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Key indicators

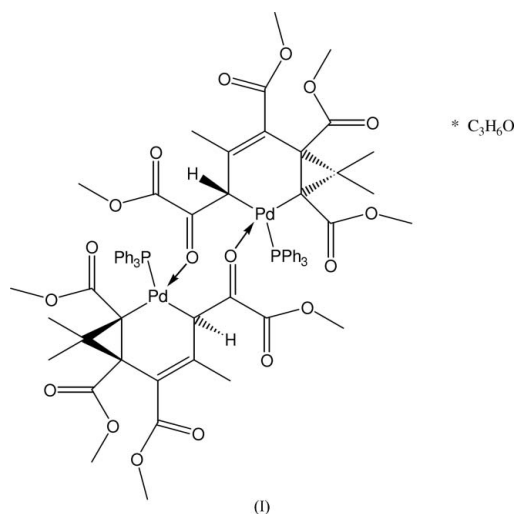
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
Disorder in solvent or counterion
 R factor = 0.059
 wR factor = 0.156
Data-to-parameter ratio = 15.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[μ -dimethyl 1-[1-methoxycarbonyl-3-(methoxyoxalyl)-2-methylpropenyl]-3,3-dimethylcyclopropane-1,2-dicarboxylato(2-)]bis[(triphenylphosphine)palladium(II)] acetone solvate

The title compound, $[\text{Pd}_2(\text{C}_{18}\text{H}_{22}\text{O}_9)_2(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{C}_3\text{H}_6\text{O}$, features a centrosymmetric dimer and an acetone molecule disordered about a centre of inversion. The Pd coordination is almost square-planar. The central eight-membered ring containing Pd and O atoms adopts a chair conformation, and the six-membered ring containing Pd adopts a half-chair conformation.

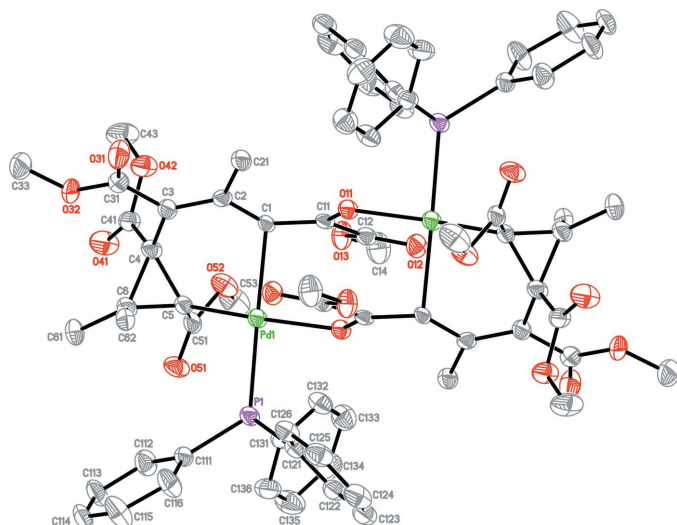
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Comment

5-Pallada-*anti*-tricyclo[4.1.0.0^{2,4}]heptanes are an interesting class of chiral organopalladium compounds which are usually stable in water and air (Hashmi, 2002). Several complexes of these compounds have been prepared (Hashmi, Naumann, Probst *et al.*, 1997; Hashmi, Naumann & Bats, 1997; Hashmi, Naumann & Bolte, 1998; Hashmi, Naumann, Bolte & Rivas Nass, 1998; Hashmi, Bats *et al.*, 1998) and their reactivity has been studied (Hashmi *et al.*, 1999). We have now tried to prepare the complex with the simple triphenylphosphine ligand, which immediately led to a precipitate with low solubility. Efforts to recrystallize this precipitate from chloroform in air and the presence of water at 321 K led to the title compound, a unique dimer of a new organometallic framework in which one of the cyclopropyl rings of the starting material was opened and oxidized. Each of the palladium centres is coordinated by only one phosphine ligand, and the other coordination site is occupied by the carbonyl-O atom of an ester group of the other palladium-organic unit. The organometallic units are still chiral; two enantiomers form the centrosymmetric dimer.



A perspective view of the title compound is shown in Fig. 1. Bond lengths and angles can be regarded as normal


Figure 1

A perspective view of the title compound with the atom numbering. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the disordered acetone molecule have been omitted for clarity. The labelled atoms indicate the asymmetric unit; the complete molecule is generated by a centre of inversion with the symmetry operator $(1 - x, 1 - y, 1 - z)$.

(Cambridge Crystallographic Database, Version 1.6 plus three updates; *MOGUL* Version 1.0; Allen, 2002). The molecule is located on a centre of symmetry. The Pd atoms show an almost ideal square-planar coordination (r.m.s. deviation for Pd and its four ligands 0.061 Å; Table 1). The central eight-membered ring adopts a chair conformation with O11, C11 and their symmetry equivalents in a common plane and the Pd1—C1 units and their symmetry equivalents deviating from this plane. The six-membered rings containing Pd adopt a half-chair conformation with C1, C2, C3 and C4 in a common plane (r.m.s. deviation 0.01 Å) and Pd1 and C5 deviating by 1.856 (8) and 0.92 (1) Å from this plane, respectively. The three ester residues adopt the *cis* conformation typical for this group.

Experimental

A solution of triphenylphosphine (94.4 mg) in acetone (1 ml) was added to a solution of tetramethyl-5-pallada-*anti*-tricyclo-[4.1.0.0^{2,4}]heptane (85.3 mg) in acetone (1 ml) in an open flask. Immediately, a new product precipitated. Acetone (3 ml) and then chloroform (5 ml) were added while heating the flask in an oil bath to 321 K. The heating was stopped, but the flask was left in the oil bath for a slow temperature decrease. Overnight, crystals of the title compound were formed.

Crystal data

$[\text{Pd}_2(\text{C}_{18}\text{H}_{22}\text{O}_9)_2(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{C}_3\text{H}_6\text{O}$
 $M_r = 1560.13$
 Triclinic, $P\bar{1}$
 $a = 9.7819$ (3) Å
 $b = 13.3852$ (3) Å
 $c = 14.4710$ (4) Å
 $\alpha = 98.446$ (1)°
 $\beta = 102.790$ (1)°
 $\gamma = 105.392$ (1)°
 $V = 1738.31$ (8) Å³

$Z = 1$
 $D_x = 1.490$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6723 reflections
 $\theta = 3.5\text{--}24.2^\circ$
 $\mu = 0.64$ mm⁻¹
 $T = 173$ (2) K
 Plate, red
 0.30 × 0.25 × 0.10 mm

Data collection

Siemens SMART CCD three-circle diffractometer
 ω scans
 Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
 $T_{\min} = 0.832$, $T_{\max} = 0.939$
 20136 measured reflections

6752 independent reflections
 3804 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.082$
 $\theta_{\max} = 26.4^\circ$
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.156$
 $S = 1.01$
 6752 reflections
 451 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0747P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.74$ e Å⁻³
 $\Delta\rho_{\min} = -0.97$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pd1—C5	2.041 (6)	Pd1—C1	2.257 (5)
Pd1—O11 ⁱ	2.144 (4)	Pd1—P1	2.3228 (16)
C5—Pd1—O11 ⁱ	171.4 (2)	C5—Pd1—P1	93.60 (16)
C5—Pd1—C1	83.4 (2)	O11 ⁱ —Pd1—P1	87.95 (10)
O11 ⁱ —Pd1—C1	93.94 (16)	C1—Pd1—P1	172.04 (16)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
C113—H113 ⁱ ⋯O1L	0.95	2.53	3.275 (14)	135
C123—H123 ⁱⁱ ⋯O1L ⁱⁱ	0.95	2.62	3.452 (13)	147

Symmetry code: (ii) $-x + 1, -y + 1, -z + 2$.

H atoms were located in a difference electron density map but refined with fixed individual displacement parameters [$U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $U(\text{H}) = 1.5 U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model, with $\text{C—H} = 0.95$ and 0.98 Å for $\text{C}_{\text{aromatic}}\text{—H}$ and $\text{C}_{\text{methyl}}\text{—H}$, respectively. The acetone molecule is disordered about a centre of inversion. Thus, the carbonyl O and C atoms and the H atoms of the methyl group were refined with a site occupation factor of 0.5 to reflect the two positions of this molecule.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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