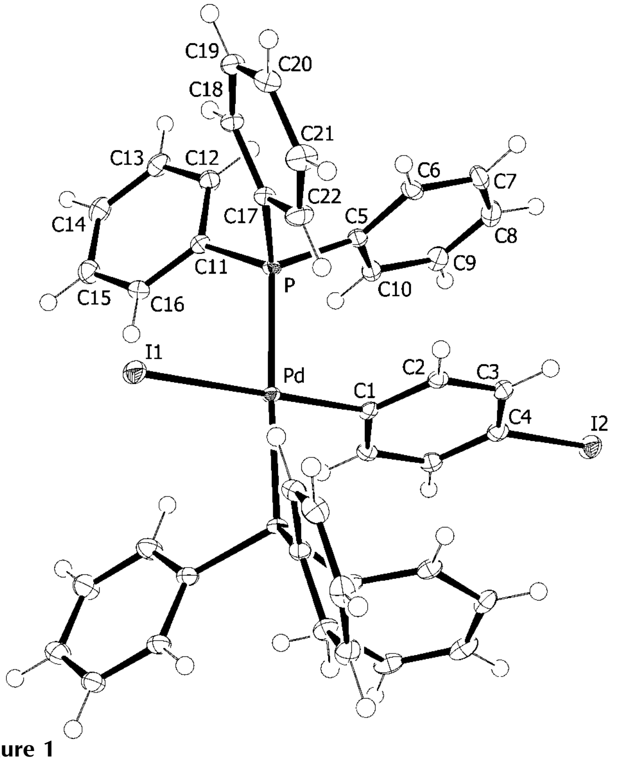

**Figure 1**
The molecular structure and atom-numbering scheme of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are related by the symmetry operation $(1 - x, y, \frac{1}{2} - z)$.

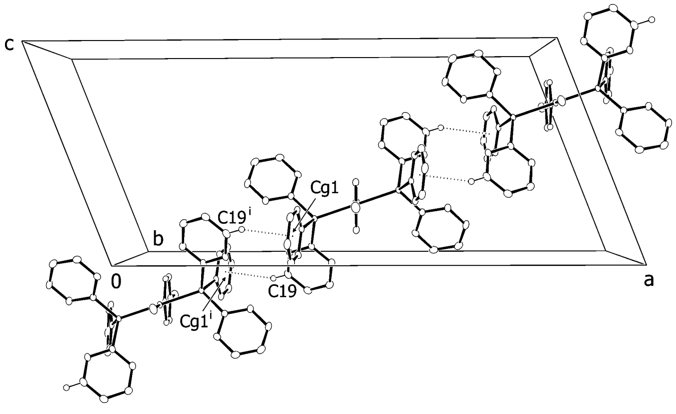

**Figure 2**
Part of the crystal structure of (I), viewed along the *b* axis. The C—H···π hydrogen bonds are represented by dotted lines. *Cg*1 represents the centroid of the C5–C10 phenyl ring. For clarity, H atoms that are not involved in these interactions have been omitted. [Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.]

All bond distances and angles in the triphenylphosphine ligands of (I) are within standard ranges (Dunne & Orpen, 1991). These ligands adopt a typical propeller-like conformation, with an essentially tetrahedral P- atom environment. The P atom deviates from the planes of the C5–C10, C11–C16 and C17–C22 phenyl rings by 0.251 (3), 0.042 (3), and 0.124 (3) Å, respectively.

The *p*-iodophenyl group of compound (I) is oriented at 72.10 (8)° with respect to the palladium coordination plane, while in an analogous complex, *trans*-[PdI(Ph)(PPh$_3$)$_2$], the phenyl ring is almost normal to the metal coordination plane (84.2°; Flemming *et al.*, 1998). Additionally, the phosphine ligands of that complex are in a twisted conformation relative to Pd—Ph, whereas in the title compound the C5–C10 ring and the *p*-iodophenyl group almost eclipse each other when viewed along the P—Pd—P axis.

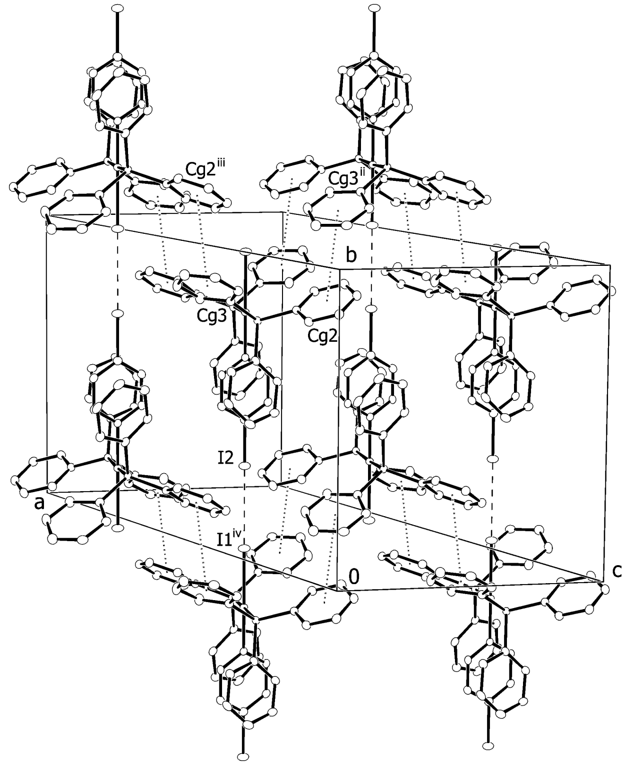

**Figure 3**
The arrangement of the molecules in the crystal structure, in a perspective view in an oblique direction. The π–π stacking interactions are represented by dotted lines, and I···I contacts by dashed lines. *Cg*2 and *Cg*3 denote the centroids of the C11–C16 and C17–C22 phenyl rings, respectively. H atoms have been omitted. [Symmetry codes: (ii) $x, 2 - y, \frac{1}{2} + z$; (iii) $x, 2 - y, -\frac{1}{2} + z$; (iv) $x, -1 + y, z$.]

The molecules of compound (I) are linked by C—H···π(arene) hydrogen bonds (Table 2). Each molecule accepts two hydrogen bonds and also donates two hydrogen bonds, thus forming chains running parallel to the [101] direction (Fig. 2). These chains are further linked (Fig. 3) by relatively short I···I contacts [I2···I1$^{iv}$ = 3.755 (2) Å; C4—I2···I1$^{iv}$ = 180°; symmetry code: (iv) $x, -1 + y, z$]. The I···I distance is 9.5% shorter than the sum of the van der Waals radii (Bondi, 1964), and the I···I interactions play a crucial role in the crystal packing.

In addition, the C11–C16 and C17–C22 phenyl rings are engaged in π–π stacking interactions (Table 3), which further assist in the stabilization of the crystal structure (Fig. 3). Even though the distance of the centroids and the offset of the interacting rings may appear to be somewhat large, it is well known that energetically favorable non-bonded aromatic interactions are generally observed at such phenyl ring centroid separation distances (McGaughey *et al.*, 1998).

*Acta Cryst.* (2006). E**62**, m1428–m1430 Gniewek *et al.* • [Pd(C$_6$H$_4$I)I(C$_{18}$H$_{15}$P)$_2$] **m1429**

## Experimental

Tetrakis(triphenylphosphine)palladium(0) (0.68 g, 0.44 mmol), obtained according to the literature (Coulson, 1972), and 1,4-diiodobenzene (0.072 g, 0.22 mmol) were mixed with dichloromethane (8 ml) at room temperature, under a nitrogen atmosphere. When the reagents were completely dissolved (after 5 min of stirring) the mixture was heated to 333 K in a thermostated oil bath. While heating, the solution changed color from yellow to light orange. After 1.5 h the solution was cooled to ambient temperature and left in a closed flask under a nitrogen atmosphere. Light-yellow prism-shaped crystals of the title compound were obtained within 48 h.

*Crystal data*

$[Pd(C_6H_4I)I(C_{18}H_{15}P)_2]$
$M_r = 960.85$
Monoclinic, $C2/c$
$a = 25.194$ (7) Å
$b = 13.375$ (3) Å
$c = 11.419$ (3) Å
$\beta = 111.49$ (3)°
$V = 3580.4$ (18) Å$^3$
$Z = 4$
$D_x = 1.783$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 2.36$ mm$^{-1}$
$T = 100$ (2) K
Prism, light yellow
0.25 × 0.15 × 0.15 mm

*Data collection*

Kuma KM-4 CCD diffractometer
$\omega$ scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{min} = 0.530$, $T_{max} = 0.713$
29727 measured reflections
8814 independent reflections
6153 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 37.5°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.064$
$S = 0.89$
8814 reflections
215 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 4.32$ e Å$^{-3}$
$\Delta\rho_{min} = -1.35$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pd—I1 | 2.7015 (6) | P—C5 | 1.837 (2) |
| Pd—P | 2.345 (1) | P—C11 | 1.824 (2) |
| Pd—C1 | 2.025 (2) | P—C17 | 1.820 (2) |
| I2—C4 | 2.099 (3) | | |
| | | | |
| P—Pd—C1 | 88.32 (2) | C11—P—C5 | 101.20 (8) |
| P—Pd—I1 | 91.68 (2) | C17—P—Pd | 111.21 (6) |
| C17—P—C11 | 107.77 (8) | C11—P—Pd | 116.59 (6) |
| C17—P—C5 | 102.63 (8) | C5—P—Pd | 116.05 (6) |
| | | | |
| I1—Pd—P—C17 | 54.11 (6) | C1—Pd—P—C5 | −9.09 (7) |
| I1—Pd—P—C11 | −69.97 (6) | P—Pd—C1—C2 | 72.10 (8) |
| I1—Pd—P—C5 | 170.91 (7) | | |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C19—H19···*Cg*1$^{i}$ | 0.95 | 2.77 | 3.629 (3) | 150 |

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

**Table 3**
Intermolecular $\pi$–$\pi$ interactions (Å, °).

*Cg*1 denotes the centroid of ring C5–C10, *Cg*2 the centroid of ring C11–C16 and *Cg*3 the centroid of ring C17–C22; *Cg*···*Cg* is the distance between ring centroids; the dihedral angle is that between the *CgI* and *CgJ* planes; the interplanar distance is the perpendicular distance of *CgI* from the plane of ring *J*; the offset is the lateral displacement of ring *I* relative to ring *J*.

| *CgI* | *CgJ* | *Cg*···*Cg* | Dihedral angle | Interplanar distance | Offset |
|---|---|---|---|---|---|
| 2 | 3$^{ii}$ | 4.122 (3) | 10.1 (2) | 3.352 (3) | 2.399 (3) |
| 3 | 2$^{iii}$ | 4.122 (3) | 10.1 (2) | 3.316 (3) | 2.448 (3) |

Symmetry codes: (ii) $x, 2 - y, \frac{1}{2} + z$; (iii) $x, 2 - y, -\frac{1}{2} + z$.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{iso}$(H)= $1.2U_{eq}$(C). The two highest residual density peaks ($Q1 = 4.32$ and $Q2 = 2.07$ e Å$^{-3}$) lie on a twofold axis. They are located 1.07 and 0.68 Å from I1 and C1, respectively. $Q1$ is 3.77 Å from Pd, which is almost exactly the same as the shortest I···I contact, and $Q2$ is 2.71 Å from Pd, which is also the same as the Pd—I1 distance. This may indicate a stacking fault with translation by the amount of the Pd—I1 bond length along the $b$ axis. This effect could be modeled by placing a small contribution of a Pd atom on $Q2$, of an I1 atom on Pd, and of I2 of the next molecule on $Q1$. We found that approximately 2% of the molecules are thus displaced. This model could not be further developed and is not included in the results presented here. The deepest hole os located 0.62 Å from atom I1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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**m1430** Gniewek *et al.* • $[Pd(C_6H_4I)I(C_{18}H_{15}P)_2]$ *Acta Cryst.* (2006). E**62**, m1428–m1430