Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Carbonyl(5-nitrotropolonato-κ^2O^1,O^2)(triphenylphosphine-κP)rhodium(I)

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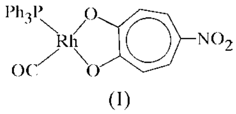
Received 26 March 2004
Accepted 7 May 2004
Online 22 June 2004

The molecule of the title complex, [Rh(5-NO_2trop)($C_{18}H_{15}P$)(CO)] (5-NO_2trop is 2-hydroxy-5-nitrocyclohepta-2,4,6-trienone, $C_7H_4NO_4$), has a distorted square-planar geometry. Strong intramolecular and weak intermolecular hydrogen bonding is observed, with H$\cdots$O distances of the order of 2.25 and 2.55 Å, respectively. The Rh—CO, Rh—O (*trans* to CO), Rh—O (*trans* to P) and Rh—P bond distances are 1.775 (7), 2.072 (4), 2.068 (4) and 2.2397 (17) Å, respectively, the O—Rh—O angle is 77.09 (16)° and the bidentate O—C—C—O torsion angle is 1.5 (7)°.

Comment

Although 5-nitrotropolone-type compounds are known for main group elements (Kubo, Tsuruta & Mori, 2001; Kubo, Yamamoto & Mori, 2001; Dittes *et al.*, 1996), very few transition metal complexes have been investigated to date. As part of our investigation into the role of functionalized tropolones (Steyl & Roodt, 2003) in rhodium(I) complexes, we present here the first crystal structure of a 5-nitrotropolone complex to be characterized for a transition group element.



(I)

The title compound, (I) (Fig. 1), crystallizes in the triclinic space group $P\overline{1}$, with Rh—O bond distances of 2.072 (4) and 2.068 (4) Å, and an O—Rh—O bite angle of 77.09 (16)°. The effective and Tolman angles observed for the triphenylphosphine ligand, 159 and 155°, respectively, agree well with observed cone angles (Tolman, 1977; Simanko *et al.*, 2000). The carbonyl C atom is displaced by 0.299 (7) Å above the plane defined by atoms Rh, P1, O12 and O11. The shortest intermolecular contact [H36$\cdots$H13($x - 1, y, z$) = 2.504 (1) Å] illustrates the generally efficient packing in the unit cell. However, high anisotropy is observed for the nitro moiety lying on the periphery of the molecule and is considered to be the result of locally weak packing forces allowing for high flexibility of the nitro group.

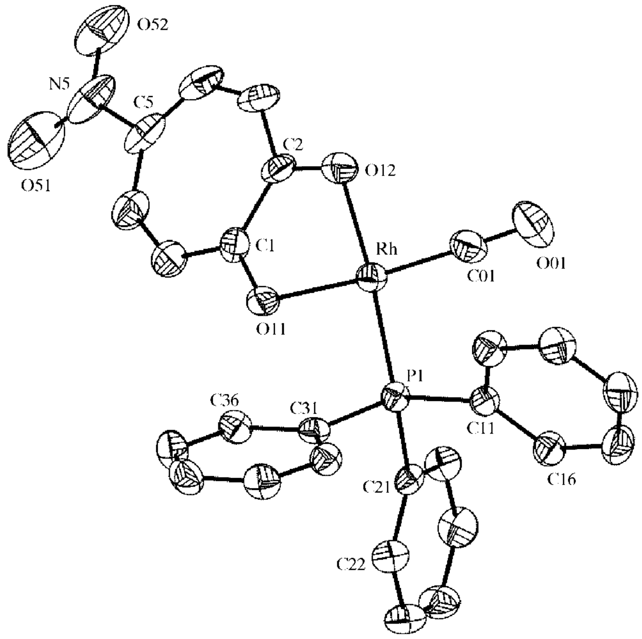


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. For clarity, only selected atoms have been numbered. For the C atoms, the first digit indicates the ring number, and the second indicates the atom number in the ring.

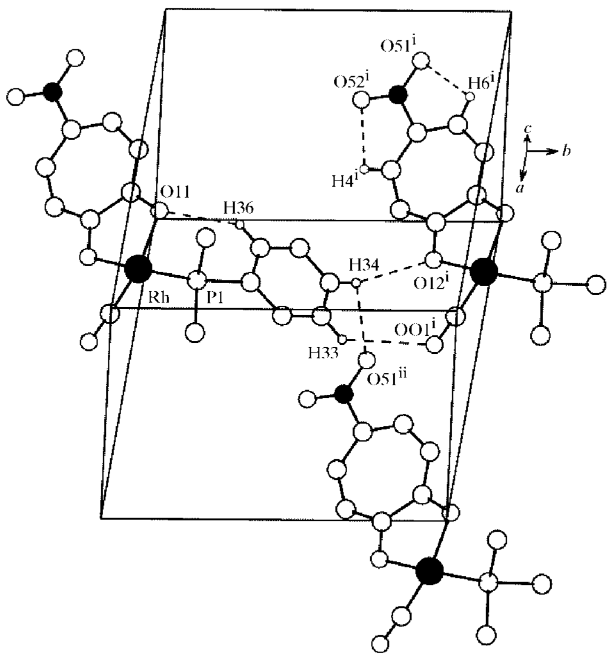


Figure 2
Part of the unit cell of (I), showing the intra- and intermolecular hydrogen bonding. Selected benzene-ring atoms have been omitted for clarity. [Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 + x, 1 + y, z$.]

DOI: 10.1107/S0108270104011102

Intramolecular hydrogen bonding exists between the nitro moiety and the troponoid H atoms (C6—H6···O51 and C4—H4···O52; see Table 2), and a further weak intramolecular hydrogen-bonding interaction is also present (C36—H36···O11). In addition, a clearly defined bifurcated hydrogen bond is observed [C34—H34···O12(x, $1 + y$, z)/O51($1 + x$, $1 + y$, z)], with the H atom lying in the plane defined by the donor/acceptor atoms (see Fig. 2). The carbonyl O atom is involved in two weak intermolecular hydrogen bonds, C6—H6···O01($x - 1$, y, z) and C33—H33···O01(x, $1 + y$, z), which might be the cause of the slight deviation from linearity of the Rh—C—O moiety [bond angle = 175.4 (5)°].

Of further interest is the similarity of the Rh—O bond distances (Table 1), in spite of the presence of different *trans* moieties (P *versus* CO). The coordination polyhedron is similar to that generally observed in square-planar rhodium(I) complexes (Leipoldt *et al.*, 1980; Steyl *et al.*, 2001). The distortion from square-planar geometry can, in part, be attributed to the strong symmetry observed in the functionalized tropolone (O12—C2 and O11—C1) bond distances (Gilli *et al.*, 1989; Bertolasi *et al.*, 1991), as well as the out-of-plane distortion of the carbonyl moiety (C01—Rh—O11; Table 1). Strong hydrogen-bonding interactions are observed for the nitrophenyl group, with closely related torsion angles for the C4—C5—N5—O52 moiety of (I). A host of nitrophenyl compounds have been characterized in the solid state and of particular interest are the similarities between these nitrophenyl compounds (André *et al.*, 1997*a*,*b*) and (I) in the nitro moiety conformation, confirming the 'aromatic' nature of the troponoid system.

In conclusion, the observed symmetry in the nitrotropolone moiety is attributed to both strong intramolecular and weak intermolecular hydrogen bonding with neighbouring nitrotropolone moieties. These hydrogen bonds probably contribute to the distorted square-planar geometry at the rhodium metal centre.

Experimental

The title compound, (I), was synthesized by dissolving [Rh(5-NO_2trop)$(CO)_2$] (10 mg, 0.031 mmol) in the minimum amount of hexane (40 ml), adding 1.1 equivalents of PPh_3 (9 mg, 0.034 mmol) and allowing crystallization to occur under slow evaporation (*ca* 1 d). ν_{CO}: 1983 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, p.p.m.): 8.2 (*m*); ^{31}P NMR ($CDCl_3$, 121.497 MHz, p.p.m.): 49.197 [*d*, ^1J(Rh—P) = 173.9 Hz].

Crystal data

$[Rh(C_7H_4NO_4)(C_{18}H_{15}P)(CO)]$
$M_r = 559.30$
Triclinic, $P\overline{1}$
$a = 9.3078\ (19)$ Å
$b = 10.329\ (2)$ Å
$c = 12.898\ (3)$ Å
$\alpha = 93.51\ (3)°$
$\beta = 105.33\ (3)°$
$\gamma = 100.75\ (3)°$
$V = 1166.9\ (5)$ Å^3
$Z = 2$
$D_x = 1.592$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}
D_m measured by flotation in aqueous KI
Mo $K\alpha$ radiation
Cell parameters from 1631 reflections
$\theta = 2–21°$
$\mu = 0.84$ mm^{-1}
$T = 293\ (2)$ K
Plate, brown
0.17 × 0.11 × 0.05 mm

Table 1
Selected geometric parameters (Å, °).

Rh—C01	1.775 (7)	O11—C1	1.275 (6)
Rh—O12	2.068 (4)	O01—C01	1.170 (6)
Rh—O11	2.072 (4)	C5—N5	1.496 (9)
Rh—P1	2.2397 (17)	O52—N5	1.217 (9)
O12—C2	1.274 (7)	O51—N5	1.234 (9)
C01—Rh—O12	94.6 (2)	O12—Rh—P1	175.38 (13)
C01—Rh—O11	168.7 (2)	O11—Rh—P1	99.41 (12)
O12—Rh—O11	77.09 (16)	O01—C01—Rh	175.4 (5)
C01—Rh—P1	89.3 (2)	O52—N5—O51	122.7 (8)
C4—C5—N5—O52	2.4 (9)	O11—C1—C2—O12	1.5 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
C36—H36···O11	0.93	2.44	3.234 (7)	143
C6—H6···O51	0.93	2.25	2.671 (9)	107
C4—H4···O52	0.93	2.27	2.673 (9)	106
C33—H33···O01^{i}	0.93	2.75	3.483 (7)	136
C34—H34···O12^{i}	0.93	2.55	3.438 (7)	159
C34—H34···O51^{ii}	0.93	2.96	3.473 (9)	116
C6—H6···O01^{iii}	0.93	2.87	3.337 (9)	112

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 + x, 1 + y, z$; (iii) $x - 1, y, z$.

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.871$, $T_{max} = 0.959$
7136 measured reflections
3988 independent reflections
2582 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.107$
$S = 1.00$
3988 reflections
307 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *SHELXL*97.

Financial assistance from the RAU is gratefully acknowledged. The University of the Witwatersrand (Professor D. Levendis, Dr D. Billing and Mr M. Fernandez) is acknowledged for the use of its diffractometer, while Mr A. Muller is thanked for the data collection. Part of this material is based on work supported by the South African National Research

Foundation (NRF) under grant No. GUN 2053397. Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1061). Services for accessing these data are described at the back of the journal.

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