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CYCLOMETALLATION REACTIONS IN COMPLEXES OF THE TYPE $\mathbf{Rh(oq)(CO)(P(\mathit{o}\text{-}BrC_6F_4)Ph_2)}$

III *. SYNTHESIS OF THE COMPOUNDS *cis*-$\mathbf{Rh(oq)Br(P(\mathit{o}\text{-}C_6F_4)Ph_2)L}$. THE MOLECULAR STRUCTURE OF *cis*-$\mathbf{Rh(oq)Br(P(\mathit{o}\text{-}C_6F_4)Ph_2)(PPh_3)}$ (oq = 8-oxyquinolinate) **

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Summary

The reaction of Rh(oq)(CO)(PCBr) (PCBr = $P(o\text{-}BrC_6F_4)Ph_2$; oq = 8-oxyquinolinate) in refluxing toluene in the presence of Et_4NBr (1/4 molar ratio) gives $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$, PC = P $(o\text{-}C_6F_4)Ph_2$, in practically quantitative yield. The water molecule is readily displaced by various P-donor ligands to give complexes of general formula $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)PR_3}$ ($PR_3 = PPh_3$, $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(OMe)_3$ and $P(OPh_3)$. The molecular structure of the compound $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(PPh_3)}$ has been determined by X-ray methods. Crystals of the title compound are monoclinic, space group $P2_1/n$ with unit cell dimensions a 11.273(4), b 20.087(8), c 17.471(7) Å and β 102.15(8)°. The final R for 2304 diffractometer data refined by least-squares is 0.0468. The compound has a distorted octahedral coordination with the phosphorus atoms in a *cis* disposition. The Rh–P bond lengths are significantly different. The P atom of the metallated phosphine, which is *trans* to N, has a Rh–P distance of 2.308(4) Å, while the PPh_3, which is *trans* to C, has a Rh–P distance of 2.422(4) Å. The most distorted angles around the rhodium atom are P(1)–Rh–P(2) 104.7(1)° and P(1)–Rh–C(1) 69.2(3)°.

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* For Part II, see ref. 2.

** Dedicated to Prof. R. Usón on the occasion of his 60th birthday.

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Introduction

Cyclometallated rhodium compounds containing four-membered metallocycles arising from cyclometallation of coordinated P-donor ligands are not common [1]. We have reported the preparation of some complexes of this type by the thermal reaction of Rh(oq)(CO)(PCBr) (oq = 8-oxyquinolinate, PCBr = $\mathrm{PPh_2}$ (o-$\mathrm{BrC_6F_4}$)). A complicated mixture of compounds was obtained from which $\overline{\mathrm{Rh(oq)_2(PC}}\mathrm{)}$ [2] and $[\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)]_2}$ [3], (PC = P(o-$\mathrm{C_6F_4}$)$\mathrm{Ph_2}$), were isolated in moderate yield. Both compounds were structurally characterized by ^{31}P NMR and single crystal X-ray methods. Both show distorted octahedral coordination and contain four-atom (–Rh–P–C–C–) metallocyclic rings generated by activation of the C–Br bond of the phosphine.

We have examined several modifications of the experimental conditions in order to achieve a more selective reaction. The only positive result was obtained by adding an excess of bromide anion to the reaction mixture. Thus the same reaction in the presence of $\mathrm{Et_4NBr}$ gives a high yield of a single new product. We report here the preparation and characterization of this new *ortho*-metallated rhodium(III) compound $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$, the synthesis of its P-donor substituted derivatives *cis*-$\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)P'}$ (P′ = $\mathrm{PPh_3}$, P(p-$\mathrm{MeC_6H_4}$)$_3$, P(p-$\mathrm{MeOC_6H_4}$)$_3$, P(p-$\mathrm{FC_6H_4}$)$_3$, $\mathrm{P(OMe)_3}$ and $\mathrm{P(OPh)_3}$, and the molecular structure of the $\mathrm{PPh_3}$ derivative *cis*-$\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(PPh_3)}$.

Results

Preparation of $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$

When a mixture of Rh(oq)(CO)(PCBr) and $\mathrm{Et_4NBr}$ (1/4 molar ratio) is refluxed in toluene the solution slowly darkens. After 15 h of reflux no starting product remains in solution. A yellow solid is filtered off from the red solution and freed from the excess of $\mathrm{Et_4NBr}$ (see Experimental). The final orange crystalline product has analytical data in good agreement with the stoicheiometry $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$.

The ^{31}P NMR spectrum (see Table 1) in $\mathrm{CDCl_3}$ at room temperature of this complex $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$ (I) shows two broad doublets at δ -24.6 ppm ^1J(Rh–P) 109 Hz and δ -48.0 ppm ^1J(Rh–P) 88 Hz, in ca. 1/3 intensity ratio. The ^{31}P NMR spectrum in $\mathrm{C_6D_6}$ at room temperature, however, shows only one resonance, at δ -47.4 ppm ^1J(Rh–P) 94 Hz (see Table 1).

The reaction of net Rh(oq)(CO)(PCBr) in refluxing toluene affords, in addition to the previously characterized $\overline{\mathrm{Rh(oq)_2(PC}}\mathrm{)}$ [2] and $[\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)]_2}$ [3], the same compound I in low yield (ca. 5%). The identity of this latter compound was established by comparison of the IR and ^{31}P NMR spectra, and analytical and TLC data with those of an authentic compound.

Preparation of species of the type cis-$\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)P'}$

The water molecule in compound I is readily displaced by various P-donor ligands according to eq. 1.

$$\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)} + \mathrm{P'} \rightarrow \overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)P'} + \mathrm{H_2O} \qquad (1)$$

Thus addition of the stoichiometric amount of $\mathrm{PPh_3}$, P(p-$\mathrm{MeC_6H_4}$)$_3$, P(p-$\mathrm{MeOC_6H_4}$)$_3$, P(p-$\mathrm{FC_6H_4}$)$_3$ or an excess of $\mathrm{P(OMe)_3}$ and $\mathrm{P(OPh)_3}$ to a $\mathrm{CH_2Cl_2}$

(Continued on p. 203)

TABLE 1

^{31}P NMR SPECTROSCOPIC DATA

Compound	δ(P) (ppm) [a]	^1J(Rh–P) (Hz)	δ(P′) (ppm) [a]	^1J(Rh–P′) (Hz)	^2J(P–P′) (Hz)
Rh(oq)Br(PC)(H_2O)	−24.6 [b] −48.0 −47.0 [c]	109 [b] 88 94 [c]	–	–	–
cis-Rh(oq)Br(PC)((PPh_3)	−45.6	92	8.5	76	–
cis-Rh(oq)Br(PC)(P(*p*-$MeC_6H_4)_3$)	−45.1	94	6.7	77	–
cis-Rh(oq)Br(PC)(P(*p*-$MeOC_6H_4)_3$)	−45.0	92	5.0	78	–
cis-Rh(oq)Br(PC)(P(*p*-$FC_6H_4)_3$)	−46.3	92	6.2	79	–
cis-Rh(oq)Br(PC)($OMe)_3$)	−36.8	92	114.0	136	–
cis-Rh(oq)Br(PC)(P($OPh)_3$)	−38.6	88	96.8	145	–
[Rh(oq)Br(PC)(H_2O)]$_2$ [3]	−22.2	107	–	–	–
trans-Rh(oq)Br(PC)(PPh_3) [3]	−42.3	71	22.6	99	538
trans-Rh(oq)Br(PC)(P(p-$MeC_6H_4)_3$) [3]	−44.2	71	22.5	100	539
trans-Rh(oq)Br(PC)(P($OMe)_3$) [3]	−48.2	63	105.4	170	813

[a] In $CDCl_3$; $\delta > 0$ for resonances downfield from H_3PO_4 15% in H_2O. [b] Relative intensities 1/3. [c] In C_6D_6.

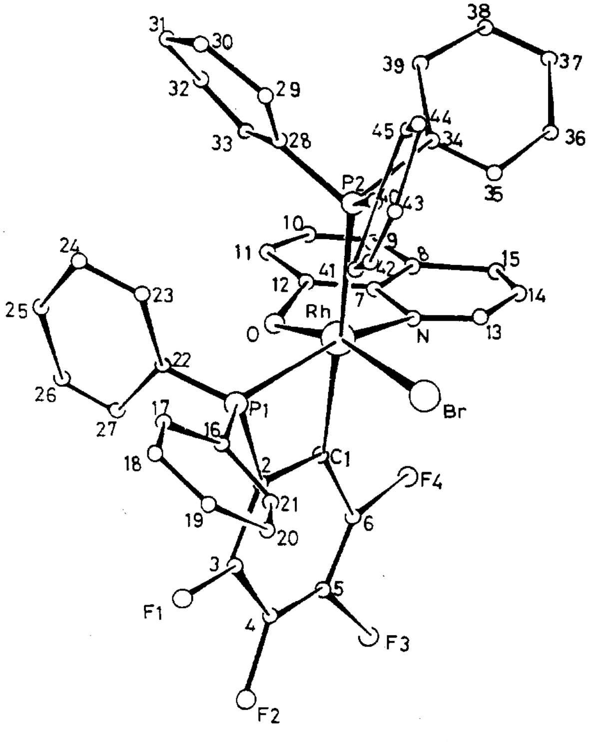


Fig. 1. A view of the compound *cis*-Rh(oq)Br(PC)(PPh_3), with the atomic numbering.

TABLE 2

FINAL ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Rh	0.0382(1)	0.5082(1)	0.7658(1)
Br	−0.0799(2)	0.5349(1)	0.8658(1)
P(1)	0.0280(3)	0.6134(2)	0.7119(2)
P(2)	0.2235(4)	0.5083(2)	0.8654(2)
F(1)	−0.2096(9)	0.6787(5)	0.5851(6)
F(2)	−0.4063(9)	0.6032(5)	0.5258(6)
F(3)	−0.4122(8)	0.4739(5)	0.5680(6)
F(4)	−0.2314(8)	0.4189(4)	0.6704(5)
O	0.1234(9)	0.4800(5)	0.6800(6)
N	0.0144(11)	0.4053(5)	0.7723(7)
C(1)	−0.1190(13)	0.5191(7)	0.6823(8)
C(2)	−0.1178(13)	0.5852(6)	0.6573(8)
C(3)	−0.2110(14)	0.6148(7)	0.6072(10)
C(4)	−0.3123(14)	0.5757(9)	0.5760(9)
C(5)	−0.3143(13)	0.5109(8)	0.5980(8)
C(6)	−0.2179(14)	0.4839(7)	0.6512(9)
C(7)	0.0567(13)	0.3741(8)	0.7141(8)
C(8)	0.0441(17)	0.3028(8)	0.7007(11)
C(9)	0.0923(20)	0.2771(10)	0.6383(12)
C(10)	0.1493(20)	0.3165(12)	0.5930(12)
C(11)	0.1619(18)	0.3870(9)	0.6049(11)
C(12)	0.1143(13)	0.4158(7)	0.6662(8)
C(13)	−0.0410(16)	0.3616(8)	0.8191(10)
C(14)	−0.0591(20)	0.3013(10)	0.8090(13)
C(15)	−0.0186(20)	0.2691(10)	0.7539(14)
C(16)	0.0061(14)	0.6948(8)	0.7543(9)
C(17)	0.0844(17)	0.7477(8)	0.7483(11)
C(18)	0.0579(25)	0.8103(9)	0.7824(14)
C(19)	−0.0397(23)	0.8147(12)	0.8181(13)
C(20)	−0.1205(21)	0.7615(11)	0.8215(13)
C(21)	−0.0946(17)	0.7018(8)	0.7879(11)
C(22)	0.1275(14)	0.6243(7)	0.6454(10)
C(23)	0.2489(16)	0.6352(8)	0.6730(10)
C(24)	0.3279(17)	0.6390(9)	0.6210(12)
C(25)	0.2820(19)	0.6318(9)	0.5412(11)
C(26)	0.1617(19)	0.6213(9)	0.5130(12)
C(27)	0.0796(17)	0.6169(9)	0.5641(10)
C(28)	0.3632(13)	0.5266(7)	0.8343(9)
C(29)	0.4531(14)	0.5712(8)	0.8728(10)
C(30)	0.5598(15)	0.5825(8)	0.8430(12)
C(31)	0.5780(17)	0.5497(10)	0.7766(12)
C(32)	0.4894(17)	0.5054(9)	0.7386(10)
C(33)	0.3830(14)	0.4943(9)	0.7655(10)
C(34)	0.2400(15)	0.4273(7)	0.9150(8)
C(35)	0.1679(16)	0.4072(8)	0.9600(9)
C(36)	0.1806(19)	0.3465(9)	0.9971(9)
C(37)	0.2805(22)	0.3053(8)	0.9900(12)
C(38)	0.3608(22)	0.3239(8)	0.9464(12)
C(39)	0.3513(19)	0.3866(8)	0.9065(10)
C(40)	0.2325(15)	0.5660(8)	0.9462(9)
C(41)	0.1849(14)	0.6307(8)	0.9334(10)
C(42)	0.2010(19)	0.6780(8)	0.9955(11)
C(43)	0.2694(16)	0.6607(9)	1.0687(11)
C(44)	0.3194(17)	0.5973(1)	1.0827(10)
C(45)	0.3016(16)	0.5488(8)	1.0227(10)

solution of compound I yields the *cis*-$\overline{\text{Rh(oq)Br(PC)}}$P′ complexes. (II, P′ = PPh_3; III, P′ = P(*p*-$MeC_6H_4)_3$; IV, P′ = P($MeOC_6H_4)_3$; V, P′ = P(*p*-$FC_6H_4)_3$; VI, P′ = $P(OMe)_3$; VII, P′ = $P(OPh_3)$. All of them are stable and yellow or orange in colour. Their elemental analyses agree with the proposed stoicheiometries.

X-Ray molecular structure of cis-$\overline{Rh(oq)Br(PC)}$(PPh_3)

Final observed and calculated structure factors, hydrogen atoms positions and thermal parameters are available from the authors.

The final coordinates for all the non-hydrogen atoms are listed in Table 2. Table 3 is a list of selected bond lengths and bond angles. Figure 1 shows the structure of the complex with the labelling scheme for the non-hydrogen atoms, projected on the plane defined by the two phosphorus atoms and the bromine atom.

The molecule shows a distorted octahedral coordination around the metal, atom with the two phosphorus atoms mutually *cis*. Bond constraints in the metallated phosphine as well as in the oq ligand make the P(1)–Rh–C(1) 69.3(2)° and O–Rh–P(1) 86.6(2)° bond angles sensibly smaller than the values expected for a regular geometry.

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Rh–Br	2.470(2)	C(1)–C(2)	1.398(18)
Rh–P(1)	2.308(4)	C(7)–C(12)	1.432(23)
Rh–P(2)	2.422(4)	C(7)–C(8)	1.453(23)
Rh–O	2.025(11)	C(8)–C(9)	1.408(31)
Rh–N	2.092(11)	C(9)–C(10)	1.377(33)
Rh–C(1)	2.057(13)	C(10)–C(11)	1.433(30)
P(1)–C(2)	1.809(4)	C(11)–C(12)	1.418(26)
P(1)–C(16)	1.832(16)	C(13)–C(14)	1.432(26)
P(1)–C(22)	1.793(19)	C(14)–C(15)	1.319(34)
P(2)–C(28)	1.808(17)	C(15)–C(8)	1.448(33)
P(2)–C(34)	1.838(15)	F(1)–C(3)	1.342(18)
P(2)–C(40)	1.815(17)	F(2)–C(4)	1.344(18)
O–C(12)	1.313(18)	F(3)–C(5)	1.342(17)
N–C(7)	1.365(21)	F(4)–C(6)	1.366(17)
N–C(13)	1.313(22)		
Br–Rh–P(2)	90.3(1)	C(2)–P(1)–C(16)	107.2(6)
N–Rh–P(2)	93.7(3)	C(2)–P(1)–C(22)	108.4(6)
O–Rh–P(2)	93.4(2)	C(16)–P(1)–C(22)	107.2(6)
P(1)–Rh–P(2)	104.7(1)	C(28)–P(2)–C(34)	104.8(6)
O–Rh–N	81.6(4)	C(28)–P(2)–C(40)	101.4(6)
N–Rh–Br	94.5(3)	C(34)–P(2)–C(40)	102.2(6)
Br–Rh–P(1)	95.9(1)	O–C(12)–C(7)	119.0(10)
P(1)–Rh–O	86.6(2)	C(7)–C(8)–C(9)	116.0(20)
Br–Rh–C(1)	88.2(3)	C(8)–C(9)–C(10)	122.0(20)
N–Rh–C(1)	92.7(4)	C(9)–C(10)–C(11)	122.0(20)
O–Rh–C(1)	88.5(4)	C(10)–C(11)–C(12)	118.0(20)
P(1)–Rh–C(1)	69.2(3)	N–C(7)–C(8)	122.0(20)
Rh–O–C(12)	113.7(8)	C(7)–C(8)–C(15)	114.0(20)
Rh–P(1)–C(2)	83.6(4)	C(8)–C(15)–C(14)	122.0(20)
Rh–P(1)–C(22)	113.1(5)	C(14)–C(13)–N	120.0(20)
Rh–C(1)–C(2)	105.0(9)		
P(1)–C(2)–C(1)	101.7(9)		

The large value of the P(1)–Rh–P(2) bond angle (104.7(1)°) reflects the marked steric interaction between the two phosphine ligands.

One of the most notable feature in the structure is the significant difference between the two Rh–P bond lengths, the Rh–P(1) bond length is 2.308(4) Å (P(1) *trans* to N) whereas the Rh–P(2) bond length is 2.422(4) Å (P(2) *trans* to C).

The oq ligand is essentially planar and the Rh atom is only 0.15 Å out of the plane.

The average C–C distance in the metallated tetrafluorophenyl ring is 1.37 Å, i.e. in the range observed in other related structures [2,3]. The fluorine atoms lie in the plane of the phenyl group, as does the P(1) atom, while the Rh atom is at a distance of 0.16 Å from it. The F–C bond lengths, between 1.342 and 1.366 Å, are normal.

There are no unusual Van der Waals contacts.

Discussion

The thermal reaction of Rh(oq)(CO)(PCBr) gives a complicated mixture of products as described in recent papers [2,3]. The nature of some of these compounds, in particular $\overline{\mathrm{Rh(oq)_2(PC}}\mathrm{)}$, indicates that a substantial ligand rearrangement has occurred during the reaction.

In order to simplify this reaction we carried it out in the presence of either PCBr, Naoq, Hoq or Et_4NBr. No significant change was observed when an equimolar amount of PCBr was added to the initial solution. Addition of Naoq or Hoq slightly increased the yield of $\overline{\mathrm{Rh(oq)_2(PC}}\mathrm{)}$, which was the only isolable product.

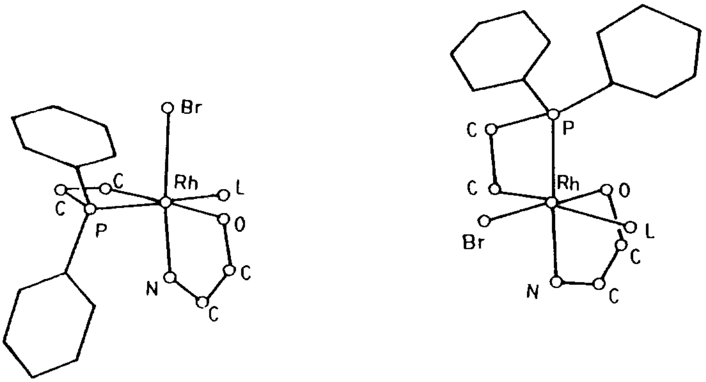
A more interesting effect occurs when a four molar excess of Et_4NBr is added. Under these conditions an insoluble yellow solid is formed, from which $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$ is isolated in about 80% yield. Small amounts of $\overline{\mathrm{Rh(oq)_2(PC}}\mathrm{)}$ are also detected in the remaining solution. We have previously isolated and characterized a compound with the same stoicheiometry as I, $[\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}]_2$ [3], (VIII), but the spectroscopic data clearly indicate that I and VIII are isomers.

Osmometry measurements in $CHCl_3$ at 40°C give molecular weight values for I higher than those for monomeric $\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}$ (847 vs. 678). This fact and the observed solvent dependence of the ^{31}P NMR spectra (see Table 1) indicate that an equilibrium between monomeric and dimeric species may exist in solution (eq. 2).

$$2\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)} \rightleftarrows \left[\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(H_2O)}\right]_2 \qquad (2)$$

We recently described this type of association for the closely related compound VIII [3]. In VIII only the associated species is present in $CHCl_3$ solution. A doublet at −22.2 ppm $^1J(\mathrm{Rh–P})$ 107 Hz appeared in the ^{31}P NMR spectrum, and in the light of that we have assigned the signal at δ −24.6 ppm in the ^{31}P NMR spectrum of I to the dimeric species and the signal at δ −48.0 ppm to the monomeric species. All the related monomeric complexes that we have prepared show also signals in the ^{31}P NMR spectra with chemical shifts of ca. −40 ppm (see Table 1). Both the molecular weight data and the ^{31}P NMR spectrum indicate that the association is small for compound I in $CHCl_3$ solution.

The X-ray structure determined for compound VIII indicates that the association involves hydrogen bonds between water molecules and the oxygen atoms of the oq ligands [3]. The same type of interaction can be responsible of the small degree of association observed for compound I in chloroform.



trans *cis*

Fig. 2. Schematic structure of *cis*- and *trans*-$\overline{\mathrm{Rh(oq)Br(PC)}}$L, showing the orientation of the phenyl groups in the metallated phosphine.

All attempts to obtain suitable crystals of I for X-ray analysis were unsuccessful. We assume that the structure of I is derived from the structure of *cis*-$\overline{\mathrm{Rh(oq)Br(PC)}}(\mathrm{PPh_3})$ by replacing $\mathrm{PPh_3}$ by a water molecule. The mild conditions under which the replacement occurs makes this assumption very probable (see Fig. 2).

The question arising is why the association is much smaller in compound I than in its isomer VIII, and we suggest that steric effects are responsible for this. The $\mathrm{PPh_2}$ group of the metallated phosphine is located *cis* to the water molecule in compound I, so creating serious steric hindrance in the dinuclear species. The same $\mathrm{PPh_2}$ fragment is *trans* to the water in compound VIII and so generates smaller steric hindrance and allows dimerization (see Fig. 2).

The nature of the P-donor derivatives of I derived by treatment with P-donors has been established from analytical data and ^{31}P NMR spectra. All of them have the composition $\overline{\mathrm{Rh(oq)Br(PC)}}$P′, and the ^{31}P NMR spectra reveal a *cis* disposition for the phosphorus nuclei.

The ^{31}P NMR spectra (see Table 1) at room temperature of all the $\overline{\mathrm{Rh(oq)Br(PC)}}$P′ compounds prepared show typical AMX patterns (A = P, M = P′, X = Rh). The absence of coupling between the P and P′ nuclei suggest a *cis* disposition for the two nuclei in all cases. Low field signals are assigned to phosphorus nuclei of the P′ ligands, the δ(P′) values being in the range expected for these coordinated ligands [4]. High field signals are assigned to phosphorus nuclei of the metallated phosphines, the δ(P) values for these indicating the presence of four-membered metallocycle rings [5]. The values of the ^{1}J(Rh–P) and ^{1}J(Rh–P′) coupling constants are normal, and similar as reported for other rhodium(III) compounds [6].

The δ(P) values are much influenced by the nature of the P′ ligands. Thus when P′ is a phosphite the signal appears at lower fields (ca. 7 ppm) than when P′ is a phosphine. This can be understood in terms mainly of electronic effects associated with the smaller steric requirements of phosphite than of phosphine ligands [4,7].

The variation in the ^{1}J(Rh–P) coupling constants on going from compound II to VII are not significant (see Table 1).

The spectra of the complexes *cis*-$\overline{\mathrm{Rh(oq)Br(PC)}}$P′ obtained from I show important differences from those of compounds *trans*-$\overline{\mathrm{Rh(oq)Br(PC)}}$P′ prepared from

VIII [3]. The δ(P) values are in the same range in both *cis* and *trans* complexes, but the δ(P′) signals for *cis*-compounds are at higher fields than those of the *trans* species (ca. 15 ppm, see Table 1). This can be interpreted in terms of the greater steric hindrance of P′ in the *cis* than in the *trans* complexes (see Fig. 2) because of the proximity of the phenyl groups of the metallated phosphine to the P′ ligand.

There are also important changes in the values of the ^1J(Rh–P′) coupling constants on going from *cis* to *trans* complexes. They can be understood in terms of the influence of the *trans* ligand on each phosphorus nucleus for each of the series of compounds [6,7,8].

Experimental

PCBr was prepared by published method [9], as was Rh(oq)(CO)(PCBr) [2]. $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(OMe)_3$ and $P(OPh)_3$ were used as purchased. PPh_3 was recrystallized from hot ethanol. Et_4NBr was recrystallized from chloroform/diethyl ether. All solvents were purified and dried by standard methods before use. All reactions were carried out under argon.

^{31}P NMR spectra were recorded on a Bruker AC200 spectrometer operating at a frequence of 81.015 MHz, in $CDCl_3$ solution with H_3PO_4 15% in H_2O as external reference.

Synthesis of $\overline{\text{Rh(oq)Br(PC)}}(H_2O)$

Rh(oq)(CO)(PCBr) (500 mg, 0.727 mmol) was dissolved in 20 ml of toluene and Et_4NBr (610 mg, 2.908 mmol) was added. The suspension was refluxed for 15 h, during which the colour of the dissolved phase changing from orange to red and a yellow solid separated out. No ν(CO) bands were detected in the infrared spectrum of the final solution, and TLC showed that no starting material remained in it. The yellow solid was filtered off and washed with toluene (15 ml). It was purified by extraction of the Et_4NBr excess with water from a dichloromethane solution of the crude product. The organic phase was dried over anhydrous Na_2SO_4 (ca. 5 g) and filtered off. Concentration under reduced pressure and addition of hexane gave an orange crystalline compound. It was identified as $\overline{\text{Rh(oq)Br(PC)}}(H_2O)$ (430 mg; 87% yield). Analysis: Found: C, 48.2; H, 2.9; N, 2.3%. $C_{27}H_{18}NO_2F_4BrPRh$ calcd.: C, 47.8; H, 2.6; N, 2.2%. Molecular weight by osmometry in $CHCl_3$ at 40°C: Found, 847; calcd. (monomeric), 678.

Synthesis of cis-$\overline{\text{Rh(oq)Br(PC)}}$*P′ compounds. General method*

$\overline{\text{Rh(oq)Br(PC)}}(H_2O)$ (0.074 mmol) was dissolved in 10 ml of dichloromethane and an equimolar amount of the phosphine ligands or an excess of the corresponding phosphite ligand was added. The colour of the solution changed immediately from red to orange. After 5 min stirring TLC showed that no starting material remained in solution. Compounds II, III, IV and V were isolated by concentration under reduced pressure followed by addition of hexane. Compounds VI and VII were isolated by evaporation to dryness and were recrystallized from diethyl ether/hexane. Yields and analytical data for these compounds are given in Table 4.

X-ray analysis

Table 5 gives details of the crystallographic study.

TABLE 4

YIELDS AND ANALYTICAL DATA FOR THE COMPLEXES *cis*-$\overline{\text{Rh(oq)Br(PC}}\text{)P}'$

Compound	Yield (%)	Analysis (Found (calcd.) (%))		
		C	H	N
$C_{45}H_{31}NOF_4BrP_2Rh$ (II)	85	58.4 (58.4)	3.3 (3.4)	1.6 (1.5)
$C_{48}H_{37}NOF_4BrP_2Rh$ (III)	87	59.8 (59.8)	3.7 (3.9)	1.6 (1.5)
$C_{48}H_{37}NO_4F_4BrP_2Rh$ (IV)	84	56.7 (56.9)	3.5 (3.7)	1.4 (1.4)
$C_{45}H_{28}NOF_7BrP_2Rh$ (V)	79	55.3 (55.6)	2.8 (2.9)	1.5 (1.4)
$C_{30}H_{25}NO_4F_4BrP_2Rh$ (VI)	87	46.1 (45.9)	3.4 (3.2)	1.8 (1.8)
$C_{45}H_{31}NO_4F_4BrP_2Rh$ (VII)	91	55.6 (55.7)	3.1 (3.2)	1.1 (1.4)

TABLE 5

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$C_{45}H_{31}NOF_4P_2BrRh$
Crystal habit	Prismatic
Crystal size (mm)	0.7×0.4×0.3
Symmetry	Monoclinic. $P2_1/n$
Unit cell determination:	
least-squares fit to	20 reflexions
Unit cell parameters (Å, °)	11.273(4), 20.087(8), 17.491(7), 102.15(8)
Packing: V (Å^3), Z	3872.12, 4
D_c, D_m (g/cm^3)	1.606, 1.571
M, $F(000)$	936.619, 1848
Experimental data	
Radiation, technique and monochromator	Mo-K_α, Siemens four-circle Diffractometer Bisecting geometry. Graphite.
Collection mode	$\omega/2\theta$ $\theta < 20°$ Scan width of 1.5°
Total independent data	3586
Observed data $I > 3\sigma(I)$	2304
Stability	Two reflexions every 90 min. No variation
Absorption: μ (cm^{-1})	16.67
Solution and refinement	
Solution mode	Direct Methods (Multan 80), Fourier (X-RAY 70) [10]
Refinement mode	Least-square on F's, observed reflex.
Final ⟨shift/error⟩	0.15
Parameters:	
No. of variables	495
Ratio of freedom	4.7
Weighting scheme	All reflexions unity
Max. thermal values (Å^2)	U_{11} (C18) 0.1345 (222)
Final R	0.0468
Atomic factors	International Tables for X-ray Crystallography [11]. Neutral atoms

X-ray data collection. Suitable orange crystals of the compound *cis*-$\overline{\mathrm{Rh(oq)Br(PC}}\mathrm{)(PPh_3)}$ were grown from dichloromethane/hexane. A crystal of appropriate dimensions was mounted on a glass fibre with epoxy adhesive.

Unit cell dimensions were obtained from 20 reflexions measured on a four-circle Siemens diffractometer. A total of 3586 reflexions were collected over the range $2° < \theta < 20°$. From these 2304 with intensities $> 3\sigma$ were used for the analysis.

Structure determination and refinement. The position of the Rh atom and of four of the atoms bonded to it were found by direct methods. The rest of the non-hydrogen atoms were located in two successive calculations of the electron density. This trial structure was refined by least-squares processes, first with isotropic and then with anisotropic temperature factors. Rh and Br atomic scattering factors were corrected for anomalous dispersion.

The calculated positions of the hydrogen atoms were confirmed on a three-dimensional difference-Fourier map which showed no significant anomalous features. The ultimate calculation of the R factor, including the hydrogen atoms positions, gave a final value of $R = 0.0468$. In this calculation isotropic temperature factors 0.01 units of U higher than those of the atoms to which they were bonded were assigned to the hydrogen atoms.

No unusual trends were observed in the analysis of the R factor as function of $\sin \theta/\lambda$ or level by level.

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