# Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 22.[1] Blue Five-co-ordinate Rhodium(III) Complexes derived from Catechol and Related Compounds

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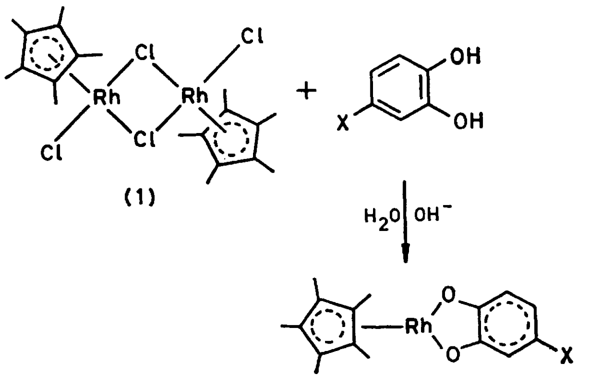
Reaction of $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_4]$ with 4-substituted catechols $4\text{-}XC_6H_3(OH)_2$ in aqueous base gives dark blue $[Rh(C_5Me_5)(4\text{-}XC_6H_3O_2)]\cdot H_2O$ (X = H, Cl, Me, or $Bu^t$). The crystal structure of the complex $[Rh(C_5Me_5)(C_6H_4O_2)]\cdot 2C_6H_4(OH)_2$ has been determined by *X*-ray diffractometry and shown to contain a $\eta^5$-pentamethylcyclopentadienylrhodium(III) *OO'*-bonded to the catecholato-ligand, which is itself further hydrogen-bonded to the two other catechols present in the lattice. The long C–O distances [av. 1.386(18) Å] indicate that the ligand is in the catecholato- and not in the *o*-quinonoid form and that the Rh is in the +III oxidation state. These catecholato-complexes show strong colours arising from ($\pi \rightarrow d$) ligand-to-metal charge-transfer bands; these bands are shifted to higher energy in more polar (better co-ordinating) solvents. The complexes also form adducts with phosphines; those with triphenylphosphine are labile and dissociate readily. $K_e$ for $[Rh(C_5Me_5)(4\text{-}XC_6H_3O_2)] + PPh_3 \rightleftharpoons [Rh(C_5Me_5)(4\text{-}XC_6H_3O_2)(PPh_3)]$ have been found to be $3.4 \times 10^3$ (X = H), $1.6 \times 10^3$ (X = Me), and $2.45 \times 10^4$ dm$^3$ mol$^{-1}$ (X = Cl) in $CH_2Cl_2$ solution. The preparation and properties of $[Rh(C_5Me_5)\{o\text{-}C_6H_4(NH)Y\}]$ (Y = O or NH) derived from *o*-aminophenol or *o*-phenylenediamine are also reported.

WE recently described the reactions of phenol with $[M(\eta^5\text{-}C_5Me_5)(solvent)_3]^{2+}$ (M = Rh or Ir) to give complexes containing $\eta^6$-phenol and $\eta^5$-oxocyclohexadienyl ligands [2] and we have now extended this work to dihydroxybenzenes and related compounds. π-Bonded rhodium complexes were obtained from resorcinol and quinol and will be described elsewhere [3] and we here report reactions with catechol, *o*-aminophenol, and *o*-phenylenediamine.

## RESULTS AND DISCUSSION

*Structure of* $[Rh(C_5Me_5)(C_6H_4O_2)]$ *and Related Complexes.*—Although catechol reacted easily with $[Rh(C_5Me_5)(MeCN)_3]^{2+}$ (ref. 4) under a variety of conditions, the products were very complex and have not yet been characterised. However, catechol reacted directly with $[Rh_2(C_5Me_5)_2Cl_4]$ (1) in aqueous base to give an immediate dark blue precipitate of $[Rh(C_5Me_5)(C_6H_4O_2)]\cdot H_2O$ (2). Since the complex was not very soluble spectroscopic investigations were difficult and in order to elucidate the structure of the compound and the reason for its remarkable colour an *X*-ray determination was carried out.



(1)

(2) X = H
(3) X = Me
(4) X = $Bu^t$
(5) X = Cl

The crystal for the determination was selected from a batch obtained by mixing very dilute solutions of catechol and (1) and allowing slow crystallisation to take place; the stoicheiometry of the product (2a) was rather different from that of (2) and the crystal structure revealed the presence of two catechol molecules of solvation linked by hydrogen bonds to the oxygens of the catecholatorhodium moiety (Figure 1). We suggest that these extra catechols are needed to stabilise the crystal lattice and that (2) and the other complexes in this series have the same basic $[Rh(C_5Me_5)(C_6H_4O_2)]$ unit but that the water, which analytical and spectroscopic data (Tables 1 and 2) show to be present, plays a similar role to that of the catechols in (2a) by stabilising the lattice through hydrogen bonding.

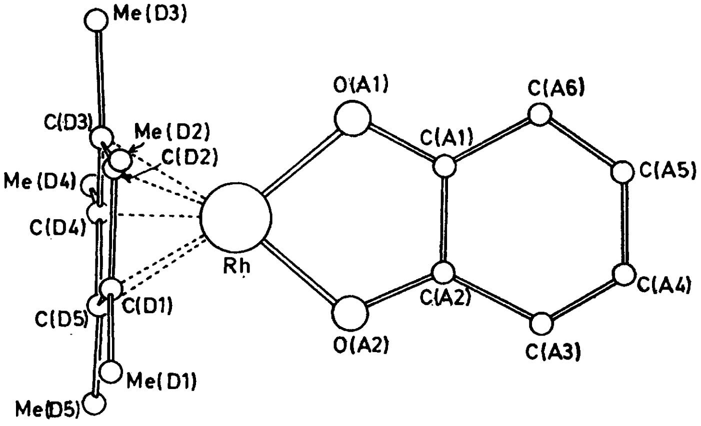


FIGURE 1 View of the $[Rh(\eta^5\text{-}C_5Me_5)(C_6H_4O_2)]$ moiety of complex (2a), projected onto the catechol plane

The structure of the $[Rh(C_5Me_5)(C_6H_4O_2)]$ unit in the crystal of (2a) is shown in Figure 2. The $\eta^5$-$C_5Me_5$ plane is inclined at 81° to the plane containing the $Rh(C_6H_4O_2)$ group, and the rhodium is *OO'*-bonded to the cate-

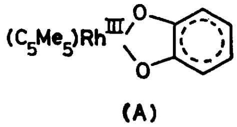
TABLE 1

Yields and analytical data (calculated values in parentheses)

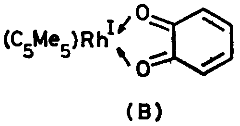
| | Complex | Yield (%) | Colour | Analysis (%) C | H | Other |
|---|---|---|---|---|---|---|
| (2) | $[Rh(C_5Me_5)(o\text{-}C_6H_4O_2)]\cdot H_2O$ | 83 | Violet-blue | 53.2 (52.8) | 5.2 (5.8) | |
| (2a) | $[Rh(C_5Me_5)(o\text{-}C_6H_4O_2)]\cdot 2o\text{-}C_6H_4(OH)_2$ | | Violet-blue | 59.2 (59.4) | 5.5 (5.5) | |
| (3) | $[Rh(C_5Me_5)(4\text{-}MeC_6H_3O_2)]\cdot H_2O$ | 75 | Violet-blue | 53.7 (54.0) | 5.5 (6.1) | |
| (4) | $[Rh(C_5Me_5)(4\text{-}Bu^tC_6H_3O_2)]\cdot H_2O$ | 39 | Dark blue | 56.9 (57.2) | 6.8 (7.0) | |
| (5) | $[Rh(C_5Me_5)(4\text{-}ClC_6H_3O_2)]\cdot H_2O$ | 73 | Violet | 48.1 (48.2) | 4.37 (5.1) | Cl 9.1 (8.9) |
| (6) | $[Rh(C_5Me_5)(C_6H_4O_2)(PPh_3)]\cdot H_2O$ | 81 | Dark green | 65.2 (65.2) | 5.4 (5.8) | |
| (7) | $[Rh(C_5Me_5)(C_6H_4O_2)(PEt_3)]\cdot H_2O$ | 82 | Brown | 54.5 (54.8) | 7.6 (7.5) | |
| (8) | $[Rh(C_5Me_5)(C_6H_4O_2)(8\text{-}HOC_9H_6N)]$ | 90 | Orange-yellow | 61.2 (61.1) | 5.4 (5.5) | N 2.8 (2.9) |
| (9) | $[Rh(C_5Me_5)(4\text{-}MeC_6H_3O_2)(PPh_3)]\cdot H_2O$ | 84 | Brown | 65.6 (66.2) | 6.0 (5.8) | |
| (10) | $[Rh(C_5Me_5)(4\text{-}ClC_6H_3O_2)(PPh_3)]\cdot H_2O$ | 78 | Brown | 62.6 (61.8) | 5.5 (5.3) | Cl 5.4 (5.4) |
| (11) | $[Rh(C_5Me_5)\{o\text{-}C_6H_4NH(O)\}]$ | 87 | Red-violet | 55.5 (55.7) | 5.4 (5.8) | N 4.3 (4.1) |
| (12) | $[Rh(C_5Me_5)\{o\text{-}C_6H_4(NH)_2\}]$ | 86 | Carmine | 55.7 (55.8) | 6.4 (6.2) | N 8.0 (8.1)<br>*M* 354 * (344) |

* Osmometric molecular weight in chloroform.

cholato-ligand. Examination of the data in Table 3 clearly shows the metal to be in the +III oxidation state and that a correct description of the bonding is given by (A) rather than (B). This can be seen from the C–O bond lengths [average 1.387(18) Å] which are close to those in catechol itself [1.371(4) Å] [5] and are very much longer than those in *o*-benzoquinone [1.220(2) Å].[6] A number of *X*-ray structure determinations of substituted (often tetrachloro-) catecholatometal complexes have been carried out. They show shorter C–O bonds {1.28 (1) Å in $[Cr(C_6Cl_4O_2)_3]$,[7] 1.31(1) Å in $[Mo_2O_5(C_{14}H_8O_2)_2]$,[8] 1.33 and 1.36(1) Å in $[Mo_2(C_6Cl_4O_2)_6]$,[9] and 1.34(1) Å in $[Pd(C_6Cl_4O_2)(PPh_3)_2]$ [10]} than in (2a) but even these are generally still closer to the catecholato- than to the *o*-quinonoid form. It is also noteworthy that, as expected, the Rh–O bonds [average 2.011(10) Å] are significantly shorter than those in the dimeric complex $[Rh_2(C_5Me_5)_2(acac)_2]^{2+}$ where the acac (pentane-2,4-dionato) ligands are *OO'*-bonded to one rhodium and *C*-bonded to the other [Rh–O 2.102(2), C–O 1.256(7) Å].[1]



**(A)**



**(B)**

TABLE 2

$^1H$ N.m.r. spectra (δ, at 60 MHz in $[^2H_6]$acetone)

| Complex | $C_5Me_5$ [a] | $H_2O$ [a] | Aromatic H [b] | Others |
|---|---|---|---|---|
| (2) | 1.96 | 2.77 | 6.65 | |
| (2) [c] | 1.95(br s) | 1.67 | 6.8 | |
| (3) | 1.91 | 2.75 | 6.5 | 2.14 (s, Me) |
| (4) | 2.00 | 2.85 | 6.93 | 1.26 (s, $Bu^t$) |
| (5) | 1.94 | 2.80 | 6.65 | |
| (5) [c] | 1.94(br s) | 1.73 | 6.7 | |
| (6) | 1.44 | 2.81 | *d* | 7.42 (m, $PPh_3$) |
| (6) [c] | 1.40 | 1.88 | 6.27 | 7.4 (m, $PPh_3$) |
| (7) | 1.62 [d, *J*(H–P) = 3 Hz] | 3.05 | 6.45 | 1.05, 1.78 (2 × m, $PEt_3$) |
| (7) [c] | 1.52 [d, *J*(H–P) = 3 Hz] | 3.25 | 6.55 | 1.07, 1.8 (2 × m, $PEt_3$) |
| (9) | 1.49 | 2.81 | *d* | 7.4 (m, $PPh_3$) |
| (9) [c] | 1.41 | n.o. | 6.17 | 7.35 (m, $PPh_3$) |
| (10) | 1.40 | 2.77 | *d* | 7.37 (m, $PPh_3$) |
| (10) [c] | 1.38 | 1.81 | 6.15 | 7.33 (m, $PPh_3$) |
| (11) [c] | 2.02 | 6.8 | | |
| (12) [c] | 2.07 | 6.82 | | |

n.o. = Not observed.

[a] Singlet, unless otherwise specified. [b] The aromatic hydrogens on the catechol ring were always seen as a broad multiplet. [c] In $[^2H]$chloroform; the complexes decompose at varying rates in this solvent, (3) and (4) reacting immediately. [d] Catechol hydrogens not observed owing to low solubility.

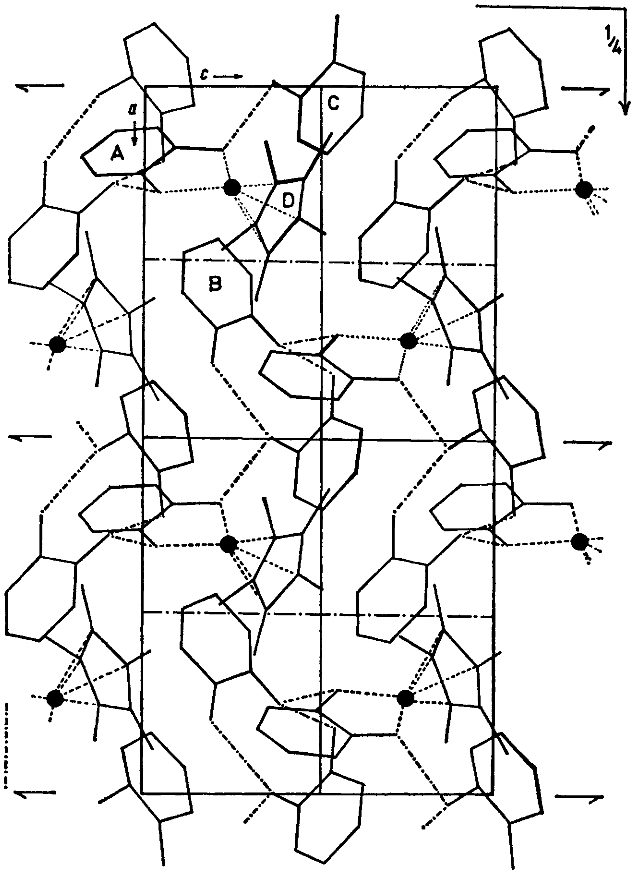


FIGURE 2 The arrangement of molecules of $[Rh(\eta^5\text{-}C_5Me_5)(C_6H_4O_2)]\cdot 2C_6H_4(OH)_2$ in the crystal lattice viewed along the *b* axis, and showing the hydrogen-bonding scheme (— · — · —)

As depicted in Figure 2 the effective co-ordination number of the rhodium(III) is five if the $\eta^5\text{-}C_5Me_5$ ligand is, as usual, regarded as a tridentate ligand. Apart from the $C_5Me_5$ carbons and the two oxygens of the one

TABLE 3

Bond lengths (Å) and angles (°) for $[Rh(\eta^5\text{-}C_5Me_5)(C_6H_4O_2)]\cdot 2o\text{-}C_6H_4(OH)_2$ (estimated standard deviations in parentheses)

| | | | |
|---|---|---|---|
| Rh–O(A1) | 2.024(11) | O(A1)–Rh–O(A2) | 81.0(4) |
| Rh–O(A2) | 1.998(10) | Rh–O(A1)–C(A1) | 112.8(9) |
| Rh ··· O(B1) | 4.09(1) | Rh–O(A2)–C(A2) | 114.0(8) |
| Rh ··· O(C1) | 4.99(1) | O(A1)–C(A1)–C(A2) | 115(1) |
| Rh ··· O(C2) | 4.09(1) | O(A2)–C(A2)–C(A1) | 116(1) |
| Rh–C(D1) | 2.130(15) | O(A1)–Rh–C(D3) | 105.2(5) |
| Rh–C(D2) | 2.133(16) | O(A1)–Rh–C(D5) | 163.8(5) |
| Rh–C(D3) | 2.183(16) | O(A2)–Rh–C(D3) | 173.3(5) |
| Rh–C(D4) | 2.153(17) | O(A2)–Rh–C(D5) | 106.8(5) |
| Rh–C(D5) | 2.170(16) | | |
| O(A1)–C(A1) | 1.398(17) | C(A6)–C(A1) | 1.400(22) |
| O(A2)–C(A2) | 1.375(18) | C(D1)–C(D2) | 1.487(22) |
| C(A1)–C(A2) | 1.403(21) | C(D2)–C(D3) | 1.438(23) |
| C(A2)–C(A3) | 1.405(23) | C(D3)–C(D4) | 1.469(23) |
| C(A3)–C(A4) | 1.361(24) | C(D4)–C(D5) | 1.465(23) |
| C(A4)–C(A5) | 1.394(24) | C(D5)–C(D1) | 1.419(22) |
| C(A5)–C(A6) | 1.386(24) | | |

Unco-ordinated catechol ring B mean distances: C–C 1.40(3), C–O 1.36(2).

Unco-ordinated catechol ring C mean distances: C–C 1.39(3), C–O 1.38(2)

Hydrogen-bonding interactions

| | | | |
|---|---|---|---|
| O(A1) ··· O(B1) | 2.592(15) | O(B1) ··· O(C1) * | 2.920(17) |
| O(A2) ··· O(C2) | 2.572(15) | O(B2) ··· O(C2) * | 2.783(18) |

* $-x, -y, z - \frac{1}{2}$.

Equations of planes:

Plane defined by C(D1)C(D2)C(D3)C(D4)C(D5)Me(D1)Me(D2)Me(D3)Me(D4)Me(D5)

$$-0.3602X + 0.5118Y - 0.7792Z = -4.545†$$

Plane defined by RhO(A1)O(A2)C(A1)C(A2)C(A3)C(A4)C(A5)C(A6)

$$-0.8467X - 0.5109Y - 0.1489Z = -2.933†$$

Angle of inclination between the planes: 80.8°.

† *X*, *Y*, and *Z* are co-ordinates in Å referred to the axes *a*, *b*, and *c*.

catechol (A) there are no other atoms within bonding distance; the closest approach is by three oxygens of two non-bonded catechols (B and C) which are at 4.09, 4.09, and 4.99 Å respectively to the metal (Table 3).

TABLE 4

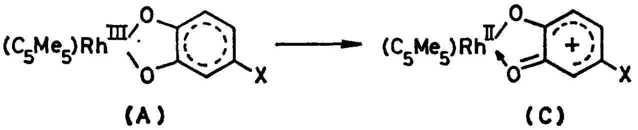
Visible spectra ($\lambda_{max.}$/nm)

| | Solvent | | | | | |
|---|---|---|---|---|---|---|
| | $C_6H_6$ | PhCl | $PhNO_2$ | $Me_2CO$ | $MeNO_2$ | $H_2O$ |
| $E_T$ values [a] | 34.5 | 37.5 | 42.0 | 42.2 | 46.3 | 63.1 |
| Complex | | | | | | |
| $[Rh(C_5Me_5)(4\text{-}XC_6H_3O_2)]\cdot H_2O$ | | | | | | |
| (5) X = Cl | 587 | 575 | 563 | 556 | 540 | 488 |
| (2) H | 594 [b] | 580 | 570 | 565 | 547 | 487 |
| (3) Me | 612 | 600 | 585 | 580 | 569 | 510 |
| (4) $Bu^t$ | 618 | 604 | 592 | 588 | 568 | *ca.* 502 |
| (11) $[Rh(C_5Me_5)\{C_6H_4NH(O)\}]$ | 565 | 563 | 560 | 557 | 547 | *c* |
| (12) $[Rh(C_5Me_5)\{C_6H_4(NH)_2\}]$ | 534 | 532 | 530 | 525 | 523 | *c* |

[a] $E_T$ values give a spectroscopic measure of the polarity of the solvent. See ref. 10. [b] $\varepsilon$ = *ca.* 11 500 dm³ mol⁻¹ cm⁻¹; all the complexes decompose in solution at varying rates and meaningful absorption coefficients are difficult to obtain. [c] Insoluble in water.

The 4-methyl-, 4-t-butyl-, and 4-chloro-catechols reacted similarly with (1) to give the complexes $[Rh(C_5Me_5)(4\text{-}XC_6H_4O)]\cdot H_2O$ [X = Me (3), $Bu^t$ (4), or Cl (5)] (Table 1). All these compounds crystallised with one equivalent of water, which was observed in the $^1H$ n.m.r. spectra (in particular in [$^2H$]chloroform solution, Table 2), and in the i.r. as broad bands at *ca.* 3 400 cm$^{-1}$ (variable intensity) and at 1 620—1 650w cm$^{-1}$. We also assign bands in the i.r. between 1 305 and 1 312m cm$^{-1}$ and at around 1 270m—s cm$^{-1}$ to ν(CO).

*Visible Spectra.*—The strong violet-blue colours of these compounds arise from ***ligand-to-metal*** charge-transfer (l.m.c.t.) bands in the visible spectrum (Table 4). This is indicated by a shift of this band to higher energy (in a given solvent) on going to more electronegative substituents.* The l.m.c.t. band is most easily understood in terms of a π→d excitation (A→C) wherein the rhodium is formally reduced to $Rh^{II}$. According to this representation the electron which is transferred to Rh comes from a π-molecular orbital of the catecholato-ligand; when X is an electron-releasing substituent ($Bu^t$, Me) the excited state (C) is stabilised and its energy is decreased causing the l.m.c.t. band to come at lower energies.



**(A)** **(C)**

A characteristic of complexes exhibiting charge-transfer bands is the effect of solvent polarity on the position (energy) of the band.[11] We have observed such an effect in complexes (2)—(5); in solvents of increasing polarity (as defined by the $E_T$ scale[12]) the bands move to progressively higher energies (Table 4 and Figure 3) and the complexes become lighter in colour. If the effect of the solvent were only to stabilise the dipolar excited state form (C) then one would expect the reverse phenomenon, a decrease in the l.m.c.t. band energy in solvents of increasing polarity. We therefore suggest that the effect of the more polar solvents is to co-ordinate more to the metal and to increase the co-ordination number of the rhodium from five in the unsolvated species to six.

Water must play a dual role here; particularly in the solids, but also in non-hydroxylic solvents, the water

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* The energy of this band decreased in the order 4-Cl > H > 4-Me > 4-$Bu^t$; however, the values for aqueous solutions are only approximate since very rapid decomposition occurs there.

of crystallisation is engaged in hydrogen bonding to the catecholato-oxygens. This is indicated by the very dark colours of both the solids and solutions in non-hydroxylic solvents. However, in water as solvent the colour rapidly fades implying that further water molecules now enter the co-ordination sphere of the metal as hydrolysis proceeds.

*Phosphine Adducts.*—We have also isolated adducts (6), (7), (9), and (10) of complexes (2), (3), and (5) with tertiary phosphines and [in one case, (8)] with 8-hydroxyquinoline. All these adducts, except (8), contain one molecule of water; this confirms that the water in (2)—(5) is hydrogen-bonded and not co-ordinated to the metal. The adduct (8) does not contain water and we presume that the 8-hydroxyquinoline is *N*-bonded to Rh and that the 8-hydroxy-group takes part in hydrogen bonding to the catecholato-oxygens. It may also be noted that pyridine does not form stable adducts with these catecholato-complexes.

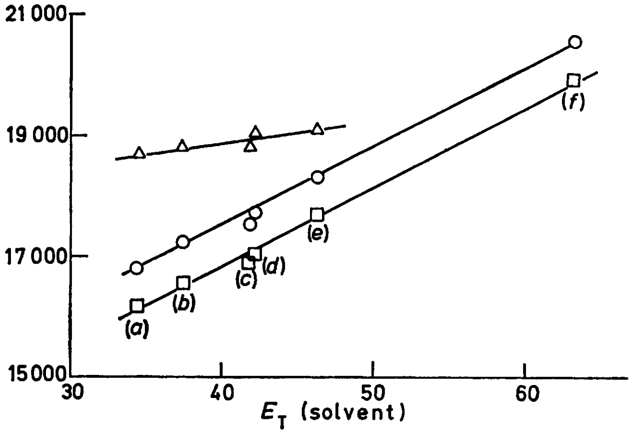
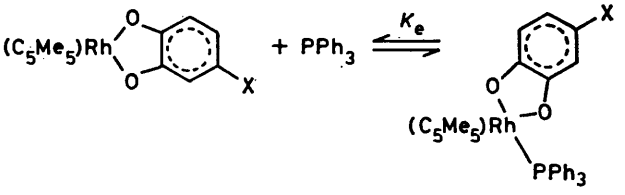


FIGURE 3 Variation of visible ($\pi \rightarrow d$) band maxima with solvent $E_T$ values for (○) [Rh(C$_5$Me$_5$)(C$_6$H$_4$O$_2$)]·H$_2$O (2), (□) [Rh(C$_5$Me$_5$)(4-Bu$^t$C$_6$H$_3$O$_2$)]·H$_2$O (4), and (△) [Rh(C$_5$Me$_5$){C$_6$H$_4$(NH)$_2$}] (12). Solvents: (*a*) benzene, (*b*) chlorobenzene, (*c*) nitrobenzene, (*d*) acetone, (*e*) nitromethane, and (*f*) water (see also Table 4)

The colours of the adducts are much lighter (brown, orange, yellow) and this is again consistent with the charge-transfer band coming at very much higher energies, both here and in solutions of (2)—(5) in co-ordinating solvents. This is not unexpected since the change in geometry, from five-co-ordinate in (2)—(5) to six-co-ordinate in the adducts (the most normal geometry for complexes of $d^6$ metals) by the entry of another ligand into the co-ordination sphere of the metal, may be expected to raise the energies of the rhodium–ligand antibonding ($\sigma^*$) orbitals. Since one of these is the orbital to which the l.m.c.t. occurs the energy of the transition will be expected to increase.

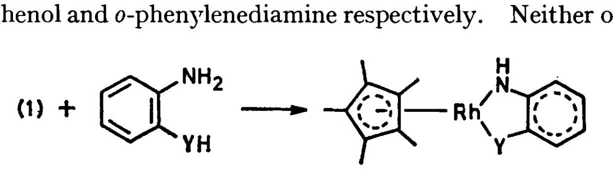
The triethylphosphine adduct (7) appears to be relatively inert; however, the triphenylphosphine adducts (6), (9), and (10) are labile to varying degrees. This is shown by the observation of coupling of the C$_5$Me$_5$ hydrogens to $^{31}$P in the n.m.r. spectrum of the triethylphosphine complex (7) (Table 2) and by its absence in complexes (6), (9), and (10). Furthermore, in these latter compounds the positions of the C$_5$Me$_5$ singlet resonances depend on the amount of PPh$_3$ present. This points to the existence of a dynamic equilibrium:



(6) X = H
(9) X = Me
(10) X = Cl

The equilibrium constants $K_e$ in dichloromethane solution have been determined (from the $^1$H n.m.r. spectra, at 34 °C) to be $3.4 \times 10^3$ (X = H), $1.6 \times 10^3$ (X = Me), and $2.45 \times 10^4$ dm$^3$ mol$^{-1}$ (X = Cl). This shows that, as expected, the stability of the PPh$_3$ adducts increases with increasing electronegativity of the X substituent. The stability of the adducts presumably depends on both steric and electronic factors and we suggest that triethylphosphine forms a more stable adduct because of its smaller size;[13] we have elsewhere noted that because of its size PPh$_3$ is rather limited in its versatility as a ligand to Rh(C$_5$Me$_5$) complexes.[14]

[Rh(C$_5$Me$_5$){C$_6$H$_4$O(NH)}] *and* [Rh(C$_5$Me$_5$){C$_6$H$_4$(NH)$_2$}] *Complexes.*—To complete the series we have also synthesised the complexes (11) and (12) from *o*-aminophenol and *o*-phenylenediamine respectively. Neither of these compounds crystallised with lattice water and they are also significantly more stable and less reactive than the catecholato-complexes. For example, neither forms adducts with phosphines; furthermore although they also have l.m.c.t. bands in their visible spectra, these show only small increases in energy on going to more polar solvents (Table 4). In less polar solvents the l.m.c.t. bands exhibit a regular progression in $\lambda_{max.}$, (2) > (11) > (12), and this effect may result from either a destabilisation of the excited state or a stabilisation of the ground state on replacing O by NH as the ligating atom. The observation that the complexes with one or two NH donor groups are reluctant to form adducts indicates that the NH is a better ligand to the rhodium and forms a stronger bond. This would imply that the ground states of these molecules are significantly stabilised on replacing O by NH.



(11) Y = O
(12) Y = NH

It is also instructive to compare these complexes to the toluene-3,4-dithiolato-analogue $[Rh_2(C_5Me_5)_2(4\text{-}MeC_6H_4S_2)_2]$;[15] the complex is again best described as having the metal in the (III) oxidation state but the high tendency for sulphur to become three-co-ordinate by binding to another metal makes the complex dimeric.

The syntheses of the complexes described in this paper. from a rhodium(III) chloride and the *o*-difunctional benzene in aqueous base, provides a versatile alternative to the one described by Sohn and Balch[16] in which *o*-benzoquinones were oxidatively added to rhodium- or iridium-(I) complexes of the type $[M(PR_3)_2(CO)Cl]$.

## EXPERIMENTAL

Microanalytical data (Table 1) were obtained by the University of Sheffield Microanalytical service; 60-MHz n.m.r. spectra (Table 2) were measured on a Perkin-Elmer R-12B spectrometer. All reactions were carried out under an atmosphere of nitrogen. Yields are given in Table 1; since the complexes were appreciably labile, recrystallisation did not in general result in purer materials and analytical and spectroscopic measurements indicated that the complexes were pure when prepared as described. Visible spectra (Table 4) were recorded on a Perkin-Elmer 137 spectrometer. In the more polar solvents reaction with solvent occurred; this had the effect of decreasing the intensity of the charge-transfer band and the solutions slowly discoloured.

$[Rh(C_5Me_5)(C_6H_4O_2)]\cdot H_2O$ (2).—Catechol (89 mg, 0.8 mmol) was added in small portions to a solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (250 mg, 0.4 mmol) and sodium carbonate (250 mg) in deoxygenated water (30 cm$^3$) with vigorous stirring. The solution changed colour rapidly from yellow to red and a very dark blue solid precipitated. The precipitate was filtered off after 1 h, washed with water (2 × 10 cm$^3$), and dried *in vacuo*.

The complexes (3)—(5) were prepared in the same way from complex (1) and the appropriate catechol, except that 4-t-butylcatechol was dissolved in acetone (2 cm$^3$) prior to addition. The reaction of (1) with *o*-phenylenediamine to give (12) was stirred for 5 h. Complex (11) was prepared analogously by adding a solution of (1) and sodium carbonate to one containing *o*-aminophenol dissolved in hot water.

X-*Ray Crystal-structure Determination of* $[Rh(C_5Me_5)(C_6H_4O_2)]\cdot 2C_6H_4(OH)_2$ (2a).—A crystal of (2a) was selected from a sample obtained by allowing a very dilute aqueous solution of complex (1), sodium carbonate, and catechol to crystallise over 3 weeks at 20 °C under $N_2$.

*Crystal data.* $C_{28}H_{31}O_6Rh$, $M = 566.46$, Orthorhombic, $a = 20.309(8)$, $b = 12.797(5)$, $c = 10.115(7)$ Å, $U = 2\,628.83$ Å$^3$, $Z = 4$, $D_c = 1.431$ g cm$^{-3}$, $F(000) = 1\,168$, space group $Pna2_1$ ($C_{2v}^9$ No. 33), crystal size 0.040 × 0.014 × 0.018 cm, $\mu = 6.75$ cm$^{-1}$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å. The unit-cell constants were determined from a least-squares fit to the setting angles of 112 reflections centred manually on the diffractometer.

TABLE 5

Atomic co-ordinates (× $10^4$, except Rh × $10^5$) for $[Rh(\eta^5\text{-}C_5Me_5)(C_6H_4O_2)]\cdot 2o\text{-}C_6H_4(OH)_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Rh | 14 085(5) | 3 925(8) | 25 265(30) |
| O(A1) | 1 465(5) | 419(9) | 530(10) |
| O(A2) | 860(5) | 1 658(8) | 2 180(9) |
| C(A1) | 1 182(7) | 1 314(11) | −21(14) |
| C(A2) | 848(7) | 1 961(12) | 876(15) |
| C(A3) | 560(8) | 2 891(13) | 416(19) |
| C(A4) | 612(8) | 3 156(13) | −882(18) |
| C(A5) | 941(8) | 2 507(14) | −1 770(17) |
| C(A6) | 1 221(9) | 1 574(13) | −1 363(16) |
| O(B1) | 1 352(6) | −1 213(9) | −971(11) |
| O(B2) | 1 145(7) | −2 613(10) | −2 970(12) |
| C(B1) | 1 821(8) | −1 288(13) | −1 908(17) |
| C(B2) | 1 712(8) | −2 033(13) | −2 929(16) |
| C(B3) | 2 180(10) | −2 178(17) | −3 907(20) |
| C(B4) | 2 749(10) | −1 566(19) | −3 891(22) |
| C(B5) | 2 870(9) | −765(18) | −2 914(21) |
| C(B6) | 2 386(9) | −668(15) | −1 900(20) |
| O(C1) | −931(6) | 3 071(10) | 5 477(13) |
| O(C2) | −55(6) | 2 392(10) | 3 673(12) |
| C(C1) | −317(8) | 3 552(12) | 5 410(17) |
| C(C2) | 140(8) | 3 221(12) | 4 439(16) |
| C(C3) | 735(9) | 3 696(15) | 4 360(19) |
| C(C4) | 897(10) | 4 532(16) | 5 177(21) |
| C(C5) | 439(10) | 4 866(14) | 6 123(21) |
| C(C6) | −170(9) | 4 365(13) | 6 230(18) |
| C(D1) | 1 823(8) | 504(12) | 4 455(15) |
| C(D2) | 2 277(8) | −71(12) | 3 559(15) |
| C(D3) | 1 949(8) | −1 005(13) | 3 125(16) |
| C(D4) | 1 288(8) | −989(13) | 3 716(16) |
| C(D5) | 1 225(8) | −63(13) | 4 560(15) |
| Me(D1) | 1 944(11) | 1 510(14) | 5 184(21) |
| Me(D2) | 2 980(8) | 230(14) | 3 201(20) |
| Me(D3) | 2 225(9) | −1 832(13) | 2 215(17) |
| Me(D4) | 762(10) | −1 843(15) | 3 513(22) |
| Me(D5) | 622(9) | 186(16) | 5 382(19) |

Three-dimensional *X*-ray data were collected with the crystal mounted along the *c* axis using a Stoe STADI-2 diffractometer in the stationary-counter–moving-crystal mode. Variable-width scans were measured with a background count at each end of the scan. Reflections with background counts differing by more than $4\sigma_B$ were rejected, as were those with $I_o < 3\sigma(I_o)$. A total of 1 929 independent reflections in the range $6.5 < 2\theta \leqslant 50°$ were corrected for Lorentz and polarisation factors; no allowance was made for absorption or extinction.

The position of the rhodium atom was obtained from a Patterson function; the subsequent Fourier synthesis indicated that the molecule did not include a crystallographic mirror plane, *i.e.* that the space group is $Pna2_1$ not *Pnma*, and this was confirmed by the subsequent refinement. The remaining non-hydrogen atoms were obtained from a series of structure-factor calculations and Fourier syntheses. Block-diagonal least-squares refinement of the atomic co-ordinates and anisotropic thermal parameters reduced *R* to 0.046. Atomic scattering factors were taken from ref. 17; calculations were performed on the Sheffield University ICL 1906 S computer using programs from the Sheffield *X*-ray system.

A diagram of the structure of the $[Rh(C_5Me_5)(C_6H_4O_2)]$ complex is given in Figure 2 together with the atom labelling. Figure 1 shows the packing in the unit cell projected down the *b* axis, and includes the hydrogen-bonding scheme. Significant bond lengths and angles are collected in Table 3. Table 5 lists the atomic co-ordinates. Tables of observed and calculated structure factors, anisotropic thermal parameters, and complete bond-length and -angle data for the structure are listed as Supplementary Publication No. SUP 22587 (38 pp.).*

$[Rh(C_5Me_5)(o\text{-}C_6H_4O_2)(PPh_3)]\cdot H_2O$ (6).—Triphenylphosphine (350 mg, 1.34 mmol) was added to a suspension of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

complex (2) (124 mg, 0.34 mmol) in deoxygenated toluene (40 $cm^3$); complex (2) dissolved and the solution turned dark green. The solution was stirred for 2 h (20 °C), then filtered, and the filtrate evaporated *in vacuo* to 3 $cm^3$; diethyl ether (30 $cm^3$) was added to dissolve the excess of $PPh_3$ and to precipitate the green complex (6). This was filtered off, washed with more ether, and dried. The same procedure was used to prepare complexes (9) and (10) and also the triethylphosphine complex (7) except that in this case light petroleum (b.p. 40—60 °C) was used to precipitate and wash the product.

Equilibrium constants for the dissociation of the triphenylphosphine complexes (6), (9), and (10) in dichloromethane were determined from the $^1H$ n.m.r. spectra. Solutions (*ca.* $10^{-4}$ mol $dm^{-3}$) of these complexes all showed a single $C_5Me_5$ resonance the position of which varied with the amount of free $PPh_3$ present. The limiting chemical shifts were taken as that of pure (2) [or (3) or (5)] and that of a solution of (6) [or (9) or (10)] containing sufficient excess of $PPh_3$ such that addition of more $PPh_3$ caused no further detectable shift in the $C_5Me_5$ resonance.

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