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tert-Butylbis(dimethylglyoximato-*N*,*N*′)(triphenylphosphine-*P*)rhodium

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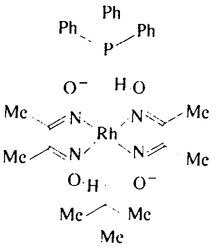
Abstract

The title structure {bis[2,3-butanedione dioximato(1−)-*N*,*N*′](*tert*-butyl)(triphenylphosphine-*P*)rhodium, [Rh($C_4H_7N_2O_2$)$_2$(C_4H_9)($C_{18}H_{15}P$)]} consists of discrete complexes in which the Rh atom displays distorted octahedral coordination, with the two dimethylglyoxime ligands in the equatorial plane and the *tert*-butyl and triphenylphosphine groups in the axial positions. The Rh atom is displaced by 0.048 (1) Å from the mean plane through the four oxime N donor atoms towards the P atom. The Rh—N distances range from 1.930 (3) to 1.982 (2) Å, while the axial Rh—P and Rh—C distances are 2.492 (1) and 2.216 (3) Å, respectively. Comparison of the results with those obtained previously for other compounds of this type indicates that the *trans* influence of *R* in the axial fragment Ph_3P—Rh—*R* is determined by its σ-donor power, while the Rh—C bond distance depends on the steric interaction of *R* with the equatorial moiety.

Comment

This work is a continuation of a project aimed at understanding the mutual electronic influence of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ-organo ligands is of particular interest. In previous papers of this series we have demonstrated (Steinborn & Ludwig, 1993; Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1994; Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1994) that in complexes of the type [Rh(dmgH)$_2$(PPh$_3$)*R*] (where dmgH is the monoanion of dimethylglyoxime and *R* is an organo group) the *trans* influence of *R*, as measured by $^1J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ coupling constants and the Rh—P bond distance, is determined by the σ-donating power of *R*, irrespective of the hybridization state of the C atom. To examine the possibility that introduction of an electron-donating substituent in *R* would enhance the *trans* influence, we prepared and determined the crystal structure of a *tert*-butyl analogue, (I). The results are described here and compared with those for other compounds of the series.



(I)

The complex crystallizes as discrete molecules in which the Rh atom exhibits distorted octahedral stereochemistry, with four oxime N donors in the equatorial positions. The two dimethylglyoximato ligands are stabilized by two intramolecular hydrogen bonds acting between atoms O(1) and O(4) [O···O 2.652 (3) Å], and O(2) and O(3) [O···O 2.694 (3) Å]. The polar H atoms were clearly located from the $\Delta\rho$ map and are bonded to atoms O(1) and O(3) (Fig. 1).

The Rh—N(1) and Rh—N(3) bond distances involving the N atoms bearing the unprotonated OH groups are equal within experimental error (Table 2) and are much shorter than the other two Rh—N distances. As found in other derivatives of the series, the two dmgH$^-$ ligands are tilted away from the triphenylphosphine ligand so that their normal vectors make an angle of 9.5 (4)° with each other. As a result, though the four oxime N donors are coplanar to within ±0.005 Å, the Rh atom is displaced by 0.048 (1) Å from their mean plane towards the P atom. The dmgH$^-$ ligands themselves are also not strictly planar. This lack of planarity originates from twisting of the two halves of the ligand about the central C—C bond, the twist angles being 3.5 (4) and 4.1 (4)° for the ligands comprising N(1), N(2), O(1), O(2) and C(1)–C(4) and N(3), N(4), O(3), O(4) and C(5)–C(8), respectively.

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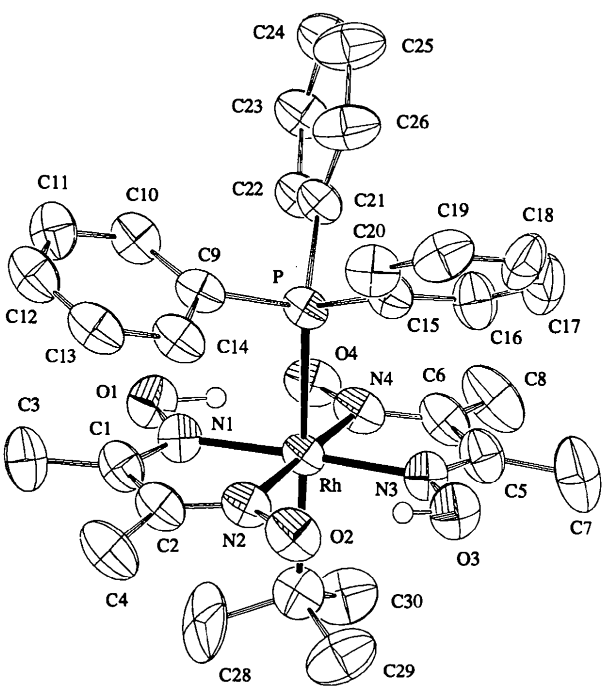

Fig. 1. *ORTEP* (Johnson, 1971) drawing of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level. Only polar H atoms (those involved in intramolecular hydrogen bonding) are shown for clarity.

As mentioned above, the *trans* influence of the axial ligands, *viz*. the σ-bonded *tert*-butyl group and the PPh_3 moiety, is of special interest here. The Rh—P and Rh—C bond lengths are 2.492 (1) and 2.216 (3) Å, respectively, and the P—Rh—C angle is 174.2 (1)°. Comparison with other $[Rh(dmgH)_2(PPh_3)R]$ complexes shows that the Rh—C bond distance varies in a rather broad range from 1.991 (3) to 2.216 (3) Å and roughly correlates with the steric volume of *R* (disregarding, of course, the phenyl group of the phenyl acetylide analogue, which is well separated from the equatorial plane). This indicates that the Rh—C bond length is determined by the steric interaction of *R* with the equatorial $dmgH^-$ ligands. In contrast, the Rh—P bond distance is determined by the electronic influence of *R* in the axial direction. This can best be demonstrated by the 0.031 (2) Å increase in the Rh—P bond length in the present complex relative to the ethyl analogue, obviously due to the increased σ-donating power of the *tert*-butyl ligand relative to the ethyl group. As the Rh—C and Rh—P bond distances depend on different factors, they are uncorrelated.

Experimental

Crystals of the title compound were obtained from ethanol. The density D_m was measured by pycnometry.

Crystal data

$[Rh(C_4H_7N_2O_2)_2(C_4H_9)(C_{18}H_{15}P)]$
$M_r = 652.54$
Triclinic
$P\bar{1}$
$a = 8.696\ (3)$ Å
$b = 10.421\ (4)$ Å
$c = 17.113\ (8)$ Å
$\alpha = 76.63\ (5)°$
$\beta = 87.31\ (6)°$
$\gamma = 72.23\ (5)°$
$V = 1436.3\ (8)$ Å^3
$Z = 2$
$D_x = 1.509$ Mg m^{-3}
$D_m = 1.50\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 6$–$17°$
$\mu = 0.68$ mm^{-1}
$T = 293$ K
Prism
$0.40 \times 0.30 \times 0.15$ mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7094 measured reflections
6659 independent reflections
5126 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.023$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -22 \rightarrow 22$
2 standard reflections
frequency: 100 min
intensity decay: 4%

Refinement

Refinement on *F*
$R = 0.055$
$wR = 0.068$
$S = 1.27$
5126 reflections
361 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0009F^2]$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Rh(1)	0.14588 (3)	0.08969 (2)	0.22915 (1)	2.72 (1)
P(1)	0.13492 (9)	0.30437 (7)	0.27280 (4)	2.58 (2)
O(1)	0.4961 (3)	−0.0029 (2)	0.2374 (1)	4.14 (6)
O(2)	−0.0455 (3)	0.2690 (2)	0.0926 (1)	4.14 (7)
O(3)	−0.2045 (3)	0.1753 (3)	0.2213 (1)	4.42 (8)
O(4)	0.3394 (3)	−0.0994 (2)	0.3627 (1)	3.91 (6)
N(1)	0.3619 (3)	0.0753 (2)	0.1908 (1)	3.05 (7)
N(2)	0.1013 (3)	0.2045 (2)	0.1188 (1)	3.16 (7)
N(3)	−0.0690 (3)	0.0964 (3)	0.2660 (1)	3.16 (8)
N(4)	0.1937 (3)	−0.0350 (2)	0.3375 (1)	3.36 (8)
C(1)	0.3773 (4)	0.1381 (3)	0.1173 (2)	3.43 (8)
C(2)	0.2262 (4)	0.2109 (3)	0.0753 (2)	3.64 (9)
C(3)	0.5352 (5)	0.1323 (4)	0.0814 (2)	5.12 (13)
C(4)	0.2096 (5)	0.2833 (4)	−0.0104 (2)	4.89 (13)
C(5)	−0.0830 (4)	0.0227 (4)	0.3360 (2)	3.87 (10)
C(6)	0.0669 (4)	−0.0550 (3)	0.3774 (2)	3.74 (9)
C(7)	−0.2424 (5)	0.0133 (5)	0.3690 (3)	5.81 (15)
C(8)	0.0848 (6)	−0.1556 (4)	0.4545 (2)	5.39 (13)
C(9)	0.2422 (4)	0.4020 (3)	0.2020 (2)	3.03 (8)
C(10)	0.3999 (4)	0.3918 (3)	0.2194 (2)	3.51 (9)
C(11)	0.4866 (4)	0.4561 (4)	0.1639 (2)	4.01 (9)
C(12)	0.4197 (5)	0.5315 (3)	0.0911 (2)	4.10 (10)
C(13)	0.2647 (5)	0.5411 (3)	0.0725 (2)	4.18 (10)
C(14)	0.1771 (4)	0.4738 (3)	0.1267 (2)	3.40 (9)

C(15)	−0.0664 (4)	0.4203 (3)	0.2798 (2)	3.24 (8)
C(16)	−0.1667 (4)	0.3702 (4)	0.3334 (2)	3.99 (10)
C(17)	−0.3154 (5)	0.4535 (5)	0.3484 (2)	5.12 (14)
C(18)	−0.3617 (4)	0.5904 (5)	0.3077 (2)	5.62 (14)
C(19)	−0.2679 (5)	0.6409 (4)	0.2559 (3)	5.19 (12)
C(20)	−0.1148 (5)	0.5590 (3)	0.2406 (2)	4.33 (10)
C(21)	0.2218 (4)	0.2996 (3)	0.3686 (2)	3.02 (8)
C(22)	0.3406 (4)	0.1870 (3)	0.4057 (2)	3.17 (8)
C(23)	0.4148 (4)	0.1894 (3)	0.4741 (2)	3.66 (10)
C(24)	0.3698 (5)	0.3046 (4)	0.5051 (2)	4.57 (11)
C(25)	0.2472 (6)	0.4147 (5)	0.4693 (3)	6.84 (17)
C(26)	0.1717 (6)	0.4137 (4)	0.4009 (2)	5.83 (14)
C(27)	0.1447 (4)	−0.0875 (3)	0.1786 (2)	3.85 (10)
C(28)	0.2846 (7)	−0.1228 (5)	0.1238 (3)	7.19 (20)
C(29)	−0.0071 (6)	−0.0545 (5)	0.1336 (3)	6.59 (17)
C(30)	0.1631 (5)	−0.2171 (4)	0.2447 (3)	5.18 (13)

Table 2. *Selected geometric parameters (Å, °)*

Rh(1)—P(1)	2.492 (1)	P(1)—C(15)	1.815 (3)
Rh(1)—C(27)	2.216 (3)	P(1)—C(21)	1.822 (3)
Rh(1)—N(1)	1.934 (3)	N(1)—O(1)	1.367 (3)
Rh(1)—N(2)	1.973 (2)	N(2)—O(2)	1.293 (4)
Rh(1)—N(3)	1.930 (3)	N(3)—O(3)	1.361 (3)
Rh(1)—N(4)	1.982 (2)	N(4)—O(4)	1.281 (4)
P(1)—C(9)	1.810 (3)		
N(1)—Rh(1)—N(2)	78.4 (1)	N(4)—Rh(1)—C(27)	89.9 (1)
N(3)—Rh(1)—N(4)	78.8 (1)	P(1)—Rh(1)—C(27)	174.2 (1)
P(1)—Rh(1)—N(1)	90.2 (1)	Rh(1)—P(1)—C(9)	109.1 (1)
P(1)—Rh(1)—N(2)	87.3 (1)	Rh(1)—P(1)—C(15)	115.4 (1)
P(1)—Rh(1)—N(3)	92.4 (1)	Rh(1)—P(1)—C(21)	122.2 (1)
P(1)—Rh(1)—N(4)	95.8 (1)	C(9)—P(1)—C(15)	106.9 (1)
N(1)—Rh(1)—C(27)	90.0 (1)	C(9)—P(1)—C(21)	102.0 (1)
N(2)—Rh(1)—C(27)	87.1 (1)	C(15)—P(1)—C(21)	99.7 (1)
N(3)—Rh(1)—C(27)	87.4 (1)		

The H(O1) and H(O3) atoms were fixed at their observed positions (from difference synthesis). All other H atoms were fixed at their calculated positions. Each H-atom displacement parameter was fixed at 0.5 Å^2 greater than the B_{eq} value of the atom to which it is bonded.

Data collection: Syntex $P2_1$ diffractometer software. Cell refinement: Syntex $P2_1$ diffractometer software. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *NRC Crystallographic Programs for the IBM*360 *System* (1970). Program(s) used to refine structure: *NRC Crystallographic Programs for the IBM*360 *System* (1970).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: HR1052). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane-*S*,*S*′)ruthenium(II) Bis(hexafluorophosphate)–Water–Methanol (1/2/1)

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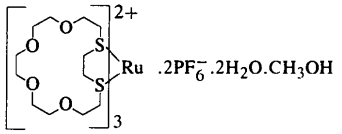
Abstract

In the title complex, $[Ru(C_{12}H_{24}O_4S_2)_3](PF_6)_2.2H_2O.CH_3OH$, the Ru^{II} ion lies on a crystallographic threefold axis and is coordinated to three symmetry-equivalent macrocyclic ligands *via* their S donor atoms [Ru—S 2.3620 (9) and 2.3859 (9) Å]. The macrocycle adopts a typical bidentate chelating coordination mode with S donors in *exo* and O donors in *endo* orientations.

Comment

Mixed O/S ionophores such as $[15]aneS_2O_3$ (1,4,7-trioxa-10,13-dithiacyclopentadecane) and $[18]aneS_2O_4$ (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane) provide atoms with contrasting donor properties within the same macrocyclic framework (Blake, Radek & Schröder, 1995). We have been interested in the coordination chemistry of these ligands with a range of metal ions (Blake, Reid & Schröder, 1990; Blake, Gould, Radek & Schröder, 1994, 1995; Bell, Blake, Gould, Parsons, Radek & Schröder, 1995) and have found that metal ions such as Ru^{II} and Pd^{II} adopt exclusively *exo* bidentate coordination modes *via* the S donors. The O donors normally remain *endo* orientated and the cavity is partially occupied by the ethylene bridge between the S donors. The structure of $[Ru([18]aneS_2O_4)_3](PF_6)_2.2H_2O.CH_3OH$, (I), displays the same chelating mode, with three $[18]aneS_2O_4$ ligands coordinated to each Ru^{II} ion.



(I)

The geometric features of the Ru—S environment [Ru—S 2.3620 (9) and 2.3859 (9) Å and chelating S—Ru—S 87.24 (3)°] are similar to those of other Ru^{II}

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