metal-organic papers

Di-μ-furan-2-selenolato-bis[(furan-2-selenolato)-(triphenylphosphine)palladium(II)]

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(C–C) = 0.009 Å
R factor = 0.042
wR factor = 0.102
Data-to-parameter ratio = 16.2

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

The title compound, $[Pd_2(C_4H_3OSe)_4(C_{18}H_{15}P)_2]$, crystallizes as a centrocymmetric furan-2-selenolate-bridged dinuclear palladium complex. The Pd atom shows a slightly distorted square-planar coordination geometry, with bridging Pd—Se distances of 2.4568 (8) and 2.4729 (8) Å, and a terminal Pd—Se distance of 2.4623 (8) Å. Terminal selenolate ligands are in *trans* positions with respect to each other.
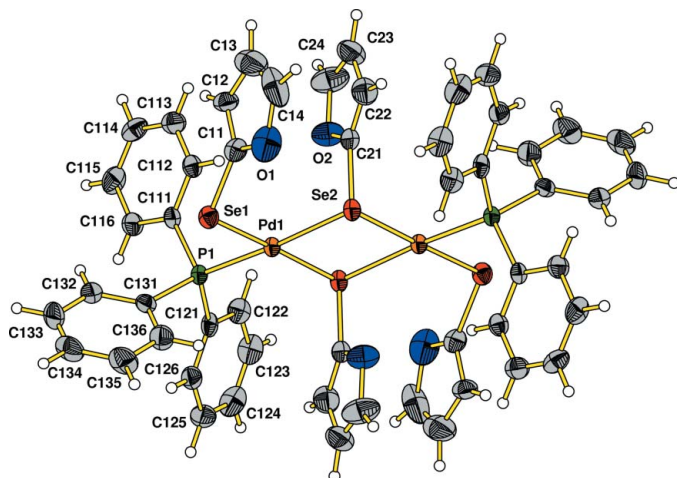
Comment

We have recently reported the synthesis of organoselenolate-bridged dimeric palladium(II) complexes $[Pd_2(\mu\text{-}SeR)_2(SeR)_2(PPh_3)_2]$ [R = 2-thienyl (Oilunkaniemi *et al.*, 1999) or phenyl (Oilunkaniemi *et al.*, 2001)] by the oxidative addition of the corresponding diorganodiselenides to $[Pd(PPh_3)_4]$ as a part of a systematic investigation of the factors affecting the preparation of palladium and platinum chalcogenolates. In this paper, the preparation and characterization of the title compound, (I), is reported. It can be synthesized in excellent yield by the reaction of lithium 2-furylselenolate with $[PdCl_2(PPh_3)_2]$. The yield is comparable to that from the method in which oxidative addition of diaryldiselenides to a Pd^0 centre is used (Oilunkaniemi *et al.*, 1999, 2001). The method reported here is, however, more convenient, because of the stability of the Pd^{II} starting material compared to the Pd^0, and the ease of preparation of the selenolate.

(I)
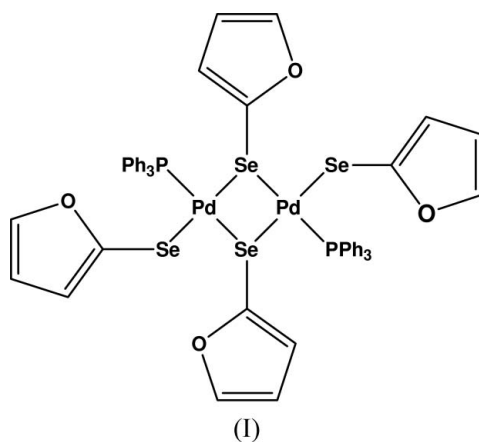
The ^{31}P NMR spectrum of (I) shows two major resonances at 28.6 and 28.0 p.p.m. These can be assigned to the *cis*- and *trans* isomers of (I). The analogous ^{31}P NMR resonances of $[Pd_2(\mu\text{-}SeR)_2(SeR)_2(PPh_3)_2]$ (R = 2-thienyl or phenyl) are found at 29.9 and 29.3 p.p.m., and at 28.9 and 27.9 p.p.m., respectively (Oilunkaniemi *et al.*, 1999, 2001).

The molecular structure and the numbering of the atoms of (I) are shown in Fig. 1. The two centrosymmetrically related

The packing of the molecules is shown in Fig. 2. The closest intermolecular contacts are Se2[ii]···H124 = 3.00 Å and O1[iii]···H135 = 2.83 Å [symmetry codes: (ii) $1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (iii) x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$].

Experimental

A solution of 2-(C4H3O)SeLi was prepared under an argon atmosphere using 1.1 ml (15 mmol) furan in 11 ml of tetrahydrofuran, 6 ml (15 mmol) of *n*-BuLi, and 1.184 g (15 mmol) selenium (Engman & Cava, 1982). 0.73 ml (0.6 mmol) of (C4H3O)SeLi solution was added to a suspension of 0.200 g (0.285 mmol) [PdCl2(PPh3)2] in 10 ml CH2Cl2. The reaction mixture was stirred at room temperature for 30 min, filtered and concentrated. The red precipitate was washed with hexane and diethyl ether, and dried (yield: 0.177 g, 94%). ^{31}P {^{1}H} NMR (CH2Cl2): 28.6 and 28.0 p.p.m. Analysis calculated for C52H24O4P2Pd2Se4: C 47.26, H 3.20%; found: C 47.09, H 3.11%. Crystals for X-ray diffraction analysis were obtained from CH2Cl2 layered with hexane and diethyl ether (1:1) at room temperature.

Crystal data

[Pd2(C4H3OSe)4(C18H15P)2]
$M_r = 1321.44$
Monoclinic, $P2_1/c$
$a = 13.045 (3)$ Å
$b = 16.394 (3)$ Å
$c = 12.233 (2)$ Å
$\beta = 110.85 (3)°$
$V = 2444.8 (10)$ Å^3
$Z = 2$

$D_x = 1.795$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3924 reflections
$\theta = 3.1$–26.0°
$\mu = 3.82$ mm^{-1}
$T = 120 (2)$ K
Block, orange
$0.15 \times 0.10 \times 0.08$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
$T_{min} = 0.638$, $T_{max} = 0.737$
17303 measured reflections

4701 independent reflections
3924 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 26.0°$
$h = -16 \rightarrow 15$
$k = -19 \rightarrow 20$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.04$
4701 reflections
290 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 10.5236P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—P1	2.2771 (13)	Pd1—Se1	2.4623 (8)
Pd1—Se2[i]	2.4568 (8)	Pd1—Se2	2.4729 (8)
P1—Pd1—Se2[i]	95.23 (4)	Se2[i]—Pd1—Se2	83.28 (3)
P1—Pd1—Se1	87.57 (4)	Se1—Pd1—Se2	94.29 (3)
Se2[i]—Pd1—Se1	175.18 (2)	Pd1[i]—Se2—Pd1	96.72 (3)
P1—Pd1—Se2	174.50 (4)		

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

H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak is located 1.27 Å from atom Pd1.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97*

Figure 1
The molecular structure of (I), with the atom-numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by $1 - x$, $-y$, $1 - z$.
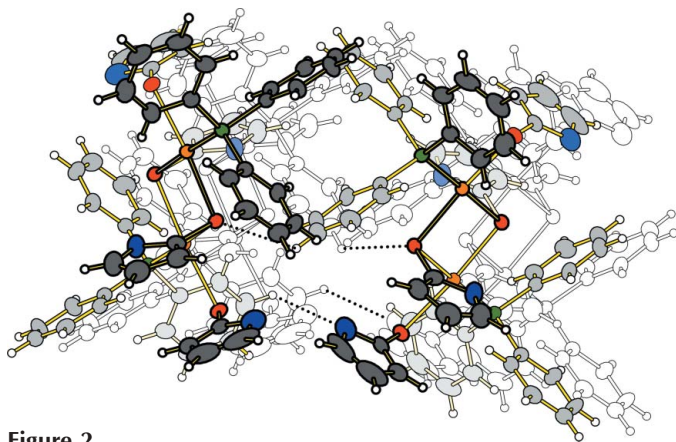
Figure 2
The packing of molecules of (I), showing the closest intermolecular contacts (dotted lines).

neighbouring coordination planes of palladium are linked together through two bridging selenolate ligands. The molecular structure is similar to those of [Pd2(μ-Se*R*)2(Se*R*)2(PPh3)2] [*R* = 2-thienyl (Oilunkaniemi *et al.*, 1999) or phenyl (Oilunkaniemi *et al.*, 2001)]. In fact, (I) is isomorphous with the 2-thienyl analogue. The Pd atoms show a slightly distorted square-planar coordination geometry (the sum of the bond angles is 360.37°). The Pd—Se1, Pd—Se2, and Pd1—Se2[i] distances are 2.4623 (8), 2.4729 (8), and 2.4568 (8) Å, respectively [symmetry code: (i) $1 - x$, $-y$, $1 - z$]. All these values are close to single bond lengths [the sum of the covalent radii of palladium and selenium is 2.45 Å; Emsley, 1998]. They can be compared to the Pd—Se distances in the thienyl complex [2.463 (1)–2.466 (1) Å] and the phenyl complex [2.461 (1)–2.494 (1) Å]. The Pd—P distance is 2.277 (1) Å, showing a typical Pd—P bond length (the sum of the covalent radii of palladium and phosphorus is 2.38 Å; Emsley, 1998). The corresponding distances in the thienyl and phenylselenolate complexes are 2.297 (2) and 2.284 (2) Å, respectively.

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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