

The Molecular Structure of the Hydrogenation Catalyst Hyridoacetatotris(triphenylphosphine)ruthenium(II)

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Summary The hydrogenation catalyst $\text{RuH}(\text{ac})(\text{PPh}_3)_3$ is monomeric with highly-distorted six-co-ordination.

THE complex $\text{RuH}(\text{ac})(\text{PPh}_3)_3$ ¹ is a strong homogeneous hydrogenation catalyst and is highly specific for alk-1-enes. Its activity is somewhat less than that of $\text{RuClH}(\text{PPh}_3)_3$ ² (though comparable), but its greater solubility makes it more amenable to kinetic studies.

The structure of $\text{RuClH}(\text{PPh}_3)_3$ has been recently determined,³ and we now report the crystal structure of the title compound. We find that the molecule is monomeric with a highly-distorted six-co-ordination, the acetate group being bidentate and loosely held.

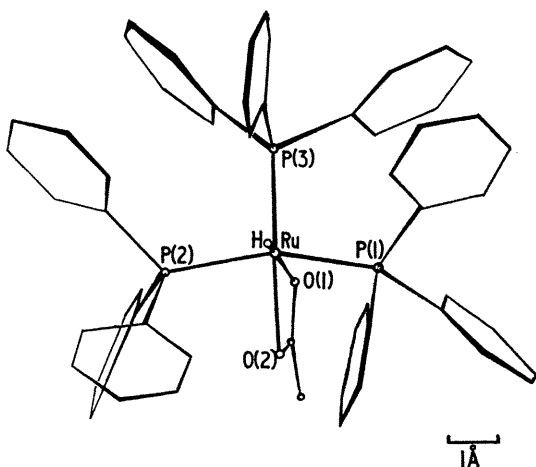


FIGURE 1. Molecular structure of $\text{RuH}(\text{ac})(\text{PPh}_3)_3$.

Hyridoacetatotris(triphenylphosphine)ruthenium(II) crystallises from methanol-benzene to form dark orange needles which are monoclinic. The unit-cell dimensions are $a = 20.68$, $b = 9.636$, $c = 26.59$ Å, $\beta = 119^\circ 35'$, $U = 4607$ Å³, $D_m = 1.39$, $Z = 4$, $D_c = 1.37$, space group $P2_1/c$.

The structure was solved by Patterson and Fourier methods from three-dimensional X-ray data recorded with Cu- K_α radiation and visually estimated. Least-squares refinement has now reached $R = 0.092$ for 4082 independent reflections.

The molecular structure and the ruthenium co-ordination are shown in Figures 1 and 2, respectively. These show

that the ruthenium atom is co-ordinated to six atoms. Apart from the acetate ligand the ruthenium environment shows a striking similarity with that found in $\text{RuHCl}(\text{PPh}_3)_3$. Thus the arrangement of the three phosphorus atoms and of the hydride hydrogen is virtually identical in both molecules. Again one Ru-P distance (the corresponding one) is considerably shorter (2.229 Å) than the other two (2.363 and 2.354 Å, respectively). The longer distances are presumably due to the mutual *trans*-influence of the PPh_3 groups.

The acetate ligand is bidentate and is rather distant from the ruthenium atom with Ru-O distances of 2.208 and 2.256 Å. These long distances suggest that the group is

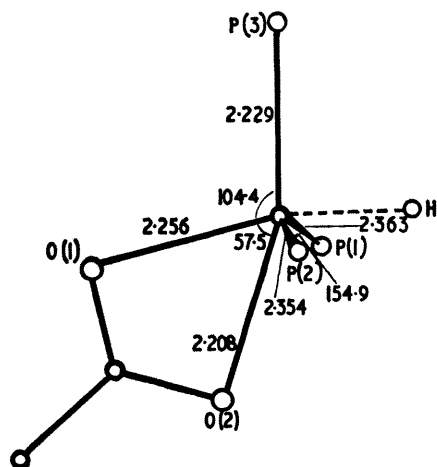


FIGURE 2. Co-ordination about the ruthenium atom. Standard deviations are: Ru-P, 0.004 Å, Ru-O, 0.010 Å; P(1)-Ru-P(2), 0.2°; P(3)-Ru-O(1); 0.3°; O(1)-Ru-O(2), 0.4°.

only loosely held, in agreement with the fact that in solution it is easily replaced by CO.¹ The longer Ru-O distance is opposite the hydride hydrogen, presumably reflecting its higher *trans*-influence compared to that of a PPh_3 group.

Although at this stage the full procedure⁴ for optimising the hydride hydrogen positions has not been applied, we find that the highest remaining peak in a difference Fourier is in the expected position at a distance *ca* 1.7 Å, as found in $\text{RuHCl}(\text{PPh}_3)_3$ and a hydridonaphthylruthenium(II) complex.⁵

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