A chloro-bridged dinuclear phosphinitopalladium complex, di-μ-chloro-bis[(diphenoxyphosphinite-κP)(diphenoxyphosphinito-κP)palladium(II)]

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The title compound, [Pd$_2$(C$_{12}$H$_{10}$O$_3$P)$_2$Cl$_2$(C$_{12}$H$_{11}$O$_3$P)$_2$], consists of a dinuclear μ-chloro-bridged palladium unit with two diphenoxyphosphinite groups per Pd atom, linked together by a hydrogen bond. The asymmetric unit contains one half of the molecule, with the other half generated by an inversion centre. The geometry around the P atoms may be described as distorted tetrahedral. Adjacent molecules of the complex are linked by weak C—H···O and C—H···Cl hydrogen bonds. The structure is additionally stabilized by π–π stacking interactions between the aryl rings. These interactions form a herring-bone pattern in the crystal structure.

Comment

Carbon–carbon bond-forming reactions are important fundamental processes in synthetic chemistry. Among such reactions the most commonly recognized are: carbonylation, which, depending on the conditions, enables the synthesis of carboxylic acids, esters or amides in a one-step process (Mägerlein *et al.*, 2000); olefination of aryl halides, the so-called Heck reaction (Beletskaya & Cheprakov, 2000); and the Suzuki process, which leads to the formation of biphenyl derivatives (Miyaura & Suzuki, 1995). Palladium compounds with phosphine ligands are frequently used as catalyst precursors in the above-mentioned reactions. Phosphinites, however, represent an interesting alternative to phosphines as ligands for metal ions employed as catalysts in organic synthesis. Such complexes have proved to be air-stable and highly active in methoxycarbonylation or the Heck reaction (Pryjomska *et al.*, 2006) and also in Suzuki cross-coupling of aryl halides (Li, 2002). In this paper, we report the synthesis and crystal structure of the title dimeric phosphinitopalladium

complex, (I), which may be successfully used as an efficient catalyst precursor.

The molecule of compound (I) (Fig. 1) contains a dimetallo-cyclic Pd$_2$Cl$_2$ core, with a crystallographic centre of inversion at the mid-point of the Pd···Pd^i line [symmetry code: (i)

(I)
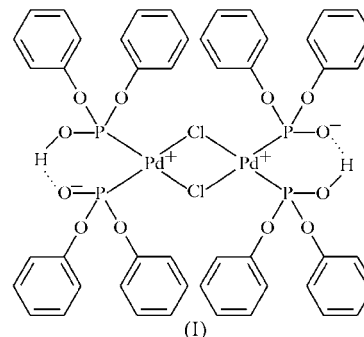
$-x + 1$, $-y + 1$, $-z + 1$]. The positive charge of each Pd atom is balanced by the O$^-$ atoms. There is clearly no Pd—Pd bond in the dimer, the Pd···Pd^i distance of 3.4830 (9) Å being too long to consider any metal–metal interaction. The Pd atoms are four-coordinated in a square-planar geometry. The angles between adjacent ligands deviate only slightly from the expected value of 90° (Table 1). As a result of the presence of the inversion centre, the Pd/Cl/Pd^i/Cl^i ring is strictly planar. The Pd—Cl and Pd—Cl^i bond lengths are quite similar [2.4139 (8) and 2.4002 (8) Å, respectively]. These distances appear to be somewhat large compared with the range reported for typical four-coordinate palladium complexes
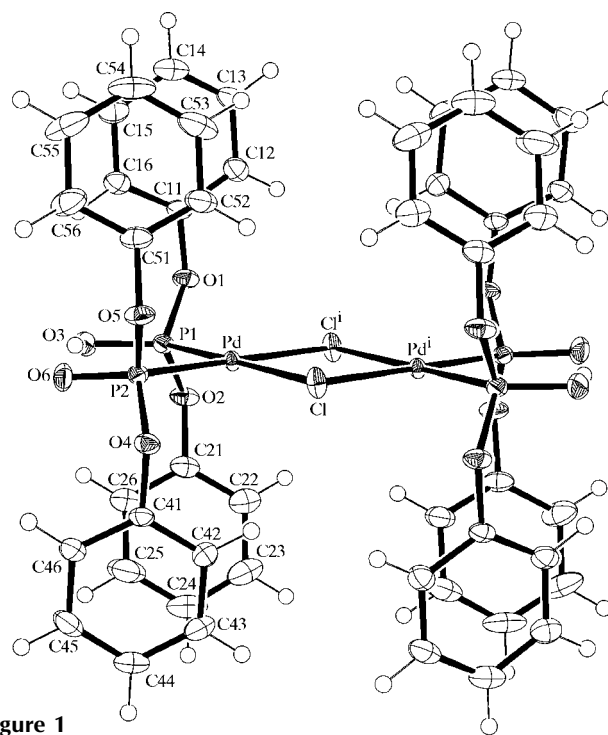

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are symmetrically dependent *via* an inversion centre. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

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(2.298–2.354 Å; Orpen *et al.*, 1989). However, such long bond distances are normally observed for analogous dinuclear *µ*-chloro-bridged palladium compounds and might be justified by the *trans* effect of the phosphorus ligands.

The geometric parameters around the four-coordinate P1 and P2 atoms indicate a noticeable deformation of the ideal tetrahedron towards a trigonal pyramid. The O3—P1—Pd and O6—P2—Pd angles differ considerably from the ideal value of 109.5° and approach 120°, while the O1—P1—O2 and O4—P2–O5 angles are very close to 90° (Table 1). Such large distortions of these angles might be explained by the steric effects of the different substituents or bond types, and are commonly observed for palladium complexes with diphenyl-phosphane ligands (Stockland *et al.*, 2004). The bond lengths
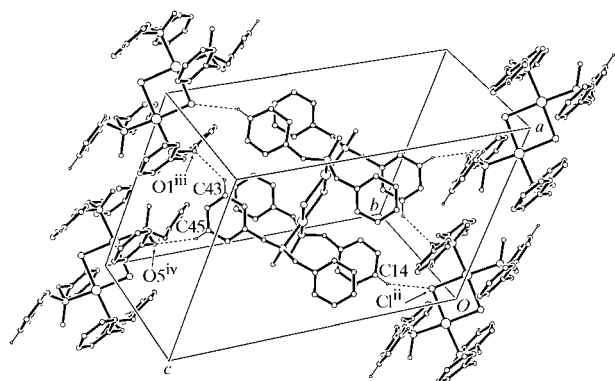

Figure 2
Part of the crystal structure of (I), viewed in an oblique direction. Weak intermolecular hydrogen bonds are represented by dashed lines. For clarity, H atoms not involved in the interactions discussed have been omitted. [Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.]
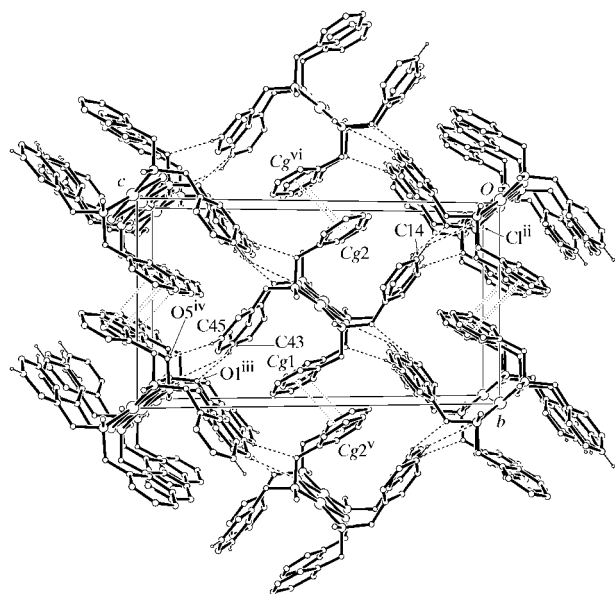

Figure 3
The arrangement of the molecules in the crystal structure of (I), viewed along the *a* axis. The hydrogen bonds are represented by dashed lines and *π*–*π* interactions by dotted lines. *Cg*1 and *Cg*2 denote the centroids of the C21–C26 and C51–C56 phenyl rings, respectively. [Symmetry codes as in Fig. 2; additionally: (v) $x, y + 1, z$; (vi) $x, y - 1, z$.]

P1—O1, P1—O2, P2—O4 and P2—O5 are typical (Allen *et al.*, 1987). In contrast, the nearly equal distances P1—O3 and P2—O6 fall between the values expected for single and double P—O bonds. As a result, the OH group on each side of the molecule forms a nearly symmetric intramolecular hydrogen bond with O⁻ (Table 2). The existence of this type of hydrogen-bond interaction was also confirmed by ¹H NMR spectroscopy (CDCl₃), which revealed a broad signal at 10 p.p.m. This O3—H3···O6 interaction generates an *S*(6) motif (Bernstein *et al.*, 1995) in the crystal structure.

Several *µ*-chloro-bridged dinuclear phosphinitopalladium complexes have previously been structurally characterized. The intramolecular hydrogen-bond geometries of such compounds are compared with that of (I) in Table 3. The O3—H3 distance of 1.08 (2) Å may at first appear to be rather large, especially when it is contrasted with the value observed for a typical hydroxy group. However, this bond length is comparable with the O—H distances found in the other characterized structures. Furthermore, there are also numerous complexes with longer O—H bond lengths, and in those cases the hydrogen-bond geometry becomes almost ideally symmetric. Finally, it is worth noting that the O···O distance observed for (I) is slightly longer than in all other palladium complexes described.

The molecules of (I) are linked by a few weak hydrogen-bond interactions of C—H···Cl and C—H···O types (Desiraju & Steiner, 1999). Aryl atoms C14, C43 and C45 act as hydrogen-bond donors (Table 2). As a consequence, a three-dimensional network of hydrogen-bond interactions is formed in the crystal structure (Fig. 2). Even though the H···Cl distance may at first appear to be fairly long compared with the expected value (Aullón *et al.*, 1998), the presence of C—H···Cl hydrogen bonds was confirmed spectroscopically for a complex with H···Cl spacings even greater than 3 Å, where Cl was bonded to Pd (Fábry *et al.*, 2004).

Additionally, the C21–C26 and C51–C56 phenyl rings are engaged in *π*–*π* stacking contacts (Fig. 3), which further assist in the stabilization of the crystal structure by assembling chains running parallel to the [010] direction. The observed distance between the centroids and the offset of the aryl rings (Table 4) are standard for energetically favourable non-bonded aromatic interactions (McGaughey *et al.*, 1998). The phenyl rings in neighbouring stacks are arranged perpendicularly, thus forming a herring-bone pattern in the crystal structure.

Experimental

PdCl₂(cod) (cod is cyclooctadiene) (0.072 g, 0.3 mmol) was dissolved in benzene (1 ml) and then diphenylphosphite (0.12 ml, 0.6 mmol) was added. A white precipitate was formed immediately. The mixture was stirred for 1 h. After that time, the product was filtered off, washed with diethyl ether and dried *in vacuo*. Finally, the product was recrystallized from chloroform. Analysis calculated: C 47.32, H 3.47%; found: C 47.18, H 3.29%. IR (KBr, *ν*, cm⁻¹): 1600 (*s*), 1480 (*vs*), 1200 (*vs*), 900 (*vs*), 750 (*m*), 700 (*m*), 500 (*m*); IR (Nujol, *ν*, cm⁻¹): 381.7, 338.0 [*m*(Pd—Cl)]; ¹H NMR (CDCl₃): *δ* 7.15 (*m*, Ph), 10.0 (*br*, OH); ³¹P NMR: *δ* 65.5.

Crystal data

$[Pd_2(C_{12}H_{10}O_3P)_2Cl_2(C_{12}H_{11}O_3P)_2]$
$M_r = 1218.40$
Monoclinic, $P2_1/n$
$a = 12.268\ (3)$ Å
$b = 10.514\ (2)$ Å
$c = 19.549\ (4)$ Å
$\beta = 106.78\ (3)°$
$V = 2414.2\ (10)$ Å^3

$Z = 2$
$D_x = 1.676$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.05$ mm^{-1}
$T = 110\ (2)$ K
Plate, colourless
$0.20 \times 0.13 \times 0.06$ mm

Data collection

Xcalibur PX diffractometer with
  Onyx CCD area detector
φ and ω scans
Absorption correction: analytical
  (*CrysAlis RED*; Oxford
  Diffraction, 2003)
  $T_{min} = 0.837$, $T_{max} = 0.933$

57621 measured reflections
12649 independent reflections
8606 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 37.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.111$
$S = 1.15$
12649 reflections
310 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.8428P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—Cl	2.4139 (8)	P2—O4	1.594 (2)
Pd—Cl^i	2.4002 (8)	P2—O5	1.590 (2)
Pd—P1	2.2248 (8)	P2—O6	1.517 (2)
Pd—P2	2.2220 (8)	O1—C11	1.410 (3)
P1—O1	1.594 (2)	O2—C21	1.416 (3)
P1—O2	1.597 (2)	O4—C41	1.407 (3)
P1—O3	1.514 (2)	O5—C51	1.418 (3)
P1—Pd—P2	92.81 (3)	O4—P2—Pd	111.87 (7)
P1—Pd—Cl^i	89.78 (3)	O5—P2—Pd	110.60 (7)
P2—Pd—Cl	90.10 (3)	O6—P2—Pd	118.50 (8)
Cl—Pd—Cl^i	87.31 (3)	O4—P2—O5	93.89 (9)
O1—P1—Pd	112.32 (7)	O4—P2—O6	108.9 (1)
O2—P1—Pd	109.25 (7)	O5—P2—O6	110.4 (1)
O3—P1—Pd	118.06 (8)	P1—O1—C11	125.1 (2)
O1—P1—O2	94.38 (9)	P1—O2—C21	118.1 (2)
O1—P1—O3	109.9 (1)	P2—O4—C41	123.4 (2)
O2—P1—O3	110.4 (1)	P2—O5—C51	121.4 (2)
Cl^i—Pd—P1—O1	48.93 (8)	Cl—Pd—P2—O6	171.69 (9)
Cl^i—Pd—P1—O2	−54.42 (8)	Pd—P1—O1—C11	68.6 (2)
Cl^i—Pd—P1—O3	178.41 (9)	Pd—P1—O2—C21	−54.8 (2)
Cl—Pd—P2—O4	43.81 (8)	Pd—P2—O4—C41	73.3 (2)
Cl—Pd—P2—O5	−59.43 (8)	Pd—P2—O5—C51	−62.3 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O6	1.08 (2)	1.40 (2)	2.435 (2)	158 (2)
C14—H14$\cdots$Cl^{ii}	0.95	2.87	3.692 (3)	145
C43—H43$\cdots$O1^{iii}	0.95	2.58	3.332 (3)	136
C45—H45$\cdots$O5^{iv}	0.95	2.63	3.466 (3)	147

Symmetry codes: (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

Table 3
Comparison of the intramolecular hydrogen-bond geometries (Å, °) in various μ-chloro-bridged dinuclear phosphinitopalladium complexes; comparative data from the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002).

CSD Refcode	O—H	H$\cdots$O	O$\cdots$O	O—H$\cdots$O	Reference
(I)†	1.08 (2)	1.40 (2)	2.435 (2)	158 (2)	a
EGEGIG‡	1.14	1.27	2.404	174	b
	1.19	1.22	2.405	175	
HAZFIY†	1.14	1.30	2.399	160	c
HEBXER§	1.21	1.21	2.408	169	d
	0.88	1.53	2.403	174	
HEBXER01§	1.16	1.26	2.402	166	c
	1.13	1.30	2.400	165	
QADTEV‡	1.20	1.23	2.394	161	e
	1.17	1.26	2.406	165	
YAZMIW†	1.04	1.30	2.406	164	f
ZATQEQ†	1.04	1.37	2.401	173	g

† Results for one centrosymmetric molecule. ‡ Results for one non-centrosymmetric molecule. § Results for two independent centrosymmetric molecules. References: (a) this work; (b) Li (2002); (c) Benito-Garagorri *et al.* (2005); (d) Ghaffar *et al.* (1994); (e) Evans *et al.* (2002); (f) Pryjomska *et al.* (2006); (g) Gebauer *et al.* (1995).

Table 4
Intermolecular π–π interactions (Å, °).

$Cg1$ denotes the centroid of ring C21–C26 and $Cg2$ the centroid of ring C51–C56. $Cg\cdots Cg$ is the distance between ring centroids. The dihedral plane is that between the CgI and CgJ planes. The interplanar distance is the perpendicular distance of CgI from the ring J plane. The offset is the lateral displacement of ring I relative to ring J.

CgI	CgJ	$Cg\cdots Cg$	Dihedral angle	Interplanar distance	Offset
1	2^v	3.750 (3)	5.1 (2)	3.671 (3)	0.766 (3)
2	1^{vi}	3.750 (3)	5.1 (2)	3.612 (3)	1.008 (3)

Symmetry codes: (v) $x, y+1, z$; (vi) $x, y-1, z$.

Carbon-bound H atoms were positioned geometrically and refined using a riding model, with aromatic C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The position of H3 was obtained from a difference Fourier map and refined, with $U_{iso}(H) = 1.5U_{eq}(O)$. The highest residual peak and the deepest hole in the final difference map are located 2.17 Å from Cl and 0.72 Å from Pd, respectively.

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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