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PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM COMPLEXES

XXVIII *. PROPERTIES AND X-RAY CRYSTAL STRUCTURES OF $[(RhC_5Me_5)_3(H)_3O]^+$ AND $[(RhC_5Me_5)_2(H)_2OAc]^+$ PREPARED FROM REACTIONS OF $[(RhC_5Me_5)_2(OH)_3]^+$ WITH ALCOHOLS **

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Summary

The tri-μ-hydroxo-dirhodium complexes $[(RhC_5Me_5)_2(OH)_3]X$ (X = Cl, PF_6, BF_4) react in isopropanol to give the tri-μ-hydrido-trirhodium complexes $[(RhC_5Me_5)_3(H)_3O]X$ (X = PF_6, BF_4, BPh_4). A combination of X-ray crystal structure determination and ^1H and ^{13}C NMR spectroscopy of $[(RhC_5Me_5)_3(H)_3O][PF_6]$ showed it to contain an equilateral triangle of rhodium, each η^5-bonded to a C_5Me_5, capped on one side by an oxygen and with each pair of rhodiums bridged on the other side by a hydride (Rh—H mean 1.7(1) Å). The molecule is quite rigid and the barrier to movement of the hydrides, $\Delta G^{\ddagger}$, is at least 21 kcal mol^{-1} at +100°C. Reasons for this rigidity are considered. The known tetrahydride complex $[(RhC_5Me_5)_4(H)_4]^{2+}$ is obtained from $[(RhC_5Me_5)_2(OH)_3]Cl$ in isopropanol using longer reaction times. Reaction of $[(RhC_5Me_5)_2(OH)_3]PF_6$ with primary alcohols (RCH_2OH) gave mixtures of $[(RhC_5Me_5)_2H(O_2CR)_2]PF_6$ and $[(RhC_5Me_5)_2(H)_2(O_2CR)]PF_6$, but only the latter could be easily isolated. A single crystal X-ray structure of $[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ showed it to be dinuclear with the two rhodiums each η^5-bonded to C_5Me_5 and bridged by two hydrides (mean Rh—H, 1.72(10) Å) and one acetate.

The pentamethylcyclopentadienyl-rhodium and -iridium halide complexes give a variety of μ-hydrido complexes when they are reacted with isopropanol (and other alcohols) in the presence of base [2,3]. For example, 1 → 2:

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* For Part XXVII, see ref. 1.
** This article is dedicated to the memory of Professor Paolo Chini.

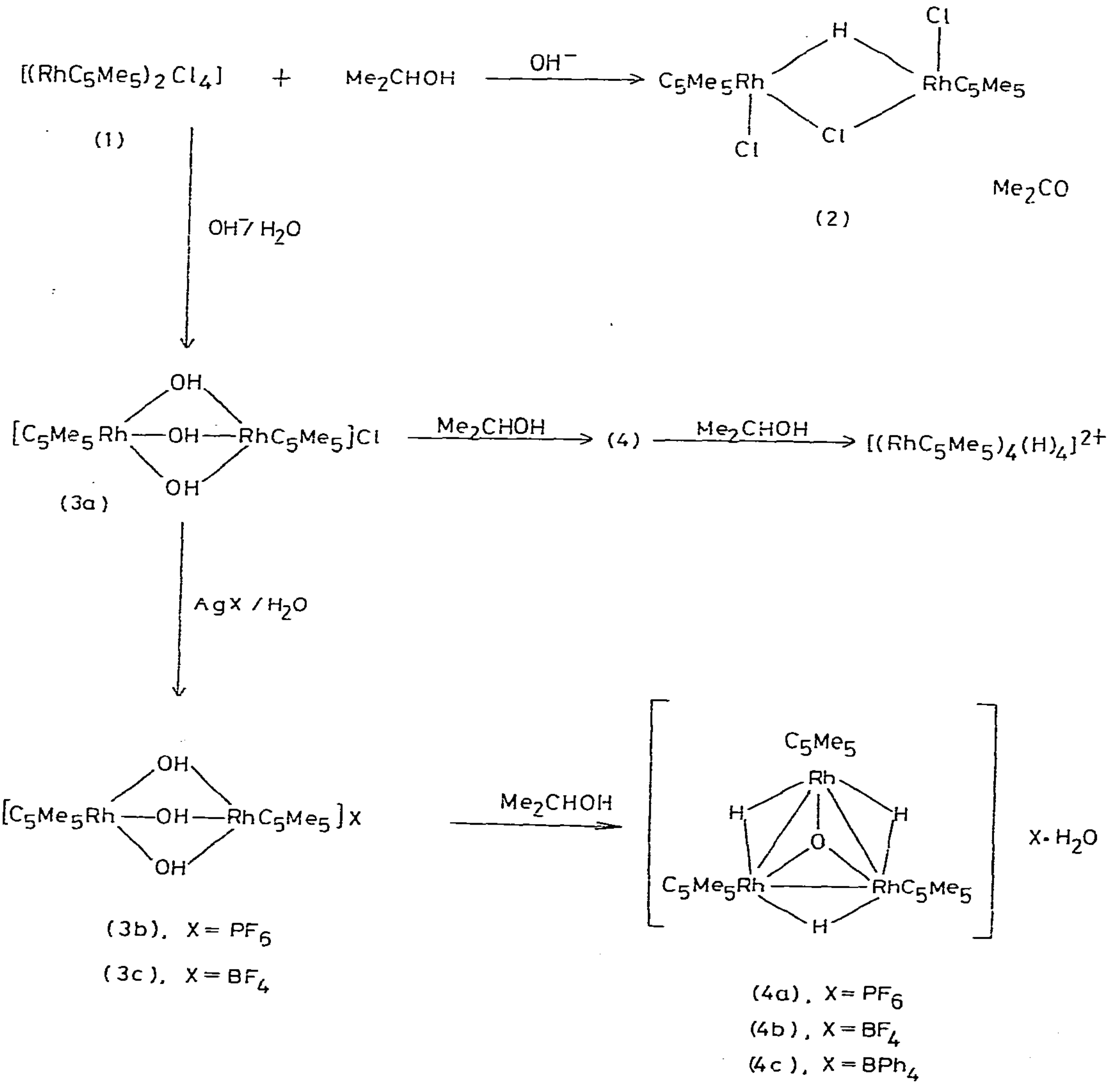
It was therefore of interest to discover what types of complexes would result from reactions of the μ-hydroxo-complex (3a) [4] and its analogues 3b and 3c [5] with alcohols. These experiments form the subject of the present paper; a part of this work was presented in a brief communication [6].

Results and discussion

Formation of [$(RhC_5Me_5)_3(H)_3O$]PF_6

When the tri-μ-hydroxo hexafluorophosphate salt 3b was allowed to react with aqueous isopropanol (3 days/50°C) a solid was obtained, the ^1H NMR spectrum of which indicated the presence of two hydrido complexes.

SCHEME 1



The minor component (ca. 25%) showed the hydride as a triplet at δ —13.9 ppm [J(Rh—H) = 30 Hz]; this was associated with a C_5Me_5 singlet (δ 2.10 ppm). The relative intensities of the two resonances suggested that two μ_2-hydrides were present for each pair of RhC_5Me_5 groups. This material has not yet been isolated pure but it is possible that it is the so far unknown di-μ-hydrido-μ-hydroxo complex, $[(RhC_5Me_5)_2(OH)(H)_2]PF_6$.

The hydrido complex present in greater amount could be isolated pure by using more dilute solutions. It was shown to be the tri-μ-hydrido trinuclear complex, $[(RhC_5Me_5)_3(H)_3O]PF_6 \cdot H_2O$ (4a) (Scheme 1) by an X-ray structure determination and by spectroscopic methods (Table 1).

When the reaction was carried out in aqueous isopropanol a stoicheiometric amount of acetone was also formed; a similar reaction occurred in butan-2-ol and in this case the organic product was butan-2-one, again formed stoicheiometrically.

Since the dinuclear hydride could not be detected when the reaction was run under more dilute conditions it is tempting to suggest that it is an intermediate in the formation of 4a.

The X-ray structure determination of 4a showed the presence of an equilateral triangle of rhodiums (mean Rh—Rh 2.758 Å) each η^5-bonded to a C_5Me_5 ligand, which is capped on one side by an oxygen (mean Rh—O 1.994 Å). This oxygen is hydrogen-bonded to a water of crystallisation [O(1)···H···O(2), 2.77 Å] which is, in turn, hydrogen-bonded to one fluorine of the PF_6^- anion ([O(2)···H···F(6), 2.96 Å] see Figs. 1 and 2 and Tables 2 and 3). The Rh_3 plane is at a mean angle of 84.3° to the C_5Me_5 planes.

A difference Fourier synthesis at R = 0.043 showed residual electron density due to a hydride bridging two of the rhodium atoms, Rh(1) and Rh(3), on the other side of the capping oxygen. This was at a mean distance of 1.7 Å from Rh(1) and Rh(3) and the angle Rh(1)—H—Rh(3) was 100°. Unfortunately the C_5Me_5 ligand bonded to Rh(2) was found to be disordered (in the relative pro-

(continued on p. 318)

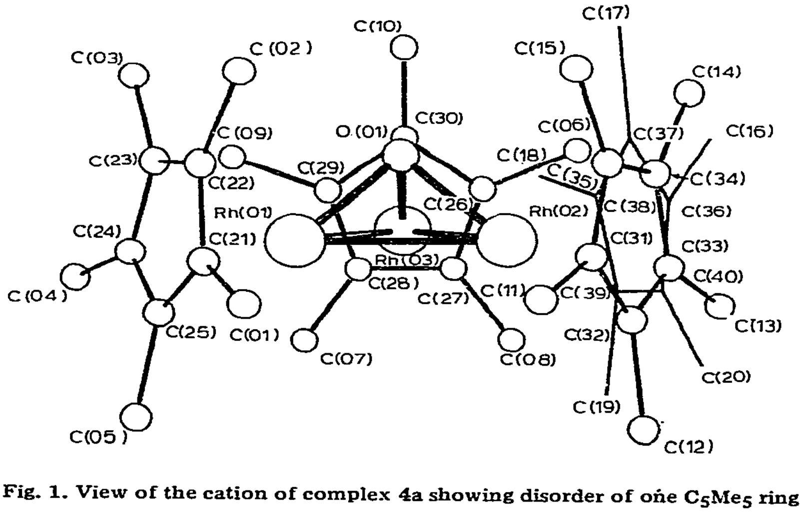


Fig. 1. View of the cation of complex 4a showing disorder of one C_5Me_5 ring (hydrogens omitted).

TABLE 1

MICROANALYTICAL AND SPECTROSCOPIC DATA

	Microanalytical data [a] (%)		^{1}H NMR spectrum (δ, ppm) in $(CD_3)_2CO$			IR spectrum (cm^{-1})	
	C	H	C_5Me_5	H	Other	ν(OH)	ν(CO)
$[(RhC_5Me_5)_3(H)_3O]PF_6 \cdot H_2O$ (4a)	39.8 (40.2)	5.9 (5.6)	2.03(s)	−18.33(m)	3.00(s, H_2O)	3663m, 3340m(br), 1630m	
$[(RhC_5Me_5)_2(H)_3O]BF_4 \cdot H_2O$ (4b)	43.1 (43.0)	6.1 (6.0)	2.07(s)	−18.13(m)	2.63(s, H_2O)	3610m, 3390m(br), 1640m	
$[(RhC_5Me_5)_3(H)_3O]BPh_4 \cdot H_2O$ (4c)	60.8 (60.6)	6.8 (6.6)	2.05(s)	−18.12(m)	2.81(s, H_2O) 7.15(m, Ph)	3400m(br), 1640m	
$[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ (8a)	38.8 (38.7)	5.2 (5.2)	1.95(s)	−11.50(t) [b]	2.23(s, Me)		1425s, 1150s
$[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ (8a)	39.7 (39.7)	5.4 (5.2)	1.95(s)	−11.42(t) [b]	1.50(t [c], Me) 2.50(q [c], CH_2)		1430s, 1547s
$[(RhC_5Me_5)_2(H)_2(O_2CPr)]PF_6$ (8c)	40.7 (40.6)	5.6 (5.5)	1.95(s)	−11.40(t) [b]	0.85(t [c], Me) 1.55(m [c], CH_2) 2.43(t [c], CH_2)		1418s, 1525s
$[(RhC_5Me_5)_2(H)_2(O_2CCHMe_2)]PF_6$ (8d)	40.4 (40.6)	5.5 (5.5)	1.95(s)	−11.41(t) [b]	1.09(d [c], Me) 1.75(septet [c], CH)		1426s, 1542s

[a] Calculated values in parentheses. [b] ^1J(Rh–H) = 33 Hz. [c] ^3J(H–H) = 7 Hz.

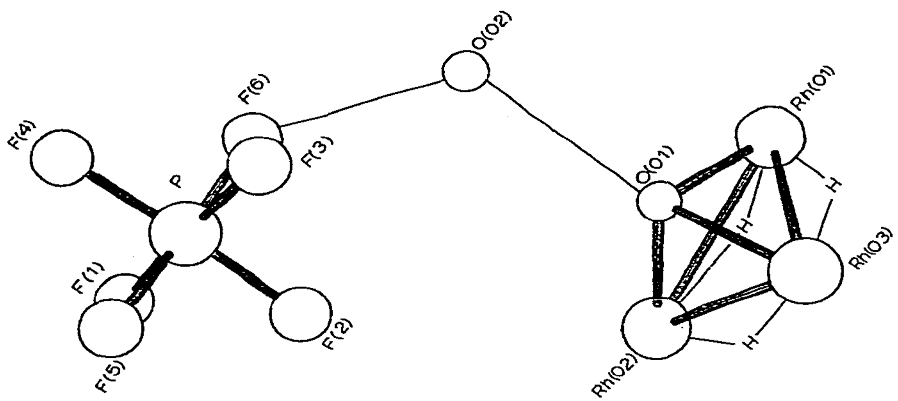


Fig. 2. View of the Rh_3H_3O core of the cation of 4a and the hydrogen bonding to H_2O and then to PF_6. Probable positions of hydrides indicated.

TABLE 2

SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(RhC_5Me_5)_3(H)_3O]PF_6 \cdot H_2O$ (4a) (e.s.d.'s IN PARENTHESES)

Rh(1)—Rh(2)	2.7551(11)	Rh(1)—Rh(2)—Rh(3)	60.32(3)
Rh(1)—Rh(3)	2.7674(10)	Rh(1)—Rh(3)—Rh(2)	69.88(3)
Rh(2)—Rh(3)	2.7527(11)	Rh(2)—Rh(1)—Rh(3)	59.80(3)
mean Rh—Rh	2.7584(11)		
Rh(1)—O(1)	1.988(6)	Rh(1)—O(1)—Rh(2)	87.4(2)
Rh(2)—O(1)	1.999(6)	Rh(1)—O(1)—Rh(3)	88.0(2)
Rh(3)—O(1)	1.995(6)	Rh(2)—O(1)—Rh(3)	87.1(2)
mean Rh—O	1.994(6)		
Rh(1)—C(21)	2.171(7)		
Rh(1)—C(22)	2.168(7)		
Rh(1)—C(23)	2.164(7)		
Rh(1)—C(24)	2.166(7)		
Rh(1)—C(25)	2.170(6)		
mean Rh(1)—C	2.168(6)		
Rh—C_5Me_5 [a]	1.809		
Rh(2)—C(31)	2.185(10)		
Rh(2)—C(32)	2.178(10)		
Rh(2)—C(33)	2.157(10)		
Rh(2)C(34)	2.150(10)		
Rh(2)—C(35)	2.168(10)		
mean Rh(2)—C [b]	2.168(10)		
Rh—C_5Me_5 [a]	1.808		
Rh(2)—C(36)	2.213(23)		
Rh(2)—C(37)	2.238(22)		
Rh(2)—C(38)	2.190(22)		
Rh(2)—C(39)	2.133(21)		
Rh(2)—C(40)	2.148(24)		
mean Rh(2)—C [b]	2.218(22)		
Rh—C_5Me_5 [a]	1.826		
Rh(3)—C(26)	2.176(9)		
Rh(3)—C(27)	2.172(10)		
Rh(3)—C(28)	2.174(9)		
Rh(3)—C(29)	2.179(9)		
Rh(3)—C(30)	2.180(9)		
mean Rh—C	2.176(9)		
Rh—C_5Me_5 [a]	1.818		
O(1)···O(2)	2.770(13)		
O(2)···F(6)	2.961(19)		

[a] Perpendicular distance. [b] The C_5Me_5 attached to Rh(2) is disordered and has two orientations in the ratio 70% [C(31)—C(35)] and 30% [C(36)—C(40)].

portions 0.7 : 0.3) and, although the three C_5Me_5Rh groups were equivalent, this disorder prevented the detection of the residual electron density due to the hydrides bridging the other two pairs of rhodium atoms.

The mean Rh—Rh separation of 2.758 Å is shorter than that in the μ-hydrido-μ-chloro dimer 2 (2.906 Å) [7] and only slightly longer than in the di-μ-hydrido-μ-acetate 8a (2.681 Å, see below). This indicates that the forces binding the metal atoms together in 4a are stronger than those in 2; in each case the metal atoms are formally in the +3 oxidation state. The oxygen in 4a is also very strongly bound and both the mean Rh—O distance of 1.994(6) Å and the mean angle RhORh (87.5°) are significantly less than the corresponding values in $[(RhC_5Me_5)(OH)_3]OH \cdot 11\ H_2O$ [2.111(4) Å, 89.6(2)°] [5]. The mean Rh—C(C_5Me_5) distances (2.171 Å) as well as the mean perpendicular Rh to C_5Me_5 ring distances (1.812 Å) [excluding those for the poorly resolved ring attached to Rh(2)] are rather longer than those typical for C_5Me_5-Rh^{III} complexes [8] and reflect some crowding in the cation. These distances are, however, less than those in $[(RhC_5Me_5)_4(H)_4]^{2+}$ [2.215(14) and 1.846 Å, respectively [9]] and we conclude that the crowding is less in 4a.

More evidence for the presence of three bridging hydrides came from the ^1H NMR spectrum. This showed a multiplet at δ −18.20 ppm and a singlet at

TABLE 3

EQUATIONS OF IMPORTANT LEAST-SQUARES PLANES IN THE FORM:

$lX + mY + nZ = d$

where XYZ are the coordinates in Å referred to the axes ab^*c'. Deviations (Å) of various atoms from these planes are listed in parentheses. Angles between the planes are at the foot of the table.

	l	m	n	d
Plane 1: C(21)—C(22)—C(23)—C(24)—C(25)				
	0.9772	−0.0091	0.2120	4.8675
[Rh(1) −1.809				
C(01) 0.10; C(02) 0.04; C(03) 0.05; C(04) 0.13; C(05) 0.15]				
Plane 2: C(26)—C(27)—C(28)—C(29)—C(30)				
	0.6585	−0.2086	−0.7231	−4.7410
[Rh(3) 1.818				
C(06) −0.14; C(07) −0.10; C(08) −0.11; C(09) −0.14; C(10) −0.04]				
Plane 3: C(31)—C(32)—C(33)—C(34)—C(35)				
	0.2043	−0.0920	0.9513	−1.4907
[Rh(2) 1.808				
C(11) −0.05; C(12) −0.12; C(13) −0.11; C(14) −0.10; C(15) −0.03]				
Plane 4: C(36)—C(37)—C(38)—C(39)—C(40)				
	0.3152	−0.1309	0.9400	−1.6244
[Rh(3) 1.826				
C(16) −0.11; C(17) −0.08; C(18) 0.00; C(19) −0.02; C(20) −0.05]				
Plane 5: Rh(1)—Rh(2)—Rh(3)				
	−0.1375	−0.9903	0.0221	−3.2184

Angles:	Plane	2	3	4	5
	1	60.5	60.7	59.4	96.9
	2		118.3	116.4	84.3
	3			2.6	85.9
	4				83.9

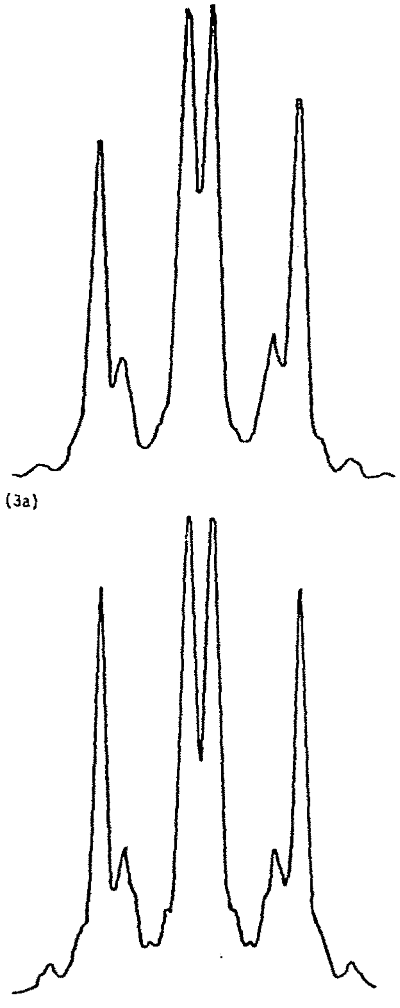
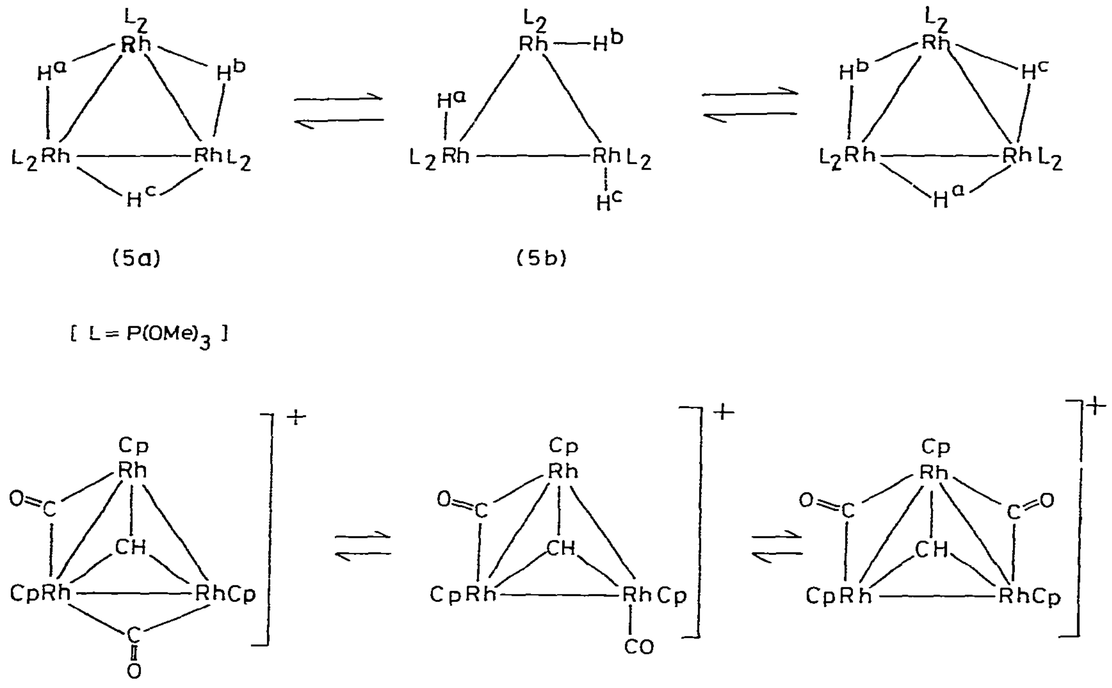


Fig. 3. a) ^{1}H NMR spectrum of the hydride resonances of $[(RhC_5Me_5)_3(H)_3O]PF_6 \cdot H_2O$ (4a) at δ −18.29 ppm. b). Computer simulation of the spectrum using ^1J(Rh—Rh) = 10.3, ^1J(Rh—H) = 26.6; ^2J(Rh—H) = 0.5 and ^2J(H—H) = 4.5 Hz.

δ 2.03 ppm (C_5Me_5) with relative intensities 1 : 15. However, the high field hydride resonance was not a 1 : 3 : 3 : 1 quartet, as would be expected if the molecule were fluxional and the three hydrogens were equally coupled to all three (equivalent) ^{103}Rh nuclei (100%; $I = \frac{1}{2}$). Instead the complex multiplet illustrated in Fig. 3a was observed, which was both field- and temperature-invariant (over the range −60 to 100°C). Further evidence that it arose from three equivalent hydrides came from the observation that the multiplet collapsed to a singlet on irradiation at the appropriate ^{103}Rh frequency (−136 ppm at a frequency of 3.16 MHz) [10].

The hydride multiplet was of the form $[AX]_3$ (A = ^{103}Rh, X = ^{1}H) and could be accurately simulated (Fig. 3b) given the observed geometry and assuming

SCHEME 2



(5a) (5b)

[L = P(OMe)3]

(6a) (6b) (6c)

the coupling constants, ^1J(Rh—Rh) 10.3, ^1J(Rh—H) 26.6, ^2J(Rh—H) 0.5, and ^2J(H—H) 4.5 Hz [6,10]. The multiplet clearly arises from a totally static situation. Indeed, since we would have been able to see a 1 Hz broadening at 100°C, we can say that the minimum $\Delta G^{\ddagger}$ for coalescence is 21 kcal mol^{-1} * using the relationship $k = \pi(h - h_0)$ where h is the linewidth of the peak, h_0 is the linewidth in the absence of exchange, and k is the rate constant for the exchange [11].

Although the X-ray structure shows the Rh_3O core in 4 to be very strongly bound, the extreme rigidity of the complex was quite surprising, particularly since hydrides normally move easily, especially in cluster complexes, and have been termed "plastic" ligands [12]. For example, the complex $[Rh_3(H)_3\{P(OMe)_3\}_6]$, 5, is highly fluxional down to —120°C and has $\Delta G^{\ddagger}$ less than 8 kcal mol^{-1} (Scheme 2) [13]. Further, the trinuclear complex 6 which, like 4, has a formal electron count of 48 and a capping ligand (though this is CH rather than the O in 4a) is reported to have fluxional carbonyls [14].

If the mechanism by which the hydrides in 5 equilibrate is as shown then the transition state 5b is one in which all three hydrides must be terminal and where the metal atoms must have a different state of hybridisation from that

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* The value of 26 kcal mol^{-1} quoted earlier [6] has now been revised.

which they have in the ground state 5a *. The molecular skeleton in 5 is presumably flexible enough to allow this to occur easily but, because of the constraints to movement and rehybridisation offered by the capping oxygen and the intermeshed methyls of the C_5Me_5 ligands, this is severely hindered in 4.

Again, an easy path to equilibration of the CO's is available in 6 since one Rh—Rh bond has no CO bridge and therefore the carbonyls can move one at a time e.g. 6a $\rightleftharpoons$ 6b $\rightleftharpoons$ 6c. This is presumably a facile process and in any case the C_5H_5 ligands would not interfere with any reorganisation (at the rhodium most involved in the transfer) to the same extent as would the C_5Me_5 ligands.

It is also possible that the reason for the lack of fluxionality of 4 may lie in electronic effects. Thus while the rhodiums in 4 are formally in the +3 oxidation state, in 5 they are +1 and in 6 $+2\frac{1}{3}$. Certainly Chini et al. have suggested that in the larger carbonyl clusters the more fluxional ones have the higher ratio of negative charge to number of metal atoms [16]. They see the higher charge leading to higher electron densities on particular metal centres which in turn helps the formation of CO bridges and hence facilitates carbonyl movements.

At present we have no means of distinguishing between the electronic and the steric effects and it is likely that both are important. The main interest in this point is because a correlation may be expected between the ease of fluxionality and the degree of kinetic lability towards, say, substitution reactions. Certainly 4 is singularly inert towards further reaction except in the presence of chloride when breakdown of the cluster slowly takes place.

The ^{13}C NMR spectrum of 4a showed a singlet at δ 11.1 ppm ($C_5\mathit{Me}_5$) and a multiplet at δ 98.5 ppm for the ring carbons (C_5Me_5). The multiplet corresponded to a rigid $[A^1X_3]$ system ($A^1 = {}^{13}C$, $X = {}^{103}Rh$) and was again successfully simulated using the parameters ${}^1J(Rh—C) = 7.0$ and ${}^2J(Rh—C) = 0$ Hz [10].

The tetrafluoroborate salt $[(RhC_5Me_5)_3(H)_3O]BF_4 \cdot H_2O$ (4b) was made analogously from $[(RhC_5Me_5)_2(OH)_3]BF_4$ (3c) in aqueous isopropanol; on reaction with $Na[BPh_4]$ it gave the tetraphenylborate $[(RhC_5Me_5)_3(H)_3O]BPh_4 \cdot H_2O$ (4c). The NMR and IR spectra were identical to those of (4a) except for bands arising from the anions, and there was no detectable fluxionality with different anions.

Formation of $[(RhC_5Me_5)_4(H)_4]^{2+}$ (7)

When the yellow tri-μ-hydroxo chloride complex 3a was reacted in aqueous isopropanol (16 h/60°C) it gave a black precipitate and a red solution. On addition of aqueous KPF_6 to the red solution, the salt 4a was again produced, in 43% yield. However, if the reaction mixture was heated longer (80 h/60°C) the solution turned deep green, and a further black precipitate was formed. Addition of aqueous KPF_6 to the green solution gave the dark green $[RhC_5Me_4)_4(H)_4][PF_6]_2$ (7) in 31% yield.

This tetranuclear complex had previously been prepared by reaction of an aqueous solution of 3a with hydrogen at 90°C [9]. During that reaction the

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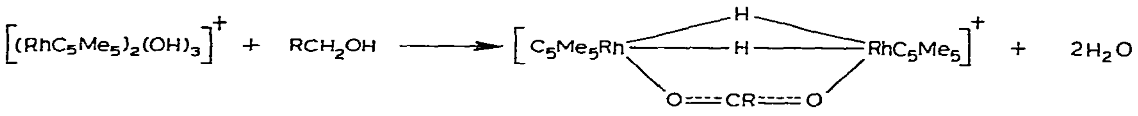
* As for example, in $[Rh_3Cp_3(CO)_3]$ [15].

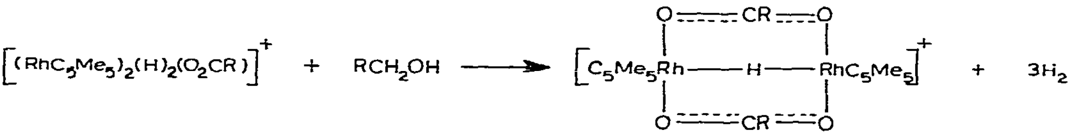
colour also changed from yellow through red to dark green and we have now found that when KPF_6 is added to the filtered aqueous red solution at the appropriate point in the reaction, the trinuclear trihydride 4a is obtained. Thus both reactions appear to proceed via the same intermediate complex to the same final product, and the function of the isopropanol is simply as a source of hydrogen. However, a variety of attempts to convert the red trinuclear into the green tetranuclear complex were unsuccessful.

Formation of $[(RhC_5Me_5)_2(H)_2(O_2CR)]^+$ (8) and $[(RhC_5Me_5)_2H(O_2CR)_2]^+$ (9)

The tri-μ-hydroxo complexes (3a—3c) all reacted analogously with primary alcohols but the reaction of the PF_6^- salt (3b) was the easiest to follow since the products could be isolated as the sparingly soluble PF_6^- salts. All the alcohols (apart from methanol) gave both the di-μ-hydrido mono-μ-carboxylato- (8) and the mono-μ-hydrido-di-μ-carboxylato complex (9). When the reactions were carried out in a large volume of solvent the less soluble dihydrides (8a—8d) could readily be obtained pure. The overall reactions appeared to be:



(8a, R = Me
8b, R = Et
8c, R = Pr^n
8d, R = Me_2CH)



(9)

The tri-μ-hydroxo chloride complex 3a reacted similarly with ethanol to give 8a and 8b. In this case small amounts (ca. 3 equivalents) of acetic acid were also detected in solution. The reaction proceeded in the same way and to the same extent under nitrogen and in degassed solvents, showing that air was not required. The source of oxygen was therefore the water and analysis of the gas phase showed that some hydrogen was produced.

Both 8a and 9a had previously been made from the rhodium acetate complex $[(RhC_5Me_5)(O_2CMe)_2 \cdot n\ H_2O]$ and were thus identified by comparison with the published data [2]. The mono-μ-hydrides 9a—9d were only observed in solution (by NMR spectroscopy) but the di-μ-hydrides 8a—8d were isolated. The complexes 8b—8d were new and were identified by analysis and NMR and IR spectroscopy.

Good crystals of the dihydrido-acetate complex 8a were obtained and an X-ray crystal structure determination on this material showed it to have the expected structure (Fig. 4 and Tables 5 and 6). The molecule is composed of

TABLE 4

ATOMIC FRACTIONAL COORDINATES FOR [$(RhC_5Me_5)_3(H)_3O$]$PF_6 \cdot H_2O$ (4a) × 10^4 (× 10^5 FOR THOSE MARKED *), ESTIMATED STANDARD DEVIATIONS ARE IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
*Rh(01)	12379(6)	20633(5)	24598(6)
*Rh(02)	—5426(7)	22328(6)	8445(6)
*Rh(03)	—13115(6)	23315(5)	32655(6)
P	—4485(3)	6942(3)	2711(3)
F(01)	—4367(12)	6835(13)	1342(10)
F(02)	—4566(25)	6028(12)	2610(22)
F(03)	—4600(11)	6986(14)	4033(9)
F(04)	—4389(20)	7850(10)	2668(23)
F(05)	—5933(8)	7373(12)	2737(11)
F(06)	—3035(9)	6551(12)	2741(12)
O(01)	—450(5)	3045(4)	2342(5)
O(02)	—640(10)	4914(7)	2702(12)
C(01)	3898(12)	1358(11)	447(11)
C(02)	2574(12)	3576(9)	1634(13)
C(03)	1710(12)	3660(8)	4426(12)
C(04)	2485(13)	1529(10)	5005(11)
C(05)	3814(12)	144(8)	2537(14)
C(06)	—4451(13)	3445(18)	3125(15)
C(07)	—1429(24)	1007(18)	5353(26)
C(08)	—3389(23)	1198(16)	3507(24)
C(09)	—1224(18)	3067(25)	6166(14)
C(10)	—3010(21)	4459(11)	4675(21)
C(11)	1674(20)	1609(23)	—1624(17)
C(12)	—165(25)	414(13)	—1354(16)
C(13)	—2919(19)	1733(17)	—290(15)
C(14)	—3039(26)	3917(14)	141(20)
C(15)	—160(37)	3852(21)	—668(23)
C(16)	—3606(42)	3494(37)	314(45)
C(17)	—1534(65)	4401(30)	—128(48)
C(18)	1219(51)	2752(48)	—1299(42)
C(19)	683(55)	744(36)	—1578(39)
C(20)	—2106(80)	1084(47)	—637(67)
C(21)	3251(6)	1751(5)	1759(4)
C(22)	2703(7)	2705(4)	2274(6)
C(23)	2310(7)	2752(4)	3509(6)
C(24)	2615(6)	1828(5)	3757(5)
C(25)	3196(6)	1209(3)	2675(6)
C(26)	—3389(7)	2931(7)	3836(7)
C(27)	—2935(10)	1987(6)	4020(8)
C(28)	—2044(9)	1895(5)	4861(9)
C(29)	—1949(7)	2783(7)	5197(6)
C(30)	—2780(9)	3422(5)	4564(8)
C(31)	202(7)	2077(8)	—1061(9)
C(32)	—541(10)	1499(5)	—941(9)
C(33)	—1811(8)	2079(7)	—460(8)
C(34)	—1853(9)	3015(6)	—283(9)
C(35)	—609(11)	3014(7)	—654(10)
C(36)	2175(15)	2780(18)	—200(21)
C(37)	—1360(21)	3303(12)	—349(20)
C(38)	—132(17)	2767(17)	—881(19)
C(39)	—188(18)	1765(14)	—1060(20)
C(40)	—1451(22)	1830(15)	—639(22)

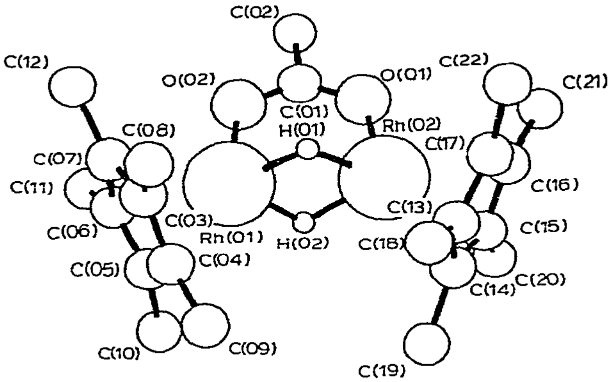


Fig. 4. View of the cation of $[(RhC_5Me_5)_2(H)_2(OAc)][PF_6]$ (8a) (methyl hydrogens omitted for clarity).

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $[(RhC_5Me_5)_2(H)_2OAc]PF_6$ (8a), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Coordination sphere of the rhodium atoms			
Rh(1)—O(2)	2.071(5)	Rh(2)—O(1)	2.070(5)
Rh(1)—H(1)	1.73(10)	Rh(2)—H(1)	1.73(10)
Rh(1)—H(2)	1.65(10)	Rh(2)—H(2)	1.75(10)
Rh(1)—C(3)	2.162(8)	Rh(2)—C(13)	2.136(10)
Rh(1)—C(4)	2.133(8)	Rh(2)—C(14)	2.141(9)
Rh(1)—C(5)	2.163(8)	Rh(2)—C(15)	2.141(9)
Rh(1)—C(6)	2.157(8)	Rh(2)—C(16)	2.171(10)
Rh(1)—C(7)	2.159(8)	Rh(2)—C(17)	2.138(11)
Rh(1)—centroid	1.779	Rh(2)—centroid	1.775
Rh(1)—Rh(2)	2.680(1)		
Rh(1)—H(1)—Rh(2)	101(5)		
Rh(1)—H(2)—Rh(2)	104(5)		
Bridging acetate group			
C(1)—O(1)	1.248(10)		
C(1)—O(2)	1.261(10)		
C(1)—C(2)	1.525(12)		
O(1)—C(1)—O(2)	124.8(7)		
O(1)—C(1)—C(2)	118.4(7)		
O(2)—C(1)—C(2)	116.9(7)		
Pentamethylcyclopentadienyl ligands			
C(3)—C(4)	1.434(12)	C(13)—C(14)	1.408(14)
C(4)—C(5)	1.436(12)	C(14)—C(15)	1.428(13)
C(5)—C(6)	1.418(12)	C(15)—C(16)	1.420(13)
C(6)—C(7)	1.454(11)	C(16)—C(17)	1.400(13)
C(7)—C(3)	1.410(11)	C(17)—C(13)	1.457(15)
C(3)—C(8)	1.522(13)	C(13)—C(18)	1.523(18)
C(4)—C(9)	1.518(14)	C(14)—C(19)	1.521(16)
C(5)—C(10)	1.508(13)	C(15)—C(20)	1.513(14)
C(6)—C(11)	1.500(13)	C(16)—C(21)	1.522(16)
C(7)—C(12)	1.513(13)	C(17)—C(22)	1.550(18)

TABLE 6

EQUATIONS OF IMPORTANT LEAST-SQUARES PLANES FOR $[(RhC_5Me_5)_2(H)_2OAc]PF_6$ (8a) IN THE FORM:

$lX + mY + nZ = d$

where XYZ are coordinates in Å referred to the axes abc^*. Deviations (Å) of various atoms from these planes are listed in parentheses. Angles between the planes are at the foot of the table.

	l	m	n	d
Plane 1: O(01)—C(01)—O(02)	0.1843	0.4338	0.8819	1.9051
[C(02) −0.010; Rh(01) 0.092; Rh(02) 0.099]				
Plane 2: Rh(01)—Rh(02)—H(01)	0.1256	−0.9744	0.1865	−3.0935
Plane 3: Rh(01)—Rh(02)—H(02)	0.1868	−0.8609	0.4732	−2.5344
Plane 4: C(03)—C(04)—C(05)—C(06)—C(07)	−0.9345	0.3496	0.0676	3.9760
[Rh(01) −1.779; C(08) 0.100; C(09) 0.136; C(10) 0.097; C(11) −0.066; C(12) 0.022]				
Plane 5: C(13)—C(14)—C(15)—C(16)—C(17)	0.7624	0.5234	−0.3804	4.6121
[Rh(02) −1.774; C(18) 0.075; C(19) 0.081; C(20) 0.034; C(21) −0.020; C(22) 0.046]				

Angles:

Plane	2	3	4	5
1	103.6	85.5	87.8	88.2
2		18.1	116.4	119.0
3			116.3	119.2
4				123.7

two rhodiums, each η^5-bonded to a C_5Me_5 ligand, and separated by 2.680 Å. The rhodiums are bridged by one acetate (Rh—O 2.070, 2.071(5) Å) and by two hydrides (Rh—H (mean) 1.72(10) Å, Rh—H—Rh 101(5), 104(5)°). As a consequence of the asymmetry of the coordination about the metal both the C_5Me_5 rings are very distorted and asymmetrically bonded. Similar effects have been noted before [17] but not in the same sense as are observed here; however the rather high e.s.d.'s on the C—C bond lengths must make any detailed analysis very tentative. The differing sizes of the hydride and the acetate bridging groups also means that the two C_5Me_5 rings are not parallel but are inclined to one another at an angle of 124°. The C_5Me_5 rings are also staggered with respect to each other so that the methyls on opposite sides mesh together in the sterically most favourable positions. Four of the methyl carbons on each C_5Me_5 are bent out of the plane of the ring away from the metal, the remaining one being slightly distorted towards the rhodium. The out-of-plane distance of the methyl groups increases as the position becomes more sterically crowded du to the inter-ring repulsions. However, since the absolute value of the deviations differs for the two rings (being 0.202 Å for one and 0.101 for the other) this suggests that the distortions cannot wholly be attributed to steric effects of this type.

Complex 8a is the first di-μ-hydride in this series to have had its crystal structure determined. It is noteworthy that the Rh—Rh distance of 2.680(1) Å falls (as might be expected) between that of the mono-μ-hydrides, 2.906(1) in $[(RhC_5Me_5)_2HCl_3]$ (2) [7] or 2.903(1) in $[(Ir(C_5Me_5)_2HCl_3]$ [18] and 2.455(1) in $[(IrC_5Me_5)_2(H)_3]^+$ [19]. Clearly bridging hydrides have the effect of pulling the C_5Me_5M units closer together and in the dinuclear hydrides the magnitude of this effect seems to be directly proportional to the number of bridging hydrides, with each successive μ-hydride leading to a further shortening of ca. 0.224 Å.

Reaction of ethanol with $[(IrC_5Me_5)_2(OH)_3]OH$ *hydrate*

The reaction of $[(IrC_5Me_5)_2(OH)_3]OH$ hydrate [5] with aqueous ethanol gave only the known tri-μ-hydrido-complex $[C_5Me_5IrH_3IrC_5Me_5][PF_6]$ [2] after the addition of hexafluorophosphate. GC analysis of the solution showed the presence of acetic acid. However, in this case the acetate was clearly not a good enough nucleophile to coordinate to the metal by displacing hydride.

Mechanism of reactions

When the yellow tri-μ-hydroxy rhodium complexes are dissolved in alcohols the initially pale solutions darken within a few minutes to red-brown (primary alcohols) or red-purple (secondary alcohols). However, the intense colours belie the very small amounts of products formed and significant quantities are only formed quite slowly. For example, on addition of NH_4PF_6 to a freshly made up red-purple solution of $[(RhC_5Me_5)_2(OH)_3]Cl$ in isopropanol an orange precipitate was obtained in high yield. This was shown to be the known tris-ammine complex $[(RhC_5Me_5)(NH_3)_3]PF_6$ (10) [20] and therefore no significant amounts of hydride complexes had yet formed.

It seems likely that, on dissolution of a tri-μ-hydroxy complex 3 in an alcohol, the tri-μ-alkoxy complex 11 is formed in equilibrium with 3. On addition of protic acids the equilibrium is then shifted, in the case of NH_4^+,towards 10

$$\underset{(3)}{[(RhC_5Me_5)_2(OH)_3]^+} + 3\ ROH \rightleftharpoons \underset{(11)}{[(RhC_5Me_5)_2(OR)_3]^+} + H_2O$$

$$11 + 6\ NH_4PF_6 \rightarrow 2\underset{(10)}{[(RhC_5Me_5)(NH_3)_3][PF_6]_2} + 3\ H^+ + 2\ PF_6^- + 3\ ROH$$

The formation of 11 may be compared to the facile formation of the tri-μ-alkoxy complexes 13 from the tri-μ-hydroxy-diruthenium arene complexes 12 [21]

$$\underset{(12)}{[C_6H_6Rh(OH)_3RuC_6H_6]^+} + 3\ ROH \rightarrow \underset{(13)}{[C_6H_6Ru(OR)_3RuC_6H_6]^+}$$

Similarly, using phenols (which cannot β-eliminate hydrogen) we have been able to prepare tri-μ-phenoxorhodium complexes [22].

The chief difference between rhodium and ruthenium in these systems therefore seems to lie in the greater ease with which the rhodium complexes β-eliminate hydrogen from alkoxy groups.

The reactions of 3 with aqueous secondary alcohols to give the trinuclear trihydride 4 presumably proceeds via intermediates such as $[(RhC_5Me_5)(OH)(H)$-

$(H_2O)]$, $[(RhC_5Me_5)(H)(H_2O)_2]^+$ and/or, $[(RhC_5Me_5)_2(H)_2(OH)]^+$, only the last of which could be detected. The organic product from the reactions in isopropanol is acetone which does not appear to react further under these conditions (however, see ref. 23).

An understanding of the reactions of 3 with primary alcohols is harder to achieve. The equation given above for the direct formation of the dihydrido-mono-carboxylato complexes 8a—8d looks persuasive but may hide a more complex situation. For example, it might reasonably be anticipated that the reaction alcohol to acid proceeds in two stages, via the aldehyde. However, if this happens here then the reaction may continue rather differently since separate studies have shown that aldehydes undergo the catalytic disproportionation reaction [24]:

$$2\ RCHO + H_2O \rightarrow RCO_2H + RCH_2OH$$

in the presence of 3 and related complexes. Indeed, both 8a and 9a are by-products of the reaction when 3b is reacted with aqueous acetaldehyde.

In that case a series of reactions such as (i)—(v) may be occurring

$$[M_2(OH)_3]^+ + RCH_2OH \rightarrow [M_2(OH)_2H]^+ + RCHO + H_2O \qquad (i)$$

$$[M_2(OH)_2H]^+ + RCH_2OH \rightarrow [M_2(OH)(H)_2]^+ + RCHO + H_2O \qquad (ii)$$

$$2\ RCHO + H_2O \rightarrow RCH_2OH + RCO_2H \qquad (iii)$$

$$[M_2(OH)_2H]^+ + 2\ RCO_2H \rightarrow [M_2(O_2CR)_2H]^+ + 2\ H_2O \qquad (iv)$$

$$[M_2(OH)(H)_2]^+ + RCO_2H \rightarrow [M_2(O_2CR)(H_2]^+ + H_2O \qquad (v)$$

[M = RhC_5Me_5; alkoxy can also replace OH]

Experimental

Solvents were redistilled before use and reactions were generally carried out under nitrogen even though none of the complexes showed any appreciable sensitivity to air. NMR spectra were run on R-12B (60 MHz ^1H), R-34 (220 MHz ^1H) or Jeol PFT-100 (^{13}C) spectrometers. Analyses are by the University of Sheffield Microanalytical Service. IR spectra were run as Nujol mulls. Analytical and spectroscopic data are collected in Table 3.

$[(RhC_5Me_5)_3(H)_3O]PF_6 \cdot H_2O$ (4a)

A solution of $[(RhC_5Me_5)_2(OH)_3]Cl \cdot 4\ H_2O$ (0.20 g, 0.32 mmol) dissolved in isopropanol/water (50 cm^3, V/V) has heated (60°C/16 h). A black precipitate was filtered off and the deep red filtrate was divided into two equal portions. To one half was added KPF_6 (0.05 g, 0.27 mmol) in water (5 cm^3); a red solid was precipitated and was characterised as $[(RhC_5Me_5)_3(H)_3O]PF_6$ (4a) (0.040 g, 43%).

The other half of the filtrate was reheated (60°C/64 h). The black precipitate formed was then filtered off and KPF_6 (0.05 g, 0.27 mmol) in water (5 cm^3) was added to the deep green solution to precipitate a green solid. This was identified as $[(RhC_5Me_5)_4(H)_4][PF_6]_2$ (7) (0.030 g, 31%) by comparison with an authentic sample.

A better preparation of complex 4a uses a solution of the hydroxy hexafluorophosphate complex 3b [5] (0.10 g, 0.14 mmol) in isopropanol/water (50 cm^3, 5% V/V). After 48 hours at 45°C the precipitate of dark red crystals of complex 4a were filtered off; further crystals were obtained on concentrating the mother liquor to 2 cm^3. The combined solids were recrystallised from acetone/diethyl ether (0.060 g, 70%).

Crystals of 4a suitable for X-ray diffraction were prepared by leaving a solution of complex 3b (0.10 g) in isopropanol/water (25 cm^3, 60% V/V) at 25°C for 10 days.

$[(RhC_5Me_5)_3(H)_3O]BF_4 \cdot H_2O$ (4b) and $[(RhC_5Me_5)_3(H)_3O]BPh_4 \cdot H_2O$ (4c)

A solution of $AgBF_4$ (0.08 g, 0.4 mmol) in water (1 cm^3) was added to a solution of complex 3a (0.25 g, 0.39 mmol) in water and the resulting mixture was stirred (1 hour/20°C). Precipitated AgCl was removed by filtration through a short column filled with powdered cellulose. Isopropanol (5 cm^3) was added to this filtrate and the resultant solution was allowed to stand at 45°C for 48 hours. The red solution was reduced in volume to 3 cm^3 and the red crystalline product was filtered off and recrystallised from acetone and diethyl ether to yield red crystals of $[(RhC_5Me_5)_3(H)_3O]BF_4 \cdot H_2O$ (4b) (0.11 g, 50%).

Addition of $NaBPh_4$ (0.05 g, 0.14 mmol) in water (2 cm^3) to a solution of 4b (0.10 g, 0.12 mmol) in water (30 cm^3) gave a red precipitate of 4c. The suspension was stirred for 1 hour at 20°C then the solid was filtered off and recrystallised from acetone/diethyl ether to give red crystals of $[(RhC_5Me_5)_3(H)_3O]BPh_4 \cdot H_2O$ (4c) (0.05 g, 69%).

$[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ (8a)

Complex $[(RhC_5Me_5)_2(OH)_3]PF_6 \cdot 3\,H_2O$ (3b) (0.15 g, 0.21 mmol) was dissolved in ethanol/water (50 cm^3, 50% V/V) and allowed to stand at 45°C for 7 days. The volume of the resulting violet solution was reduced to 5 cm^3 and a solid was obtained which was crystallised from acetone/diethyl ether to give dark red crystals of $[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ (8a) (0.10 g, 67%). Crystals suitable for X-ray diffraction were obtained from a solution of 3b in 10% V/V ethanol/water after 3 days at 45°C.

When the reaction in ethanol/water was repeated using higher concentrations of 3b, mixtures of the monohydride 9a and the dihydride 8a were obtained.

$[(RhC_5Me_5)_2(H)_2(O_2CR)]PF_6$ (8b–8d)

The reactions were carried out as described above for the preparation of 8a. Conditions used were: 0.25 g 3b in propan-1-ol/water (100 cm^3, 10% V/V), 45°C/14 days, yield of 8b 0.06 g, 24%; 0.25 g 3b in butan-1-ol/water (100 cm^3, 7% V/V), 45°C/14 days, yield of 8c, 0.04 g, 16%; 0.25 g 3b in 2-methylpropan-1-ol/water (100 cm^3, 7% V/V), 45°C/14 days, yield of 8d, 0.05 g, 18%.

Reaction of $[(RhC_5Me_5)_2(OH)_3]Cl$ with aqueous ethanol

A solution of complex 3 [25 mg, 0.04 mmol] in ethanol/water (10% V/V, 5 cm^3) was heated (60°C/16 h). Acetic acid was detected by GC (Poropak Q columns, FID detector) and estimated to be 0.12 mmol by comparison with a calibrated sample. A second determination after 40 h/60°C showed no change.

X-ray crystal structure determination of $[(RhC_5Me_5)_3(H)_3O][PF_6]\cdot H_2O$ *(4a)*

Crystal data: $[C_{30}H_{48}ORh_3]PF_6 \cdot H_2O$, $M = 896.0$, triclinic, $a = 11.065(12)$, $b = 15.282(17)$, $c = 11.230(28)$ Å, $\alpha = 96.80(3)$, $\beta = 85.31(3)$, $\gamma = 70.27(1)°$, (The Delaunay cell is 11.065, 17.520, 11.231, 119.09, 94.69, 106.54 — it was not used in the calculations but is quoted for reference), $U = 1759.8$ Å^3. $Z = 2$, $D_{obs} = 1.63$, $D_{calc} = 1.690$ g cm^{-3}, space group $P\bar{1}$, Mo-K_α X-radiation (graphite monochromator) $\lambda = 0.71069$, μ(Mo-K_α) = 14.7 cm^{-1}. The unit cell parameters were obtained from a least squares fit to the setting angles of 50 reflections centred manually on a Stoe STADI-2 diffractometer.

A dark red brick-shaped crystal of approximate dimensions 0.045 × 0.040 × 0.017 cm, was used for data collection with a Syntex *P*3 four circle diffractometer. Data in the range $3.5 < 2\theta < 50°$ were collected using an omega scan of 1.90 degrees for each reflection with the detector arm fixed; the scan rate was varied between 1.01 and 14.65 deg min^{-1}, dependent on prescan intensity; "weak" reflections having this prescan intensity less than 100 counts were not measured. Background scatter was measured at each end of the scan such that the total background counting time was equal to the time spent scanning the reflection. 4365 independent reflections with intensity $I > 3\sigma$ (I_{obs}) and background difference $\Delta < 4\sigma B$ were corrected for Lorentz and polarisation effects.

The structure was solved using Patterson and Fourier methods and refined using block diagonal matrix least-squares refinement. Individual atom refinement proceded satisfactorily using anisotropic thermal parameters for all non-hydrogen atoms and *R* convergenced at 0.052. At this stage a distance-angle calculation showed on of the pentamethylcyclopentadienyl rings to be ill-defined, a difference Fourier synthesis at this stage showed this ring also had randomly arranged residual peaks associated with it. The ring carbon atoms of each of the pentamethylcyclopentadienyl rings were therefore treated as groups of fixed overall geometry in the structure factor calculation and allowed to refine both in translation and rotation; the methyl substituents were left as individual atoms in the calculation and refinement. A difference Fourier synthesis now showed an alternative position for the carbon atoms of the suspect pentamethylcyclopentadienyl ring, such that the alternative position is related by rotation about an axis approximately through the centre of the ring and perpendicular to the plane of the five carbon atoms. The thermal parameters of the two rings were returned to isotropic values and their relative populations adjusted until they showed similar thermal parameters — at this stage the relative populations were 70 : 30%. Finally methyl carbon substituents on the low population ring were included, and *R* converged at 0.043. A difference Fourier synthesis at this stage showed the maximum residual electron density to be 0.78 *e* Å^{-3}; electron density between Rh(1) and Rh(3) was interpreted as due to a hydride but this was not included in the calculation.

The overall geometry of the molecule is shown in Figs. 1 and 2, atomic coordinates are in Table 4, distance-angle values in Table 2, and equations of some important molecular planes in Table 3. Structure factors and anisotropic thermal parameters can be obtained from the authors.

Atomic scattering factors for neutral Rh, C, O, F, P were used with corrections for real and imaginary components of anomalous dispersion [25]. Calculations were computed on the University of Sheffield ICL 1906S computer, using programs from the Sheffield X-ray system.

X-ray crystal structure determination of $[(RhC_5Me_5)_2(H)_2(O_2CMe)]PF_6$ *(8a)*

Crystal data: $[C_{22}H_{35}O_2Rh_2]PF_6$; $M = 682.3$; Monoclinic, $a = 20.893(9)$, $b = 16.447(12)$, $c = 15.752(12)$ Å, $\beta = 90.44(5)°$, $U = 5368$, $Z = 8$, $D_m = 1.70$ (flotation), $D_c = 1.688$ g cm^{-3}, $F(000) = 2736$. Systematic absences are consistent with spacegroups $Cc(C^4{}_s$, no. 9) and $C2/c(C^6{}_{2h}$, no. 15), Mo-K_α X-radiation (graphite monochromator) $\lambda = 0.71069$, μ(Mo-K_α) = 13.26 cm^{-1}.

Single crystal X-ray data in the range $3.5 < 2\theta < 50$ were collected on a Syntex P3 four circle diffractometer. For each reflection, omega was scanned with the detector arm in a fixed position, the scan rate being in the range 3.0 to 29.3 deg min^{-1}, dependent on prescan intensity. Weak reflections having prescan intensities below 38 counts were omitted. Background counts were accumulated at each end of the scan such that the total background counting time equalled the total time spent scanning the reflections. 2576 independent reflections with intensity $I > 3\sigma(I)$ and background difference $\Delta < 4\sigma B$ were cor-

TABLE 7

ATOMIC FRACTIONAL COORDINATES FOR $[(RhC_5Me_5)_2(H)_2OAc]PF_6$ (8a) $\times 10^4$ ($\times 10^5$ FOR THOSE MARKED *), ESTIMATED STANDARD DEVIATIONS ARE IN PARETNTHESES

Atom	x/a	y/b	z/c
*Rh(01)	—4623(3)	19514(4)	5838(4)
*Rh(02)	7394(3)	20804(4)	1752(4)
P	2072(1)	4637(2)	7654(2)
F(01)	2012(6)	3732(5)	7663(10)
F(02)	1346(4)	4716(7)	7345(6)
F(03)	2132(5)	5568(5)	7640(8)
F(04)	2799(4)	4571(6)	7974(6)
F(05)	2216(5)	4630(9)	6728(5)
F(06)	1915(5)	4646(9)	8550(5)
O(1)	845(3)	922(3)	688(4)
O(2)	—151(3)	816(3)	1031(4)
C(01)	413(4)	552(3)	1009(5)
C(02)	570(5)	—284(5)	1402(7)
C(03)	—1385(4)	2291(5)	—108(5)
C(04)	—1097(4)	2968(5)	371(5)
C(05)	—1043(4)	2752(5)	1261(6)
C(06)	—1260(4)	1941(5)	1327(5)
C(07)	—1477(4)	1655(5)	464(5)
C(08)	—1582(5)	2270(7)	—1072(6)
C(09)	—981(5)	3809(6)	24(8)
C(10)	—808(5)	3312(6)	1994(7)
C(11)	—1259(5)	1433(7)	2118(6)
C(12)	—1767(5)	827(6)	242(7)
C(13)	945(5)	2961(7)	—749(6)
C(14)	1175(5)	3249(5)	76(6)
C(15)	1653(4)	2694(5)	460(6)
C(16)	1722(4)	2062(7)	—135(6)
C(17)	1287(5)	2207(7)	—873(6)
C(18)	454(6(	3386(10)	—1399(9)
C(19)	995(6)	4037(6)	491(9)
C(20)	2045(5)	2775(7)	1334(6)
C(21)	2175(5)	1338(7)	32(9)
C(22)	1208(7)	1691(11)	—1704(7)
H(01)	—42(50)	1875(63)	—292(63)
H(02)	250(48)	2333(62)	958(64)

rected for Lorentz and polarisation effects, no allowance was made for absorption and extinction.

The structure was solved using Patterson and Fourier methods, with the Patterson function indicating the centric space group. Block diagonal matrix least squares refinement reduced R to 0.063 with all atoms having isotropic temperature factors. Introduction of anisotropy on all atoms further reduced R to 0.032. At this stage, a difference Fourier synthesis using the 750 reflections at lowest angle ($\sin \theta/\lambda < 0.34$) clearly showed the presence of electron density in the position bridging the two rhodium atoms. The methyl hydrogen atom positions were calculated at 10° intervals around an annulus 0.95 Å from the methyl carbon atom and making an angle of 109.5° with the carbon—carbon bond; the electron density was calculated at each of these points, but well defined positions for these hydrogen atoms could not be found. Structure factors were calculated with the two bridging hydrogen atoms included but not allowed to refine, the final R-factor being 0.031.

Atomic scattering factors were taken from ref. 25. Calculations were computed on the University of Sheffield ICL 1906S computer using programs from the Sheffield X-ray system. The final structural parameters with e.s.d.'s are listed in Table 7, bond lengths and bond angles are listed in Table 5, important least squares planes in Table 6 and the structure is depicted in Figure 4. Structure factors and anisotropic thermal parameters may be obtained from the authors.

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