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

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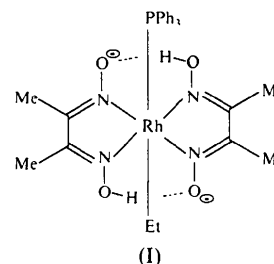
Abstract

The structure of $[\text{Rh}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_5)(\text{C}_{18}\text{H}_{15}\text{P})]$ consists of discrete complex molecules in which the Rh atom displays distorted octahedral coordination;

the two dimethylglyoxime ligands lie in the equatorial plane and the ethyl and triphenylphosphine groups occupy the axial positions. The Rh atom is displaced by 0.130(1) Å from the mean plane through the four oxime N donor atoms in the direction of the P atom. The Rh—N distances range from 1.903(6) to 1.993(6) Å, while the axial Rh—P and Rh—C distances are 2.461(2) and 2.064(7) Å, respectively. Comparison of the results with those obtained previously for analogous compounds containing the axial fragment $\text{Ph}_3\text{P—Rh—X}$ indicates that the *trans* influence of X is determined by its σ -donor power.

Comment

This work is part of a more general study aimed at understanding the mutual electronic influences of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ -organo ligands is of particular interest. In this paper we report the crystal structure of $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{Et}]$ (dmgH = mono-anion of dimethylglyoxime), (I). The molecular structure and the numbering scheme are shown in Fig. 1.



The complex crystallizes with discrete molecules, in which the Rh atom exhibits a distorted octahedral stereochemistry, with four oxime N donor atoms in the equatorial positions. The two dimethylglyoxime ligands are stabilized by two intramolecular hydrogen bonds acting between O(1) and O(4) [O...O = 2.560(7) Å] and between O(2) and O(3) [O...O = 2.671(7) Å]. Although the H atoms were not located from the $\Delta\rho$ map, on the basis of the oxime N—O distances (Table 2) it appears that the protons are more tightly bonded to O(4) and O(2) than to O(1) and O(3). In this respect the title structure agrees with those of analogous complexes which have pyridine as the axial base, $[\text{Rh}(\text{dmgH})_2(\text{py})\text{R}]$ (Bresciani Pahor, Dreos-Garlatti, Geremia, Randaccio, Tazher & Zangrando, 1990; Randaccio, Geremia, Dreos-Garlatti, Tazher, Asaro & Pellizer, 1992).

The Rh—N bond distances range from 1.903(6) to 1.993(6) Å. These values are slightly shorter than those in the closely related complex $[\text{Rh}(\text{dmgH})_2-$

(PPh₃)Cl] (Cotton & Norman, 1971). The Rh(dmgH)₂ system is not strictly planar; the two dmgH⁻ ligands are tilted away from the phenyl groups so that their normal vectors make an angle of 13.5 (5)° with each other. Though the four oxime N donor atoms are coplanar to within ± 0.005 Å, the Rh atom is displaced by 0.130 (1) Å from their mean plane toward the P atom. In the two crystallographically independent molecules of the corresponding pyridine complex [Rh(dmgH)₂(py)Et] (Bresciani Pahor, Dreos-Garlatti, Geremia, Randaccio, Tazher & Zangrando, 1990), the bending angles and the displacements of the Rh atom out of the N₄ plane are 13° and 0.07 Å, and 0.5° and 0.02 Å, respectively.

The dmgH⁻ ligands themselves are not strictly planar; the lack of planarity originates from a twisting of the two halves of the ligand about the central C—C bond, the twist angles being 2.7 (8) and 7.6 (8)° for ligands N(1), N(2), O(1), O(2), C(1)—C(4) and N(3), N(4), O(3), O(4), C(5)—C(8), respectively.

As mentioned above, the *trans* influence of the axial ligands, *viz.* the σ -bonded ethyl group and the PPh₃ moiety, is of special interest here. The Rh—P and Rh—C bond lengths are 2.461 (2) and 2.064 (7) Å, respectively, and the P—Rh—C angle is 173.6 (2)°. The Rh—C bonds in the two molecules of the corresponding pyridine derivative are slightly longer [2.077 (2) and 2.080 (3) Å] but the N—Rh—C

units are less bent [177.7 (1) and 177.9 (1)°] (Bresciani Pahor, Dreos-Garlatti, Geremia, Randaccio, Tazher & Zangrando, 1990) than the P—Rh—C unit in the title complex.

Comparison of the Rh—P bond length with those found previously for other complexes containing the axial Ph₃P—Rh—X fragment has shown that the Rh—P bond distance is strongly dependent on the nature of the *trans* atom and is shortest (2.28–2.32 Å) when X is bonded to the Rh atom through an electronegative atom, *e.g.* Cl, N, O, S, *etc.* (Bosman & Gal, 1975, 1976; Thackray, Ariel, Leung, Menon, James & Trotter, 1986; Chambron, Eichhorn, Franczyk & Stearns, 1991; Sellmann, Fetz, Moll & Knoch, 1989; van Aswegen, Leipoldt, Potgieter, Lamprecht, Roodt & van Zyl, 1991; Kuzmenko, Zhilyaev, Porai-Koshits & Barabovskii, 1990). As expected, on the basis of greater σ -donor power of the C atom, the Rh—P bond in the title compound is almost 0.2 Å longer than those found in the aforementioned analogues.

To our knowledge, besides the present structure determination, only one structure of this type has been established by X-ray methods (Vicente, Martin, Solans & Font-Altaba, 1989), namely, the structure of (chloro)bis(2-nitrophenyl-*C,O*)(triphenylphosphine)rhodium(III), in which a σ -bonded C atom (β C atom of the 2-nitrophenyl ligand) lies opposite the PPh₃ group. In the latter derivative, the geometry of the axial fragment [Rh—P = 2.434 (2), Rh—C = 2.043 (6) Å, P—Rh—C = 172.5 (2)°] is very close to that found in the present complex in spite of the rather different substance type.

Recent NMR investigations of [Rh(dmgH)₂-(PPh₃)R] complexes (Steinborn & Ludwig, 1993) demonstrate that the *trans* influence of the organo group, R, as determined from ¹J(¹⁰³Rh—³¹P) coupling constants, is nearly the same for the sp³-hybridized ethyl group and the sp²-hybridized vinyl and phenyl groups. More structural data are needed to solve the problem of how the displacement of the Rh atom out of the N₄ plane and the π -accepting capability of the PPh₃ ligand affect the *trans* influence of R, measured by NMR spectroscopy.

Experimental

Crystal data

[Rh(C₄H₇N₂O₂)₂(C₂H₅)(C₁₈H₁₅P)]

M_r = 624.5

Monoclinic

*P*2₁

a = 8.707 (4) Å

b = 15.490 (10) Å

c = 10.476 (5) Å

β = 105.74 (6)°

Mo K α radiation

λ = 0.71069 Å

Cell parameters from 15

reflections

θ = 8–16°

μ = 0.71 mm⁻¹

T = 293 K

Prism

0.40 × 0.20 × 0.15 mm

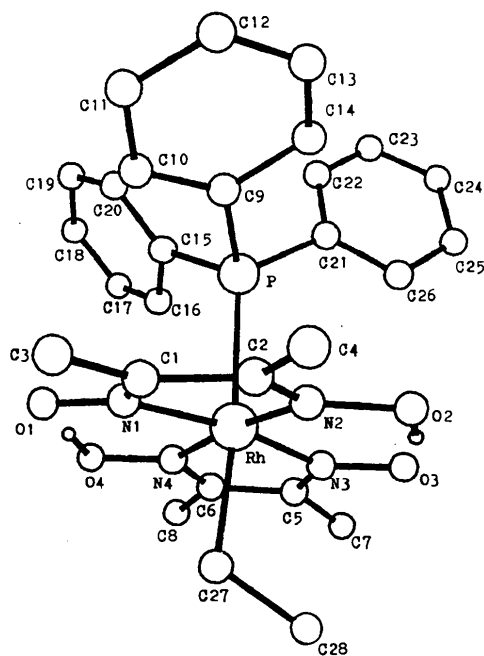


Fig. 1. Perspective drawing of the title compound and atom-numbering scheme. Only polar H atoms (involved in intramolecular hydrogen bonds) are shown for clarity.

$V = 1360 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.525 \text{ Mg m}^{-3}$
 $D_m = 1.53 \text{ Mg m}^{-3}$
 D_m measured by flotation in
 CHBr₃-cyclohexane

Brownish yellow
 Crystal source: slow
 evaporation of acetone
 solution at room
 temperature

| | | | | |
|-------|--------------|------------|--------------|-----------|
| C(23) | -0.2610 (11) | 0.1883 (7) | -0.2514 (9) | 4.92 (37) |
| C(24) | -0.3208 (11) | 0.1183 (5) | -0.2102 (8) | 2.87 (25) |
| C(25) | -0.2701 (11) | 0.0963 (6) | -0.0749 (10) | 4.33 (36) |
| C(26) | -0.1622 (10) | 0.1472 (5) | 0.0187 (10) | 3.45 (33) |
| C(27) | 0.3078 (10) | 0.2259 (5) | 0.5005 (8) | 3.35 (30) |
| C(28) | 0.2477 (15) | 0.1549 (7) | 0.5767 (10) | 7.42 (47) |

Data collection

Syntex P2₁ diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 empirical (ψ scan)
 $T_{\min} = 0.71$, $T_{\max} = 1.0$
 3442 measured reflections
 3256 independent reflections
 1841 observed reflections
 $[I \geq 2\sigma(I)]$

$R_{\text{int}} = 0.039$

$\theta_{\text{max}} = 27.5^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 20$

$l = -13 \rightarrow 12$

2 standard reflections

frequency: 90 min

intensity variation: < 4%

Refinement

Refinement on F
 $R = 0.052$
 $wR = 0.050$
 $S = 1.42$
 1841 reflections
 343 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F_o) + 0.0009(F_o)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.06$

$\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------------|-----------|-------------------|-----------|
| Rh(1)—P(1) | 2.461 (2) | P(1)—C(15) | 1.815 (8) |
| Rh(1)—C(27) | 2.064 (7) | P(1)—C(21) | 1.815 (8) |
| Rh(1)—N(1) | 1.993 (6) | N(1)—O(1) | 1.286 (8) |
| Rh(1)—N(2) | 1.970 (6) | N(2)—O(2) | 1.366 (8) |
| Rh(1)—N(3) | 1.954 (6) | N(3)—O(3) | 1.306 (8) |
| Rh(1)—N(4) | 1.903 (6) | N(4)—O(4) | 1.364 (7) |
| P(1)—C(9) | 1.811 (8) | | |
| N(1)—Rh(1)—N(2) | 79.0 (2) | Rh(1)—C(27)—C(28) | 116.9 (6) |
| N(3)—Rh(1)—N(4) | 78.0 (2) | Rh(1)—P(1)—C(9) | 116.8 (3) |
| P(1)—Rh(1)—N(1) | 90.1 (2) | Rh(1)—P(1)—C(15) | 108.8 (3) |
| P(1)—Rh(1)—N(2) | 92.4 (2) | Rh(1)—P(1)—C(21) | 122.2 (3) |
| P(1)—Rh(1)—N(3) | 97.8 (2) | C(9)—P(1)—C(15) | 105.1 (4) |
| P(1)—Rh(1)—N(4) | 95.0 (2) | C(9)—P(1)—C(21) | 99.2 (4) |
| P(1)—Rh(1)—C(27) | 173.6 (2) | C(15)—P(1)—C(21) | 102.7 (5) |

All calculations were performed with the *NRC* program system (Ahmed & Singh, 1973).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and interatomic distances have been deposited with the IUCr (Reference: KA1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

| | $B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$ | | | |
|-------|---|-------------|-------------|-----------------|
| | x | y | z | B_{eq} |
| Rh(1) | 0.1753 (1) | 0.2486 (1) | 0.3080 (1) | 2.44 (1) |
| P(1) | 0.0265 (3) | 0.2926 (1) | 0.0826 (2) | 2.04 (6) |
| O(1) | 0.3388 (7) | 0.4107 (4) | 0.3399 (6) | 3.69 (20) |
| O(2) | -0.1152 (6) | 0.2110 (4) | 0.3836 (6) | 4.02 (20) |
| O(3) | 0.0384 (6) | 0.0819 (6) | 0.3020 (6) | 2.88 (18) |
| O(4) | 0.4802 (7) | 0.2845 (3) | 0.2617 (6) | 3.71 (20) |
| N(1) | 0.2161 (8) | 0.3722 (4) | 0.3591 (5) | 2.34 (20) |
| N(2) | -0.0068 (7) | 0.2741 (5) | 0.3797 (6) | 3.52 (27) |
| N(3) | 0.1594 (7) | 0.1238 (4) | 0.2808 (5) | 1.49 (20) |
| N(4) | 0.3677 (6) | 0.2235 (3) | 0.2624 (6) | 1.65 (20) |
| C(1) | 0.1151 (11) | 0.4062 (5) | 0.4090 (8) | 3.53 (29) |
| C(2) | -0.0168 (14) | 0.3526 (6) | 0.4202 (8) | 5.29 (39) |
| C(3) | 0.1267 (12) | 0.4932 (6) | 0.4573 (10) | 4.61 (36) |
| C(4) | -0.1449 (14) | 0.3816 (8) | 0.4768 (11) | 6.61 (45) |
| C(5) | 0.2773 (10) | 0.0868 (5) | 0.2545 (8) | 2.85 (28) |
| C(6) | 0.4007 (9) | 0.1462 (6) | 0.2411 (8) | 2.67 (27) |
| C(7) | 0.2952 (12) | -0.0085 (7) | 0.2482 (10) | 5.27 (40) |
| C(8) | 0.5519 (10) | 0.1157 (6) | 0.2131 (10) | 4.29 (34) |
| C(9) | 0.1433 (9) | 0.3261 (6) | -0.0278 (8) | 2.77 (26) |
| C(10) | 0.2621 (9) | 0.2712 (4) | -0.0368 (8) | 2.48 (27) |
| C(11) | 0.3482 (10) | 0.2859 (5) | -0.1256 (9) | 3.25 (24) |
| C(12) | 0.3315 (11) | 0.3624 (7) | -0.1878 (9) | 4.28 (36) |
| C(13) | 0.2160 (10) | 0.4195 (7) | -0.1824 (9) | 4.81 (37) |
| C(14) | 0.1247 (11) | 0.4018 (6) | -0.0946 (8) | 3.40 (32) |
| C(15) | -0.0968 (10) | 0.3852 (5) | 0.0941 (7) | 2.42 (26) |
| C(16) | -0.0344 (9) | 0.4649 (5) | 0.1239 (7) | 1.85 (25) |
| C(17) | -0.1395 (12) | 0.5314 (6) | 0.1359 (9) | 4.32 (37) |
| C(18) | -0.2990 (10) | 0.5120 (5) | 0.1228 (9) | 2.93 (29) |
| C(19) | -0.3557 (9) | 0.4339 (5) | 0.0953 (8) | 2.27 (25) |
| C(20) | -0.2649 (10) | 0.3694 (5) | 0.0770 (9) | 3.45 (31) |
| C(21) | -0.1130 (8) | 0.2210 (4) | -0.0287 (8) | 2.30 (26) |
| C(22) | -0.1607 (9) | 0.2352 (6) | -0.1638 (7) | 3.55 (28) |

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