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

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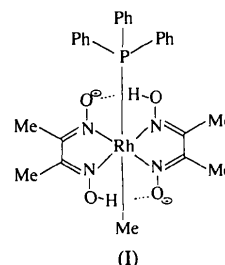
### Abstract

The structure of  $[\text{Rh}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{CH}_3)(\text{C}_{18}\text{H}_{15}\text{P})]$  consists of discrete complexes in which the Rh atom displays distorted octahedral coordination. The two dimethylglyoxime ligands lie in the equatorial plane, with the methyl and triphenylphosphine groups occupying axial positions. The Rh atom is displaced by 0.1293 (7) Å from the mean plane through the four oxime N-donor atoms towards the P atom. The average Rh—N distance is 1.976 (9) Å, while the axial Rh—P and Rh—C distances are 2.4543 (11) and 2.119 (4) Å, respectively. Comparison of the results with those obtained previously for other compounds of this type indicates that the *trans* influence of group *R* in the axial fragment  $\text{Ph}_3\text{P—Rh—R}$  is determined by its  $\sigma$ -donor power.

### Comment

This work is a continuation of a project aimed at understanding the mutual influence of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of  $\sigma$ -organo ligands is of particular interest. We have demonstrated (Steinborn & Ludwig, 1993a; Ludwig & Steinborn, 1995) that in complexes of the type  $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{R}]$  (dmgH is the monoanion of dimethylglyoxime and *R* is an organo group), the *trans* influence of the *R* group, as measured by  $^1J(^{103}\text{Rh—}^{31}\text{P})$  coupling constants, is in the unusual order  $^t\text{Bu} \gg \text{cyclohexyl} > ^i\text{Pr} > \text{CPr}=\text{CH}_2 > \text{CH}_2\text{OMe} > \text{CH}=\text{CHPr} \approx ^t\text{Bu} \approx ^n\text{Pr} \approx \text{Ph} \approx \text{Et} \approx ^n\text{Bu} \approx \text{CH}=\text{CHPh} > \text{CH}=\text{CH}_2 > \text{CH}_2\text{SiMe} \approx \text{Me} > \text{CH}_2\text{Cl} \approx \text{CH}_2\text{SPh} \approx \text{Bz} \approx \text{CH}_2\text{Br} \gg \text{C}\equiv\text{CPh}$ . In order to investigate the dependence of the *trans* influence, measured by NMR spectroscopy, on the structure of complexes, we decided to systematically change the type of hybridization of the donor orbital (*R* = Et,  $\text{CH}=\text{CH}_2$ ,  $\text{C}\equiv\text{CPh}$ ), as well as changing the branching within

the alkyl ligands (*R* = Me, Et,  $^i\text{Pr}$ ,  $^t\text{Bu}$ ) ( $\text{C}\equiv\text{CPh}$ : Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1995;  $\text{CH}=\text{CH}_2$ : Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1994; Et: Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1994;  $^t\text{Bu}$ : Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1995). Here we report the structure of the methyl complex (I). The X-ray structure analysis of the isopropyl complex is in progress.



The  $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{Me}]$  complex crystallizes as discrete molecules in which the Rh atom has a distorted octahedral environment, with four oxime N-donor atoms in equatorial positions. The two dimethylglyoximate ligands are stabilized by two intramolecular hydrogen bonds acting between atoms O1 and O4 [O...O 2.699 (4) Å], and between O2 and O3 [O...O 2.608 (5) Å]. On the basis of the refined H-atom positions, both hydrogen bridges in the  $\text{Rh}(\text{dmgH})_2$  unit are unsymmetrical [O1—H1 0.81 (5), O4...H1 1.90 (5), O3—H3 0.82 (5), O2...H3 1.79 (5) Å].

The four Rh—N bond distances range from 1.964 (3) to 1.986 (3) Å, with a mean value of 1.976 (9) Å. This value is longer than those in both the vinyl and *tert*-butyl derivatives [1.957 (2) and 1.955 (3) Å, respectively] (Dunaj-Jurčo *et al.*, 1994; Kettmann *et al.*, 1995), but is comparable with that in the phenylacetylide complex [1.971 (2) Å] (Dunaj-Jurčo *et al.*, 1995). As found in other derivatives of the series, the two  $\text{dmgH}^-$  ligands are tilted away from the triphenylphosphine ligand so that their normal vectors make an angle of 12.69 (8)° with one another. As a result, though the four oxime N donors are coplanar to within  $\pm 0.005$  Å, the Rh atom is displaced by 0.1293 (7) Å from their mean plane towards the P atom. Also, the  $\text{dmgH}^-$  ligands themselves are not strictly planar; the lack of planarity originates from twisting of the two halves of the ligand about the central C—C bond, the twist angles being 3.7 (2) and 6.7 (2)°, respectively, for ligands N1, N2, O1, O2, C1—C4 and N3, N4, O3, O4, C5—C8.

As mentioned above, the *trans* influence of the axial ligands, *i.e.* the  $\sigma$ -bonded methyl group and  $\text{PPh}_3$  moiety, is of special interest here. The Rh—P and Rh—C bond lengths are 2.4543 (11) and 2.119 (4) Å, respectively, and the P—Rh—C angle is 176.97 (13)°. Comparison with other  $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{R}]$  complexes shows that the Rh—C bond length value is somewhat

longer than the value found for the ethyl derivative [2.064 (7) Å], but is considerably shorter than that found for the *tert*-butyl derivative [2.216 (3) Å], which is in line with the steric demand of the *tert*-butyl ligand. The Rh—C distance found in the similar compound [Rh(dmgh)<sub>2</sub>(pyridine)CH<sub>3</sub>] is shorter [2.063 (5) Å] than the Rh—C distance found in the title compound, which is in agreement with the smaller *trans* influence of the pyridine ligand in comparison with the PPh<sub>3</sub> group (Bresciani Pahor, Dreos-Garlatti, Geremia, Randaccio, Tazher & Zangrando, 1990). The Rh—P bond distance is determined by the electronic influence of the R group in the axial direction. This is demonstrated by comparison of the Rh—P bond length in the present complex [2.4543 (11) Å] with those in the *tert*-butyl and ethyl analogues, where this length decreases from 2.492 (1) Å for R = *tert*-butyl to 2.461 (2) Å for R = ethyl, obviously due to the decreased  $\sigma$ -donating power of the methyl group relative to the *tert*-butyl and the ethyl groups. But this distance is still longer than the distance for R = vinyl [2.447 (1) Å] and R = phenyl-acetylide [2.409 (1) Å] with smaller  $\sigma$ -donating power.

$M_r = 610.45$   
 Monoclinic  
 $P2_1$   
 $a = 8.849 (2) \text{ \AA}$   
 $b = 15.530 (3) \text{ \AA}$   
 $c = 10.422 (3) \text{ \AA}$   
 $\beta = 108.04 (2)^\circ$   
 $V = 1361.8 (6) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.489 \text{ Mg m}^{-3}$   
 $D_m = 1.47 (1) \text{ Mg m}^{-3}$

Cell parameters from 25 reflections  
 $\theta = 5.82\text{--}9.665^\circ$   
 $\mu = 0.725 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prism  
 $0.6 \times 0.55 \times 0.4 \text{ mm}$   
 Brownish yellow

#### Data collection

Syntex P2<sub>1</sub> diffractometer  
 $\theta$ – $2\theta$  scans  
 Absorption correction:  
 $\psi$  scans of 10 reflections  
 (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.895$ ,  $T_{\max} = 0.991$   
 3450 measured reflections  
 3264 independent reflections

2990 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.0235$   
 $\theta_{\max} = 27.58^\circ$   
 $h = 0 \rightarrow 11$   
 $k = 0 \rightarrow 20$   
 $l = -13 \rightarrow 12$   
 2 standard reflections monitored every 98 reflections  
 intensity decay: none

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.0202$   
 $wR(F^2) = 0.1229$   
 $S = 0.981$   
 3257 reflections  
 345 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0193P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.028$

$\Delta\rho_{\max} = 0.337 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.518 \text{ e \AA}^{-3}$   
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4  
 Absolute configuration:  $\chi = 0.00 (2)$  (Flack, 1983)

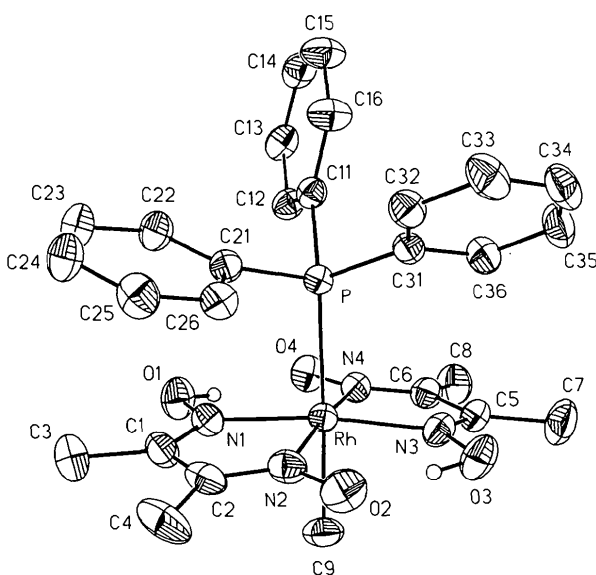


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound (40% probability level) showing the atom-numbering scheme.

#### Experimental

Crystals of bis(dimethylglyoximate-*N,N'*)(methyl)(triphenylphosphine)rhodium(III) were prepared according to Steinborn & Ludwig (1993*b*). The crystal density  $D_m$  was measured by flotation in water–KI solution.

#### Crystal data

[Rh(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>)-  
(C<sub>18</sub>H<sub>15</sub>P)]

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$

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

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

|     | <i>x</i>    | <i>y</i>    | <i>z</i>    | $U_{eq}$    |
|-----|-------------|-------------|-------------|-------------|
| Rh  | 0.68100 (2) | 0.74733 (2) | 0.81527 (2) | 0.03210 (6) |
| P   | 0.52643 (9) | 0.79236 (5) | 0.58652 (7) | 0.0300 (2)  |
| N1  | 0.5013 (3)  | 0.7703 (2)  | 0.8843 (3)  | 0.0424 (8)  |
| N2  | 0.7162 (4)  | 0.8701 (2)  | 0.8686 (3)  | 0.0439 (7)  |
| N3  | 0.8770 (3)  | 0.7231 (2)  | 0.7710 (3)  | 0.0424 (7)  |
| N4  | 0.6646 (3)  | 0.6208 (2)  | 0.7868 (3)  | 0.0366 (6)  |
| O1  | 0.3992 (4)  | 0.7063 (2)  | 0.8936 (3)  | 0.0581 (7)  |
| O2  | 0.8384 (3)  | 0.9119 (2)  | 0.8527 (3)  | 0.0582 (7)  |
| O3  | 0.9811 (3)  | 0.7872 (2)  | 0.7685 (3)  | 0.0589 (7)  |
| O4  | 0.5484 (3)  | 0.5768 (2)  | 0.8092 (3)  | 0.0478 (6)  |
| C1  | 0.4910 (5)  | 0.8463 (3)  | 0.9304 (3)  | 0.0486 (9)  |
| C2  | 0.6154 (5)  | 0.9051 (2)  | 0.9213 (3)  | 0.0478 (8)  |
| C3  | 0.3629 (6)  | 0.8718 (4)  | 0.9889 (5)  | 0.0757 (14) |
| C4  | 0.6319 (7)  | 0.9957 (3)  | 0.9688 (4)  | 0.0711 (13) |
| C5  | 0.9055 (4)  | 0.6448 (3)  | 0.7497 (4)  | 0.0447 (8)  |
| C6  | 0.7844 (4)  | 0.5845 (2)  | 0.7608 (3)  | 0.0414 (7)  |
| C7  | 1.0516 (5)  | 0.6174 (3)  | 0.7167 (5)  | 0.0683 (12) |
| C8  | 0.8011 (5)  | 0.4889 (3)  | 0.7540 (4)  | 0.0581 (10) |
| C9  | 0.8140 (5)  | 0.7152 (3)  | 1.0161 (3)  | 0.0526 (9)  |
| C11 | 0.3857 (4)  | 0.7206 (2)  | 0.4694 (3)  | 0.0353 (7)  |
| C12 | 0.3277 (4)  | 0.6482 (2)  | 0.5147 (3)  | 0.0411 (7)  |
| C13 | 0.2167 (4)  | 0.5965 (2)  | 0.4239 (4)  | 0.0456 (8)  |
| C14 | 0.1681 (4)  | 0.6156 (3)  | 0.2889 (4)  | 0.0521 (9)  |
| C15 | 0.2256 (5)  | 0.6868 (3)  | 0.2434 (4)  | 0.0600 (11) |
| C16 | 0.3339 (4)  | 0.7391 (4)  | 0.3325 (3)  | 0.0524 (9)  |
| C21 | 0.4014 (4)  | 0.8833 (2)  | 0.5967 (3)  | 0.0337 (6)  |

|     |            |            |            |             |
|-----|------------|------------|------------|-------------|
| C22 | 0.2431 (4) | 0.8698 (2) | 0.5873 (3) | 0.0438 (8)  |
| C23 | 0.1509 (5) | 0.9368 (3) | 0.6069 (4) | 0.0542 (9)  |
| C24 | 0.2132 (5) | 1.0174 (3) | 0.6348 (4) | 0.0591 (10) |
| C25 | 0.3724 (5) | 1.0323 (2) | 0.6461 (4) | 0.0508 (9)  |
| C26 | 0.4651 (4) | 0.9647 (2) | 0.6299 (3) | 0.0411 (7)  |
| C31 | 0.6456 (4) | 0.8261 (2) | 0.4799 (3) | 0.0334 (6)  |
| C32 | 0.6264 (4) | 0.9031 (2) | 0.4102 (3) | 0.0414 (7)  |
| C33 | 0.7140 (5) | 0.9194 (3) | 0.3234 (4) | 0.0544 (10) |
| C34 | 0.8190 (5) | 0.8594 (3) | 0.3064 (4) | 0.0561 (10) |
| C35 | 0.8378 (5) | 0.7830 (3) | 0.3728 (4) | 0.0540 (9)  |
| C36 | 0.7512 (4) | 0.7650 (2) | 0.4605 (3) | 0.0452 (9)  |

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

|          |             |           |             |
|----------|-------------|-----------|-------------|
| Rh—N3    | 1.964 (3)   | P—C31     | 1.830 (3)   |
| Rh—N1    | 1.970 (3)   | P—C11     | 1.828 (3)   |
| Rh—N2    | 1.984 (3)   | N1—O1     | 1.366 (4)   |
| Rh—N4    | 1.986 (3)   | N2—O2     | 1.315 (4)   |
| Rh—C9    | 2.119 (4)   | N3—O3     | 1.362 (4)   |
| Rh—P     | 2.4543 (11) | N4—O4     | 1.314 (4)   |
| P—C21    | 1.818 (4)   |           |             |
| N3—Rh—N1 | 172.59 (13) | N1—Rh—P   | 91.89 (9)   |
| N3—Rh—N2 | 100.14 (13) | N2—Rh—P   | 89.44 (10)  |
| N1—Rh—N2 | 78.36 (13)  | N4—Rh—P   | 98.27 (9)   |
| N3—Rh—N4 | 78.74 (12)  | C9—Rh—P   | 176.97 (13) |
| N1—Rh—N4 | 101.76 (12) | C21—P—C31 | 106.8 (2)   |
| N2—Rh—N4 | 172.3 (2)   | C21—P—C11 | 102.2 (2)   |
| N3—Rh—C9 | 85.8 (2)    | C31—P—C11 | 99.84 (15)  |
| N1—Rh—C9 | 86.9 (2)    | C21—P—Rh  | 109.32 (11) |
| N2—Rh—C9 | 87.6 (2)    | C31—P—Rh  | 114.76 (11) |
| N4—Rh—C9 | 84.7 (2)    | C11—P—Rh  | 122.30 (11) |
| N3—Rh—P  | 95.35 (9)   |           |             |

Data reduction was performed using *XP21* (Pavelčík, 1993). Intensities were corrected for Lorentz and polarization factors using *XP21*. The structure was solved by heavy-atom methods with *XFPS* (Pavelčík, Rizzoli & Andreotti, 1990) and subsequent Fourier syntheses using *SHELXL93* (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. Both hydroxyl H atoms were located from difference Fourier maps and refined with isotropic displacement factors fixed at  $0.06 \text{ \AA}^2$ . The H atoms attached to carbon were apparent in difference maps and were included as riding atoms in calculated positions with isotropic displacement factors. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL93*. *ORTEP* (Johnson, 1965) was employed to produce the figure. *SHELXL93* was used to prepare the material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2,4,6-Tris(2-pyridyl)-1,3,5-triazine-Lithium Tetraphenylborate Bis(ethanol) Solvate

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## Abstract

The first crystal structure determination of an alkali metal complex of 2,4,6-tris(2-pyridyl)-1,3,5-triazine reveals a five-coordinate Li cation with three contacts to the N atoms and two more to the O atoms of the ethanol solvent, *i.e.* bis(ethanol-*O*)[2,4,6-tris(2-pyridyl)-*N*<sup>2</sup>,*N*<sup>6</sup>-1,3,5-triazine-*N*<sup>1</sup>]lithium tetraphenylborate, [Li-(C<sub>18</sub>H<sub>12</sub>N<sub>6</sub>)(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>][(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B]. The tetraphenylborate anion is not in contact with the cation.

## Comment

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (TPTZ) has been used for the spectrophotometric analytical determination of iron(II), cobalt(II) and ruthenium(II) (Janmohamed & Ayres, 1972). However, very few structures of its transition metal complexes have been determined so far. TPTZ acts as mono-, bi- or tridentate ligand, in