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PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM COMPLEXES

XXV *. RHODIUM COMPLEXES DERIVED FROM *m*- AND *p*-DIHYDROXYBENZENES

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Summary

The acetonitrile complex $[Rh(\eta^5\text{-}C_5Me_5)(MeCN)_3](PF_6)_2$ (Ib) reacts with hydroquinone (*p*-dihydroxybenzene) or resorcinol (*m*-dihydroxybenzene) to give three types of different complexes, $[Rh_2(C_5Me_5)_2(HOC_6H_4O\cdots H\cdots OC_6H_4OH)](PF_6)_3$ (II), $[Rh(C_5Me_5)(\cdots OC_6H_4OH)]_n(PF_6)_n$ (III), and $[Rh(C_5Me_5)(\cdots H\cdots OC_6H_4O\cdots H\cdots OC_6H_4O\cdots)]_n$, (IV), [$C_6H_4(OH)_2$ = hydroquinone or resorcinol] depending on the amount of base present and on the ratio of diol to Ib. Spectroscopic data indicate that the $C_6H_4O_2$ ligands are π-bonded to the metal in II and III, and that one is π-bonded and the other hydrogen-bonded to it in IV. All these complexes are rather insoluble in organic solvents but do dissolve in water; this leads to a breakdown of the hydrogen-bonding interactions between the complexed diols. The nature of the bonding of the $C_6H_4O_2$ ligands to the metal in the various complexes is discussed.

We have previously described the reactions of $[M(C_5Me_5)(solvent)_3](PF_6)_2$ (Ia, M = Rh or Ir; solvent = acetone) with phenol to give η^6-phenol and η^5-oxocyclohexadienyl complexes [2] and also of $[Rh_2(C_5Me_5)_2Cl_4]$ with catechol (*o*-dihydroxybenzene) and substituted catechols in the presence of base to give the *O,O'*-bonded $[Rh(C_5Me_5)(O_2C_6H_4)]$ [3]. It was therefore of interest to extend this to the preparation of complexes derived from *m*- and *p*-dihydroxybenzenes (resorcinol and hydroquinone).

Results and discussion

The most convenient starting material for these reactions was found to be the acetonitrile solvent complex (Ib, M = Rh, solvent = MeCN) [4]. Both hy-

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* For Part XXIV see ref. 1.

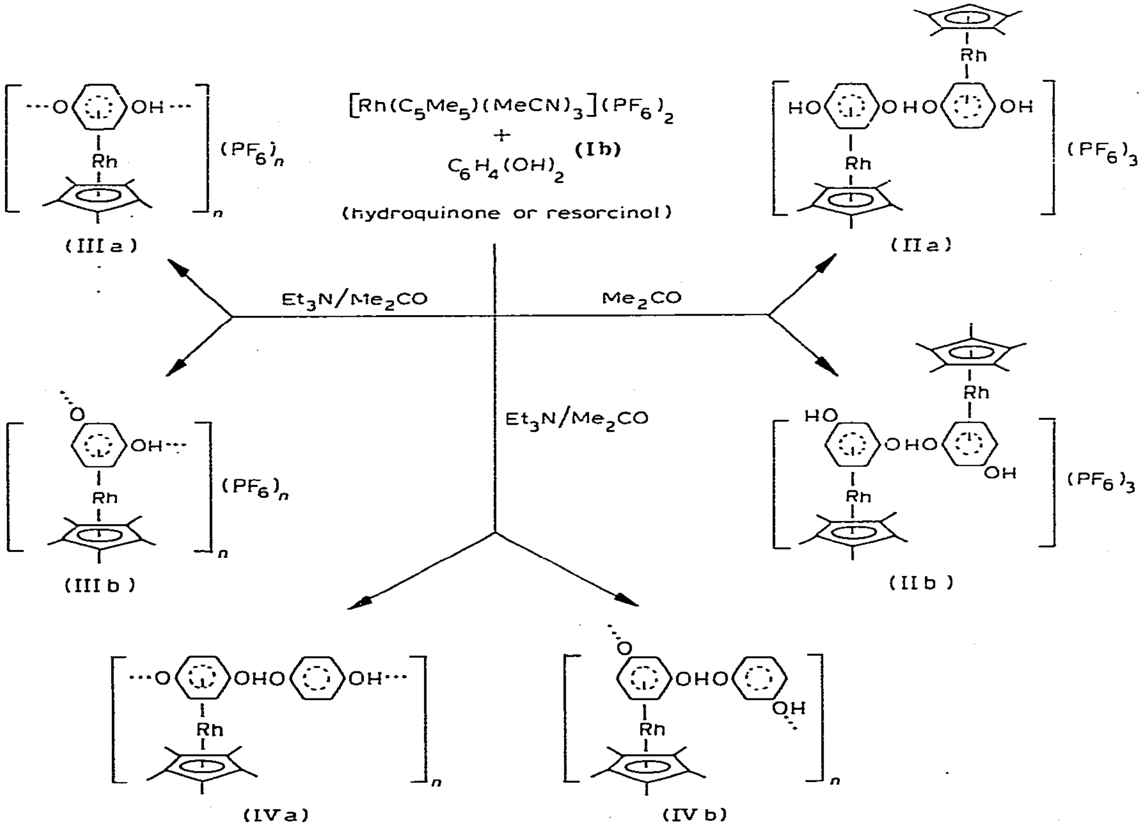
droquinone and resorcinol underwent very similar reactions. For both reactants three types of product could be isolated, each containing complexed and partly deprotonated hydroquinone (or resorcinol), the precise stoicheiometries of which depended on the ratios of reactants and Ib and the amount of base present.

When an excess of the diol was added to a solution of complex Ib in acetone (no base present) the products obtained (IIa or IIb) had analyses corresponding to $[Rh_2(C_5Me_5)_2\{C_6H_4(OH)(O)\}_2H](PF_6)_3$ (Table 1). This implied that one HPF_6 had been spontaneously lost from two molecules of $[Rh(C_5Me_5)\{C_6H_4(OH)_2\}](PF_6)_2$.

When equimolar amounts of diol and Ib were allowed to react, in the presence of an excess of base, different products (IIIa or IIIb) were obtained in which one HPF_6 had been lost from each $[Rh(C_5Me_5)\{C_6H_4(OH)_2\}](PF_6)_2$. The third set of products (IVa or IVb) was obtained under these conditions when two equivalents of diol per Ib were used and showed the presence of an extra diol.

We formulate the complexes II—IV as shown (Scheme 1) on the following spectroscopic evidence (Table 2).

SCHEME 1.



Complexes IIa and IIb each show a medium intensity ν(OH) band at 3083 (or 3090) cm^{-1} in the infrared which is assigned to the terminal OH's of the

TABLE 1

YIELDS AND ANALYTICAL DATA (calculated values in patenthesis)

	Yield (%)	C (%)	H(%)
$[Rh_2(C_5Me_5)_2(HOC_6H_4O\cdots H\cdots OC_6H_4OH)](PF_6)_3$			
(IIa)	92	33.6 (34.0)	3.6 (3.5)
(IIb)	95	33.5	3.3
$[Rh(C_5Me_5)(\cdots OC_6H_4O\cdots H\cdots)]_n(PF_6)_n$			
(IIIa)	72	39.0 (39.0)	3.6 (4.1)
(IIIb)	64	39.4	4.0
$[Rh(C_5Me_5)(\cdots H\cdots OC_6H_4O\cdots H\cdots OC_6H_4O\cdots)]_n$			
(IVa)	73	57.7 (57.9)	5.7 (5.5)
(IVb)	67	57.5	5.2

complexed diol as well as a very broad medium intensity band at ca. 2500 cm^{-1} which we assign to a hydrogen bridge between the oxygens of two complexed $C_6H_4(OH)O$ ligands.

It is instructive to note that the initial product, $[Rh_2(C_5Me_5)_2$-

TABLE 2

^1H NMR (60 MHz) AND IR (Nujol) SPECTROSCOPIC DATA

	^1H NMR (δ)			IR (cm^{-1})		
	C_5Me_5	OC_6H_4O	OH	ν(OH)	ν(C=O)/ν(C=C)	ν(PF_6^-)
Hydroquinone^a	—	6.67(s)	7.60(s)	3250s(br)	1515s 1465vs	
Hydroquinone^b	—	6.81(s)	^{c}			
IIa^a	2.25	6.71(s)	4.04(s)	3083m 2470 2590m(br)	1577s 1503vs 1400m	840vs
IIa^b	2.05^d	5.87(s)^d	^{c}	2690		
IIIa^b	2.10	6.02(s)	^{c}	3080m 1580—800^f	1475s(br)	840vs
IVa^b	2.04^e	5.64(s)^e 6.98(s)^e	^{c}	2640 m(br) 2720	1565(sh) 1537s 1470vs	
Resorcinol^{a,b}	—	6.5(m, 3 H) 7.15(m, H)	^{c}	3200s(br)	1609vs, 1385m-s 1490vs, 1295m-s	
IIb^a	2.31	6.1—7.3(m)	^{c}	3090m 2500m (v. br.)	1574m-s 1548m-s 1490m(sh)	840vs
IIb^b	2.08	5.1—6.7(m)	^{c}			
IIIb^a	2.21	5.5—6.9(m)	3.66(s)	3092m 1580—900^f	1460s 1392s	840vs
IIIb^b	2.04	5.0—6.5(m)	^{c}			
IVb^b	2.04	7.2(m), 6.5(m) 5.5(m), 5.0(m)	^{c}	2590 m-s(br) 2650	1606m-w 1540vs(br) 1505vs(br)	

[a] In $(CD_3)_2CO$ relative to TMS. [b] In D_2O relative to $Me_3Si(CH_2)_3SO_3Na$. [c] Not observed; coincident with HOD solvent resonance. [d] Chemical shifts are concentration-dependent. [e] Intensity ratios: 15(C_5Me_5): 4($C_6H_4O_2$, complexed): 4($C_6H_4O_2$, free). [f] Broad envelope, see text.

$\{C_6H_5O{\cdots}H{\cdots}OC_6H_5\}](PF_6)_3$, from the reaction of phenol with Ia (M = Rh) in the absence of base was of precisely the same type [2]. Again here a broad ν(OH) was seen at 2350 cm^{-1}, and in addition that complex also showed a strong band at 1570 cm^{-1}, which compares with that at 1577 cm^{-1} for IIa. The resorcinol complex IIb also showed a medium intensity doublet (at 1574 and 1548 cm^{-1}) in this region.

While the positions of the aromatic H's in ^1H NMR spectrum of IIa in $(CD_3)_2CO$ were not very different from those of hydroquinone in this solvent, there was a marked shift (of ca. 1 ppm to higher field) in the spectrum of IIa in D_2O. This we suggest is evidence for a π-bonding of the hydroquinone ligand to the metal (see also below). The complexity of the spectra of the resorcinol complex IIb precluded detailed analysis; however, it is clear that in this complex there has also been a shift of the aromatic H's to higher field compared with those for resorcinol. Since all these complexes are rather insoluble in solvents other than water, it is probable that some change occurs on dissolution in water involving breaking of the $>CO{\cdots}H{\cdots}OC<$ bridges and, in this case, possibly also a deprotonation to form a species with a lower overall positive charge.

The analytical data of complexes II and III clearly indicate that loss of a further H^+ has taken place in the formation of III. The very low solubility of IIIa and IIIb, even in polar organic solvents, suggest a polymeric-ionic formulation as shown. The IR spectra in Nujol again show only a medium-intensity band due to ν(OH) (at 3080 and 3092 cm^{-1}), but do not show the broad bands at ca. 2500 cm^{-1} observed in II. However, the region from ca. 1500—800 cm^{-1} is very poorly resolved for these complexes and can best be described as consisting of medium-intensity bands (ν(CH), ν(CC) and ν(CO)) on top of a very broad, unresolved, and rather intense envelope of absorption. We tentatively suggest that this broad absorption arises from (O—H···O) bending modes [5].

The ^1H NMR spectra of both IIIa and IIIb again show the aromatic H's shifted to higher field by comparison with the free diols; presumably a breakdown of the polymeric ions again occurs in solution.

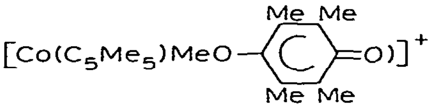
Final proof that the hydroquinone ligand in IIIa is π- and not *O*-bonded to the rhodium comes from the $^{13}C\{^1H\}$ NMR spectrum in D_2O. This shows the aromatic *C*H's as a doublet at δ 91.8 ppm [*J*(Rh—C) 6.1 Hz], in addition to the $C_5\mathit{Me}_5$ at δ 9.9 s ppm and the C_5Me_5 at 107.0 ppm [d, *J*(Rh—C) 9 Hz]. The low solubility prevented the observation of the aromatic *C*O's.

The ^1H NMR spectrum of complex IVa in D_2O shows three singlets at δ 2.04, 5.64 and 6.98 ppm in the ratio of 15/4/4 which we assign to the C_5Me_5, the complexed hydroquinone, and uncomplexed hydroquinone, respectively. Although the aromatic resonance at δ 5.64 ppm is most correctly described as a singlet, under optimum resolution it was possible to see some splitting (<1 Hz) which may be due to *J*(Rh—H). The ^1H NMR spectrum of complex IVb derived from resorcinol was again more complicated but it too showed two regions of absorption in the aromatic region (δ 5.0, 5.5 and 6.5, 7.2 ppm), which may be identical with the complexed and uncomplexed ligand.

Medium-strong broad absorptions in the 2500—2700 cm^{-1} region of the IR were again observed for IVa and IVb, which are identified as ν(O—H···O) hydrogen-bonding vibrations. In the region 1480—1610 cm^{-1}, which may be assigned to ν(CC) and ν(CO) [6], these complexes show features present both in the free diols and in II.

The hydrogen-bonded interaction between complexed and free $C_6H_4O_2$ ligands in IV has a precedent in the complex $[(OC)_3FeC_5H_4O\cdots H—OC_6H_4O—H\cdots OC_5H_4Fe(CO)_3]$, obtained from iron carbonyl and acetylene, which contains two cyclopentadienoneiron tricarbonyl groups hydrogen-bonded to a hydroquinone [7].

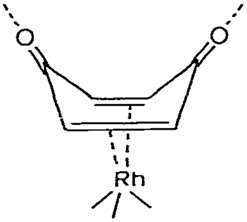
Complexes of tetrasubstituted *p*-benzoquinones in which the quinone is functioning as an η^4-1,4-diene to the metal are well-known [8—12]. *p*-Benzoquinone itself also functions as a ligand but relatively fewer complexes have been made with it; again, it usually prefers to bind as a 1,4-diene [13]. The only types of π-bonded hydroquinone complexes that appear to have been reported are those obtained in solution by protonation of $[M(C_5H_5)(Dqu)]$ (M = Co, Rh, or Ir; Dqu = duroquinone). In the ^{13}C NMR spectrum of the rhodium complex it has been shown that the carbonyl carbons of Dqu are coupled to rhodium in D_2SO_4 whereas no coupling is seen in $CDCl_3$ solution [14]. Conclusive evidence for a diprotonated species has very recently been obtained from the isolation of the diprotonated form of $[Co(C_5Me_5)(Dqu)]$ and from the monoprotonation in strong acid [15] of:



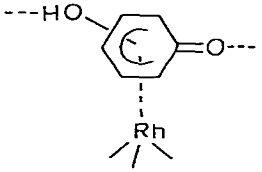
$[Co(C_5Me_5)MeO—C_6Me_4=O)]^+$

Such resorcinol complexes as have been reported apparently all contain the ligand *O*-bonded to the metal.

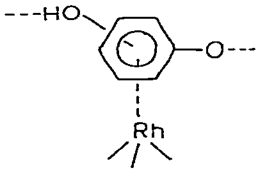
Given that the bonding of the ligands in complexes II—IV is via a π-interaction rather than through the oxygens, there appear to be three ways in which the bonding may be represented, 1,2 : 4,5-η^4 as in (A), 2-6-η^5- as in (B), and η^6- as in (C).



(A)



(B)



(C)

Since the complexes derived from hydroquinone so closely parallel those from resorcinol in their stoicheiometries and spectroscopic behaviour and since a structure analogous to A is not possible for a ligand based on a *meta*-disposition of the oxygens in a benzene ring, we can rule that structure out of consideration.

It is more difficult to decide between structures B and C and the IR evidence suggests that both forms may be present.

We favor form B for IIa and IIb since both show bands, at 1577, 1574 and 1548 cm^{-1} respectively, in the ν(C=O)/ν(C=C) region associated with hydrogen-bonded η^5-oxocyclohexadienyl or η^4-benzoquinone complexes (1536—1575 cm^{-1}) [2,9,15,16]. For similar reasons we favour the presence of form B in IVa and IVb. However, the spectra of IIIa and IIIb show no distinct peaks in this region, but only poorly defined weak to medium intensity shoulders at ca. 1560 cm^{-1}. Based on these spectroscopic data one would therefore be tempted to describe the bonding in complexes IIIa and IIIb in the solid state in terms of the η^6-bonded form C.

Preliminary data from the X-ray crystal structure determination of $[Co(\eta^5\text{-}C_5Me_5)(OC_6Me_4OH)]^+$ shows that the protonated duroquinone possesses a mirror plane perpendicular to the O···O vector and that the two oxygens appear to participate equally in the hydrogen-bonding [17]. This corresponds to a bonding situation between B and C above.

Experimental

All reactions were carried out under nitrogen. Microanalytical data, determined by the University of Sheffield Micronanalytical Laboratory, are collected in Table 1 together with the isolated yields of the complexes. NMR (60 MHz, Perkin—Elmer R-12B) and IR data are given in Table 2. Typical preparations of the complexes are given below.

$[Rh_2(C_5Me_5)_2(HOC_6H_4O\cdots H\cdots OC_6H_4OH)](PF_6)_3$ (II)

Quinol (or resorcinol) (101 mg, 0.92 mmol) was added to a solution of Ib (300 mg, 0.46 mmol) in acetone (10 cm^3). The resulting solution was stirred (18 h/20°C) and then the volume was reduced to ca. 5 cm^3. Diethyl ether was added to precipitate an oil which slowly solidified on stirring. This pale yellow solid (II) was filtered off, washed with ether and dried.

$[Rh(C_5Me_5)(\cdots OC_6H_4O\cdots H\cdots)]_n(PF_6)_n$ (III)

Quinol (or resorcinol) (51 mg, 0.46 mmol) was added to a solution of Ib (300 mg, 0.46 mmol). The resulting solution was stirred (2 h/20°C) and then an excess of triethylamine (0.3 cm^3, 2.2 mmol) was added. A pale yellow crystalline solid (III) began to precipitate, the formation of which was complete after a further 5 h stirring. It was then filtered off, washed with acetone and dried.

$[Rh(C_5Me_5)(\cdots H\cdots OC_6H_4O\cdots H\cdots OC_6H_4O\cdots)]_n$ (IV)

Quinol (or resorcinol) (101 mg, 0.92 mmol) was added to a solution of Ib (300 mg, 0.46 mmol) in acetone (10 cm^3). After 5 min stirring excess triethylamine (0.3 cm^3, 2.2 mmol) was added; this caused the precipitation of a pale yellow crystalline solid (IV), the formation of which was complete after a further 2 h stirring. The crystals were filtered off, washed with acetone and dried.

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