

**(Tricyclohexylphosphine)bis(tropolonato)-palladium(II)****Gideon Steyl**

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa

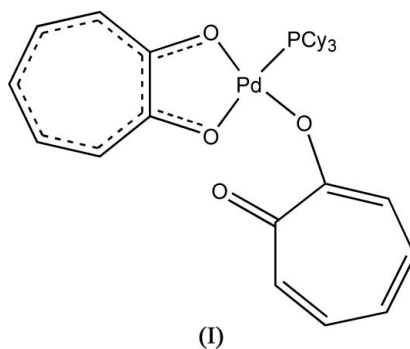
Correspondence e-mail: geds12@yahoo.com

**Key indicators**Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.024  
 $wR$  factor = 0.078  
Data-to-parameter ratio = 21.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A new type of  $\alpha$ -diketone palladium(II) complex containing a tertiary phosphine, namely the title compound,  $[\text{Pd}(\text{C}_7\text{H}_5\text{O}_2)_2(\text{C}_{18}\text{H}_{33}\text{P})]$ , crystallizes with a square-planar geometry about the palladium(II) metal centre. One tropolonate ligand is bonded in a bidentate chelating mode, while the second one is bonded through a single O atom to the palladium(II) metal centre. The Pd—O distances range from 1.9907 (13) to 2.0702 (12) Å, and the O—Pd—O bite angle for the bidentate tropolonate ligand is 80.30 (5)°.

**Comment**

A variety of bis- $\beta$ -diketonate palladium(II) complexes have been characterized to date for acetylacetonato type ligands (Cambridge Structural Database; Version 5.27; Allen, 2002). The addition of tertiary phosphines to these types of complex has resulted in only three reported structures (Okeya *et al.*, 1984; Ooi *et al.*, 1983; Siedle *et al.*, 1982). To date, no  $\alpha$ -diketone palladium(II) complexes containing a phosphine ligand have been reported. In the current paper, a tricyclohexylphosphine derivative of bis(tropolonato)palladium(II) (Steyl, 2005) is presented as an example of a mono/bidentate tropolonate complex.

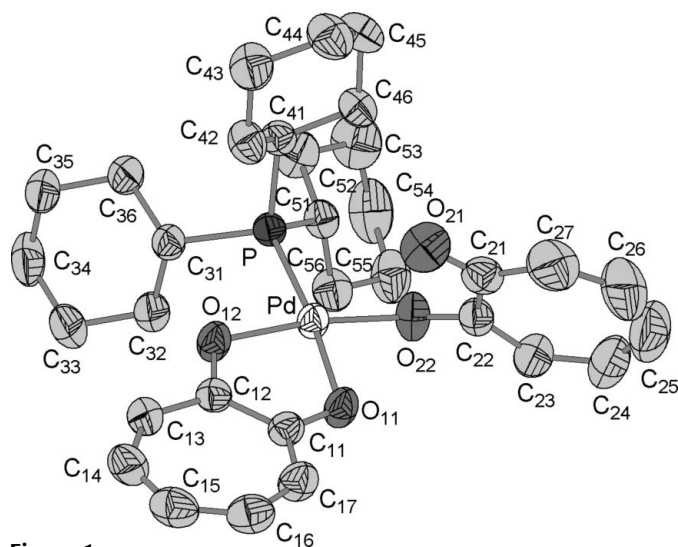


The title compound, (I), crystallizes with a slightly distorted square-planar geometry about the palladium(II) metal centre. The palladium atom is elevated by 0.0501 (1) Å above the plane defined by the four coordinated atoms, *viz.* O11, O12, O22 and P. The Pd—O distances do not differ from those observed for the bis(tropolonato)palladium(II) complex (Steyl, 2005). The O12—Pd—O11 bidentate bite angle [80.30 (5)°; Table 1] is less than the value of 81.8 (1)° observed in the bis(tropolonato)palladium(II) complex.

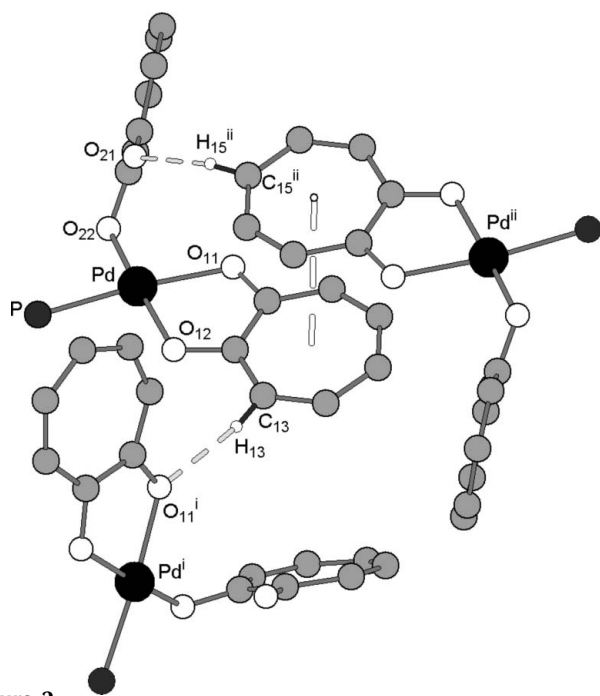
An interesting feature in (I) is the rotation of one tropolonato group to form a monodentate ligand (Fig. 1). A similar situation was observed in  $[\text{Rh}(\text{tropBr}_3)\text{CO}(\text{PPh}_3)]$  (trop is 2-hydroxy-2,4,6-cycloheptatrienone) and  $[\text{Rh}(\text{tropBr}_3)\text{CO}-$

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



**Figure 2**  
A fraction of the unit cell contents, showing the intermolecular hydrogen bonding and  $\pi$ - $\pi$  stacking as dashed lines [symmetry codes: (i)  $x, -y, z - \frac{1}{2}$ ; (ii)  $-x, -y, -z$ ].

(AsPh<sub>3</sub>)] (Roodt *et al.*, 2003), although a formal monodentate ligand system was not apparent. The monodentate tropolonate ligand is nearly perpendicular [ $78.4(1)^\circ$ ] to the mean plane defined by the four atoms coordinating the palladium metal centre. Uncoordinated atom O21 lies  $2.812(2)$  Å from the Pd atom and is displaced from the apical position with a Pd—O22...O21 angle of  $72.4(2)^\circ$ . The short interplanar distance of  $3.51(1)$  Å between the two bidentate tropolonate ligands related by the symmetry operation  $(-x, -y, -z)$  indicates the presence of  $\pi$ - $\pi$  interactions.

In conclusion, the addition of tertiary phosphine to the bis(tropolonato)palladium(II) complex resulted in the weakening of the bidentate character of one tropolonate ligand. However, complete dissociation or the formation of a Pd—C(tropolonato) bond as found in acetylacetonate-type complexes (Ooi *et al.*, 1983) were not observed.

## Experimental

The title complex was synthesized by the addition of PCy<sub>3</sub> (88 mg, 0.316 mmol) to an acetone solution of the bis(tropolonato)palladium(II) complex (100 mg, 0.287 mmol). The solution changed colour from orange to red. On evaporation of the solvent, crystals suitable for X-ray diffraction were obtained (yield: 60 mg, 33%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.28 MHz):  $\delta$  7.24 (*d*, 4), 7.17 (*dd*, 4), 6.74 (*t*, 2), 2.05 (*m*, 3), 1.75 (*m*, 24), 1.25 (*m*, 6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.97 MHz):  $\delta$  183.2 (C11, C12, C21, C22), 136.0 (C14, C16, C24, C26), 126.3 (C13, C17, C23, C27), 124.3 (C15, C25), 32.01 (*d*, C31, C41, C51), 28.27 (C32, C36, C42, C46, C52, C56), 27.45 (C33, C35, C43, C45, C53, C55), 26.25 (C34, C44, C54) with positions of C atoms confirmed by HSQC and HMBC data. Exchange is observed in CDCl<sub>3</sub> of tropolonate moieties. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242.98 MHz):  $\delta$  42.31 (*s*).

## Crystal data

[Pd(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>18</sub>H<sub>33</sub>P)]  
*M<sub>r</sub>* = 629.05  
Monoclinic, *C*2/*c*  
*a* = 17.6699 (4) Å  
*b* = 27.7962 (6) Å  
*c* = 12.2289 (2) Å  
 $\beta$  = 94.523 (1) $^\circ$   
*V* = 5987.6 (2) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.396 Mg m<sup>-3</sup>  
Mo *K* $\alpha$  radiation  
Cell parameters from 7765 reflections  
 $\theta$  = 2.5–28.2 $^\circ$   
 $\mu$  = 0.71 mm<sup>-1</sup>  
*T* = 293 (2) K  
Plate, red  
0.37 × 0.31 × 0.10 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
*T<sub>min</sub>* = 0.776, *T<sub>max</sub>* = 0.936  
81120 measured reflections

7406 independent reflections  
6361 reflections with  $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.030  
 $\theta_{\max}$  = 28.3 $^\circ$   
*h* = -23 → 23  
*k* = -37 → 37  
*l* = -16 → 16

## Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.078$   
*S* = 1.12  
7406 reflections  
343 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 3.4366P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.29$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

Pd—O12	1.9907 (13)	Pd—O11	2.0702 (12)
Pd—O22	2.0132 (13)	Pd—P	2.2342 (4)
O12—Pd—O11	80.30 (5)	O12—Pd—P	93.23 (4)
O22—Pd—O11	95.13 (5)	O22—Pd—P	91.32 (4)
O11—C11—C12—O12	-6.6 (3)	O21—C21—C22—O22	5.3 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C46—H46A $\cdots$ O21	0.97	2.43	3.348 (3)	159
C13—H13 $\cdots$ O11 <sup>i</sup>	0.93	2.56	3.456 (2)	161
C15—H15 $\cdots$ O21 <sup>ii</sup>	0.93	2.44	3.309 (3)	155

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with  $C-H = 0.93-0.98$  Å and  $U_{iso}(H) = 1.2U_{eq}$  of the parent atom.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; 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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