Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 31.[1] Tri-μ-phenoxo-rhodium Complexes and a Facile H/D Exchange Reaction

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$[\{Rh(C_5Me_5)\}_2(OH)_3][PF_6]$ reacts with phenol to give $[\{Rh(C_5Me_5)\}_2(OPh)_3][PF_6]$ (3), containing three μ-phenoxo-ligands. The related complexes $[\{Rh(C_5Me_5)\}_2(OH)_3]X$ (X = Cl or OH) react with phenol to give $[\{Rh(C_5Me_5)(OPh)_2(PhOH)_2\}_n]$ which is formulated as the tri-μ-phenoxo-complex $[\{Rh(C_5Me_5)\}_2(OPh)_3]$-$[(PhO)_5H_4]$ (4), largely on the basis of the ^{13}C n.m.r. spectra. The methyl hydrogens in (4) [but not in (3)] exchange very rapidly for deuterium in $[^2H_6]$acetone solution.

WE have previously found that although the tri-μ-hydroxo-dirhodium complexes (1) [and their iridium analogues] are easily obtained and stable,[2,3] all attempts to isolate their μ-alkoxo-analogues have failed. We believe this to be not because they do not form readily but because they decompose easily, in many cases to give μ-hydrido-complexes.[4] By contrast, the tri-μ-hydroxo-bis(benzeneruthenium) cation (2) readily forms the tri-μ-ethoxo- and -methoxo-complexes in ethanol and methanol

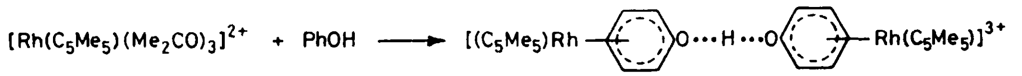
$$\underset{(2)}{[\{Ru(\eta^6\text{-}C_6H_6)\}_2(OH)_3]^+} + ROH \longrightarrow [\{Ru(\eta^6\text{-}C_6H_6)\}_2(OR)_3]^+ \quad (1)$$

respectively,[5] equation (1). Presumably, the hydrogen transfer to the metal does not occur quite as easily here as for the pentamethylcyclopentadienyl-rhodium or -iridium systems.

We have now found that phenol reacts readily with (1) to form tri-μ-phenoxo-rhodium complexes; these complexes are easily isolated and, because they have no hydrogens that are readily lost to the metal, they are quite stable.

RESULTS AND DISCUSSION

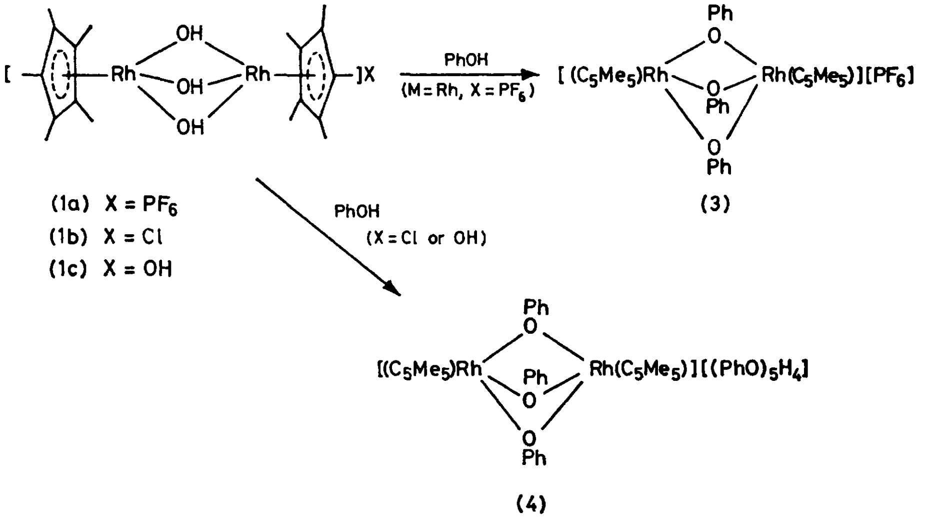
μ-Phenoxo-complexes.—The tri-μ-hydroxo-rhodium hexafluorophosphate complex (1a) reacted with an aqueous solution of phenol to give a phenoxo-hexafluorophosphate complex (3). Analytical and spectroscopic data agreed with a formulation in which 1.5 phenoxo-groups per $Rh(C_5Me_5)$ were incorporated into the molecule. The complex (3) showed four singlet resonances in the aromatic region of the ^{13}C n.m.r. spectrum due to the *o*-, *m*-, *p*-, and *i*-carbons. The absence of any doublets arising from coupling to ^{103}Rh ($I = \frac{1}{2}$, 100%) indicates that the ring carbons of the phenoxo-ligand are not directly bonded (π or σ) to the metal, and therefore the ligands must be O-bonded. The dinuclear structure (3) then follows unambiguously.



(2)

This bonding pattern contrasts sharply with the π-bonded (η^5 or η^6) phenoxo-complexes derived from the reaction (2).[6]

Defined examples of μ-phenoxo-complexes are still relatively unusual but Lappert and co-workers[7] have recently described the dinuclear μ-phenoxo-lithium complexes $[Li_2(OR)_2(OEt_2)]$ (R = aryl).



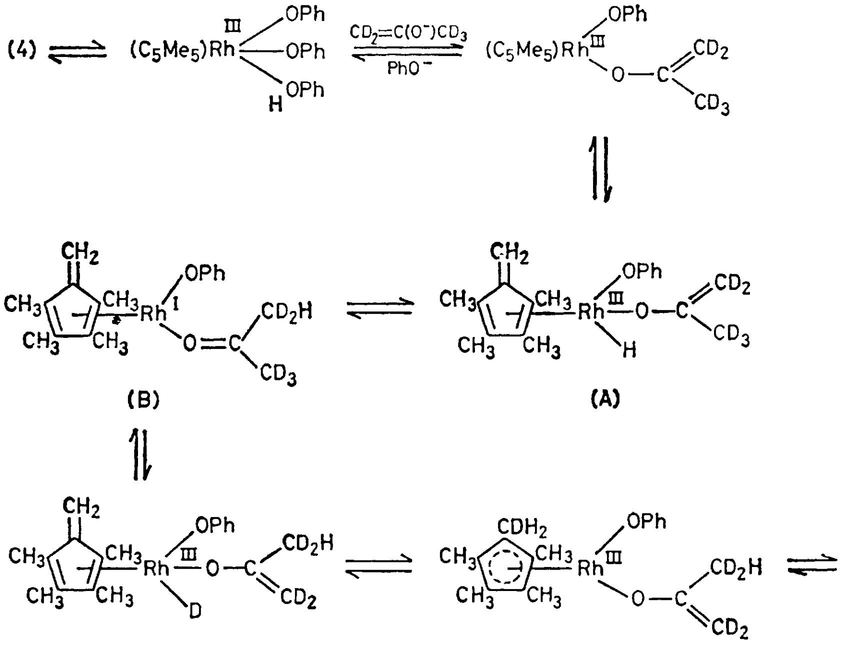
(1a) X = PF6
(1b) X = Cl
(1c) X = OH

(3)

(4)

Both the hydroxo-chloride (1b) and the hydroxo-hydroxide (1c) also reacted with phenol in water to give the same product (4), which analysed for $[\{Rh(C_5Me_5)(OPh)_2(PhOH)_2\}_n]$. The ^1H n.m.r. spectrum of this material showed, in addition to a singlet C_5Me_5 resonance (δ 0.73 p.p.m.) and a multiplet for the aromatic protons (δ 7.00), a singlet at δ 11.07 due to *H*-OPh. Integration confirmed the empirical formula above.

The structure of the compound was quite readily established from the ^{13}C n.m.r. spectrum. In addition to the C_5Me_5 resonances this showed seven singlet peaks in the aromatic region; however, one was of considerably greater intensity than all the others and we propose that this arises from the accidental overlap of two resonances. Of these eight resonances, four have the same chemical shift as those of the tri-μ-phenoxo-ligands in (3) and the remaining four come between the corresponding resonances for phenol and those for the phenolate ion.[8] We propose therefore that these latter resonances arise from unco-ordinated PhOH and PhO^- groups, which exchange quickly with each other, but *not* with the μ-phenoxo-ligands.



SCHEME 1

Inspection of the two sets of PhO^- ^{13}C resonances shows that each of those arising from a μ-phenoxo-ligand has just 60% of the intensity of the corresponding resonance of the uncomplexed phenoxy-group. Although ^{13}C-$\{^1H\}$ intensities are normally a poor guide to relative abundances, we feel that in this case they are meaningful since within each pair the n.O.e. enhancements will be the same, as the resonances arise from identical types of carbon. This analysis therefore leads to the conclusion that for every two $Rh(C_5Me_5)$ groups there are three μ-phenoxo-ligands [as in (3)] and that the counter-ion is a composite hydrogen-bonded anion $[4PhOH{\cdot}PhO^-]$ which for simplicity we designate as $[(PhO)_5H_4]^-$. Its exact nature is not clear.

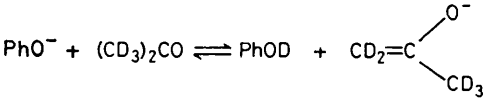
H/D *Exchange*. When the complex (4) was dissolved in $[^2H_6]$acetone the ^1H n.m.r. spectrum changed with time. Three effects were noted: (*i*) the C_5Me_5 singlet rapidly decreased in intensity, (*ii*) the *H*-OPh signal disappeared, and (*iii*) the quintet arising from CHD_2 in the $[^2H_6]$acetone increased in intensity.

These effects are explained by an H/D exchange between the acetone and the C_5Me_5 hydrogens (as well as the phenol protons, OH). This was confirmed by a ^2D n.m.r. spectrum of the exchanged, deuterio-complex (4) (in $CDCl_3$) which showed a singlet resonance at δ 0.73 arising from a $C_5(CD_3)_5$ ligand. The ^1H complex (4) showed the C_5Me_5 resonance in the ^1H n.m.r. at δ 0.73. Aromatic hydrogens in (4) were unaffected and did not exchange.

Exchange of the C_5Me_5 methyl hydrogens in $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$ for deuterium in D_2O–NaOD was noted some time ago,[3] but the conditions were moderately severe and required 70 °C/72 h for complete exchange. By contrast, the exchange of (4) with $[^2H_6]$acetone was very much faster with $t_{\frac{1}{2}}$ *ca.* 40 min at 20 °C and achieved a 98% deuteriation after 4 h. An analysis of the spectra with time showed that the reaction was first order in complex (4).

This exchange appears to be highly specific; for example, the methyl hydrogens in the very basic $[\{Rh(C_5Me_5)\}_2(OH)_3]OH{\cdot}11H_2O$ *did not* exchange in $[^2H_6]$acetone–D_2O mixture. Thus while formation of the enolate ion $CD_2{=}C(O^-)CD_3$ seems to be necessary for exchange, it is not by itself sufficient. Further, we did not observe exchange in the system $C_6(CH_3)_6$–$(CD_3)_2CO$–$CDCl_3$–base; this implies that the metal plays an important role in the reaction.

We propose that the phenoxo-groups in complex (4) play two roles. One is that the PhO^- in the counter-ion acts as a base to form the enolate ion (see below). This also accounts for the H/D exchange on the phenol OH.

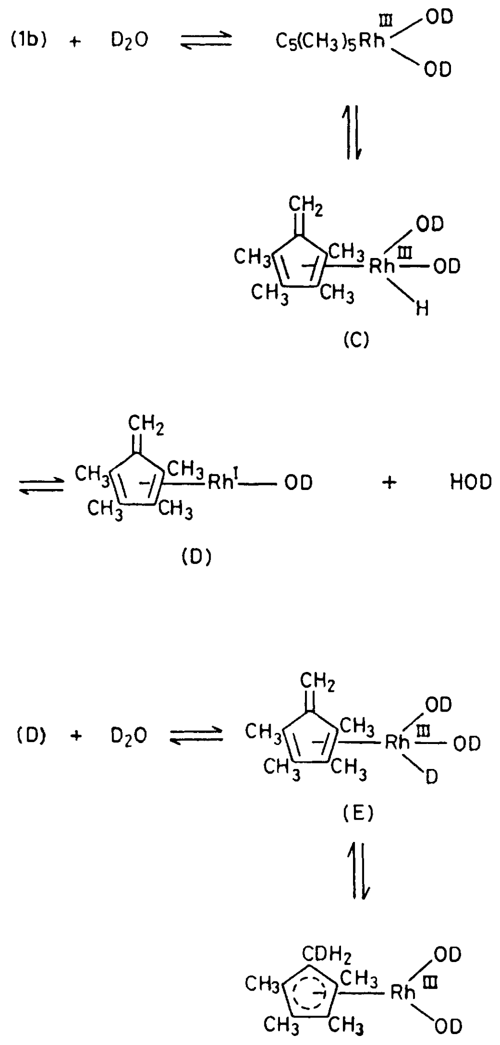


$$PhO^- + (CD_3)_2CO \rightleftharpoons PhOD + CD_2{=}C(O^-)CD_3$$

$$PhOH + CD_2{=}C(O^-)CD_3 \rightleftharpoons (CD_2H)C{=}O(CD_3) + PhO^- \quad \textit{etc.}$$

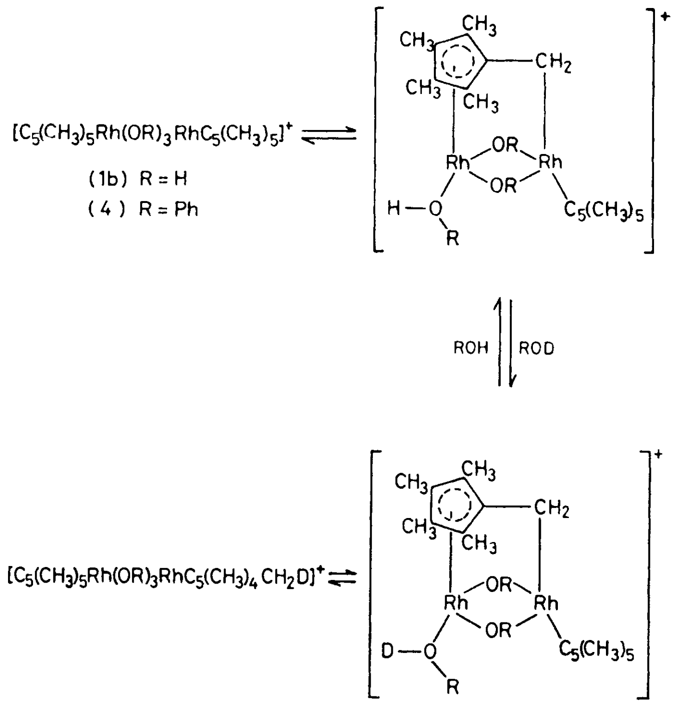
The second role may well be to facilitate the formation of a mononuclear species at which reaction can occur. Studies of a number of reactions catalysed by dinuclear $Rh(C_5Me_5)$ complexes have shown them to proceed *via* active mononuclear intermediates.[9,10]

We previously suggested [3] that the slow H/D exchange observed in $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$ (1b) (D_2O–NaOD) took place through the formation of a fulvene–rhodium hydride species and a similar series of intermediates is postulated here (Scheme 1).



Scheme 2

The difference between the two reactions presumably lies in the ease with which the methyl hydrogen can be transferred to the metal and then eliminated. In the reaction under discussion here this can occur as in (A) ⟶ (B) by transfer to enolate to give co-ordinated acetone.* In the exchange involving (1b) (D_2O–NaOD) the analogous steps are (C) ⟶ (D) ⟶ (E) and involve reductive elimination of HOD followed by oxidative addition of D_2O (Scheme 2).



Scheme 3

The steps (C) ⟶ (D) and (D) ⟶ (E) might well be quite difficult since we have no evidence from other work that oxidative addition of water occurs easily in pentamethylcyclopentadienylrhodium complexes.

However, we cannot exclude an alternative binuclear process since the $\eta^1:\eta^5$-$C_5(CH_3)_4CH_2$ ligand is readily formed and can bridge two metal atoms.[11] In this case a process such as is shown in Scheme 3 could be operating for both these exchange reactions. The ease of exchange would then depend on the relative ease of oxidatively adding $-CH_2$-H to the metal when different types of R group are present.

The hydroxoiridium acetate complex $[\{Ir(C_5Me_5)\}_2(OH)_3]O_2CMe{\cdot}14H_2O$ [2] also reacted readily with phenol; however, in this case the ^1H n.m.r. spectrum of the product showed the presence of several C_5Me_5 resonances suggesting that several species had been formed.

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* Step A⟶B is probably more complex than written and may involve a π-complexed enolate intermediate.

Attempts to separate them were not successful. We did, however, observe that at least some of the components of the mixture underwent H/D exchange with [$^2H_6$]-acetone.

We also note that an aqueous suspension of the phenoxorhodium complex (4) was very readily carbonylated (20 °C, 1 atm *) to [$Rh(C_5Me_5)(CO)_2$].[12] No other products could be detected.

EXPERIMENTAL

Complexes (1a), (1b), (1c), and (2) were prepared by literature methods.[1,2] N.m.r. spectra were run on Perkin-Elmer R-12B (^1H, 60 MHz) and JEOL PFT-100 (^{13}C) spectrometers; microanalyses were carried out by the University of Sheffield Microanalytical Service. Reactions were carried out under nitrogen but the products were not air-sensitive.

[{$Rh(C_5Me_5)$}$_2(OPh)_3$][PF_6]$\cdot 2H_2O$ (3).—A solution of phenol (0.25 g, 2.66 mmol) in water (5 cm^3) was added to a solution of [{$Rh(C_5Me_5)$}$_2(OH)_3$][PF_6]$\cdot 3H_2O$ (1a) (0.20 g, 0.28 mmol) in water (5 cm^3) and the resultant solution was stirred (20 °C, 3 h). A solid precipitated which was filtered off, washed, dried, and crystallised from chloroform–diethyl ether to give yellow crystals of complex (3) (0.21 g, 78%) (Found: C, 48.5; H, 4.9. $C_{38}H_{49}F_6O_5PRh_2$ requires C, 48.7; H, 5.3%). ^1H N.m.r. ($CDCl_3$): δ (p.p.m.) 0.86 (s, 30 H, C_5Me_5) and 7.15 (m, 15 H, Ph). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 7.7 (s, C_5Me_5), 90.3 [d, C_5Me_5, *J*(Rh-C) 10 Hz], 122.1 (s, OPh, *p*-),† 122.3 (s, OPh, *o*-),† 129.2 (s, OPh, *m*-),† and 164.5 (s, OPh, *i*-).† I.r. (Nujol): ν(OH) 3 530s, ν(Ph-O) 1 227s, ν(PF_6) 840vs cm^{-1}.

[{$Rh(C_5Me_5)$}$_2(OPh)_3$][$(PhO)_5H_4$] (4).—The yellow crystalline complex (4) was obtained (0.18 g, 47%) from complex (1b) (0.20 g) in the same way as described for (3) (Found: C, 67.0; H, 6.1. $C_{68}H_{75}O_8Rh_2$ requires C, 66.7; H, 6.1%). ^1H N.m.r. ($CDCl_3$): δ (p.p.m.) 0.73 (s, 30 H, C_5Me_5), 7.00 (m, 40 H, Ph), and 11.07 (s, 4 H, PhO*H*). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 7.6 (s, C_5Me_5), 90.1 [d, C_5Me_5, *J*(Rh-C) 10 Hz]; liganded OPh† 121.8 (s, *p*-) 122.1 (s, *o*-), 128.9 (s, *m*-, overlap with *m*- of non-liganded OPh) 164.4 (s, *i*-); non-liganded OPh† 116.5 (s, *p*-), 117.2 (s, *o*-), 128.9 (s, *m*-, overlap with *m*- of liganded OPh), and 159.3 (s, *i*-).† The intensities of the liganded phenoxo-carbon resonances averaged 60% of the intensities of the corresponding non-liganded phenoxo-carbon resonances. I.r.: ν(Ph-O) 1 227s, ν(OH) 3 200m, br cm^{-1}.

H/D *Exchange in Complex* (4).—Complex (4) (70 mg, 0.06 mmol) was dissolved in a mixture of $CDCl_3$ (0.40 cm^3) and $(CD_3)_2CO$ (0.50 cm^3, 6.8 mmol) containing $SiMe_4$ as reference. The C_5Me_5 and $SiMe_4$ peaks in the ^1H n.m.r. spectrum were integrated against each other at 10-min intervals over 130 min at 30 °C. During this time the C_5Me_5 resonance decreased and the acetone resonance increased in size.

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* Throughout this paper: 1 atm = 101 325 N m^{-2}.

† Assignments of phenoxo-carbons based on peak heights and literature values (ref. 8).

REFERENCES

[1] Part 30, K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1981, 2003.

[2] Part 29, A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1981, 1997.

[3] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **30**, 127.

[4] A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Organomet. Chem.*, 1981, **213**, 313.

[5] D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1978, **157**, C47.

[6] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **127**, 415.

[7] B. Cetinkaya, I. Gümrükcü, M. F. Lappert, J. L. Atwood, and R. Shakir, *J. Am. Chem. Soc.*, 1980, **102**, 2086.

[8] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, p. 197.

[9] D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 617.

[10] J. Cook, J. E. Hamlin, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1980, 144.

[11] See for example, F. J. Bottomley, I. J. B. Lin, and P. S. White, *J. Am. Chem. Soc.*, 1981, **103**, 703.

[12] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **26**, 393.