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Carbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)(triphenylphosphine-*P*)rhodium(I)

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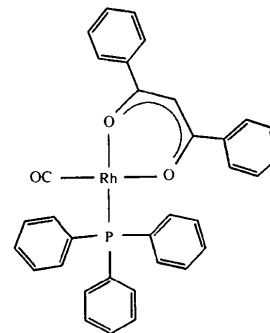
Abstract

One carbonyl group in dicarbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)rhodium(I) was substituted by triphenylphosphine to yield the title compound, [Rh(C₁₅H₁₁O₂)(C₁₈H₁₅P)(CO)], which has a square-planar

geometry about the Rh atom. There are two crystallographically independent molecules in the asymmetric unit.

Comment

The title compound, [Rh(DBM)(CO)(PPh₃)] (DBM is the 1,3-diphenyl-1,3-propanedionate anion), (I), was prepared and its crystal structure solved as part of our study of the relationship between the chemical oxidation of Rh^I to Rh^{III} in these compounds by iodo-methane, and the electrochemical oxidation by means of cyclic voltametry. To minimize the effect of different groups on the monocharged β-diketonate ligand, we have chosen the symmetrical β-diketone 1,3-diphenyl-1,3-propanedione.



(I)

The asymmetric unit consists of two crystallographically independent molecules of the title compound. These molecules form a very closely centrosymmetric pair, but this is not a crystallographic inversion center. One of the molecules of (I) is illustrated in Fig. 1. The square-planar coordination of the Rh atom is clear from the bond angles in Table 1. The partial overlapping of the chelate ring of one molecule with a phenyl ring of the other molecule can be attributed to π–π interactions by considering the intermolecular distances in Table 2.

The Rh1 and Rh2 atoms lie 0.012 and –0.015 Å from their respective coordination planes. The distances Rh1–O2 [2.081 (9) Å] and Rh2–O5 [2.072 (7) Å] when compared with Rh1–O1 [2.038 (10) Å] and Rh2–O4 [2.040 (7) Å] illustrate clearly the larger *trans* influence of triphenylphosphine compared with a carbonyl group. The same tendency with similar bond lengths was found in structures of the following compounds which also contain symmetrical β-diketones: [Rh(acac)(CO)(PPh₃)] (acac is acetylacetonate) (Leipoldt, Basson, Bok & Gerber, 1978) and [Rh(TROP)(CO)(PPh₃)] (TROP is tropolonate) (Leipoldt, Bok, Basson & Meyer, 1980). In a previous paper (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1991), the authors claimed that the Rh–P distance could be used to estimate the relative *trans* influence of different donor atoms in the chelate rings. In this case,

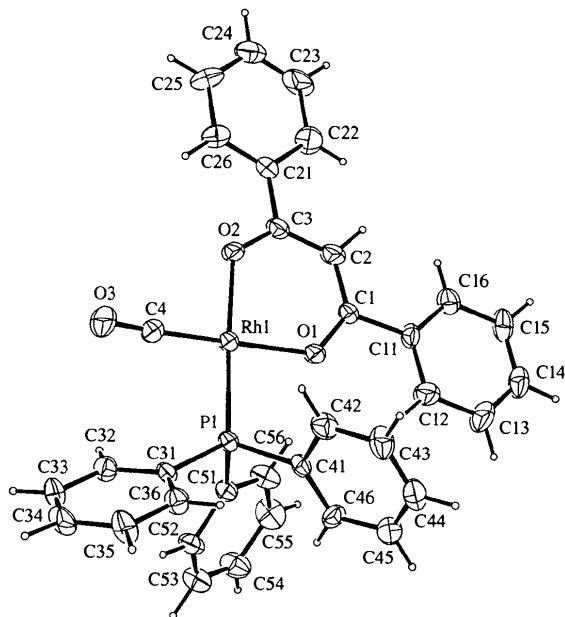


Fig. 1. The structure of one of the two independent molecules with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

however, the differences between Rh1—P1 [2.237 (7) Å] and Rh2—P2 [2.245 (3) Å] may be ascribed to a packing effect.

Experimental

The Rh^I β-diketonato complex [Rh(DBM)(CO)₂] was prepared from RhCl₃·3H₂O, *N,N*-dimethylformamide and 1,3-diphenyl-1,3-propanedione by previously described methods (Leipoldt & Grobler, 1982; Varshavskii & Cherkasova, 1967). The title compound was prepared by dissolving [Rh(DBM)(CO)₂] in the minimum quantity of acetone at ca 313 K and an equivalent amount of triphenylphosphine was added. Upon cooling, the title compound precipitated and was recrystallized from acetone.

Crystal data

[Rh(C₁₅H₁₁O₂)(C₁₈H₁₅P)(CO)]

M_r = 616.46

Monoclinic

Cc

a = 30.404 (4) Å

b = 10.276 (1) Å

c = 18.742 (3) Å

β = 108.92 (1)°

V = 5539 (1) Å³

Z = 8

D_x = 1.478 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 26

reflections

θ = 15.5–17.5°

μ = 0.695 mm⁻¹

T = 163 K

Rhombic

0.78 × 0.45 × 0.20 mm

Yellow

Data collection

Mac Science MXC18
diffractometer

ω/2θ scans

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)

T_{min} = 0.781, *T_{max}* = 0.870

7056 measured reflections

6231 independent reflections

5972 reflections with

I > 2σ(*I*)

R_{int} = 0.015

θ_{max} = 26.43°

h = -39 → 37

k = -13 → 0

l = 0 → 24

3 standard reflections

every 150 reflections

intensity decay: 9.5%

Refinement

Refinement on *F*²

R = 0.035

wR = 0.043

S = 2.564

5972 reflections

701 parameters

H atoms riding with *U*(H) =

1.3*U*_{eq}(C)

w = 1/[σ²(*F*) + 0.001*F*²]

(Δ/σ)_{max} = 0.023

Δρ_{max} = 0.55 e Å⁻³

Δρ_{min} = -0.84 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Rh1—P1	2.237 (7)	Rh2—O4	2.040 (7)
Rh1—O1	2.038 (10)	Rh2—O5	2.072 (7)
Rh1—O2	2.081 (9)	Rh2—C8	1.794 (10)
Rh1—C4	1.812 (13)	O3—C4	1.154 (13)
Rh2—P2	2.245 (3)	O6—C8	1.161 (12)
P1—Rh1—O1	87.7 (3)	P2—Rh2—O4	87.8 (2)
P1—Rh1—O2	175.2 (4)	P2—Rh2—O5	174.0 (2)
P1—Rh1—C4	91.1 (5)	P2—Rh2—C8	91.8 (3)
O1—Rh1—O2	88.5 (5)	O4—Rh2—O5	89.1 (3)
O1—Rh1—C4	175.3 (6)	O4—Rh2—C8	172.6 (4)
O2—Rh1—C4	92.9 (5)	O5—Rh2—C8	91.9 (4)

Table 2. Contact distances (Å)

C1···C66	3.39 (2)	C5···C16	3.39 (1)
C2···C65	3.57 (2)	C6···C15	3.56 (1)
C2···C66	3.56 (2)	C6···C16	3.57 (1)
C3···C64	3.55 (2)	C7···C14	3.44 (1)
C3···C65	3.54 (1)	C7···C15	3.54 (1)

The systematic absences (*hkl*, *h* + *k* = 2*n* + 1; *h0l*, *l* = 2*n* + 1) of (I) agree with both *C2/c* and *Cc*. The absence of Patterson vectors related to twofold rotation and screw axes, and the successful structural solution and refinement showed that the correct space group of (I) is *Cc*. The structure was solved by direct methods.

Data collection: *MXC Diffractometer Control Software* (MAC Science, 1989). Cell refinement: *MXC Diffractometer Control Software*. Data reduction: *CRYSTAN* (Edwards, Gilmore, Mackay & Stewart, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTAN*. Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN* and *BOND* (Yoshioka & Hirotsu, 1980).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1166). Services for accessing these data are described at the back of the journal.

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***trans*-[Bis-2,6-(2-benzimidazolyl- κ N²)-pyridine- κ N]nitrobis(triphenylphosphine-*P*)ruthenium(II) Perchlorate Ethanol Solvate**

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Abstract

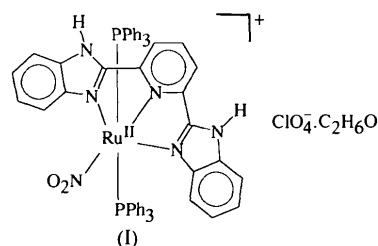
In the title compound, $[\text{Ru}(\text{NO}_2)(\text{C}_{19}\text{H}_{13}\text{N}_5)(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{ClO}_4\cdot\text{C}_2\text{H}_6\text{O}$, the two phosphine ligands are in *trans* positions. The Ru atom and imidazolylpyridine moiety are almost coplanar, with the fused ring of the imidazolyl groups somewhat bent from the plane due to the steric hindrance of the phosphine phenyl groups. The nitro ligand is coordinated so that the NO₂ group is rotated 40.5 (1)° from the imidazolylpyridine plane.

Comment

There has been considerable interest in transition metal complexes containing a nitro ligand because of their capability to transfer oxygen to a number of organic and inorganic substrates (Leising & Takeuchi, 1987). Nitro-ruthenium complexes involving terpyridine (terpy) or bis(pyrazolyl)pyridine have been studied with respect to their reactivity and the coordination environment

around the central metal atom (Bailey & Drago, 1987; Bessel, See, Jameson, Churchill & Takeuchi, 1993; Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990). The orientation of the NO₂ plane is dependent on the meridional ligands. For example, the angles between the NO₂ and meridional coordination planes are almost 90° in the Ru–nitro complex containing 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Bessel, See, Jameson, Churchill & Takeuchi, 1993) and almost 0° in the complex containing 2,6-bis(pyrazol-1-yl)pyridine (Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990).

We report here the orientation of the NO₂ ligand in the title compound, (I), in which it is bound to the metal atom. The Ru atom is also coordinated by a pyridine ring carrying two benzimidazolyl groups rather



than substituted imidazole rings. An *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 1. The structure reveals that a bis(2-benzimidazolyl)pyridine (BIP) moiety, an NO₂ and two triphenylphosphine (PPh₃) groups are bound to the Ru atom, with ClO₄[−] as anion. The two phosphine ligands are in an almost *trans* arrangement, with a P1–Ru–P2 angle of 178.79 (8)°.

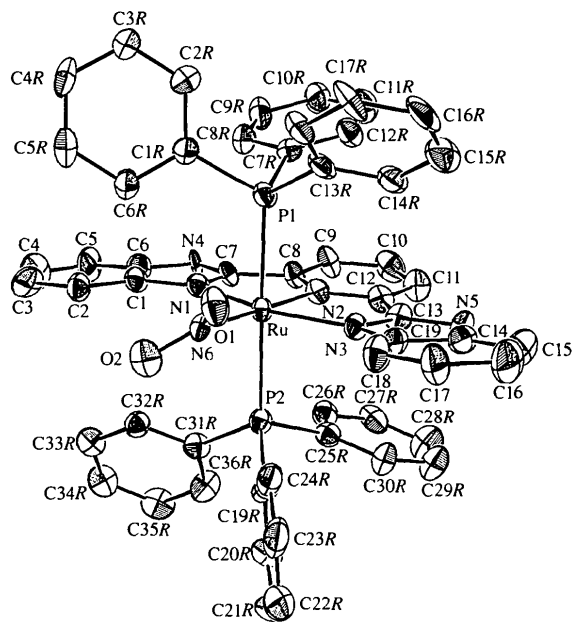


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 40% probability level.