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Key indicators

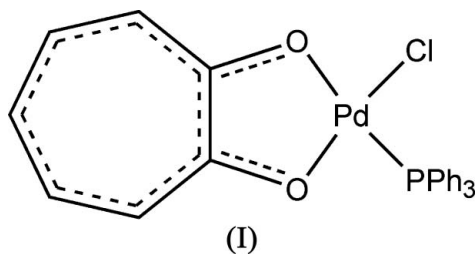
Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.024
 wR factor = 0.056
Data-to-parameter ratio = 20.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Chloro(triphenylphosphine)(tropolonato)-
palladium(II)

The title compound, $[\text{Pd}(\text{C}_7\text{H}_5\text{O}_2)\text{Cl}(\text{C}_{18}\text{H}_{15}\text{P})]$, is a new type of α -diketone palladium(II) complex containing a tertiary arylphosphine. It crystallizes with a distorted square-planar geometry about the palladium(II) metal centre. The most important bond distances and angles include $\text{Pd}-\text{O}$ (*trans* P) = 2.0481 (12) Å, $\text{Pd}-\text{O}$ (*trans* Cl) = 2.0016 (12) Å, $\text{Pd}-\text{P}$ = 2.2268 (4) Å, $\text{Pd}-\text{Cl}$ = 2.2770 (5) Å, $\text{O}-\text{Pd}-\text{O}$ = 80.22 (5)° and $\text{O}-\text{C}-\text{C}-\text{O}$ = 3.7 (2)°. A π - π stacking interaction is observed between neighbouring tropolonate groups, with an interplanar distance of 3.377 (6) Å.

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Comment

A variety of bis- β -diketonato-palladium(II) complexes have been characterized to date for acetylacetonate-type ligands (Cambridge Structural Database; Version 5.27; Allen, 2002). The addition of tertiary aryl phosphines to these types of complexes has resulted in a limited number of reported structures (Okeya *et al.*, 1984; Ooi *et al.*, 1983; Siedle *et al.*, 1982). The inclusion of a chloro derivative with an α - (Lang *et al.*, 1999) or β -diketone (Woisetschlager *et al.*, 2000; Navarro *et al.*, 2005) has attracted less attention. In a previous study (Steyl, 2006), we reported the structure of $[(\text{PCy}_3)(\text{Trop})_2\text{Pd}]$ (Cy = cyclohexyl and Trop = 2-hydroxy-2,4,6-cycloheptatrienone). The title compound, (I), is presented as an example of a monotropolonate-palladium(II) complex containing chloro and triphenylphosphine ligands.



The molecule of (I) crystallizes with a slightly distorted square-planar geometry about the palladium(II) metal centre. The Pd^{II} atom is elevated by 0.0068 (1) Å above the plane defined by the four coordinated atoms (O11, O12, P, Cl). The $\text{Pd}-\text{O}$ bond distances (Table 1) do not differ from those observed for the bis(tropolonato)palladium(II) (Steyl, 2005) or the tricyclohexyl (Steyl, 2006) derivatives. The bidentate bite angle of 80.22 (5)° (Table 1) does not differ significantly from that in the previously reported tropolonate structures of palladium(II). A torsional twist is observed for the tropolonate ligand (see values of torsion angles in Table 1).

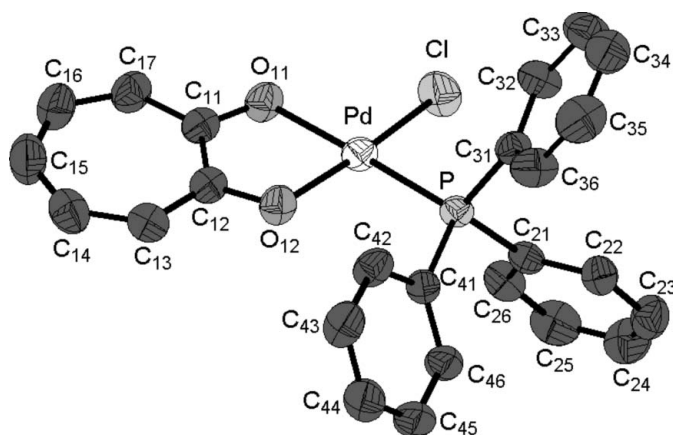


Figure 1
The molecular structure of (I), showing the numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

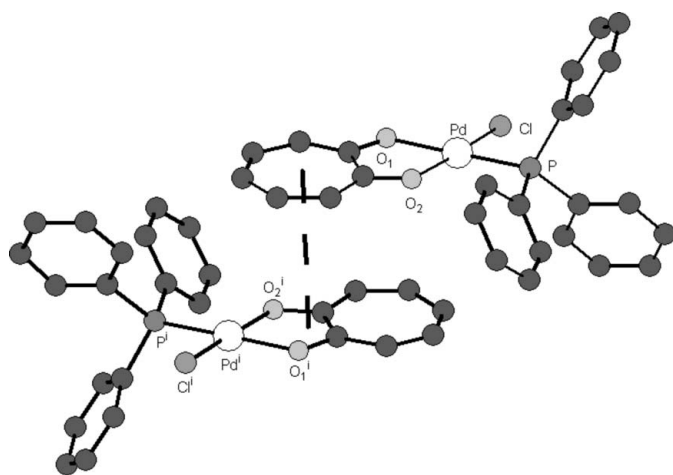


Figure 2
A pair of moleculesⁱ, showing the stacking [symmetry code: (i) $-x, 2 - y, -z$]. H atoms have been omitted.

A weak intramolecular C—H \cdots Cl hydrogen bond (Table 2) is found in (I). π – π Stacking between parallel troponate ring systems (Fig. 2) is observed, with an interplanar distance of 3.377 (6) Å, which is significantly shorter than that [3.51 (1)–3.80 (2) Å] in the previously published troponate–palladium(II) complexes (Steyl, 2005, 2006). This close interaction can be attributed to the shift of the troponate ring system to form an eclipsed conformation of the C11–C17 seven-membered ring.

In conclusion, the substitution of a chloro group for a troponate {[PCy₃(Trop)₂Pd^{II}]; Steyl, 2006} ligand does not significantly alter the bonding mode of the remaining troponate ligand to the Pd^{II} atom.

Experimental

The title complex was synthesized by the addition of PPh₃ (83 mg, 0.316 mmol) to an acetone solution (10 ml) of the bis-troponato-

palladium(II) complex (100 mg, 0.287 mmol) containing hydrochloric acid (0.5 ml). The suspension dissolved and gave an orange solution; on evaporation of the solvent, crystals suitable for X-ray crystallography were obtained. Yield 45 mg (30%).

Crystal data

[Pd(C₇H₅O₂)Cl(C₁₈H₁₅P)]
 $M_r = 525.23$
 Triclinic, $P\bar{1}$
 $a = 9.8561$ (3) Å
 $b = 9.9719$ (2) Å
 $c = 13.2792$ (3) Å
 $\alpha = 85.851$ (1)°
 $\beta = 72.262$ (1)°
 $\gamma = 63.317$ (1)°

$V = 1107.51$ (5) Å³
 $Z = 2$
 $D_x = 1.575$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.05$ mm⁻¹
 $T = 273$ (2) K
 Prism, red
 $0.25 \times 0.14 \times 0.11$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.782$, $T_{\max} = 0.897$
 24655 measured reflections

5506 independent reflections
 4981 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 28.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.057$
 $S = 1.04$
 5506 reflections
 271 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 3.4366P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pd—O11	2.0481 (12)	C11—O11	1.291 (2)
Pd—O12	2.0016 (12)	C12—O12	1.295 (2)
Pd—P	2.2268 (4)	C12—C11	1.462 (2)
Pd—Cl	2.2770 (5)		
O11—Pd—Cl	93.10 (4)	O12—Pd—P	95.01 (4)
O12—Pd—O11	80.22 (5)	P—Pd—Cl	91.818 (18)
O12—C12—C11—O11	3.7 (2)	C13—C12—C11—C17	5.2 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C32—H32 \cdots Cl	0.93	2.67	3.496 (2)	148
C25—H25 \cdots O11 ⁱⁱ	0.93	2.46	3.333 (3)	157

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2004); software used to prepare material for publication: SHELXL97.

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