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Carbonyl(triphenylarsine)(tropolonato)rhodium(I)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.016 Å
R factor = 0.070
wR factor = 0.186
Data-to-parameter ratio = 16.3

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

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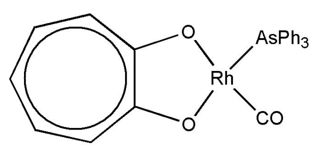
The title complex, $[Rh(C_7H_5O_2)(C_{18}H_{15}As)(CO)]$, has a distorted square-planar geometry. The most important bond distances and angles include Rh—C = 1.788 (10) Å, Rh—O(*trans* to CO) = 2.039 (6) Å, Rh—O(*trans* to As) = 2.059 (6) Å, Rh—As = 2.3507 (13) Å, O—Rh—O = 78.1 (2)° and O—C—C—O = 3.4 (12)°. The short interplanar distances between the tropolonate ligands [3.57 (5) Å] and phenyl groups [3.51 (5) Å] of neighbouring molecules indicate π–π stacking interactions, which stabilize the crystal packing.

Comment

The first known structure of a group 15 rhodium tropolonate (Trop) compound was reported for the analogous triphenylphosphine derivative (Leipoldt *et al.*, 1980) of the title compound. The current structure investigation was undertaken to evaluate the role that the other group 15 ligands play in affecting the solid-state behaviour of these complexes, since only a small number of phosphine complexes are known to date containing tropolone ligands (Steyl *et al.*, 2001; Steyl & Roodt, 2003, Crous *et al.*, 2005). In this paper, we present the crystal structure of the title compound, (I) (Fig. 1).



(I)

In (I), the Rh—O bond lengths of 2.039 (6) and 2.059 (6) Å, and the O—Rh—O bite angle of 78.1 (2)° (Table 1) are comparable with those observed in the phosphine derivative (Leipoldt *et al.*, 1980), *viz*. 2.034 (7) and 2.081 (7) Å, and 77.8 (3)°, respectively. The tropolone ring system has a distorted geometry, confirmed by the non-zero torsion angles O11—C1—C2—O12 [−3.4 (12)°] and C7—C1—C2—C3 [−9.7 (16)°], and by the C—C bond distances in the seven-membered ring (Table 1). The Rh atom is slightly elevated by 0.0481 (8) Å above the plane defined by the four ligand donor atoms of the square-planar coordination (C01, As1, O12 and O11). Intramolecular C—H···O hydrogen bonding is observed in (I) (Table 2). The shortest intermolecular contact [H13···H36(x + 1, y, z) = 2.495 (8) Å] illustrates the efficient packing in the unit cell. Due to the efficient packing of the system, intermolecular interactions, with a C···O distance of 3.42 (2) Å and a C—H···O angle of 140.5 (8)°, are observed (C4—H4···O01).

Although (I) crystallizes in a similar fashion (square-planar configuration) as $[Rh(L,L'\text{-Bid})CO(PPh_3)]$ (L,L'-Bid = α- and

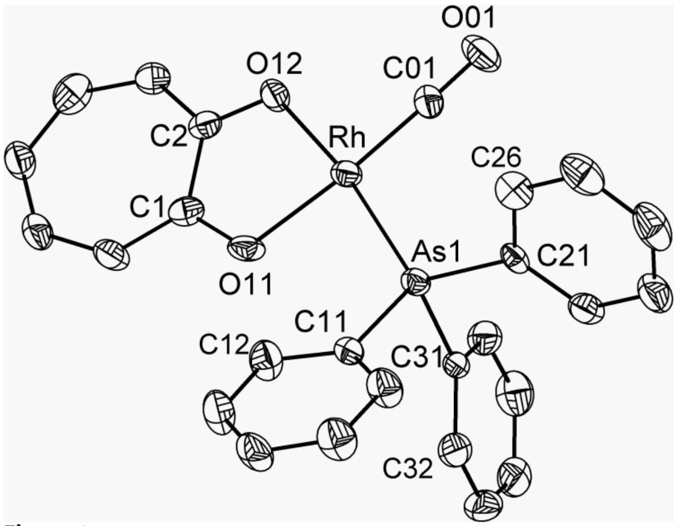


Figure 1
View of (I), showing the numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. The numbering for the other atoms in the rings follows consecutively from those shown.

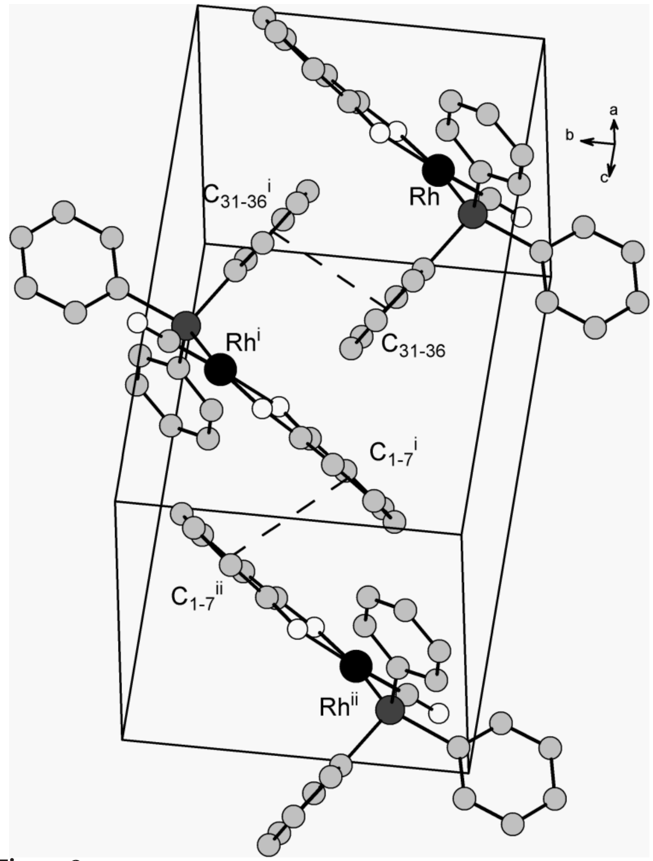


Figure 2
The packing of (I) showing π–π stacking interactions (dashed lines). H atoms have been omitted for clarity. [Symmetry codes: (i) $2 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $-z$].

β-diketone) complexes (Leipoldt *et al.*, 1980; Steyl & Roodt, 2003; Crous *et al.*, 2005), the effective and Tolman cone angles (Tolman, 1977; Otto *et al.*, 2000) of the triphenylarsine ligand in (I) are significantly larger than those in the related structures (Table 3). The Rh—As—C angles lie in the range 110–121° (Table 1); this can be attributed to the π–π stacking interaction between the C31–C36 and symmetry-related [symmetry code: $(2 - x, -y, 1 - z)$] phenyl rings, with an interplanar distance of 3.51 (5) Å. The half-angle contribution of the arsine derivative is *ca* 5° greater than that in the related complexes known to date (Table 3). The π–π interaction is also observed for the C1–C7 tropolone and symmetry-related [symmetry code: $(2 - x, 1 - y, -z)$] ring systems (Fig. 2), with an interplanar distance of 3.57 (3) Å. The dihedral angle between the C1–C7 and C31–C36 planes is 89.8 (3)°. In the phosphine derivative (crystallized under similar conditions), where no π–π stacking interactions are observed for either the tropolone ring or phenyl rings, the O—C—C—O and C—C—C—C torsion angles of −1.6 and −2.8°, respectively, demonstrate significantly less distortion compared with (I).

Theoretical calculations were employed to determine the extent of the packing effect on the system compared to the optimized gas-phase structure. The geometry of (I) was optimized with no restraints using *Gaussian03W B3LYP/Lan2DZ* (Frisch *et al.*, 2003) and characterized as a minimum from the vibrational analysis. The overlay of the calculated and solid state structures is in a good agreement (0.3 Å; Pretorius *et al.*, 2004), with the largest differences observed in the distortion of the tropolonato ring system as well as small torsion angle changes in the phenyl rings.

Experimental

The title compound, (I), was synthesized by dissolving $[Rh(Trop)(CO)_2]$ (10 mg, 0.036 mmol) in the minimum amount of acetone (10 ml), adding 1.1 equivalents of $AsPh_3$ (11.6 mg, 0.038 mmol) and allowing crystallization to occur under slow evaporation (*ca* 1 h). IR: ν_{CO} 1969 cm^{-1}, ^1H NMR ($CDCl_3$, 300 MHz): δ 7.64 (*m*), 7.39 (*m*).

Crystal data

$[Rh(C_7H_5O_2)(C_{18}H_{15}As)(CO)]$	$Z = 2$
$M_r = 558.25$	$D_x = 1.656$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.996$ (5) Å	Cell parameters from 1266 reflections
$b = 9.387$ (5) Å	$\theta = 2.5$–$22.1°$
$c = 14.137$ (5) Å	$\mu = 2.25$ mm^{-1}
$\alpha = 96.550$ (5)°	$T = 295$ (2) K
$\beta = 103.623$ (5)°	Block, orange
$\gamma = 101.722$ (5)°	0.15 × 0.14 × 0.08 mm
$V = 1119.5$ (9) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	4552 independent reflections
ω scans	2446 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	$R_{int} = 0.063$
$T_{min} = 0.729$, $T_{max} = 0.840$	$\theta_{max} = 26.4°$
7120 measured reflections	$h = -11 \rightarrow 10$
	$k = -11 \rightarrow 11$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.1006P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.186$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.92$	$\Delta\rho_{max} = 1.63$ e Å^{-3}
4552 reflections	$\Delta\rho_{min} = -1.49$ e Å^{-3}
280 parameters	

Table 1
Selected geometric parameters (Å, °).

Rh—C01	1.788 (10)	C1—C7	1.392 (13)
Rh—O11	2.039 (6)	C1—C2	1.470 (13)
Rh—O12	2.059 (6)	C7—C6	1.393 (13)
Rh—As1	2.3507 (13)	C2—C3	1.403 (12)
O12—C2	1.266 (11)	C5—C6	1.349 (14)
C01—O01	1.151 (11)	C5—C4	1.368 (15)
C1—O11	1.309 (10)	C3—C4	1.385 (14)
O11—Rh—O12	78.1 (2)	C11—As1—Rh	117.6 (3)
C31—As1—Rh	109.7 (2)	O01—C01—Rh	177.0 (10)
C21—As1—Rh	120.8 (3)		
C01—Rh—As1—C31	−110.7 (4)	O11—C1—C2—O12	−3.4 (12)
C01—Rh—As1—C21	8.7 (4)	C7—C1—C2—C3	−9.7 (16)
C01—Rh—As1—C11	133.9 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$\cdots$O11	0.93	2.30	3.152 (13)	152

Table 3
Effective and Tolman angles (°) for [Rh(X)($AsPh_3$)$_n$(CO)] compounds.

Compound	Effective cone angle[a]	Tolman cone angle[b]
Rh(Trop)CO($AsPh_3$)[c]	156	159
Rh(TFBA)CO($AsPh_3$)[d]	152	154
Rh(DBBT)CO($AsPh_3$)[e]	145	149
Rh(H_2O)CO($AsPh_3$)$_2$[f]	151	152

Notes: (*a*) Otto *et al.* (2000); (*b*) Tolman (1977); (*c*) present study; (*d*) Ebenebe *et al.* (1996); (*e*) Kemp *et al.* (1996); (*f*) Hursthouse *et al.* (1995).

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq} of the parent atom. The highest and lowest electron-density peaks are 0.98 and 0.91 Å, respectively, from atom Rh.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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