

Dicarbonyl(tropolonato)rhodium(I),
a redetermination

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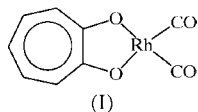
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The molecules of the title complex, $[\text{Rh}(\text{Trop})(\text{CO})_2]$ (Trop is 2-hydroxycyclohepta-2,4,6-trienonate, $\text{C}_7\text{H}_5\text{O}_2$), exhibit symmetrical but non-crystallographic square-planar molecular geometry, with Rh—C distances of 1.825 (10) and 1.826 (9) Å, Rh—O distances of 2.021 (5) and 2.032 (5) Å, and an O—Rh—O bite angle of 79.4 (2)°. Strong Rh···Rh and Rh···C intermolecular interactions of 3.683 (3) and 3.650 (5) Å, respectively, are also observed.

Comment

The first known crystal structure of a rhodium–tropolonate compound was reported for the title compound, (I) (Manojlovic-Muir & Muir, 1975), but unfortunately the authors did not publish the atomic coordinates. As a result of our interest in tropolonate tertiary aryl phosphine compounds of rhodium(I) (Steyl *et al.*, 2001; Roodt *et al.*, 2003; Steyl & Roodt, 2004), the current investigation was undertaken to clarify the solid-state behaviour of (I).



Dicarbonyl(tropolonato)rhodium(I) crystallizes in the monoclinic crystal system with one molecule per asymmetric unit (Fig. 2). The molecular geometry is distorted square planar, with an O—Rh—O bite angle of 79.4 (2)° and an intracarbonyl C—Rh—C angle of 88.3 (4)°. The molecule displays non-crystallographic internal symmetry that approaches C_{2v} , with Rh—C bond distances of 1.825 (10) and 1.826 (9) Å, and Rh—O bond distances of 2.021 (5) and 2.032 (5) Å. A minor distortion in symmetry is observed for the tropolone C—O bond distances [1.267 (9) and 1.324 (8) Å, as listed in Table 1]. High anisotropy is observed for the carbonyl C and O atoms lying on the periphery of the molecule, thus allowing for high flexibility of the carbonyl group.

The whole molecule, including the tropolone ring, is close to being planar, as was established by calculating the least-squares plane containing all the non-H atoms. The mean

deviation of the fitted atoms is 0.052 Å, with a maximum deviation of 0.104 (6) Å for carbonyl atom O02. The shortest intermolecular contact, between atoms H3 and $\text{C4}(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ [1.941 (8) Å], illustrates the efficient packing in the unit cell.

Theoretical calculations were performed on the system using B3LYP/Lan2DZ (GAUSSIAN03; Frisch *et al.*, 2003), with no symmetry restraints on the optimization. The stationary point was characterized as a minimum by means of frequency analysis. An r.m.s. overlay of the calculated and solid-state structures gave an error of less than 0.142 Å. A comparison of the geometric parameters for the solid-state data in Table 1 and the calculated structure (Rh—C = 1.872 and 1.872 Å, Rh—O = 2.061 and 2.061 Å, O—Rh—O = 78.6°, C—Rh—O = 94.7 and 94.7°, and C—Rh—C = 92.0°) for the ligands coordinated to the metal centre shows a good correlation. The absence of large-scale distortions in the crystal structure indicates that packing effects do not play a major role in the solid state.

The structure is similar to those of other Rh complexes of this type in that close intermolecular Rh···Rh contacts, roughly perpendicular to the molecular plane, are present. The molecules stack as infinite chains along the *a* axis, with an Rh···Rh distance of 3.683 (3) Å (Fig. 2). This is longer than examples that have been observed to date (see Table 2), but the Rh···Rh interactions are not perfectly perpendicular to the molecular planes as a result of the monoclinic stacking.

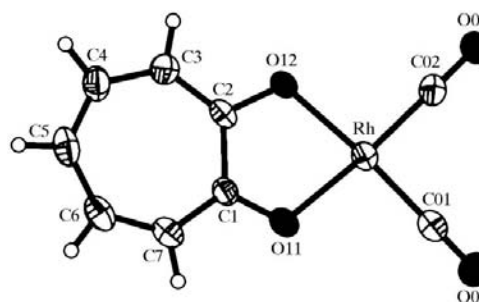


Figure 1

The molecular conformation of (I), with anisotropic displacement ellipsoids shown at the 30% probability level (Brandenburg & Berndt, 2001).

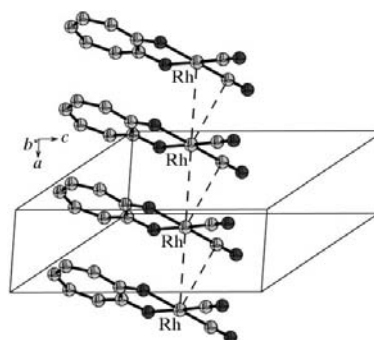


Figure 2

Part of the unit cell of (I), showing the stacking pattern and the intermolecular Rh···Rh and Rh···C interactions.

Because of this offset, a second close intermolecular contact, that between Rh and C02 [3.650 (5) Å], is also observed (Fig. 2).

A further deviation from the stacking pattern normally observed in other crystal structures, listed in Table 2, is the unique occurrence of head-to-head stacking in the title compound. All the other complexes pack in a head-to-tail pattern or a close variant thereof. This effect is illustrated by the range of O—Rh··Rh—O pseudo-torsion angles listed in Table 2 and could be the result of the small steric demand of the tropolonate moiety, which is indicated by the fact that the bidentate bite angle (O—Rh—O) in (I) is small compared with that in other dicarbonyl complexes.

Experimental

The title compound, (I), was synthesized by dissolving [Rh(μ -Cl)(CO)₂]₂ (45 mg, 0.116 mmol) in methanol (30 ml), adding 2.2 equivalents of tropolone (30.9 mg, 0.253 mmol) and allowing crystallization to occur under slow evaporation (ca 1 d) (yield 58.5 mg, 90%). IR: ν_{CO} 2074, 2014 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.55 (*m*, 5H).

Crystal data

[Rh(C ₇ H ₅ O ₂)(CO) ₂]	$D_x = 2.058 \text{ Mg m}^{-3}$
$M_r = 280.04$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 48 reflections
$a = 3.683 (1) \text{ \AA}$	$\theta = 4.1\text{--}13.3^\circ$
$b = 21.856 (4) \text{ \AA}$	$\mu = 1.87 \text{ mm}^{-1}$
$c = 11.296 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.32 (2)^\circ$	Prism, orange
$V = 903.8 (4) \text{ \AA}^3$	$0.23 \times 0.15 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Philips PW1100 diffractometer	$R_{\text{int}} = 0.085$
ω - 2θ scans	$\theta_{\text{max}} = 26.0^\circ$
Absorption correction: Gaussian	$h = 0 \rightarrow 4$
(<i>ABSORB</i> in <i>Xtal3.6</i> ; Hall <i>et al.</i> , 1999)	$k = -26 \rightarrow 26$
$T_{\text{min}} = 0.673$, $T_{\text{max}} = 0.872$	$l = -13 \rightarrow 13$
3331 measured reflections	1 standard reflection every 50 reflections
1784 independent reflections	intensity decay: none
1049 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1784 reflections	$\Delta\rho_{\text{max}} = 1.26 \text{ e \AA}^{-3}$
127 parameters	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Rh—C01	1.825 (10)	O11—C1	1.267 (9)
Rh—C02	1.826 (9)	O12—C2	1.324 (8)
Rh—O12	2.021 (5)	C01—O01	1.139 (9)
Rh—O11	2.032 (5)	C02—O02	1.145 (9)
C01—Rh—C02	88.3 (4)	C02—Rh—O12	96.1 (3)
O12—Rh—O11	79.4 (2)	C01—Rh—O11	96.3 (3)
O11—C1—C2—O12	−1.4 (11)	C3—C4—C5—C6	−1.6 (17)
C7—C1—C2—C3	−3.8 (14)		

Table 2

Comparative data (Å, °) for dicarbonyl diketone rhodium complexes.

Complex ^a	Rh··Rh	O—Rh··Rh—O	O—Rh—O	N_C^b
Rh(Trop)(CO) ₂ ^c	3.683 (5)	0.0 (2)	79.4 (2)	5
Rh(DBSQ)(CO) ₂ ^d	3.252 (6)	139.0 (4)	80.1 (4)	5
Rh(TDN)(CO) ₂ ^e	—	—	80.46 (1)	5
Rh(TMOX)(CO) ₂ ^f	3.243 (1)	180.0 (1)	81.0 (2)	5
Rh(TECA)(CO) ₂ ^g	3.213 (14)	124.4 (1)	80.0 (1)	5
Rh(ACAC)(CO) ₂ ^h	3.253 (1)	−180.0 (1)	88.93 (1)	6
Rh(BTAC)(CO) ₂ ⁱ	3.537 (1)	155.6 (2)	89.8 (1)	6
Rh(TACC)(CO) ₂ ^j	3.352 (1)	−139.4 (1)	92.6 (2)	6
Rh(TAMO)(CO) ₂ ^k	3.401 (3)	−132.8 (2)	86.8 (2)	6
Rh(HGCA)(CO) ₂ ^l	3.419 (1)	168.4 (2)	90.2 (2)	6
Rh(HGCA)(CO) ₂ ^l	3.315 (1)	−169.1 (2)	90.4 (2)	6

Notes: (a) Cambridge Structural Database (Allen, 2002) reference code; (b) number of atoms in chelate; (c) present study, where Trop is tropolonate; (d) Lange *et al.* (1992), where DBSQ is 3,6-di-*tert*-butyl-1,2-semiquinonate; (e) Ragaini *et al.* (1992), where TDN is bis(triphenylphosphino)iminium-*N*-(3,4-dichlorophenyl)nitrosobenzene-carboxylate; (f) Real *et al.* (1989), where TMOX is oxalate; (g) Elduque *et al.* (1999), where TECA is chloranilate; (h) Huq & Skapski (1974), where ACAC is acetylacetonate; (i) Leipoldt *et al.* (1977), where BTAC is benzoyl-1,1,1-trifluoroacetate; (j) Schurig *et al.* (1983), where TACC is (1*S*)-3-trifluoroacetylcamphorate; (k) Schurig *et al.* (1985), where TAMO is (1*RS*,4*SR*)-trifluoroacetylmenthonate; (l) Schurig *et al.* (1989), where HGCA is 3,3'-hexafluoroglutaryl-bis-(1*R*)-camphorate.

Data collection: *PWPC* (Gomm, 1998); cell refinement: *PWPC*; data reduction: *Xtal3.6* (Hall *et al.*, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1251). Services for accessing these data are described at the back of the journal.

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