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CYCLOMETALLATION REACTIONS IN COMPLEXES OF THE TYPE Rh(oq)(CO)[P(*o*-BrC$_6$F$_4$)Ph$_2$]. THE MOLECULAR STRUCTURE OF Rh(oq)$_2$[P(*o*-C$_6$F$_4$)Ph$_2$] (oq = 8-hydroxyquinolinate)

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Summary

Cyclometallation occurs when a solution of the complex Rh(oq)(CO)(PCBr), (PCBr = 2-bromo-3,4,5,6-tetrafluorophenyldiphenylphosphine; oq = 8-hydroxyquinolinate) in toluene is refluxed, giving Rh(oq)$_2$(PC) (PC = P(C$_6$F$_4$)(C$_6$H$_5$)$_2$) and a dimeric compound, not yet completely characterized, formulated as Rh$_2$Br(oq)(PCBr)$_2$. Rh(oq)$_2$(PC) was characterized by elemental analysis, by conductance measurements, and by ^{19}F, ^{31}P NMR and infrared spectroscopy. Its molecular structure was determined by single-crystal X-ray methods and refined by standard procedures to final agreement factors R and R_w of 0.067 and 0.060 for 5346 observed data. Lattice constants are 15.8494(6), 14.7188(5), 14.6675(5) Å and β 96.933(3)°, with monoclinic symmetry. The complex has a distorted octahedral geometry with a four atom metallocycle-ring (Rh–P–C–C) showing distorted angles of 69.8(2) and 84.8(2)° at Rh and P atoms, respectively. The analogous compound Rh(5-moq)$_2$(PC), (5-moq = 5-methyl-8-hydroxyquinolinate), can be obtained by heating Rh(5-moq)(CO)(PCBr).

Introduction

The cyclometallation reactions of coordinated P-donor ligands have received considerable attention [1] and there are many reports of activation of C–H bonds in aryl [2], and, more recently, in alkyl groups [3].

There are many examples of cyclometallated phosphines and aryl phosphites containing five-membered rings. Many fewer examples are known of cyclometallated

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compounds containing four-membered rings, and only a few of them have been studied crystallographically [4,5].

We report in this paper the preparation, spectroscopic evidences and X-ray structure of a new four-membered cyclometallated compound, $\overline{\mathrm{Rh(oq)_2(PC)}}$. Some related species have also been synthesized.

Results and discussion

Preparation of species of the type Rh(oq)(CO)(PCBr)

Rh(oq)(CO)(PCBr) (I) was prepared by treatment of $\mathrm{Rh(oq)(CO)_2}$ with a stoichiometric amount of the phosphine PCBr in CH_2Cl_2. The reaction is rapid and the infrared spectrum of the product exhibits a sharp carbonyl band at 1967 cm^{-1}, a value normal for monocarbonyl compounds of rhodium(I) with oxinate ligands [6].

The same type of compound can be prepared with 5-moq and 5,7-Cl_2oq, from the analogous dicarbonyl complexes [7].

$$\mathrm{Rh(oq)(CO)_2 + PCBr \rightarrow Rh(oq)(CO)(PCBr) + CO}$$

All these compounds are yellow, air stable solids, and show a single ν(CO) band in the IR.

Addition of a stoichiometric amount of triphenylphosphine, triphenyl phosphite or trimethyl phosphite, to compound I in toluene causes replacement of the phosphine PCBr and gives the corresponding Rh(oq)(CO)L species (L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$ or $P(OCH_3)_3$).

$$\mathrm{Rh(oq)(CO)(PCBr) + L \rightarrow Rh(oq)(CO)L + PCBr}$$

Preparation of $\overline{Rh(oq)_2(PC)}$

A solution of Rh(oq)(CO)(PCBr) in toluene was refluxed under N_2, the reaction being monitored by infrared spectroscopy and thin layer chromatography. The colour of the solution changed from orange to red and after 2 h compound I had disappeared and no carbonyl bands were observed in the infrared spectrum. Two new products II and III were isolated from the product mixture by chromatography. Both were air stable as solids and were soluble in chlorinated solvents, acetone, benzene, toluene and tetrahydrofuran.

The yellow crystalline compound II was identified as $\overline{\mathrm{Rh(oq)_2(PC)}}$ by elemental analysis, ^{19}F, ^{31}P NMR and infrared spectra. It is non-conducting in acetone. The infrared spectrum (KBr mull) shows the characteristic C–F stretching bands of the ligand PCBr at 1000–1100 cm^{-1}. Compound II gives four fluorine resonances in the ^{19}F NMR spectrum and a single resonance in the ^{31}P NMR spectrum at δ −33.8 ppm (^1J(Rh–P) 99.7 Hz) (see Table 1). This high field resonance with a Δ_R value [8] of −79.8 ppm is characteristic of a four-membered metallocycle, in contrast with the low field resonance (positive Δ_R values) observed for five-membered species.

The value of Δ_R was calculated relative to Rh(oq)(CO)(PCBr), which gives a peak at δ +46.0 ppm (^1J(Rh–P) 174.6 Hz) in the ^{31}P NMR spectrum.

The ratio of the values of the ^1J(Rh–P) coupling constants in compounds II and I is 0.57, in satisfactory agreement with the value of 0.66 expected on the assumption of an oxidation state of III for the rhodium atom in compound II.

The ^{1}H NMR shows a signal at δ 5.2 ppm assigned to dichloromethane, one molecule per rhodium atom.

TABLE 1

^{31}P AND ^{19}F NMR SPECTROSCOPIC DATA

Compound	δ_P [a] (ppm)	^1J(Rh–P) (Hz)	δ_F [b] (ppm)
Rh(oq)(CO)(PCBr)	46.0	174.6	35.4
			33.7
			10.2
			5.2
$Rh(oq)_2(PC)$	−33.8	99.7	23.9 [c]
			10.3
			−1.9

[a] $\delta_p = 0.0$ ppm H_3PO_4 85% in D_2O. Negative values of δ_p for high field shift. [b] $\delta_F = 0.0$ ppm C_6F_6. Negative values of δ_F for high field shift. [c] Relative intensities 2/1/1.

The molecular structure of II was determined by X-ray crystallography.

The second product isolated from the reaction, compound III, has not been definitively identified. The analytical data and the molecular weight determination in benzene by osmometry indicate a dimeric composition Rh_2Br $(oq)(PCBr)_2$.

This compound III showed no clear signal in the ^{31}P NMR spectrum and only broad peaks in the ^{19}F NMR spectrum. As the infrared spectrum in KBr shows characteristic bands of the phosphine at 1000–1100 cm^{-1}, the absence of signals in the ^{31}P spectrum suggests the presence of paramagnetic species in solution. Magnetic measurements on III in the solid state at room temperature gave a high value for the atomic paramagnetic susceptibility.

Product III reacts with two equivalents of $AgClO_4$; the reaction with triphenylphosphine gives two major species as detected by TLC. These results indicate that one of the two phosphines in compound III must be metallated and that two bromines are bridging two non-equivalent rhodium atoms. We can formulate III as $Rh_2Br_2(oq)(PC)(PCBr)$. Studies of molecular structure and magnetic behaviour of this compound are in progress.

As compounds II and III constitute more than 75% of the reaction products, we can depict the thermal reaction as follows:

$$3\ \mathrm{Rh(oq)(CO)(PCBr)} \xrightarrow[-3\ \mathrm{CO}]{\Delta} \mathrm{Rh(oq)_2(PC)} + \mathrm{Rh_2Br_2(oq)(PC)(PCBr)}$$

A similar compound $Rh(5\text{-}moq)_2(PC)$ can be isolated from the reaction of Rh(5-moq)(CO)(PCBr) in refluxing toluene. However, $Rh(5,7\text{-}Cl_2oq)(CO)(PCBr)$ gives a very complex mixture of compounds under the same conditions. Attempts to identify any of the products have so far been unsuccesful.

Crystal structure

Coordination around the Rh atom. The metal shows octahedral coordination with the two enantiomeric configurations shown in Fig. 1. The octahedron is considerably distorted due to the strain in the metallated tetrafluorophenyl group (see Table 2). The length of the metal–ligand bonds are within the expected ranges [9]. The three four atom sets defining the octahedra are not strictly planar (the spread of deviations

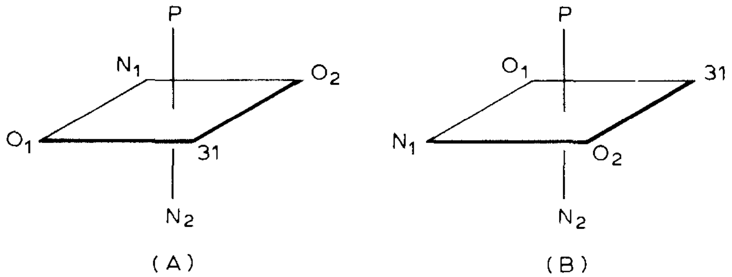

Fig. 1. The two configurations in the structure for the coordination octahedron.

being +/− 0.044(5) to +/− 0.165(5) Å), the Rh atom being within the deviation of the defining atoms. Their least-squares planes intersect each other at angles of 84.5(1), 83.7(1) and 80.4(1)°.

The four-membered ring. The four atoms ring is virtually planar (the deviation being +/− 0.003(1) to +/− 0.006(6) Å) and it forms angles of 81.1(1), 88.9(1), 3.1(2) and 87.1(2)° with the other two coordinating 8-hydroxyquinolinate groups, with the tetrafluorophenyl ring, and with the P, C(41) C(51) plane, respectively. The geometry within the ring is considerably distorted, especially the angles, but this is

TABLE 2

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (DEGREES)

Rh–O(1)	2.034(4)	O(2)–C(29)	1 313(8)
Rh–N(1)	2.093(5)	N(2)–C(27)	1.324(8)
Rh–O(2)	2.039(4)	N(2)–C(28)	1.359(8)
Rh–N(2)	2.089(5)	C(31)–C(32)	1.411(8)
Rh–C(31)	2 038(5)	C(32)–P	1.800(5)
Rh–P	2 274(1)	P–C(41)	1.798(6)
O(1)–C(19)	1.321(7)	P–C(51)	1.805(6)
N(1)–C(17)	1.328(9)	C(11)–C(60)	1.833(–)
N(1)–C(18)	1.361(8)	C(12)–C(60)	1.935(–)
C(31)–Rh–P	69.8(2)	Rh–O(2)–C(29)	111.6(4)
N(2)–Rh–P	1.67 5(1)	Rh–N(2)–C(28)	110 6(4)
N(2)–Rh–C(31)	97.8(2)	Rh–N(2)–C(27)	128 9(4)
O(2)–Rh–P	96.8(1)	Rh–C(31)–C(36)	138.5(5)
O(2)–Rh–C(31)	90.9(2)	Rh–C(31)–C(32)	105 4(4)
O(2)–Rh–N(2)	81.3(2)	C(31)–C(32)–P	100 1(4)
N(1)–Rh–P	99.1(1)	C(33)–C(32)–P	136 3(5)
N(1)–Rh–C(31)	168 2(2)	Rh–P–C(32)	84 8(2)
N(1)–Rh–N(2)	93.4(2)	C(32)–P–C(51)	111.2(3)
N(1)–Rh–O(2)	94.7(2)	C(32)–P–C(41)	109 3(3)
O(1)–Rh–P	88.5(1)	Rh–P–C(51)	117.6(2)
O(1)–Rh–C(31)	94.2(2)	Rh–P–C(41)	124.4(2)
O(1)–Rh–N(2)	94.3(2)	C(41)–P–C(51)	106.8(2)
O(1)–Rh–O(2)	173 6(2)	P–C(41)–C(46)	119 4(5)
O(1)–Rh–N(1)	81.0(2)	P–C(41)–C(42)	120 8(5)
Rh–O(1)–C(19)	111.0(4)	P–C(51)–C(56)	118 0(5)
Rh–N(1)–C(18)	110.6(4)	P–C(51)–C(52)	121.2(4)
Rh–N(1)–C(17)	129.4(5)	C(11)–C(60)–C(12)	95.2(–)

TABLE 3

SELECTED TORSION ANGLES (DEGREES)

Rh-N(2)-C(28)-C(29)	-3.6(6)	Rh-N(1)-C(18)-C(19)	-4.5(7)
N(2)-C(28)-C(29)-O(2)	2.8(8)	N(1)-C(18)-C(19)-O(1)	-3.0(9)
C(28)-C(29)-O(2)-Rh	-0.4(7)	C(18)-C(19)-O(1)-Rh	8.9(7)
C(29)-O(2)-Rh-N(2)	-1.2(4)	C(19)-O(1)-Rh-N(1)	-8.4(4)
O(2)-Rh-N(2)-C(28)	2.6(4)	O(1)-Rh-N(1)-C(18)	7.0(4)
C(31)-Rh-P-C(32)	0.5(3)	Rh-P-C(51)-C(52)	69.6(5)
Rh-P-C(32)-C(31)	-0.6(3)	Rh-P-C(51)-C(56)	-103.4(5)
P-C(32)-C(31)-Rh	0.7(4)	Rh-P-C(41)-C(42)	-171.0(5)
C(32)-C(31)-Rh-P	-0.6(3)	Rh-P-C(41)-C(46)	7.4(6)

consistent with literature reports [4]. The main distortions are that P-Rh-C(31) 69.8(2), Rh-P-C(32), 84.8(2)°; P-C(32)-C(31) 100.1(4), Rh-C(31)-C(32) 105.4(4), compared with Rh-C(31)-C(36) of 138.5(5)°.

The other parts of the complex are normal (see Table 2). Except for C(13)-C(14) and C(12)-C(13), the $C(sp^2)$-$C(sp^2)$ bond lengths are in the range 1.340(16) to 1.428(8) Å, and the angles range between 115.7(5) and 124.2(9)°. The plane formed by P, C(41), and C(51) forms angles of 45.9(3) and 39.2(3)° with its phenyl groups, which lie at 71.7(3)° to each other (see Table 3 for angular conformation). The C-F distances fall between 1.341(10) and 1.360(8) Å [10]. The geometry of the dichloromethane group is an average because of the disorder at C(60).

Experimental

Reagents and chemicals

PCBr was prepared by a published method [11]; as was Rh(acac)$(CO)_2$ [12]. All solvents were purified and dried by standard methods before use. All reactions were carried out under dry nitrogen.

Synthesis of Rh(oq)(CO)(PCBr)

When Rh(acac)$(CO)_2$ (300 mg, 1.16 mmol) and Hoq (169 mg, 1.16 mmol) were stirred together in dichloromethane (15 ml) for 90 min a dark solid separated from the orange solution. When PCBr (480 mg, 1.16 mmol) was added to this suspension some gas was evolved and the mixture turned orange. The reaction was considered to be complete when the infrared spectrum of the solution showed only one band, at 1967 cm^{-1}, in the carbonyl region. The solvent was partly removed under reduced pressure and hexane was added to precipitate Rh(oq)(CO)(PCBr) (750 mg, 93% yield) a yellow air stable solid. Analysis: Found: C, 48.5; H, 2.7; N, 2.7. $C_{28}H_{16}O_2NBrPRh$ calcd.: C, 48.7; H, 2.3; N, 2.1%. ν(CO) (in KBr) 1965 cm^{-1}.

Synthesis of Rh(5-moq)(CO)(PCBr) and Rh(5,7-Cl_2oq)(CO)(PCBr)

The procedure used for Rh(oq)(CO)(PCBr) was employed.

Rh(5-moq)(CO)(PCBr) 92% yield. Analysis: Found: C, 50.2; H, 2.7; N, 2.0. $C_{29}H_{18}O_2NBrF_4PRh$ calcd.: C, 49.6; H, 2.6; N, 2.0%; ν(CO) (in KBr) 1970 cm^{-1}.

Rh(5,7-Cl_2oq)(CO)(PCBr) 95% yield. Analysis: Found: C, 43.3; H, 2.0; N, 1.8. $C_{28}H_{14}O_2NBrF_4Cl_2PRh$ calcd.: C, 44.4; H, 2.0; N, 1.8%; ν(CO) (in KBr) 1960 cm^{-1}.

Synthesis of $\overline{Rh(oq)_2(PC)}$

A solution of Rh(oq)(CO)(PCBr) (500 mg, 0.76 mmol) in toluene was refluxed. The colour changed from orange to dark green during 30 min, and after 2 h became

TABLE 4

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$[Rh(C_9H_6NO)_2(PPh_2C_6F_4)]\cdot CH_2Cl_2$
Crystal habit	Yellow, prismatic
Crystal size (mm)	0.14×0.14×0.18
Symmetry	$2/m$, monoclinic, $P2_1/n$
Unit cell determination, least-squares fit to θ(Cu) < 45°	68 reflexions
Unit cell dimensions (Å)	a 15.8494(6), b 14.7188(5), c 14.6675(5) β 96.933(3)°
Packing: V(Å^3), Z	3396.7(3), 4
D(g cm^{-3}), M, F(000)	1.583, 809.388, 1624
Experimental data	
Radiation and technique	Cu-K_α, Philips diffractometer, PW 1100 Bisecting geometry
Monochromator	Graphite-oriented
Sample orientation	$00l$: X −22°, ϕ 354° $hh0$: X 2°, ϕ 270°
Collection mode	$w/2\theta$, 1×1° det apertures, θ < 65°, 1 min refl^{-1}; scan width of 1.5°
Total independent data	5898
Observed data $I < 2\sigma(I)$	5346
Stability	Two reflexions every 90 min; no variation
Absorption:	
faces	+/− (110, 101, $1\bar{1}0$)
μ (cm^{-1})	66.02
Min-max transmissions	0.421–0.627
Solution and refinement	
Solution mode	Patterson, Dirdif 81 [15], X-Ray 76 System [16] Vax 11/750
Refinement mode	Least-squares on F's, observed reflexions only; 2 blocks in the final cycles
Final shift/error	0.50
Parameters:	
no. of variables	517
degrees of freedom	4829
ratio of freedom	10.3
Weighting scheme	Empirical as to give no trends in $\langle w\Delta^2\rangle$ vs. $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$.
Max. thermal values (Å^2)	U_{22}(C(60)) = 0.50(4)
Final ΔF-peaks	About 1 eÅ^{-3} around C60
Final R, R_w	0.067, 0.060
Atomic factors	International Tables for X-Ray Crystallography [17] Neutral atoms. Real part of anomalous dispersion applied for Rh atom

TABLE 5

THERMAL PARAMETERS AS $U_{eq} = \frac{1}{3}\Sigma(U_{ij}a_i^{\star}a_j^{\star}a_ia_j\cos(a_i,a_j))$ ($\times 10^4$)

Atom	x/a	y/b	z/c	U_{eq}
Rh	0.08350(2)	0.11298(2)	0.26950(3)	330(1)
O(1)	0.0259(3)	0.0098(3)	0.3306(3)	429(12)
N(1)	−0.0039(3)	0.0730(3)	0.1583(3)	437(14)
C(11)	−0.0990(6)	−0.0815(6)	0.3085(7)	739(30)
C(12)	−0.1700(7)	−0.1101(9)	0.2496(10)	1026(45)
C(13)	−0.1842(7)	−0.0856(10)	0.1629(11)	1055(50)
C(14)	−0.1276(5)	−0.0203(7)	0.1249(7)	706(27)
C(15)	−0.1418(7)	0.0155(9)	0.0365(7)	884(37)
C(16)	−0.0864(8)	0.0784(9)	0.0120(6)	891(38)
C(17)	−0.0164(6)	0.1064(6)	0.0737(5)	647(25)
C(18)	−0.0583(4)	0.0095(4)	0.1852(5)	481(18)
C(19)	−0.0412(4)	−0.0201(4)	0 2770(5)	467(18)
O(2)	0.1421(3)	0.2067(3)	0.1964(3)	444(12)
N(2)	0.1802(3)	0.0309(3)	0.2298(3)	388(13)
C(21)	0.2594(5)	0.2218(5)	0.1107(5)	589(23)
C(22)	0.3315(6)	0.1836(6)	0.0794(6)	676(26)
C(23)	0.3548(5)	0.0951(6)	0.0981(6)	634(24)
C(24)	0.3044(4)	0.0407(5)	0.1503(4)	486(18)
C(25)	0.3214(5)	−0.0505(6)	0.1712(5)	584(22)
C(26)	0.2670(5)	−0.0992(5)	0.2192(6)	639(24)
C(27)	0.1958(4)	−0.0560(4)	0.2481(4)	488(19)
C(28)	0.2325(3)	0.0799(4)	0.1816(4)	404(15)
C(29)	0.2088(4)	0.1723(4)	0.1638(4)	416(16)
C(31)	0.1468(3)	0.1601(4)	0.3894(4)	381(15)
C(32)	0.0904(3)	0.2213(4)	0.4246(4)	407(16)
C(33)	0.1110(4)	0.2716(5)	0.5031(5)	506(19)
C(34)	0.1924(5)	0.2635(6)	0.5483(5)	629(23)
C(35)	0.2480(4)	0.2030(6)	0.5174(5)	631(23)
C(36)	0.2254(4)	0.1521(5)	0.4387(5)	516(19)
F(1)	0.0564(3)	0.3302(4)	0.5350(4)	757(17)
F(2)	0.2162(4)	0.3116(5)	0.6247(4)	928(21)
F(3)	0.3264(3)	0.1948(5)	0.5627(4)	980(23)
F(4)	0.2842(2)	0.0936(3)	0.4121(4)	687(15)
P	0.00062(7)	0.21243(8)	0.33721(9)	314(3)
C(41)	−0.0279(3)	0.3238(4)	0.2934(4)	418(16)
C(42)	−0.0687(5)	0.3851(5)	0.3449(6)	660(25)
C(43)	−0.0859(6)	0.4718(6)	0.3135(8)	832(33)
C(44)	−0.0646(7)	0.4974(6)	0.2258(10)	886(39)
C(45)	−0.0257(7)	0.4372(6)	0.1765(8)	812(33)
C(46)	−0.0067(5)	0.3492(5)	0.2081(5)	565(20)
C(51)	−0.0912(3)	0.1675(4)	0.3836(4)	394(15)
C(52)	−0.0827(5)	0.1124(4)	0.4609(4)	451(17)
C(53)	−0.1537(5)	0.0710(5)	0.4887(5)	570(21)
C(54)	−0.2319(5)	0.0844(6)	0.4402(6)	701(27)
C(55)	−0.2407(4)	0.1385(8)	0.3635(7)	820(32)
C(56)	−0.1705(4)	0.1812(6)	0.3340(6)	605(22)
Cl(1)	0.5261(8)	0.1688(6)	0.4504(4)	2250(52)
Cl(2)	0.4882(10)	0.2628(8)	0.2860(10)	2361(59)
C(60)	0.4400(−)	0.1680(−)	0.3550(−)	3283(190)

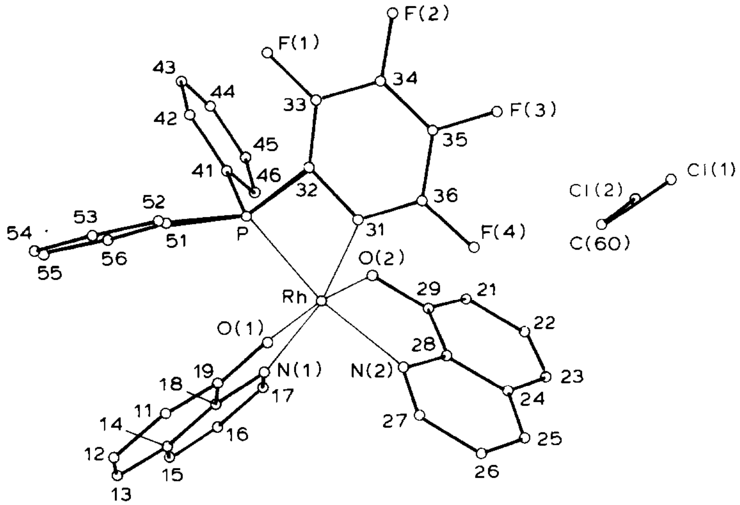

Fig. 2. A view of the complex showing the atomic numbering.

red; no ν(CO) bands were then present in the infrared spectrum. TLC on a sample of the solution showed that no starting material remained and that two new products had been formed. The toluene was removed under reduced pressure and the residual red oil dissolved in chloroform (3 ml). Hexane (3 ml) was added, and the resulting solution chromatographed (silica gel suspended in hexane as support). The first elution with chloroform/hexane (1/1) gave a yellow fraction. Further elution with diethyl ether gave an orange fraction. The yellow fraction was evaporated under reduced pressure and the residue was crystallized from dichloromethane/hexane to give $Rh(oq)_2(PC) \cdot CH_2Cl_2$ (120 mg; 22% yield) a yellow air stable solid. Analysis: Found: C, 55.6; H, 3.1; N, 3.8. $C_{37}H_{24}O_2N_2F_4Cl_2PRh$ calcd.: C, 54.9; H, 2.9; N, 3.5%. The orange fraction likewise gave $Rh_2Br_2(oq)(PC)(PCBr)$ as an orange air stable solid. $Rh_2Br_2(oq)(PC)(PCBr)$ (260 mg; 55% yield) Found: C, 43.3; H, 2.6; N, 1.3. $C_{45}H_{26}ONBr_3F_8P_2Rh_2$ calcd.: C, 43.0; H, 2.1; N, 1.1%. Molecular weight: found, 1220; calcd., 1256.

X-Ray analysis

Table 4 shows the experimental details. The weighting scheme was tested by a δR plot [16] which gave satisfactory results. Table 5 lists the atomic coordinates with numbering as in Fig. 2). Lists of structure factors, thermal parameters and hydrogen atomic coordinates can be obtained from the authors on request. The CH_2Cl_2 group caused disorder problems, and we had to fix the C(60) atom in the least-squares refinement cycles as well as some H atoms which showed abnormal thermal factors or bond distances.

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