Synthesis and Structure (*X*-Ray Diffraction and Spectroscopy) of an Extremely Rigid and Non-fluxional Trinuclear Trihydride, $[Rh_3H_3(\eta^5\text{-}C_5Me_5)_3O]PF_6\cdot H_2O$

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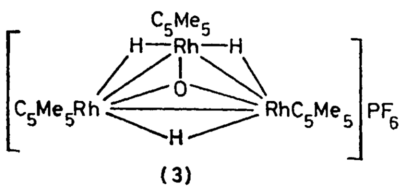
Summary The trinuclear trihydride $[Rh_3H_3(\eta^5\text{-}C_5Me_5)_3O]\cdot PF_6\cdot H_2O$ has been synthesised and characterised by *X*-ray diffraction and spectroscopy; the ^1H n.m.r. spectrum shows the molecule to be extremely rigid with a *minimum* $\Delta G^\ddagger$ for fluxionality of 109 kJ mol^{-1}.

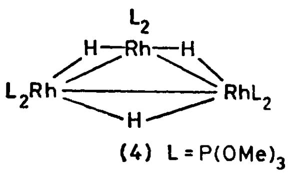
We recently reported[1] the structure of the tetrarhodium tetrahydride complex $[Rh_4H_4(\eta^5\text{-}C_5Me_5)_4]^{2+}$ (**2**) and its synthesis by reaction of hydrogen (90 °C, 1 atm) with an aqueous solution of $[Rh_2(C_5Me_5)_2(OH)_3]Cl$ (**1**).[2] During this reaction the colour changes from the yellow-orange of (**1**) through deep red to the dark green characteristic of (**2**). A similar series of colour changes, which we have shown to arise from the formation of the same species, also occurs on warming a solution of (**1**) in aqueous propan-2-ol and if the reaction is carried out at 45 °C a new red-brown complex (**3**) can be isolated on addition of hexafluorophosphate after 24 h. Crystals suitable for *X*-ray analysis were grown from a slowly reacting solution.

$[C_5Me_5Rh(OH)_3RhC_5Me]Cl$ (1)

$[Rh_4H_4(C_5Me_5)_4][PF_6]_2$ (2)



(3)



(4) L = P(OMe)$_3$

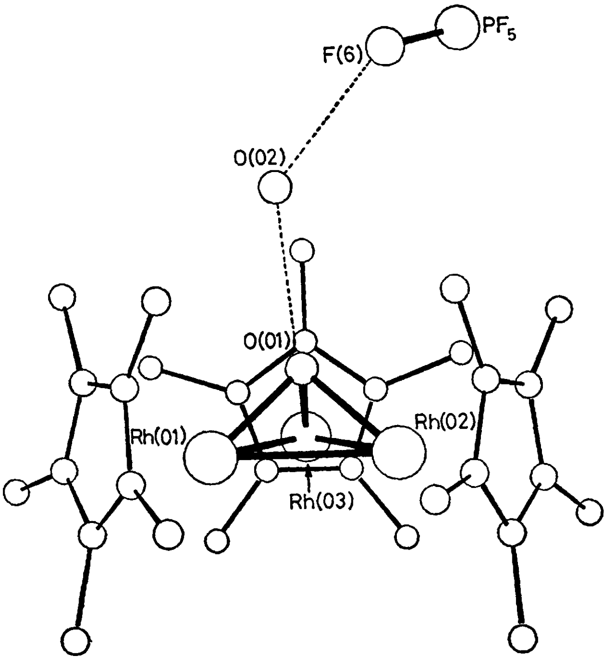


Figure 1. View of the structure of complex (**3**), *all* hydrogen atoms and carbon atom labels omitted for clarity. Important bond lengths (e.s.d.'s in parentheses): Rh(1)–Rh(2), 2·757(1); Rh(1)–Rh(3), 2·770(1); Rh(2)–Rh(3), 2·755(1); Rh–O (mean), 2·001(6); Rh–C (C_5Me_5) (mean), 2·17 Å. Rh–O(1)–Rh' (mean) 87·2°.

Crystal data: $[C_{30}H_{48}ORh_3]PF_6\cdot H_2O$, $M = 896{\cdot}0$, triclinic, $a = 11{\cdot}065(12)$, $b = 15{\cdot}282(17)$, $c = 11{\cdot}230(28)$ Å, $\alpha = 96{\cdot}80(3)$, $\beta = 85{\cdot}31(3)$, $\gamma = 70{\cdot}27(1)^\circ$, $U = 1759{\cdot}8$ Å^3, $Z = 2$, $D_{obs} = 1{\cdot}632$, $D_{calc} = 1{\cdot}69$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å. Three-dimensional *X*-ray data were collected on a Stoe STADI-2 diffractometer in the stationary-counter–moving-crystal mode. 4744 Independent reflections in the range $6{\cdot}5 < 2\theta \leqslant 50^\circ$ with $I_{obs} \geqslant 3\sigma(I_{obs})$ were obtained. The structure was solved using Patterson and Fourier methods and refined using block diagonal matrix least squares refinement; each pentamethylcyclopentadienyl ring had the ring carbon atoms present in the calculation as a group of fixed geometry and the methyl substituents as individual atoms. At an advanced stage of the refinement, a difference Fourier synthesis showed that there was some disorder associated with one of the pentamethylcyclopentadienyl rings and this was likewise introintroduced into the structure factor calculation. The populations of the two positions of the rings were adjusted until both showed similar isotropic temperature factors for the ring carbon atoms; at this stage the relative populations were 0·7 : 0·3 and the *R* factor was 0·049.

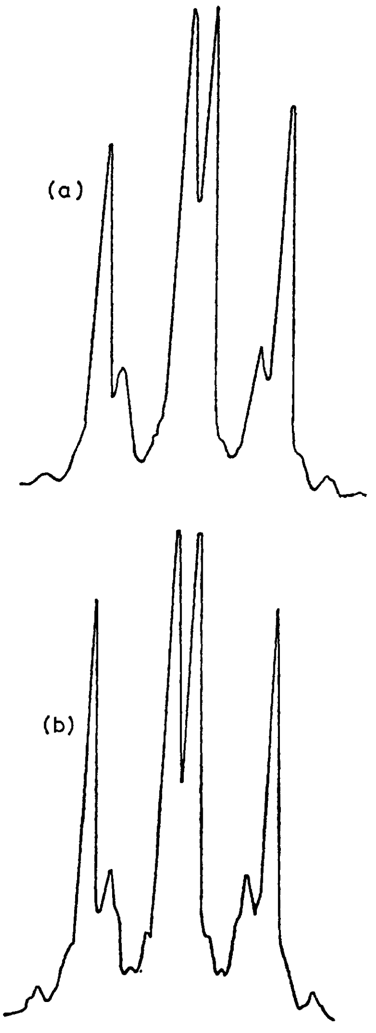
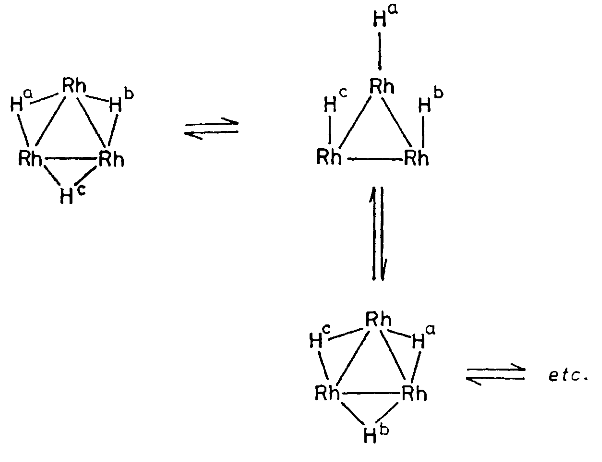


FIGURE 2. (a) ^1H n.m.r. spectrum (hydride region) of complex (**3**); (b) computer simulation using parameters detailed in text.

The molecular structure of (**3**) consists of a triangle of rhodiums (each η^5-bonded to a C_5Me_5 ligand) capped on one side by an oxygen (Figure 1). This oxygen is hydrogen-bonded to a water of crystallisation which is, in turn, hydrogen-bonded to one F of the PF_6^- group. A difference Fourier synthesis at $R = 0{\cdot}049$ shows residual electron density due to a hydride in a position bridging two rhodium atoms[†] [Rh–H = 1·7 Å (mean), Rh–H–Rh = 100°] on the opposite side to the capping oxygen.

Integration of the ^1H n.m.r. spectrum shows the presence of one hydride (at δ $-18{\cdot}20$) per C_5Me_5 (at δ 2·03), showing (**3**) to be a trihydride cluster. The surprising feature of this cluster is the $[AX]_3$ pattern (A = ^{103}Rh, X = ^1H) of the hydride resonance (Figure 2a). Inspection shows that it is not the 1 : 3 : 3 : 1 quartet that would be expected from the coupling of three equivalent (on the n.m.r. time-scale) hydrogens with three equivalent rhodiums. The spectrum can be accurately simulated (Figure 2b) on the basis of the observed geometry using the parameters ^1J(Rh–Rh) 10·3, ^1J(Rh–H) 26·6, ^2J(Rh–H) 0·5, and ^2J(H–H) 4·5 Hz.[‡] The shape of the hydride resonance remains unchanged over the temperature range -60 to $+100$ °C and we estimate a minimum $\Delta G^\ddagger$ for fluxionality to be 26 kcal mol^{-1} (109 kJ mol^{-1}).

The molecular core of (**3**) is therefore extremely rigid; this may be contrasted with the complex $[Rh_3H_3\{P(OMe)_3\}_6]$ (**4**) which also contains a triangular array of rhodiums bridged by hydrides and which is fluxional down to -120 °C and with $\Delta G^\ddagger$ less than 8 kcal mol^{-1}.[3] We suggest that this remarkable difference arises because complex (**4**) is flexible enough to allow ready movement of the hydrides; for example it may occur by a process similar to that which has been



SCHEME.

[†] Although the other two edge-bridging hydrides are equivalent, residual electron density in these positions was not found on the function, presumably because of the disorder of the one C_5Me_5 ligand. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[‡] The ^{13}C n.m.r. spectrum of the ring carbons (δ 98·5) is of the AX_3 type and can also be accurately simulated with ^1J(Rh–C) = 7·0 and ^2J(Rh–C) = 0 Hz.

proposed for the equilibration of the carbonyl ligands in $[Rh_3Cp_3(CO)_3]$[4] (Scheme).

Similar deformations in complex (**3**) will, however, be resisted by (a) the capping oxygen and (b) the intermeshed methyls of the C_5Me_5 ligands and hence (**3**) is quite rigid. This observation further suggests that in cluster complexes even the movement of hydrides, which have been termed extremely 'plastic' ligands,[5] requires some substantial movement or rehybridisation of the associated metal atoms. However, (**3**) is formally a complex of Rh^{III}, whereas (**4**) contains Rh^{I}, and the possibility that part, at least, of the barrier to fluxionality is due to electronic effects cannot be excluded.

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