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Bis(dimethylglyoximato-*N*,*N'*)(isopropyl)-(triphenylphosphine)rhodium(III)

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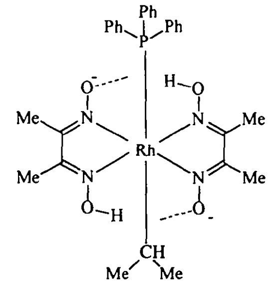
Abstract

The structure of the title compound, $[Rh(C_4H_7N_2O_2)_2\{CH(CH_3)_2\}\{P(C_6H_5)_3\}]$, consists of discrete complexes in which the Rh atom has distorted octahedral coordination. The two dimethylglyoximato ligands lie in the equatorial plane and the isopropyl and triphenylphosphine species occupy the axial positions. The Rh atom is displaced by 0.096 (1) Å from the mean plane through the four oxime N donor atoms towards the P atom. The average Rh—N distance is 1.975 (10) Å, while the axial Rh—P and Rh—C distances are 2.489 (2) and 2.146 (6) 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.

Comment

This work is a continuation of a project aimed at the elucidation of the mutual influence of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ-organo ligands is of particular interest. We have demonstrated (Steinborn & Ludwig, 1993*a*; Ludwig & Steinborn, 1996) that in complexes $[Rh(dmgH)_2(PPh_3)R]$ (dmgH = monoanion of dimethylglyoxime, PPh_3 = triphenylphosphine, *R* = organo group) the *trans* influence of *R*, as measured by $^1J(^{103}Rh–^{31}P)$ coupling constants, is in the unusual order ^{t}Bu $\gg$ cyclohexyl > ^{i}Pr > CPr=CH_2 > CH_2OMe > CH=CHPr = ^{i}Bu = ^{n}Pr = Ph = Et = ^{n}Bu = CH=CHPh > CH=CH_2 > CH_2SiMe_3 = Me > CH_2Cl = CH_2SPh = Bz = CH_2Br $\gg$ C≡CPh. To investigate the dependence of the *trans* influence measured by NMR spectroscopy on the structure of the complexes, we decided to study the structures of the complexes by systematically changing the type of hybridization of the donor orbital (*R* = Et, CH=CH_2 and C≡CPh) as well as the branching within the alkyl ligands (*R* = Me, Et, ^{i}Pr and ^{t}Bu) (C≡CPh: Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1995; CH=CH_2: Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1994; Et: Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1994; ^{t}Bu: Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1996; Me: Potočňák, Dunaj-Jurčo, Ludwig & Steinborn, 1996). Here we report the structure of the isopropyl complex, (I).



(I)

The $[Rh(dmgH)_2(PPh_3)^i Pr]$ complex crystallizes with discrete molecules, in which the Rh atom exhibits distorted octahedral coordination, with four oxime N donors in the equatorial positions. The two dimethylglyoximato ligands are stabilized by two intramolecular hydrogen bonds, acting between O1 and O4 [O···O = 2.686 (7) Å] and between O2 and O3 [O···O = 2.692 (7) Å]. On the basis of the refined H-atom positions, both hydrogen bridges in the $Rh(dmgH)_2$ unit are asymmetric [O1···H4 = 1.93 (7), O4—H4 = 0.78 (7), O3···H2 = 2.01 (7), O2—H2 = 0.69 (7) Å].

The four Rh—N bond distances range from 1.963 (5) to 1.990 (5) Å, with a mean value of 1.975 (10) Å. This value is larger than those of the vinyl and the *tert*-butyl derivatives [1.957 (2) and 1.955 (3) Å, respectively (Dunaj-Jurčo *et al.*, 1994*b*; Kettmann *et al.*, 1996)] but is similar to those of the phenylacetylide and methyl complexes [1.971 (2) and 1.976 (9) Å, respectively (Dunaj-Jurčo *et al.*, 1994*a*; Potočňák *et al.*, 1996)]. 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 9.74 (7)° with each other. As a result, though the four oxime N donors are coplanar to within ±0.002 Å, the Rh atom is displaced by 0.0961 (10) Å from their mean plane toward the P atom. The $dmgH^-$ ligands themselves are also not strictly planar; the lack of planarity originates from twisting of the two halves of the ligand about the central C—C bond, the dihedral angle formed by the planes O1—N1—C1—C3 and O2—N2—C2—C4 being 2.9 (3)° and that formed by

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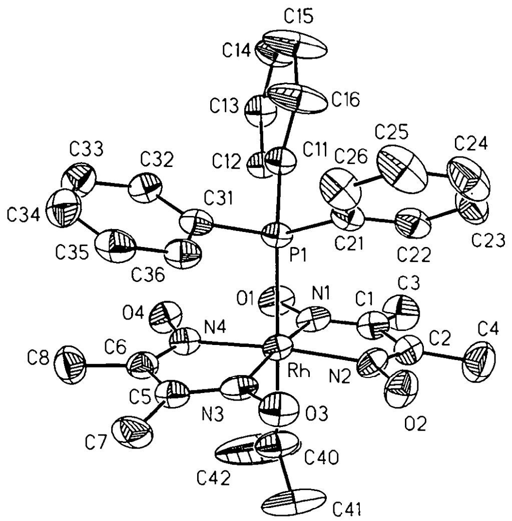

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound showing the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level.

the planes O3—N3—C5—C7 and O4—N4—C6—C8 being 3.6 (3)°.

As mentioned above, the *trans* influence of the axial ligands, *i.e.* the σ-bonded isopropyl group and PPh_3 moiety, is of special interest here. The Rh—P and Rh—C bond lengths are 2.489 (2) and 2.146 (6) Å, respectively, and the P—Rh—C angle is 176.1 (2)°. Comparison with other [Rh(dmgH)$_2$(PPh$_3$)*R*] complexes shows that the Rh—C bond length is somewhat longer than that found for the methyl and the ethyl derivatives [2.119 (4) and 2.064 (7) Å, respectively] but it is considerably shorter than that found for the *tert*-butyl derivative [2.216 (3) Å], which is in line with the sterical demand of the *tert*-butyl ligand.

The Rh—C distance found in the similar compound [Rh(dmgH)$_2$(pyridine)C(CH$_3$)$_2$] is shorter [2.085 (3) Å] than the Rh—C distance found in the title compound, in agreement with the smaller *trans* influence of the pyridine ligand in comparison with that of the PPh_3 group (Pahor *et al.*, 1990). The Rh—P bond distance is determined by the electronic influence of *R* in the axial direction. This is demonstrated by comparison of the Rh—P bond length in the present complex [2.489 (2) Å], which is similar that in the *tert*-butyl complex [2.492 (1) Å], with those in the methyl and ethyl analogues [2.454 (1) and 2.461 (2) Å, respectively]. The former are longer obviously due to increased σ-donating power of the isopropyl and *tert*-butyl groups relative to the methyl and the ethyl groups.

Experimental

Preparation of the title compound is described by Steinborn & Ludwig (1993*b*). The crystal density D_m was measured by flotation in water–KI.

Crystal data

[Rh(C$_4$H$_7$N$_2$O$_2$)$_2$(C$_3$H$_7$)-(C$_{18}$H$_{15}$P)]
$M_r = 638.49$
Triclinic
$P\bar{1}$
$a = 8.815$ (2) Å
$b = 10.154$ (2) Å
$c = 17.277$ (4) Å
$\alpha = 76.49$ (2)°
$\beta = 87.98$ (2)°
$\gamma = 74.55$ (2)°
$V = 1448.7$ (6) Å^3
$Z = 2$
$D_x = 1.464$ Mg m^{-3}
$D_m = 1.46$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 21 reflections
$\theta = 6.34$–12.63°
$\mu = 0.672$ mm^{-1}
$T = 293$ (2) K
Prism
0.5 × 0.3 × 0.25 mm
Brownish yellow

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: ψ scan (Pavelčík, 1993)
$T_{min} = 0.396$, $T_{max} = 0.520$
3802 measured reflections
3802 independent reflections
3211 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 22.50°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -22 \rightarrow 22$
2 standard reflections monitored every 98 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0469$
$wR(F^2) = 0.1256$
$S = 1.073$
3798 reflections
362 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 4.0832P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.049$
$\Delta\rho_{max} = 2.433$ e Å^{-3}
$\Delta\rho_{min} = -0.646$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh	0.14417 (5)	0.09184 (4)	0.23172 (3)	0.0364 (2)
P1	0.1467 (2)	0.31117 (15)	0.27194 (8)	0.0369 (4)
N1	0.1847 (6)	−0.0366 (5)	0.3395 (3)	0.0441 (12)
N2	−0.0712 (5)	0.0965 (5)	0.2666 (3)	0.0458 (12)
N3	0.1040 (6)	0.2033 (5)	0.1209 (3)	0.0446 (12)
N4	0.3603 (5)	0.0706 (5)	0.1928 (3)	0.0416 (12)
O1	0.3294 (5)	−0.1008 (4)	0.3667 (3)	0.0548 (11)
O2	−0.2018 (6)	0.1763 (6)	0.2203 (3)	0.0618 (14)
O3	−0.0402 (5)	0.2707 (4)	0.0938 (2)	0.0553 (11)
O4	0.4892 (5)	−0.0074 (5)	0.2398 (3)	0.0552 (12)
C1	0.0601 (8)	−0.0589 (6)	0.3776 (4)	0.050 (2)
C2	−0.0883 (8)	0.0188 (7)	0.3352 (4)	0.052 (2)
C5	0.2283 (8)	0.2041 (6)	0.0762 (4)	0.048 (2)
C6	0.3771 (7)	0.1277 (6)	0.1190 (4)	0.048 (2)
C3	0.0727 (10)	−0.1622 (8)	0.4555 (4)	0.073 (2)
C4	−0.2448 (9)	0.0091 (10)	0.3664 (5)	0.084 (2)
C7	0.2125 (9)	0.2732 (8)	−0.0100 (4)	0.064 (2)
C8	0.5336 (8)	0.1163 (8)	0.0822 (4)	0.070 (2)
C11	0.2383 (7)	0.3088 (6)	0.3660 (3)	0.0419 (14)

C12	0.3513 (7)	0.1936 (6)	0.4050 (3)	0.0439 (14)
C13	0.4287 (8)	0.1981 (7)	0.4715 (4)	0.051 (2)
C14	0.3956 (9)	0.3137 (8)	0.5001 (4)	0.065 (2)
C15	0.2822 (13)	0.4258 (9)	0.4638 (6)	0.114 (4)
C16	0.2043 (11)	0.4252 (8)	0.3967 (5)	0.097 (3)
C21	−0.0475 (7)	0.4309 (6)	0.2784 (3)	0.0426 (14)
C22	−0.1515 (8)	0.3792 (7)	0.3299 (4)	0.055 (2)
C23	−0.2945 (9)	0.4642 (10)	0.3431 (5)	0.072 (2)
C24	−0.3362 (10)	0.6010 (11)	0.3042 (5)	0.083 (3)
C25	−0.2366 (11)	0.6560 (9)	0.2535 (5)	0.083 (3)
C26	−0.0917 (9)	0.5720 (7)	0.2404 (4)	0.064 (2)
C31	0.2563 (7)	0.4090 (5)	0.1990 (3)	0.0401 (14)
C32	0.4101 (7)	0.4017 (6)	0.2141 (4)	0.0475 (15)
C33	0.4989 (9)	0.4675 (7)	0.1572 (4)	0.060 (2)
C34	0.4255 (9)	0.5452 (7)	0.0858 (4)	0.063 (2)
C35	0.2723 (9)	0.5530 (7)	0.0688 (4)	0.057 (2)
C36	0.1883 (8)	0.4829 (6)	0.1242 (3)	0.048 (2)
C40	0.1368 (9)	−0.0887 (7)	0.1891 (5)	0.067 (2)
C41	0.0192 (13)	−0.0651 (9)	0.1258 (6)	0.110 (4)
C42	0.2441 (18)	−0.2119 (10)	0.2171 (10)	0.203 (9)

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

Rh—N2	1.963 (5)	P1—C11	1.832 (6)
Rh—N4	1.972 (5)	N1—O1	1.315 (6)
Rh—N3	1.974 (5)	N2—O2	1.374 (7)
Rh—N1	1.990 (5)	N3—O3	1.316 (6)
Rh—C40	2.146 (6)	N4—O4	1.365 (6)
Rh—P1	2.489 (2)	C40—C42	1.346 (11)
P1—C31	1.830 (6)	C40—C41	1.468 (10)
P1—C21	1.833 (6)		
N2—Rh—N4	174.3 (2)	N3—Rh—P1	88.19 (14)
N2—Rh—N3	101.1 (2)	N1—Rh—P1	97.31 (14)
N4—Rh—N3	78.7 (2)	C40—Rh—P1	176.1 (2)
N2—Rh—N1	78.7 (2)	C31—P1—C21	107.0 (3)
N4—Rh—N1	100.9 (2)	C31—P1—C11	101.7 (3)
N3—Rh—N1	174.5 (2)	C21—P1—C11	100.2 (3)
N2—Rh—C40	85.9 (3)	C31—P1—Rh	108.8 (2)
N4—Rh—C40	88.4 (3)	C21—P1—Rh	115.3 (2)
N3—Rh—C40	88.0 (2)	C11—P1—Rh	122.3 (2)
N1—Rh—C40	86.6 (2)	C42—C40—C41	124.3 (7)
N2—Rh—P1	94.33 (15)	C42—C40—Rh	119.3 (6)
N4—Rh—P1	91.33 (14)	C41—C40—Rh	116.2 (5)

Intensities were corrected for Lorentz and polarization factors and absorption using *XP*21 (with a modified version of *EMPABS*) (Pavelčík, 1993). The structure was solved by heavy-atom methods with *XFPS* (Pavelčík, Rizzoli & Andreeti, 1990) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. Highly anisotropic displacement parameters of atoms C41 and C42 indicate possible disorder of the isopropyl group orientation around the Rh—C40 bond, but splitting of C41 and C42 into two or more corresponding pairs did not yield better results. Both (O)H atoms were located from the difference Fourier map and refined with isotropic displacement parameters fixed at 0.06 $Å^2$. The (C)H atoms were apparent in the difference map, but they were included in the refinement as riding atoms in calculated positions with isotropic displacement parameters. The only exception were the isopropyl H atoms which were not included because of high anisotropic displacement parameters of C41 and C42 atoms. $\Delta\rho_{max} = 2.4$ e $Å^{-3}$ near Rh (1.57 Å) allows no reasonable crystallochemical explanation and is considered to be false. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium Bis(isothiocyanato)-triphenylstannate

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Abstract

The $[Sn(C_6H_5)_3(NCS)_2]^-$ organotin anion of the title compound, $(C_8H_{20}N)[Sn(C_6H_5)_3(NCS)_2]$, lies on a crystallographic twofold axis and the trigonal bipyramidal