

CYCLOMETALLATION REACTIONS IN COMPLEXES OF THE TYPE $\text{Rh}(\text{oq})(\text{CO})(\text{P}(\text{o}-\text{BrC}_6\text{F}_4)\text{Ph}_2)$

II *. THE MOLECULAR STRUCTURE OF $[\text{Rh}(\text{oq})\text{Br}(\text{P}(\text{o}-\text{C}_6\text{F}_4)\text{Ph}_2)(\text{H}_2\text{O})]_2$ (oq = 8-oxyquinolate)

FRANCISCO BARCELÓ, PASCUAL LAHUERTA, M. ANGELES UBEDA,

*Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Valencia,
 Dr. Moliner 50, Burjassot-Valencia (Spain)*

CONCEPCIÓN FOCES-FOCES, FELIX H. CANO and MARTÍN MARTINEZ-RIPOLL

Departamento de Rayos X, Instituto Rocasolano, C.S.I.C., Serrano 119, 28006 Madrid (Spain)

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Summary

The complex $[\text{uRh}(\text{oq})\text{Br}(\text{P}(\text{o}-\text{C}_6\text{F}_4)\text{Ph}_2)(\text{H}_2\text{O})]_2$ is obtained by refluxing a solution of $\text{Rh}(\text{oq})(\text{CO})(\text{P}(\text{o}-\text{BrC}_6\text{F}_4)\text{Ph}_2)$ (oq = 8-oxyquinolate) in toluene. The structure of this compound has been determined by X-ray diffraction and refined to $R = 0.061$ and $R_w = 0.065$ factors. The cell has monoclinic symmetry, space group $P2_1/n$; a 19.513(2), b 17.049(1), c 16.898(1) Å and β 99.69(1)°. The structure consists of two independent $\text{Rh}(\text{oq})\text{Br}(\text{P}(\text{o}-\text{C}_6\text{F}_4)\text{Ph}_2)(\text{H}_2\text{O})$ units linked by hydrogen bonds between the coordinated water molecules and oq ligands to form a distorted boat (six atom ring of junction between the two units). In each unit the metal atom has a distorted octahedral coordination, with a four-atom metallocyclic ring ($-\text{uRh}-\text{P}-\text{C}-\text{Cu}-$) with $\text{C}-\text{Rh}-\text{P}$ and $\text{Rh}-\text{P}-\text{C}$ angles 69.3(2) and 85.3(3)°, respectively, in one unit, and 70.0(2) and 81.1(2)° in the other. The water molecule is readily displaced by a variety of phosphorus donor ligands to form the complexes $\text{uRh}(\text{oq})\text{Br}(\text{P}(\text{o}-\text{C}_6\text{F}_4)\text{Ph}_2)\text{P}'$, $\text{P}' = \text{PPh}_3$, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{P}(\text{OCH}_3)_3$, in which the P atoms are in *trans*-dispositions.

Introduction

We previously reported [1] that cyclometallation occurs when $\text{Rh}(\text{oq})(\text{CO})(\text{PCBr})$, ($\text{PCBr} = 2\text{-bromo-3,4,5,6-tetrafluorophenyldiphenylphosphine}$), is refluxed in

* For Part I, see ref. 1.

toluene. $\overline{\text{Rh}(\text{oq})}_2(\text{PC})$. ($\text{PC} = \text{P}(o\text{-C}_6\text{F}_4)\text{Ph}_2$) was isolated and structurally characterized by single crystal X-ray methods, showing a distorted octahedral coordination around the rhodium with a four-atom metallocycle ring ($-\text{Rh}-\text{P}-\text{C}-\text{C}-$). Chromatography gave a second, ill-defined product. On the basis of the analytical data and molecular weight determination in benzene a dimeric composition was proposed. We report here further information about this cyclometallation reaction, and also describe the crystal structure and reactions of a new rhodium(III) compound $[\text{Rh}(\text{oq})\text{Br}(\text{PC})(\text{H}_2\text{O})]_2$ (I), which involves hydrogen bonds between the water molecules and the oxygen of the oq groups.

Results and discussion

Preparation of $[\text{Rh}(\text{oq})\text{Br}(\text{PC})(\text{H}_2\text{O})]_2$

When a toluene solution of $\text{Rh}(\text{oq})(\text{CO})(\text{PCBr})$ was refluxed for 2 h under argon no carbonyl bands remained in the infrared spectrum. When this solution was chromatographed on alumina, rather than the silica gel used in previous experiments [1], a complex pattern of bands was obtained and a new compound, I, was isolated in addition to the previously described $\text{Rh}(\text{oq})_2(\text{PC})$ [1].

The molecular structure of compound I was determined by single crystal X-ray crystallography. The structure consists of two independent $\text{Rh}(\text{oq})\text{Br}(\text{PC})(\text{H}_2\text{O})$ units linked via hydrogen bonds between the oq ligands and the coordinating water molecules. The metal atoms have an octahedral coordination composed of the four-membered ring of the metallated phosphine, a five-membered ring of the

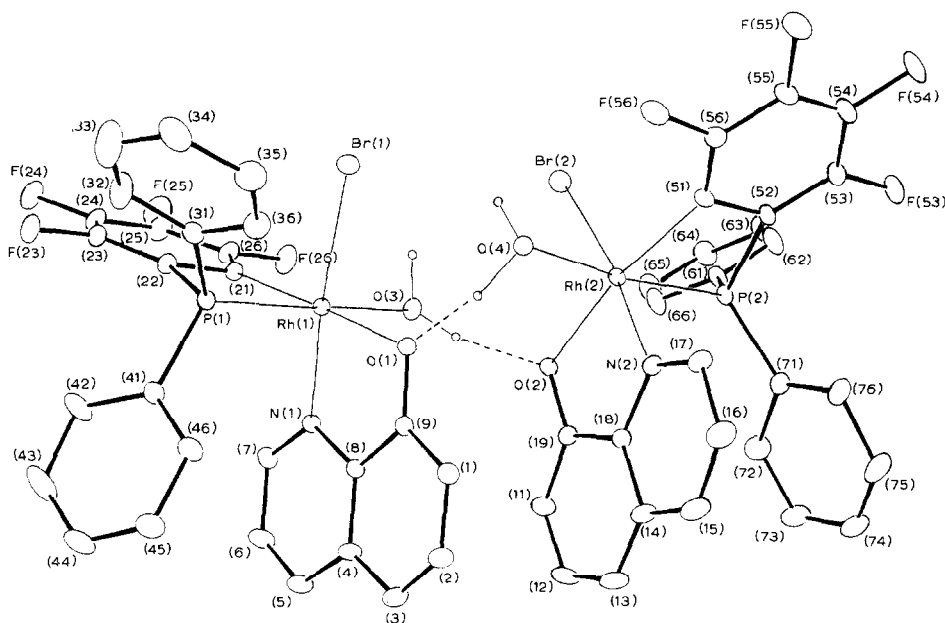


Fig. 1. ORTEP view of the complex dimer, showing the atomic numbering. The hydrogen interactions, with the assigned hydrogen bonds (*), are ($\text{\AA}$ and $^\circ$): $\text{H}(1)(\text{O}(4))-\text{Br}(1)$ 2.65(1), $\text{H}(2)(\text{O}(3))-\text{Br}(1)$ 2.38(1), $\text{H}(2)(\text{O}(4))-\text{O}(1)$ 1.49(1) $^\circ$, $\text{H}(1)(\text{O}(3))-\text{O}(2)$ 1.79(1) $^\circ$, $\text{O}(4)-\text{H}(1)(\text{O}(4))-\text{Br}(1)$ 132(3), $\text{O}(3)-\text{H}(2)(\text{O}(3))-\text{Br}(1)$ 144(3), $\text{O}(4)-\text{H}(2)(\text{O}(4))-\text{O}(1)$ 162(2)*, $\text{O}(3)-\text{H}(1)(\text{O}(3))-\text{O}(2)$ 160(2)*.

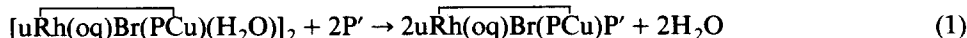
8-oxyquinolate group, a bromine atom, and a water molecule which is *trans* to the phosphorus atom (Fig. 1).

The infrared spectrum (KBr pellet) of compound I shows the characteristic C–F stretching bands for the PCBr ligand in the 1000–1100 cm^{−1} region. This compound is a non-conductor in acetone solution. The molecular weight determined by osmometry in CHCl₃ suggests that the strong intermolecular association persists in solution (see Experimental).

The ³¹P NMR spectrum of compound I shows a doublet at δ −22.2 ppm with a coupling constant ¹J(Rh–P) 107 Hz. This chemical shift is consistent with the presence of a four-atom metallocycle [2] (–Rh–P–C–C–). The value of the coupling constant is in good agreement with those observed for other rhodium(III) compounds [3,4].

Preparation of species of the type Rh(oq)Br(PC)P'

Displacement of the water molecules in compound I is readily brought about, as shown in eq. 1, in which P' represents a P-donor ligand. Thus addition of a stoi-



cheiometric amount of PPh₃, P(*p*-CH₃C₆H₄)₃, or an excess of P(OCH₃)₃ to a solution of compound I in CH₂Cl₂ results in rapid replacement of the coordinated water to give the corresponding compounds II–IV (II, P' = PPh₃; III, P' = P(*p*-CH₃C₆H₄)₃; IV, P' = P(OCH₃)₃). These new compounds are orange air-stable solids, which are non-conductors in acetone solution. Their elemental analyses (see Experimental) are in good agreement with the proposed stoichiometries.

The ³¹P NMR spectra of these compounds at room temperature (Table 1) show typical AMX patterns, and are consistent with a *trans* disposition of the two phosphorus nuclei. The low field signals are assigned to the resonances of the phosphorus nuclei of the ligands P' [3], and the high field signals to the resonances of the phosphorus nuclei of the metallated phosphines [2]. The large values observed for the ²J(P–P') coupling constants and the small values of the ¹J(Rh–P) and ¹J(Rh–P') coupling constants are in agreement with the assigned *trans* configuration (Fig. 2).

The replacement of water by a P-donor ligand produces a shift towards higher field in the resonance of the metallated phosphine (from δ −22.2 to ca. −45 ppm). At the same time the value of ¹J(Rh–P) for the metallated phosphine decreases from 107 to 63 Hz upon going from compound I to compound IV. As expected, the

TABLE 1

³¹P NMR SPECTROSCOPIC DATA FOR THE COMPOUNDS Rh(oq)Br(PC)L

L	δ(P) (ppm) ^a	δ(P') (ppm) ^a	¹ J(Rh–P) (Hz)	¹ J(Rh–P') (Hz)	² J(P–P') (Hz)
H ₂ O	−22.2	—	107	—	—
PPh ₃	−42.3	22.6	71	99	538
P(<i>p</i> -CH ₃ C ₆ H ₄) ₃	−44.2	22.5	71	100	539
P(OCH ₃) ₃	−48.2	105.4	63	170	813

^a δ = 0 ppm H₃PO₄ 85% in H₂O as external reference. δ < 0 for resonances upfield. For notation P and P' see Fig. 2.

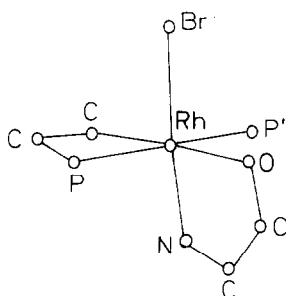


Fig. 2. Schematic structure of the $\overline{\text{Rh(oq)Br(PC)P'}}$ compounds.

increase in $^2J(\text{P-P}')$ is accompanied by a decrease in $^1J(\text{Rh-P})$. Both steric and electronic effects can be invoked [5] to explain these spectroscopic features, which must certainly reflect relevant structural changes, probably a lengthening of the Rh-P bond. Structural studies are in progress in order to correlate structural and spectroscopic parameters for this particular series of compounds.

We also attempted the preparation of other $\overline{\text{Rh(oq)Br(PC)L}}$ compounds in which L is a N-donor ligand. None of the isolated solids gave good analytical data and all decomposed quite rapidly when their solutions were exposed to air.

Compound I in CHCl_3 was reversibly carbonylated (one atmosphere pressure and room temperature), resulting in the appearance of two $\nu(\text{CO})$ carbonyl bands at 2035(s) and 2115(m) cm^{-1} in the infrared spectrum of the solution. Purging of the solution with argon or evacuation yielded the starting material. All attempts to isolate the carbonylated species were unsuccessful.

Crystal structure

The crystal structure of the complex $[\overline{\text{Rh(oq)Br(PC)}(\text{H}_2\text{O})}]_2$ consists of two units interlinked by two hydrogen bonds (Fig. 1). This leads to a central six-membered ring (excluding H atoms) with a distorted boat conformation (Table 2) with flaps at O(1) and at O(2). This arrangement has a pseudo-twofold axis relating both units. The Rh-Rh distance is 5.111(1) Å.

The metal atoms have a distorted octahedral coordination, which includes a metallated tetrafluorophenyl group and a five-membered ring with the oq ligand. All coordination distances are shorter than those in related complexes [1,6] except for those to the oxygen of the oq ligand, which are longer. The chelating ligands produce

TABLE 2

MAIN TORSION ANGLES (°)

O(1)-Rh(1)-O(3)-O(2)	6.4(3)	O(2)-Rh(2)-O(4)-O(1)	13.3(3)
Rh(1)-O(3)-O(2)-Rh(2)	-85.9(3)	Rh(2)-O(4)-O(1)-Rh(1)	-94.7(3)
O(3)-O(2)-Rh(2)-O(4)	47.9(2)	O(4)-O(1)-Rh(1)-O(3)	53.4(2)
O(3)-Rh(1)-P(1)-C(22)	-12.9(8)	O(4)-Rh(2)-P(2)-C(52)	-9.4(9)
O(3)-Rh(1)-P(1)-C(31)	-130.4(8)	O(4)-Rh(2)-P(2)-C(61)	-124.5(9)
O(3)-Rh(1)-P(1)-C(41)	94.8(8)	O(4)-Rh(2)-P(2)-C(71)	103.0(9)

TABLE 3
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Rh(1)–Br(1)	2.467(1)	Rh(2)–Br(2)	2.464(1)
Rh(1)–P(1)	2.241(2)	Rh(2)–P(2)	2.234(2)
Rh(1)–O(1)	2.121(5)	Rh(2)–O(2)	2.107(5)
Rh(1)–O(3)	2.175(6)	Rh(2)–O(4)	2.167(5)
Rh(1)–N(1)	2.016(6)	Rh(2)–N(2)	2.008(6)
Rh(1)–C(21)	2.016(8)	Rh(2)–C(51)	2.036(7)
P(1)–C(22)	1.800(8)	P(2)–C(52)	1.788(8)
P(1)–C(31)	1.803(9)	P(2)–C(61)	1.804(8)
P(1)–C(41)	1.806(8)	P(2)–C(71)	1.809(9)
C(21)–C(22)	1.389(12)	C(51)–C(52)	1.415(11)
O(1)–C(9)	1.315(9)	O(2)–C(19)	1.322(9)
C(9)–C(8)	1.428(10)	C(19)–C(18)	1.415(12)
C(8)–N(1)	1.382(9)	C(18)–N(2)	1.390(10)
O(3)–Rh(1)–Br(1)	89.0(2)	O(4)–Rh(2)–Br(2)	86.7(1)
O(3)–Rh(1)–C(21)	98.6(3)	O(4)–Rh(2)–C(51)	100.6(3)
O(3)–Rh(1)–P(1)	167.8(2)* ^a	O(4)–Rh(2)–P(2)	170.3(1)*
O(3)–Rh(1)–N(1)	88.0(2)	O(4)–Rh(2)–N(2)	88.2(2)
O(3)–Rh(1)–O(1)	88.9(2)	O(4)–Rh(2)–O(2)	89.3(2)
Br(1)–Rh(1)–C(21)	86.5(2)	Br(2)–Rh(2)–C(51)	91.4(2)
Br(1)–Rh(1)–P(1)	92.1(1)	Br(2)–Rh(2)–P(2)	94.7(1)
Br(1)–Rh(1)–N(1)	174.3(2)	Br(2)–Rh(2)–N(2)	172.0(2)
Br(1)–Rh(1)–O(1)	94.4(1)	Br(2)–Rh(2)–O(2)	92.7(1)
C(21)–Rh(1)–P(1)	69.3(2)*	C(51)–Rh(2)–P(2)	70.0(2)*
C(21)–Rh(1)–N(1)	98.8(3)	C(51)–Rh(2)–N(2)	95.6(3)
C(21)–Rh(1)–O(1)	172.4(3)	C(51)–Rh(2)–O(2)	169.5(3)
P(1)–Rh(1)–N(1)	91.8(2)	P(2)–Rh(2)–N(2)	91.4(2)
P(1)–Rh(1)–O(1)	103.1(1)*	P(2)–Rh(2)–O(2)	100.2(2)*
N(1)–Rh(1)–O(1)	80.7(2)*	N(2)–Rh(2)–O(2)	81.1(2)*
Rh(1)–P(1)–C(22)	85.3(3)*	Rh(2)–P(2)–C(52)	86.0(3)*
Rh(1)–P(1)–C(31)	120.8(3)	Rh(2)–P(2)–C(61)	119.6(3)
Rh(1)–P(1)–C(41)	119.0(3)	Rh(2)–P(2)–C(71)	118.0(3)
C(22)–P(1)–C(31)	115.9(4)	C(52)–P(2)–C(61)	113.7(4)
C(22)–P(1)–C(41)	107.8(4)	C(52)–P(2)–C(71)	111.7(4)
C(31)–P(1)–C(41)	106.3(4)	C(61)–P(2)–C(71)	106.6(4)
Rh(1)–C(21)–C(22)	106.7(6)	Rh(2)–C(51)–C(52)	105.0(5)
C(21)–C(22)–P(1)	98.3(5)	C(51)–C(52)–P(2)	99.1(5)
Rh(1)–O(1)–C(9)	109.9(4)	Rh(2)–O(2)–C(19)	110.1(5)
O(1)–C(9)–C(8)	120.0(7)	O(2)–C(19)–C(18)	118.7(7)
C(9)–C(8)–N(1)	115.4(6)	C(19)–C(18)–N(2)	116.7(7)
C(8)–N(1)–Rh(1)	113.4(5)	C(18)–N(2)–Rh(2)	112.0(5)
Rh(1)–C(21)–C(26)	135.9(6)*	Rh(2)–C(51)–C(56)	137.8(6)*
P(1)–C(22)–C(23)	138.9(7)*	P(2)–C(52)–C(53)	138.6(6)*
Rh(1)–N(1)–C(7)	127.2(5)*	Rh(2)–N(2)–C(17)	128.4(6)*
O(1)–C(9)–C(1)	124.6(7)*	O(2)–C(19)–C(11)	125.4(8)*

^a * see text.

severe distortion from the theoretical angles (see values with asterisk in Table 3) and in consequence the angles at the P atoms are distorted from tetrahedral values.

Two characteristics distinguish the PCBr and oq ligands from the previous features [1,6]: The P–C phenyl bonds are shorter and the N–C bond in the coordinating ring is larger.

The C–C bonds in the phenyl rings are in the range 1.309(18)–1.410(14) Å and the C–F bonds in the 1.341(11)–1.172(11) Å range.

Experimental

PCBr was prepared by a published method [7], as was Rh(oq)(CO)(PCBr) [1]. Hoq, P(OCH₃)₃ and P(*p*-CH₃C₆H₄)₃ were used as purchased. PPh₃ was recrystallized from hot ethanol prior to use. All solvents were purified and dried by standard procedures. All reactions were carried out under dry argon.

Crystals of compound I suitable for X-ray studies were obtained by slow diffusion of hexane into a solution of I in dichloromethane/hexane.

³¹P NMR spectra were recorded on a Varian XL 200 or a Bruker WP-80 spectrometer, in CDCl₃ with H₃PO₄ 85% in H₂O as external reference.

Preparation of [Rh(oq)Br(PC)(H₂O)]₂

A solution of Rh(oq)(CO)(PCBr) (500 mg, 0.76 mmol) in 20 ml of toluene was refluxed for 2 h during which the colour changed from orange to deep red. No ν (CO) bands were detected in the infrared spectrum of the resulting solution, and TLC showed that no starting material remained. The toluene was removed under reduced pressure and the residual oil dissolved in chloroform (3 ml). Hexane (3 ml) was added and the solution chromatographed (alumina suspended in hexane as support). Elution with chloroform/hexane (1/1) yielded a yellow fraction which contained the previously reported Rh(oq)₂(PC). The column was washed with acetone and then with 2-propanol. Further elution with methanol quickly gave an orange fraction and this was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane/hexane to give an orange solid, identified as [Rh(oq)Br(PC)(H₂O)]₂ (150 mg, 29.5% yield). Analysis: Found C, 46.4; H, 2.7; N, 1.8. C₅₄H₃₆N₂O₄F₈P₂Br₂Rh₂ · 1/2(CH₂Cl₂) calcd.: C, 46.3; H, 2.5; N, 2.0%. Molecular weight by osmometry in chloroform (at 40°C): Found 1500; calcd.: 1398.

Preparation of Rh(oq)Br(PC)(PPh₃)

To a solution of [Rh(oq)Br(PC)(H₂O)]₂ (50 mg, 0.035 mmol) in 10 ml of dichloromethane was added PPh₃ (19 mg, 0.070 mmol). The colour of the solution changed immediately from red to orange, and TLC showed that no starting complex remained. The solution was concentrated under reduced pressure and hexane was added to precipitate an air-stable orange product, identified as Rh(oq)Br(PC)(PPh₃) (46 mg, 69% yield). Analysis: Found C, 58.0; H, 3.4; N, 1.3. C₄₅H₃₁NOF₄P₂BrRh calcd.: C, 58.4; H, 3.4; N, 1.5%. Molecular weight by osmometry in chloroform (at 40°C): Found 1109; calcd. 922.

*Preparation of Rh(oq)Br(PC)(P(*p*-CH₃C₆H₄)₃)*

To a solution of [Rh(oq)Br(PC)(H₂O)]₂ (50 mg, 0.035 mmol) in 10 ml of dichloromethane was added P(*p*-CH₃C₆H₄)₃ (22 mg, 0.070 mmol). The colour of the solution changed from red to orange, and TLC showed that no starting product remained. The solution was concentrated under vacuum and slow addition of hexane gave an orange air-stable solid, identified as Rh(oq)Br(PC)(P(*p*-CH₃C₆H₄)₃) (50 mg, 72% yield). Analysis: Found C, 59.0; H, 3.9; N, 1.4. C₄₈H₃₇NOF₄P₂BrRh calcd.: C, 59.8; H, 3.9; N, 1.5%.

Preparation of $\text{Rh}(\text{aq})\text{Br}(\text{PC})(\text{P}(\text{OCH}_3)_3)$

To a solution of $[\text{Rh}(\text{aq})\text{Br}(\text{PC})(\text{H}_2\text{O})_2]$ (50 mg, 0.035 mmol) in 10 ml of dichloromethane was added an excess of $\text{P}(\text{OCH}_3)_3$ (ca. 0.5 ml). The solution rapidly became orange. It was evaporated to dryness under vacuum to remove the excess ligand, and the resulting oil was crystallized from dichloromethane/hexane to give an orange air-stable solid, $\text{Rh}(\text{aq})\text{Br}(\text{PC})(\text{P}(\text{OCH}_3)_3)$ (39 mg, 67% yield). Analysis: Found C, 45.7; H, 3.3; N, 1.8. $\text{C}_{30}\text{H}_{25}\text{NO}_4\text{F}_4\text{P}_2\text{BrRh}$ calcd.: C, 45.9; H, 3.2; N, 1.8%.

TABLE 4

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

<i>Crystal data</i>	
Formula	$\text{C}_{27}\text{H}_{18}\text{NOF}_4\text{PBrRh} \cdot \text{H}_2\text{O} \cdot \frac{1}{4}\text{Cl}_2\text{CH}_2$
Crystal habit	Prismatic, yellow
Crystal size (mm)	$0.48 \times 0.31 \times 0.37$
Symmetry	Monoclinic. $P2_1/n$
Unit cell determination:	
least-squares fit to	81 reflexions
$\theta(\text{Cu}) < 45^\circ$	
Unit cell parameters ($\text{\AA}$, $^\circ$)	19.513(2), 17.049(1), 16.898(1), 99.69(1)
Packing: $V(\text{\AA}^3)$, Z	5541.4(7), 8
$D(\text{g cm}^{-3})$, M , $F(000)$	1.64, 683.74, 2772
<i>Experimental data</i>	
Radiation, technique and monochromator	Cu- K_α . PW1100 Philips diffractometer. Bisecting geometry. Graphite oriented
Collection mode	$\omega/2\theta$, 1×1 deg. det. apertures, $\theta \leq 60^\circ$, 1 min/reflex. Scan width of 1.5 deg.
Total independent data	8213
Observed data $I > 3 \sigma(I)$	7001
Stability	Two reflexions every 90 min. No variation
Absorption: $\mu(\text{cm}^{-1})$	78.24
Min-max transmissions	0.116–0.688
<i>Solution and refinement</i>	
Solution mode	Patterson, XRAY76 [8], DIRDIF83 [9] VAX 11/750
Refinement mode	Least-squares on F 's, observed reflex. only, 3 blocks in the final cycles
Final $\langle \text{shift/error} \rangle$	0.15
Parameters:	
No. of variables	694 (H atoms fixed)
Ratio of freedom	10.1
Weighting scheme	Empirical as to give no trends in $\langle w \Delta^2 \rangle$ vs. $\langle F_0 \rangle$ and $\langle \sin \theta / \lambda \rangle$
Max. thermal values ($\text{\AA}^2$)	$U_{33} \text{ Cl}(1) = 0.27(2)$
Final F peaks	About $0.8 \text{ e \AA}^{-3}$ around Cl(1) atom
Final R , R_w	0.061, 0.065
Atomic factors	International Tables for X-ray Crystallography [10]. Neutral atoms

TABLE 5

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS: $U_{eq} = \frac{1}{3} \sum (U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cdot \cos(a_i a_j)) \times 10^4$

Atom	x/a	y/b	z/c	U_{eq}
Rh(1)	0.22837(3)	0.22930(3)	-0.04452(3)	361(2)
Br(1)	0.34964(4)	0.26626(6)	0.00861(6)	656(3)
O(3)	0.22373(28)	0.16849(31)	0.06758(32)	504(18)
O(1)	0.18506(25)	0.32966(28)	0.00243(30)	416(16)
N(1)	0.12662(30)	0.20472(33)	-0.07841(35)	387(19)
C(1)	0.07363(43)	0.39296(47)	-0.00787(53)	530(28)
C(2)	0.00324(48)	0.39004(54)	-0.03530(64)	653(34)
C(3)	-0.02896(46)	0.32754(58)	-0.07361(65)	662(35)
C(4)	0.01121(39)	0.26167(48)	-0.08878(52)	503(27)
C(5)	-0.01569(44)	0.19273(53)	-0.12972(63)	630(33)
C(6)	0.02645(47)	0.13390(53)	-0.14236(65)	659(34)
C(7)	0.09916(43)	0.14121(45)	-0.11726(48)	504(27)
C(8)	0.08331(37)	0.26491(41)	-0.06301(42)	394(23)
C(9)	0.11727(40)	0.33055(42)	-0.02099(44)	427(25)
P(1)	0.23866(10)	0.26657(11)	-0.16915(11)	399(6)
C(21)	0.26845(39)	0.14187(48)	-0.10286(45)	462(26)
C(22)	0.27768(43)	0.17181(45)	-0.17679(49)	490(27)
C(23)	0.30884(46)	0.12943(55)	-0.23099(52)	567(31)
F(23)	0.31640(33)	0.15943(36)	-0.30241(32)	796(22)
C(24)	0.32879(49)	0.05514(55)	-0.21256(60)	614(34)
F(24)	0.35818(36)	0.01106(36)	-0.26376(41)	921(26)
C(25)	0.32002(52)	0.02255(49)	-0.14032(67)	665(36)
F(25)	0.34102(42)	-0.05088(34)	-0.12090(48)	1032(30)
C(26)	0.29130(45)	0.06629(50)	-0.08467(55)	559(30)
F(26)	0.28424(34)	0.03154(31)	-0.01454(34)	801(23)
C(31)	0.29140(43)	0.34988(50)	-0.18559(48)	524(28)
C(32)	0.32988(95)	0.35088(90)	-0.24431(83)	1202(68)
C(33)	0.36229(134)	0.42355(130)	-0.26056(108)	1680(109)
C(34)	0.36160(87)	0.48479(89)	-0.21213(91)	1112(62)
C(35)	0.32504(71)	0.48233(66)	-0.15181(91)	939(52)
C(36)	0.29002(60)	0.41507(62)	-0.13929(72)	786(42)
C(41)	0.16162(44)	0.27178(46)	-0.24498(48)	495(27)
C(42)	0.15464(69)	0.22712(76)	-0.31257(73)	953(47)
C(43)	0.09130(101)	0.23219(100)	-0.36828(89)	1308(70)
C(44)	0.03893(63)	0.28365(87)	-0.35544(81)	911(49)
C(45)	0.04847(56)	0.33020(67)	-0.29294(74)	783(41)
C(46)	0.11039(50)	0.32657(54)	-0.23578(57)	635(32)
Rh(2)	0.23458(3)	0.31095(3)	0.24762(3)	371(2)
Br(2)	0.32916(5)	0.21509(6)	0.24835(6)	663(3)
O(4)	0.26439(25)	0.35803(29)	0.13926(30)	434(16)
O(2)	0.16151(26)	0.23819(30)	0.17651(30)	448(17)
N(2)	0.15319(33)	0.38473(36)	0.23095(37)	445(21)
C(11)	0.03701(47)	0.23258(63)	0.13543(62)	682(36)
C(12)	-0.02591(49)	0.26928(84)	0.12707(74)	854(46)
C(13)	-0.03053(48)	0.34654(80)	0.15016(78)	834(45)
C(14)	0.02654(44)	0.38755(59)	0.18327(59)	617(33)
C(15)	0.02801(54)	0.46793(65)	0.20494(73)	760(42)
C(16)	0.08936(57)	0.50402(59)	0.23572(77)	799(42)
C(17)	0.15173(44)	0.46012(47)	0.25049(58)	559(31)
C(18)	0.09239(40)	0.34783(48)	0.19486(45)	472(26)
C(19)	0.09882(40)	0.26975(47)	0.16862(47)	470(26)
P(2)	0.21440(10)	0.27905(11)	0.36985(11)	408(6)

TABLE 5 (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>
C(51)	0.29463(38)	0.37749(43)	0.33233(46)	440(25)
C(52)	0.27872(40)	0.35091(43)	0.40647(45)	452(25)
C(53)	0.31019(49)	0.38176(50)	0.47898(52)	573(31)
F(53)	0.29488(34)	0.35732(36)	0.54966(31)	820(33)
C(54)	0.35892(53)	0.44029(57)	0.47868(59)	681(35)
F(54)	0.39091(38)	0.47064(39)	0.54870(37)	987(26)
C(55)	0.37367(47)	0.46680(53)	0.40725(62)	648(34)
F(55)	0.42396(36)	0.52337(38)	0.40928(42)	960(26)
C(56)	0.34254(44)	0.43625(50)	0.33489(55)	546(30)
F(56)	0.36344(31)	0.46347(37)	0.26820(35)	815(22)
C(61)	0.23532(45)	0.18180(45)	0.40852(45)	492(27)
C(62)	0.26624(61)	0.16943(51)	0.48671(56)	702(36)
C(63)	0.28189(63)	0.09346(62)	0.51265(61)	801(41)
C(64)	0.26617(60)	0.03183(51)	0.46346(69)	738(40)
C(65)	0.23565(68)	0.04369(56)	0.38546(65)	782(42)
C(66)	0.21933(57)	0.11982(49)	0.35858(49)	641(34)
C(71)	0.13055(44)	0.30365(48)	0.39522(49)	513(28)
C(72)	0.07465(58)	0.25090(67)	0.37535(75)	817(43)
C(73)	0.00997(60)	0.27062(90)	0.38991(87)	923(52)
C(74)	-0.00173(64)	0.34157(103)	0.42118(85)	960(56)
C(75)	0.04937(75)	0.39518(87)	0.43735(91)	1029(59)
C(76)	0.11874(58)	0.37606(67)	0.42526(71)	811(43)
Cl(1) ^a	0.05649(67)	0.05622(54)	0.44611(102)	1798(66)
Cl(2) ^a	0.03435(55)	-0.09072(74)	0.36201(77)	1596(50)
C(80) ^a	0.07317(211)	-0.04376(208)	0.43725(335)	1524(209)

^a Means population parameter = 0.5.

X-ray analysis

Details of the crystallographic study are given in Table 4. One water molecule is present per Rh atom and coordinated to it, as well as 1/4 of a dichloromethane molecule (Cl–C 1.58(5) Å, Cl–C–Cl/119(3)°). Table 5 gives the final fractional coordinates. Structural parameters for the complex are presented in Tables 2 and 3. Lists of structure factors, thermal parameters and hydrogen coordinates can be obtained from the authors on request.

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References

- 1 F.L. Barceló, J.C. Besteiro, P. Lahuerta, C. Foces-Foces, F.H. Cano and M. Martínez-Ripoll, J. Organomet. Chem., 270 (1984) 343.
- 2 P. Garrou, Chem. Rev., 81 (1981) 229.

- 3 P.E. Pregosin and R.W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer-Verlag, Berlin, 1979.
- 4 M. Sanaú, Ph.D. Thesis, Universidad de Valencia (Spain), 1982.
- 5 C.A. Tolman, Chem. Rev., 77 (1977) 313.
- 6 F.L. Barceló, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano and M. Martinez-Ripoll, J. Chem. Soc., Chem. Commun., (1985) 43.
- 7 P.G. Eller and D.W. Meek, J. Organomet. Chem., 22 (1970) 631.
- 8 J.M. Stewart, P.A. Machin, C.W. Dickinson, H.L. Ammon, H. Heck and H. Flack, The X-Ray System (1976), University of Maryland, USA.
- 9 P.T. Beurskens, W.P. Bosman, H.N. Doesburg, R.O. Gould, Th.E.M. van den Hark, P.A.J. Prick, J.H. Noordik, G. Beurskens, V. Parthasarathi, H.J. Brunis Slot and R.C. Haltiwanger, Dirdif System (1983), Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands.
- 10 International Tables for X-Ray Crystallography (1974) Vol. IV, Birmingham, Kynoch Press, England.