Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

An organometallic compound with Z' = 4: {2-[2-(benzylideneamino)-phenyl]-1,2-bis(methoxycarbonyl)-ethenyl-κ^2C^1,N}iodo(triphenyl-phosphine-κP)palladium(II)

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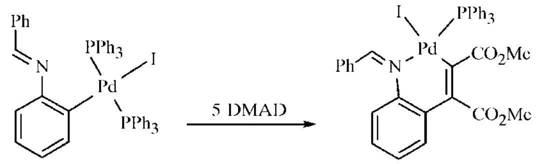
Received 29 November 2006
Accepted 30 November 2006
Online 23 December 2006

The title compound, $[Pd(C_{19}H_{17}NO_4)I(C_{18}H_{15}P)]$, crystallizes with four independent molecules in the asymmetric unit. The main difference between the molecules is the disposition of the PPh_3 ligand, for which in each molecule one ring is perpendicular to the ligand plane, but may be directed in either direction away from the plane; of the four molecules, two represent each possible direction. The independent molecules are arranged to form a chain parallel to [101] with an approximate translation of $(a+c)/4$ between successive molecules, excluding the PPh_3 rings. This leads to a systematic weakness of the reflections with $h + l \neq 4n$.

Comment

The title compound, (I), was synthesized during a study of aryl palladium complexes bearing functionalized susbtituents on the *ortho* position. In these investigations, oxidative addition of Pd^0 precursors to aryl halides yielded organometallic compounds that are models of intermediates in palladium-catalysed organic syntheses (Vicente *et al.*, 2005) and may lead to new coordination modes for the ligands. There are a large number of known palladium–diimine complexes; a search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) revealed 106 hits for α-diimine complexes of palladium, *e.g.* de Pater *et al.* (2005). However, the double bond in the imine group of (I) does not form part of the heterocycle.

Compound (I) crystallizes in the solvent-free form with four independent molecules in the asymmetric unit. Molecules 1 and 3 are shown in Figs. 1 and 2, respectively; a similar numbering scheme was used for all the molecules, replacing the first digit '1' in molecule 1 with the appropriate molecule number 2, 3 or 4. In all four molecules, the Pd atom shows the expected planar four-coordination, albeit with slight but



(I)

significant deviations from planarity (r.m.s. deviations of the five atoms Pd, I, P, N and C from their least-squares plane are 0.01, 0.04, 0.05 and 0.08 Å, respectively, for molecules 1–4). The bond lengths at Pd are consistent over all four molecules (see below for one possible exception). The bite of the C,N-bidentate ligand is constant at *ca* 82° (important molecular dimensions are given in Table 1). The chelate rings display a configuration whereby atoms Pdn, Cn01, Cn02 and Cn12 are coplanar (r.m.s. deviations $\leq$ 0.02 Å for all four molecules), and the other two atoms, Nn and Cn11, are displaced from this plane to the same side. The double-bond positions Cn01=Cn02 are unambiguously established by the bond lengths. The carboxylate groups are disposed such that the absolute torsion angles Cn02=Cn01—Cn03=On01 lie in the range 9–17° and Cn01=Cn02—Cn04=On02 in the range 90–97°.

Despite the above-mentioned similarities, the molecules differ in one important respect, namely the disposition of the triphenylphosphine ligand. For each molecule, one phenyl ring of PPh_3 is approximately perpendicular to the coordination plane (*cf.* torsion angles I—Pd—P—C_{ipso} in Table 1; in each

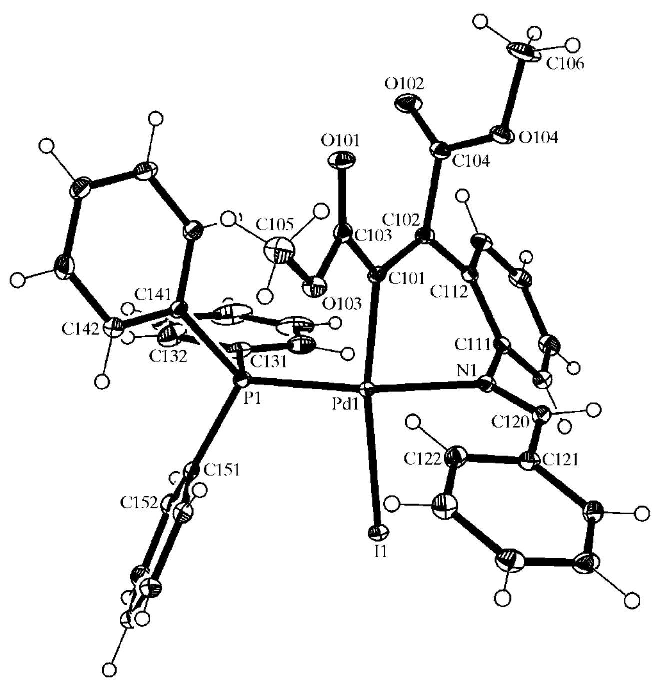


Figure 1
The first independent molecule of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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case, there is one ring with an absolute value of *ca* 90°). However, in molecules 1 and 4, the ring at C*n*31 points out of the coordination plane to the same side as ring C*n*11, whereas in molecules 2 and 3 (Fig. 2), the ring at C*n*51 points to the other side of the plane from C*n*11, *viz*. to the same side as C*n*21. The differing Pd—P bond lengths (slightly longer for molecules 2 and 3) and the markedly irregular Pd—P—C bond angles for molecules 1 and 4, with wide angles of *ca* 120° to C*n*41 to avoid closer contact between the phenyl ring and the methoxycarbonyl group at C*n*01, also reflect these differences. Even within this loose classification as two pairs of similar molecules, there are considerable differences in the I—Pd—P—C and Pd—P—C—C torsion angles for either given pair.

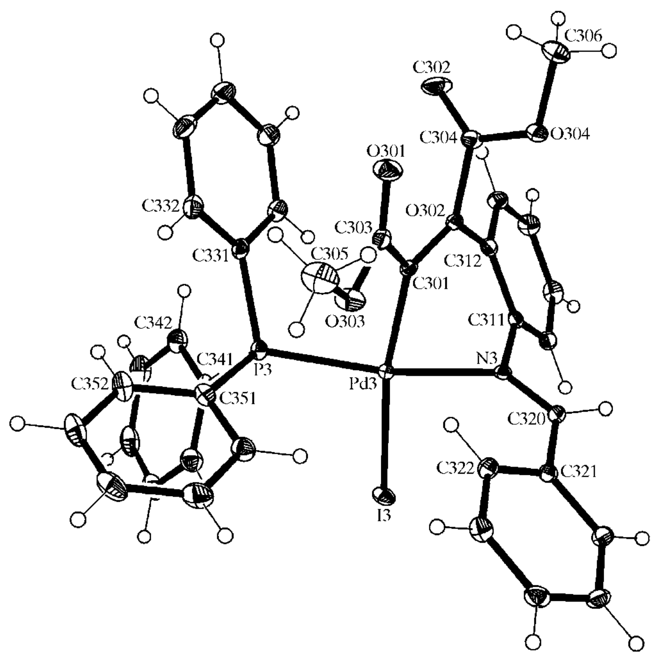

Figure 2
The third independent molecule of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

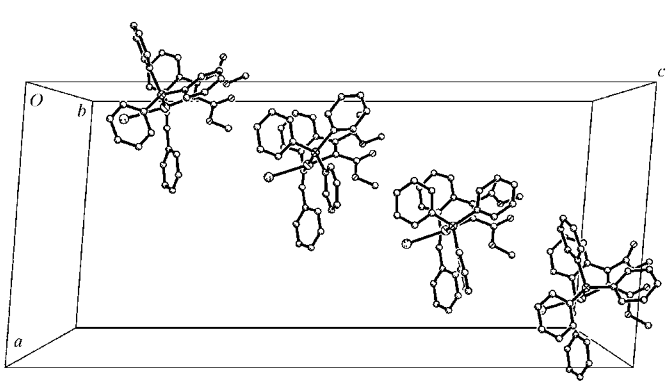

Figure 3
The four independent molecules of (I) in the unit cell, running in order from molecule 1 (bottom right) to molecule 4 (top left). H atoms have been omitted.

In the CSD, there are 25 examples of palladium complexes with a coordination sphere of C/N(chelating)/P/I. However, the bond lengths at Pd vary over a very wide range (*e.g.* Pd—N = 2.09–2.32 Å), making generalization difficult, and the iodo ligand may be *trans* to C or P. There are no examples with P *trans* to C for this donor atom set; consistent with the great extent of P/C 'transphobia' (Vicente *et al.*, 1997, 2002, 2006), the P- and C-atom donors are mutually *cis* in (I) and in the other literature examples.

The molecular packing of (I) is noteworthy. The molecules are associated into chains parallel to [101] (Fig. 3), in which neighbouring molecules, except for the PPh_3 phenyl groups as noted above, adopt positions related by the non-crystallographic translation of (*a*+*c*)/4. This pseudosymmetry is responsible for the fact that reflections with $h + l \neq 4n$ are systematically weak. However, the seven non-classical ('weak') hydrogen-bonding interactions (Desiraju & Steiner, 1999; Table 2), of which five involve *para*-H atoms of the PPh_3 ligands, are not formed within the chains.

Experimental

Under a dinitrogen atmosphere, dimethyl acetylenedicarboxylate (DMAD) (94 µl, 0.7 mmol) was added to a solution of *trans*-[$(C_6H_4N{=}CH_2Ph$-2)I$(PPh_3)_2$Pd] (Vicente *et al.*, 1999) (125 mg, 0.13 mmol) in degassed CH_2Cl_2 (5 ml) and the reaction mixture was stirred overnight (16 h). The solvent was removed and the residue was treated with diethyl ether (5 ml). The solid was collected by filtration, washed with diethyl ether (3 × 3 ml) and dried in air to yield complex (I) as a yellow powder (yield 80 mg, 73%). Single crystals were obtained by slow diffusion of Et_2O into a solution of complex (I) in $CDCl_3$. IR (Nujol, ν, cm^{-1}): 1726 (CO); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (*d*, $^3J_{H,H}$ = 7 Hz, 2H), 8.40 (*d*, $^1J_{H,H}$ = 13.5 Hz, 1H), 7.68–7.33 (several *m*, 22H, 4Ph + $2H_{arom}$), 3.69 (*s*, 3H, OMe), 3.06 (*s*, 3H, OMe); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.44 (PPh_3). Analysis calculated for $C_{37}H_{31}INO_4PPd$: C 54.33, H 3.82, N 1.71%; found: C 54.53, H 3.86, N 1.67%.

Crystal data

[Pd($C_{19}H_{17}NO_4$)I($C_{18}H_{15}P$)]
M_r = 817.90
Monoclinic, $P2_1/c$
a = 16.6938 (11) Å
b = 22.1074 (15) Å
c = 36.666 (3) Å
β = 94.460 (4)°
V = 13490.8 (17) Å^3
Z = 16
D_x = 1.611 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.55 mm^{-1}
T = 133 (2) K
Prism, yellow
0.38 × 0.22 × 0.20 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.653, T_{max} = 0.733
261441 measured reflections
39449 independent reflections
27970 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 30.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.070
S = 0.95
39449 reflections
1629 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 1.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—C101	2.019 (2)	Pd3—C301	2.023 (2)
Pd1—N1	2.0744 (18)	Pd3—N3	2.0727 (17)
Pd1—P1	2.2524 (6)	Pd3—P3	2.2700 (6)
Pd1—I1	2.6716 (3)	Pd3—I3	2.6595 (3)
C101—C102	1.338 (3)	C301—C302	1.344 (3)
Pd2—C201	2.020 (2)	Pd4—C401	2.024 (2)
Pd2—N2	2.0813 (19)	Pd4—N4	2.0654 (18)
Pd2—P2	2.2833 (6)	Pd4—P4	2.2660 (6)
Pd2—I2	2.6683 (3)	Pd4—I4	2.6877 (3)
C201—C202	1.346 (3)	C401—C402	1.347 (3)
C101—Pd1—N1	82.16 (8)	C301—Pd3—N3	82.01 (8)
C101—Pd1—P1	93.37 (6)	C301—Pd3—P3	91.08 (6)
N1—Pd1—P1	165.77 (5)	N3—Pd3—P3	170.16 (5)
C101—Pd1—I1	168.71 (6)	C301—Pd3—I3	168.52 (6)
N1—Pd1—I1	88.46 (5)	N3—Pd3—I3	87.45 (5)
P1—Pd1—I1	94.253 (17)	P3—Pd3—I3	98.796 (17)
C131—P1—Pd1	108.64 (8)	C331—P3—Pd3	109.98 (7)
C141—P1—Pd1	120.28 (7)	C341—P3—Pd3	118.36 (8)
C151—P1—Pd1	112.94 (7)	C351—P3—Pd3	114.94 (8)
C201—Pd2—N2	81.95 (8)	C401—Pd4—N4	82.05 (8)
C201—Pd2—P2	93.81 (7)	C401—Pd4—P4	95.77 (6)
N2—Pd2—P2	175.10 (5)	N4—Pd4—P4	168.13 (5)
C201—Pd2—I2	170.30 (7)	C401—Pd4—I4	167.88 (7)
N2—Pd2—I2	89.52 (5)	N4—Pd4—I4	87.77 (5)
P2—Pd2—I2	94.495 (17)	P4—Pd4—I4	92.847 (16)
C231—P2—Pd2	114.28 (8)	C431—P4—Pd4	108.49 (8)
C241—P2—Pd2	115.85 (8)	C441—P4—Pd4	122.76 (7)
C251—P2—Pd2	112.67 (8)	C451—P4—Pd4	113.26 (7)
I1—Pd1—P1—C131	−87.82 (8)	I3—Pd3—P3—C331	−148.06 (8)
I1—Pd1—P1—C141	155.74 (9)	I3—Pd3—P3—C341	−29.18 (9)
I1—Pd1—P1—C151	29.24 (9)	I3—Pd3—P3—C351	88.14 (9)
Pd1—P1—C131—C132	−174.63 (19)	Pd3—P3—C331—C332	−125.79 (19)
Pd1—P1—C141—C142	−111.48 (19)	Pd3—P3—C341—C342	−108.0 (2)
Pd1—P1—C151—C152	−110.40 (18)	Pd3—P3—C351—C352	−179.46 (19)
C102—C101—C103—O101	17.2 (3)	C302—C301—C303—O301	13.1 (4)
C101—C102—C104—O102	−95.5 (3)	C301—C302—C304—O302	−94.4 (3)
I2—Pd2—P2—C231	−165.59 (9)	I4—Pd4—P4—C431	−80.69 (8)
I2—Pd2—P2—C241	−43.87 (9)	I4—Pd4—P4—C441	162.79 (9)
I2—Pd2—P2—C251	74.91 (9)	I4—Pd4—P4—C451	38.86 (8)
Pd2—P2—C231—C232	−128.6 (2)	Pd4—P4—C431—C432	−174.12 (17)
Pd2—P2—C241—C242	−93.2 (2)	Pd4—P4—C441—C442	−129.76 (17)
Pd2—P2—C251—C252	−169.81 (19)	Pd4—P4—C451—C452	−113.42 (18)
C202—C201—C203—O201	17.3 (4)	C402—C401—C403—O401	9.4 (4)
C201—C202—C204—O202	−97.0 (3)	C401—C402—C404—O402	−90.4 (3)

Because of the large number of parameters, full-matrix refinement was not possible, and the refinement was therefore split into two blocks consisting of molecules 1 and 2, and molecules 3 and 4, respectively. Methyl H atoms were identified in difference syntheses, idealized, and refined as rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model. C—H bond lengths were fixed at 0.98 (methyl C) or 0.95 Å (Csp^2), and methyl H—C—H angles were fixed at 109.5°. U_{iso}(H) values were fixed at 1.2 times U_{eq} of the parent atom. The maximum residual electron density of 1.3 e Å^{-3} is associated with the methoxy group at C401, and may indicate slight disorder of this group. The next five difference peaks (down to 0.8 e Å^{-3}) all lie close to Pd or I atoms.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C154—H154···O401^{i}	0.95	2.44	3.325 (3)	155
C254—H254···O402^{i}	0.95	2.49	3.334 (3)	148
C313—H313···O302^{ii}	0.95	2.42	3.170 (3)	136
C354—H354···O102^{iii}	0.95	2.59	3.536 (3)	174
C454—H454···O301^{iii}	0.95	2.45	3.088 (3)	124
C133—H133···I3^{iv}	0.95	2.99	3.805 (3)	145
C444—H444···I1^{v}	0.95	2.99	3.780 (2)	141

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

The authors thank Professor J. Vicente, University of Murcia, for his continuing support and encouragement.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3068). Services for accessing these data are described at the back of the journal.

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