

The Preparation and Crystal and Molecular Structure of Di- μ -acetatobis(dimethylglyoximate)bis(triphenylphosphine)dirhodium(II)

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Summary The preparation of $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2$ and the determination of its structure by single crystal X-ray diffraction are described; the Rh-Rh bond length is 2.618(5) Å.

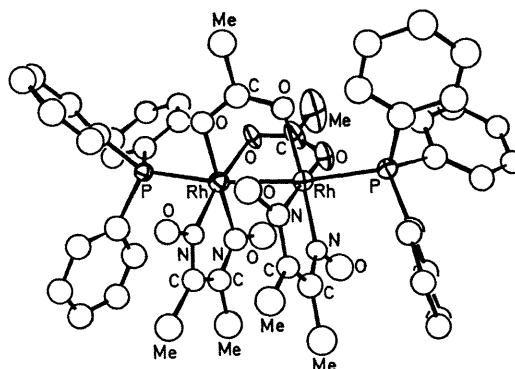
In the course of attempting to prepare rhodium(II) compounds of the type $\text{Rh}_2(\text{dmg})_2\text{L}_2$ (where dmg^- is the mono-anion of dimethylglyoxime and L is a neutral ligand such as a phosphine) by reaction of the corresponding $\text{Rh}_2(\text{OAc})_4\text{L}_2$ compounds with dimethylglyoxime, we succeeded in isolating the intermediate mixed-ligand complex, $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2$ (1). In view of the considerable recent interest in the structural features, notably the Rh-Rh bond lengths, of such binuclear rhodium(II) compounds,¹ we communicate here the results of a single-crystal X-ray structure determination of (1).

Warming 10 ml of a methanol solution of $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ (0.1 g) and dimethylglyoxime (0.06 g) under nitrogen for 40 min resulted in the formation of a black precipitate of $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{H}_2\text{O})_2$ which was converted into (1) by dissolving in 25 ml of methanol containing 0.12 g PPh_3 . Slow evaporation of the resulting solution yielded deep red crystals of $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2 \cdot \text{H}_2\text{O}$, one of which was subjected to a single-crystal X-ray structure determination.†

The crystal belonged to the space group $P2_1/b$ with lattice constants $a = 15.21(2)$, $b = 28.88(3)$, $c = 13.79(2)$ Å, $\gamma = 125.55(3)^\circ$. The unit cell contained four asymmetric units of formula $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2 \cdot \text{H}_2\text{O}$. X-Ray data were collected on a Picker FACS I diffractometer with a graphite monochromator. Approximately 3000 independent reflections with intensities $> 1\sigma$, collected out to $2\theta = 40^\circ$ (Mo- K_α), were employed. After the measured intensities were corrected for Lorentz and polarization effects, the structure was solved by Patterson and Fourier

techniques. Full-matrix least-squares refinement, treating the phenyl groups as rigid bodies and varying the temperature factors of the Rh and P atoms, as well as the atoms of one of the acetate ligands, anisotropically, led to a final value of $R_w = 0.064$.

The molecular structure of $\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2$ is depicted in the Figure.‡ Not unexpectedly, the molecule



FIGURE

possesses structural features in common with those of the previously determined structures $\text{Rh}_2(\text{dmg})_4(\text{PPh}_3)_2$ (2) and of $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ (3).^{1a,b} The bridging of the two Rh atoms by the OAc^- ligands and the co-ordination of each of the dmg^- ligands to one of the Rh atoms to form a normal five-atom chelate ring resemble the corresponding roles of the same ligands in (2) and (3), respectively. The Rh-Rh bond length of 2.618(5) Å is intermediate between those of (2) and (3) [2.934(2) and 2.386(3) Å, respectively].^{1a,b} Each OAc and dmg unit is essentially planar (to within

† The absorption spectrum of (1) in benzene solution features an intense band with a maximum at 412 nm ($\epsilon \sim 3.7 \times 10^4$). The ^1H n.m.r. spectrum in CDCl_3 exhibited the following features. PPh_3 : τ 2.66 (multiplet); OAc : τ 8.10 (singlet); dmg : $\tau(\text{CH}_3)$ 8.57 (singlet), $\tau(\text{OH})$ 4.80 (broad). The PPh_3 and dmg n.m.r. spectra are similar to those previously reported for $\text{Rh}_2(\text{dmg})_4(\text{PPh}_3)_2$.²

‡ It is likely that this structure is also characteristic of another known class of rhodium(II) compounds, namely $\text{Rh}_2(\text{OAc})_2(\beta\text{-diketonato})_2\text{L}_2$ (where L = water or pyridine).³

0.1 Å). One dmg ligand is rotated about the Rh–Rh axis by 20° from an eclipsed configuration relative to the other dmg ligand [compared with approximately 90° in (2)]^{1a}. The angle between the planes defined by each of the dmg ligands is approximately 15° with the dmg ligands directed away from each other so that their separation is greatest in the region of the methyl groups. The Rh–Rh–P angles are 172–173°, the Rh–P bonds being bent slightly away from the dmg ligands. The metal–ligand–atom distances, Rh–O, 2.081(7)—2.094(6) Å; Rh–N, 1.952(4)—1.996(6) Å; Rh–P, 2.476(9)—2.494(9) Å, are close to the corresponding distances in (2) and (3).

The principal questions raised by earlier interpretations¹ of the structural features of (2) and (3) concern the degree to which various factors including (i) multiple Rh–Rh bonding in (3), (ii) repulsive interactions between the dmg

ligands on the two Rh atoms in (2), and (iii) constraints imposed by the bridging OAc ligands in (3), contribute to the striking differences in the Rh–Rh bond lengths in the two compounds. While the additional structural information on the present mixed-ligand complex (1) contributes little to an assessment of the role of multiple bonding in these compounds, certain features, notably the staggering of the two dmg ligands and the deflection of their planes away from each other, do seem to emphasize the importance of repulsive interactions of the dmg ligands with each other and with the adjacent PPh₃ ligands.

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