

***trans*-(6-Amino-2-pyridinio)iodobis-(triphenylphosphine)palladium(II) iodide ethyl acetate solvate**William Clegg* and
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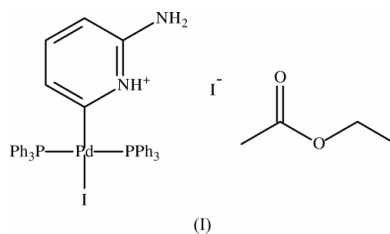
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Key indicatorsSingle-crystal X-ray study
 $T = 160\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
Disorder in main residue
 R factor = 0.025
 wR factor = 0.066
Data-to-parameter ratio = 18.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{Pd}(\text{C}_5\text{H}_6\text{N}_2)((\text{C}_6\text{H}_5)_3\text{P})_2]\text{I}\cdot\text{C}_4\text{H}_8\text{O}_2$, has a square-planar geometry for Pd, coordinated by two *trans*-phosphines, an iodo, and an aminopyridyl ligand. The cation, anion and solvent molecule all lie on a crystallographic mirror plane, and are connected together by $\text{N}-\text{H}\cdots\text{I}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

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The title compound, (I), was obtained unexpectedly as a by-product in a reaction exploring the synthesis of enantiomerically pure pyridylamino acids *via* palladium-catalysed cross-coupling of serine-derived organozinc reagents with various halopyridines (Tabanella *et al.*, 2003). It is presumably derived from the product of oxidative addition of 2-amino-6-bromopyridine to bis(triphenylphosphine)-palladium(0), followed by exchange of bromide for iodide, originating from the zinc reagent. Similar products have been obtained by other researchers in related reactions (Spee *et al.*, 2000; Bocelli *et al.*, 1998).



The complex cation (Fig. 1) contains Pd in a square-planar coordination environment, bonded to two *trans*-triphenylphosphine ligands, one iodide, and an amino-substituted pyridyl group through its *ortho*-C atom. This pyridyl ligand is protonated on the ring N atom, and it forms two hydrogen bonds to the uncoordinated second iodide anion, one from the pyridinium $\text{N}-\text{H}$ and the other from the 6-amino NH_2 group. The second H atom of the amino group is hydrogen bonded to the ethyl acetate solvent molecule (Fig. 2), which has relatively large anisotropic displacement parameters and may be subject to unresolved disorder in addition to the disorder detected and modelled for its two methyl groups. The Pd atom, both iodides, all atoms of the pyridyl ligand, and all non-H atoms of the solvent molecule lie in a crystallographic mirror plane, which relates the two phosphine ligands to each other. Deviations from ideal square-planar coordination geometry are small, as can be seen in Table 1 and in the figures. Apart from the hydrogen bonding, there are no significant intermolecular interactions.

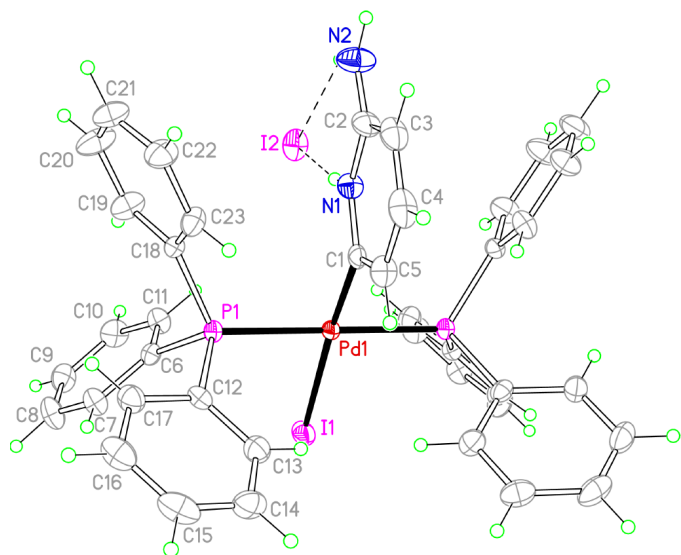


Figure 1
The structure of the cation and anion, with atom labels and 50% probability ellipsoids for non-H atoms. Hydrogen bonds are shown as dashed lines. The solvent molecule is not shown.

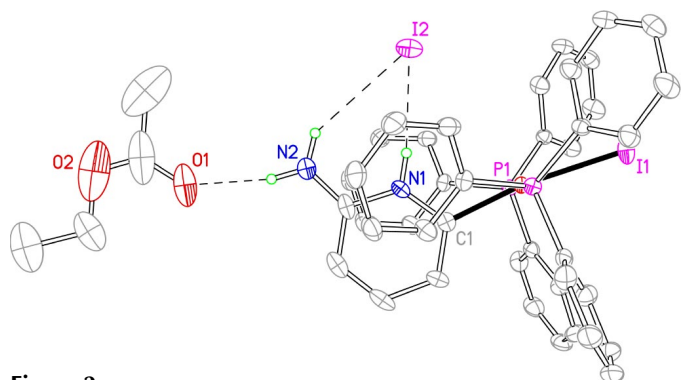


Figure 2
The cation, anion and solvent molecule, viewed perpendicular to the mirror plane. H atoms not involved in hydrogen bonding have been omitted; hydrogen bonds are shown as dashed lines.

Pyridyl complexes of palladium with a Pd–C bond are not unknown, but there are few reported crystal structures. A search of the Cambridge Structural Database (CSD, Version 5.24 with two updates, April 2003; Allen, 2002) finds seven. In every case, the other ligands are a combination of phosphines and halides. Except for one complex with a chelating diphosphine, which imposes a *cis* configuration (Chin *et al.*, 1998), the pyridyl ligand always lies *trans* to a halide (Cave *et al.*, 1999; Isobe *et al.*, 1980; Newkome *et al.*, 1987; Benetollo *et al.*, 1991), as is the case here.

The CSD contains 100 structures of bis(phosphine) complexes of palladium with a Pd–C bond *trans* to a halide ligand. 12 of these have iodine as the halogen, nine of them with a substituted or unsubstituted phenyl or pyridyl ligand. For these, the Pd–C distances range from 2.009 to 2.048 Å, and the Pd–I distances from 2.680 to 2.706 Å. The title complex thus has both the shortest Pd–I bond and (marginally) the shortest Pd–C bond. The values are in accordance

with the known relative *trans* influences of aryl and iodo ligands (e.g. Spee *et al.*, 2000; Vicente *et al.*, 1999; Flemming *et al.*, 1998).

Experimental

The synthetic strategy for the preparation of pyridylalanines and the reaction leading to the formation of the title compound are described by Tabanella *et al.* (2003). A zinc reagent derived from iodoalanine was treated with 2-amino-6-bromopyridine and with dichlorobis(triphenylphosphine)palladium as a coupling catalyst, and the title compound was isolated by recrystallization of the crude reaction mixture from ethyl acetate.

Crystal data

[Pd(C₅H₆N₂)(C₁₈H₁₅P)₂]₂I·C₄H₈O₂
M_r = 1066.96
 Orthorhombic, *Cmc*2₁
a = 15.0297 (9) Å
b = 16.9603 (10) Å
c = 17.2897 (11) Å
V = 4407.3 (5) Å³
Z = 4
D_x = 1.608 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 13025 reflections
 θ = 2.2–28.8°
 μ = 1.93 mm⁻¹
T = 160 (2) K
 Plate, pale yellow
 0.40 × 0.21 × 0.10 mm

Data collection

Bruker SMART 1K CCD diffractometer
 Narrow-frame ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
T_{min} = 0.600, *T_{max}* = 0.824
 14181 measured reflections

5016 independent reflections
 4828 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
 θ_{max} = 28.8°
h = −19 → 19
k = −22 → 17
l = −23 → 19

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.026
wR (*F*²) = 0.066
S = 1.04
 5016 reflections
 270 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.905P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.71 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983);
 2220 Friedel pairs
 Flack parameter = −0.005 (16)

Table 1

Selected geometric parameters (Å, °).

Pd1–I1	2.6580 (5)	Pd1–P1	2.3313 (7)
Pd1–C1	2.006 (4)		
I1–Pd1–C1	171.95 (14)	C1–Pd1–P1	89.06 (2)
I1–Pd1–P1	90.81 (2)	P1–Pd1–P1 ⁱ	177.49 (5)

Symmetry code: (i) 1 − *x*, *y*, *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1...I2	0.88	2.52	3.393 (4)	173
N2–H2A...I2	0.88	3.05	3.806 (5)	146
N2–H2B...O1	0.88	2.08	2.950 (6)	168

H atoms were placed geometrically and refined with a riding model (including free rotation about C–C bonds), and with *U_{iso}* constrained to be 1.2 (1.5 for methyl groups) times *U_{eq}* of the carrier atom; N–H distances were set at 0.88 Å, and C–H to 0.95

(aromatic), 0.98 (methyl) or 0.99 Å (methylene). Both methyl groups of the solvent molecule were found to be disordered, each with two sets of H atoms, which were constrained to ideal tetrahedral angles and assigned equal occupancy factors. The largest peaks in the final difference synthesis lie close to the Pd and I atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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