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[1,2-Bis(diphenylphosphino)ethane]dinitratopalladium(II)

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The Pd atom in the title complex, $[Pd(C_{26}H_{24}P_2)(NO_3)_2]$, exists in a distorted square-planar geometry defined by an O_2P_2 donor set provided by the bidentate phosphine ligand and two monodentate nitrate groups.

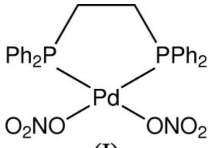
Key indicators

Single-crystal X-ray study
T = 113 K
Mean σ(C–C) = 0.004 Å
R factor = 0.018
wR factor = 0.046
Data-to-parameter ratio = 14.6

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

Comment

The title complex, $[Pd(NO_3)_2\{Ph_2P(CH_2CH_2)PPh_2\}]$, (I), is isomorphous with the Pt^{II} analog (Arendse *et al.*, 2001) and was investigated in relation to our continuing interest in the coordination chemistry of cationic Pd complexes (Zhu *et al.*, 2004; Adrian *et al.*, 2006). The Pd atom in (I) (Fig. 1 and Table 1) is coordinated in a square-planar fashion by two P atoms derived from the chelating diphosphine ligand and two O atoms derived from two monodentate nitrate groups. The deviations of atoms P1, P2, O1 and O4 from their least-squares plane are 0.0901 (7), −0.0835 (7), −0.0928 (7) and 0.0862 (7) Å, respectively, and the Pd atom lies 0.0270 (7) Å out of this plane. While atoms O2 and O5 are orientated towards the Pd atom, the Pd···O2/O5 distances of 2.889 (2) and 2.835 (2) Å, respectively, are not considered to represent significant bonding interactions.



(I)

The structure of (I) has been refined in *Cc*, as indeed was the Pt^{II} analog (Arendse *et al.*, 2001). While the molecule of (I) ostensibly has twofold symmetry and comparable interatomic parameters are experimentally equivalent or close to equivalent, significant differences in the orientations of the nitrate groups contradict the higher symmetry space group *C*2/*c* where crystallographic twofold symmetry would be imposed. This is evidenced in the following pairs of torsion angles: Pd—O1—N1—O2 and Pd—O4—N2—O5 of 2.2 (3) and 17.1 (3)°, respectively, and P1—Pd—O4—N2 and P2—Pd—O1—N1 of −156.1 (3) and 122.5 (6)°, respectively. The coordination geometry and geometric parameters in (I) match closely those found in the bis(diphenylphosphino)methane analog (Rath *et al.*, 1999). In the latter, the Pd—P bond distances were 2.2241 (7) and 2.2346 (7) Å, and the Pd—O distances were 2.103 (2) and 2.130 (2) Å. The primary intermolecular contacts in the crystal structure of (I) are of types C—H···O and C—H···π. Each of the O atoms, with the exception of O1, forms at least one close C—H···O contact, the shortest of these being 2.36 Å for C25—H25···O5^{i}, so that C25···O5^{i} is

3.249 (4) Å and the angle at H is 156° [symmetry code: (i) $-1 + x, y, z$]. The C—H$\cdots$O interactions serve to link a total of five molecules to the asymmetric unit. The closest C—H$\cdots\pi$ interactions of 1.78 and 1.79 Å, respectively, occur between C23—H23 and the ring centroid of (C1–C6)$^{\rm ii}$, and C18—H18 and the ring centroid of (C21–C26)$^{\rm iii}$ with angles subtended at H of 146 and 155°, respectively [symmetry codes: (ii) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$]. A view of the packing is shown in Fig. 2.

Experimental

Complex (I) was prepared by adding solid $AgNO_3$ (88.7 mg, 0.522 mmol) to an acetonitrile solution (70 ml) of $[PdCl_2\{Ph_2P(CH_2CH_2)PPh_2\}]$ (0.150 g, 0.261 mmol; Aldrich). The mixture was stirred for 2 h and filtered to remove AgCl. The solution was concentrated to approximately 3 ml by slow evaporation at 333 K. As the solution cooled, X-ray diffraction quality crystals formed (yield 0.044 g, 79%; m.p. 511–517 K).

Crystal data

$[Pd(C_{26}H_{24}P_2)(NO_3)_2]$
$M_r = 628.81$
Monoclinic, *Cc*
$a = 10.383$ (5) Å
$b = 15.442$ (5) Å
$c = 16.278$ (5) Å
$\beta = 101.135$ (16)°
$V = 2560.7$ (16) Å^3

$Z = 4$
$D_x = 1.631$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.90$ mm^{-1}
$T = 113$ (2) K
Plate, yellow
0.35 × 0.31 × 0.14 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
ω scans
Absorption correction: numerical (Katayama, 1986; Paturle & Coppens, 1988)
$T_{\rm min} = 0.745$, $T_{\rm max} = 0.885$

13230 measured reflections
4845 independent reflections
4791 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\rm max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
$S = 1.08$
4845 reflections
332 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 3.1937P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983), 2326 Friedel pairs
Flack parameter: −0.003 (15)

Table 1
Selected geometric parameters (Å, °).

Pd—P1	2.2148 (8)	Pd—O1	2.1034 (18)
Pd—P2	2.2239 (9)	Pd—O4	2.1137 (18)
P1—Pd—P2	84.73 (3)	O1—Pd—O4	86.94 (7)
P1—Pd—O1	90.02 (6)	Pd—P1—C13	110.03 (9)
P1—Pd—O4	175.42 (6)	Pd—P2—C14	108.30 (9)
P2—Pd—O1	171.82 (5)	Pd—O1—N1	114.33 (14)
P2—Pd—O4	98.66 (6)	Pd—O4—N2	111.20 (15)

The H atoms were included in the riding-model approximation, with C—H = 0.95 (aromatic H) and 0.99 Å (methylene H), and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

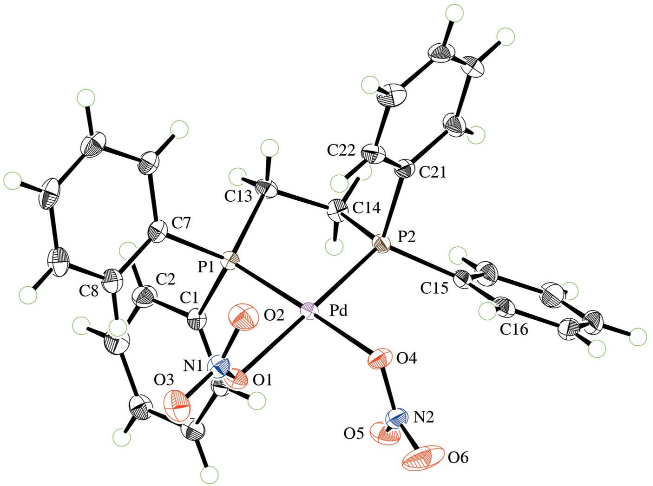


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme; ring C atoms are numbered sequentially. Displacement ellipsoids are drawn at the 50% probability level.

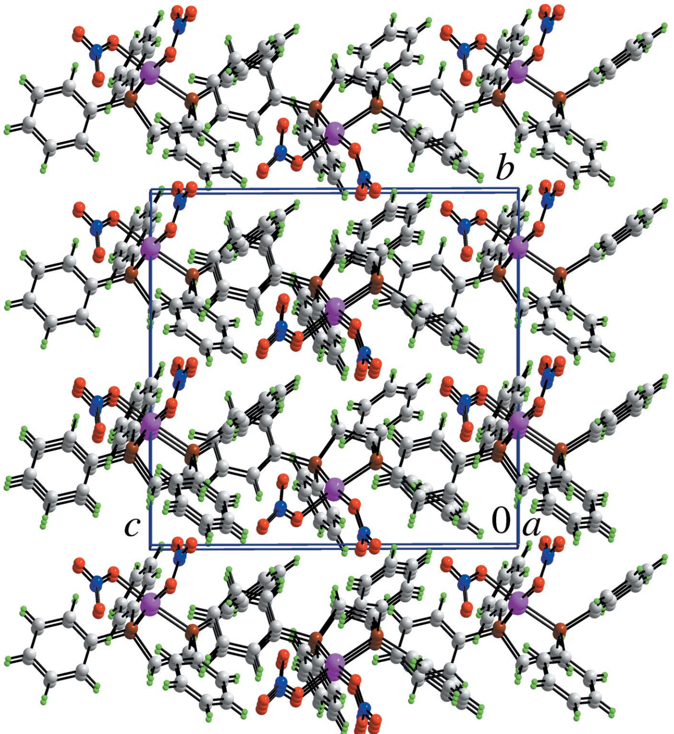


Figure 2
The crystal packing in (I), viewed down the *a* axis. Color code: Pd violet, P brown, O red, N blue, C grey and H green.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Crystal Impact, 2006; software used to prepare material for publication: *SHELXL97*.

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