Molecular Structure of the Hydrogenation Catalyst Hydridochlorotris(triphenylphosphine)ruthenium(II)

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THE COMPLEX $RuClH(PPh_3)_3$ is the most active homogeneous hydrogenation catalyst yet known and is highly specific for alk-1-enes of formula $RCH{=}CH_2$.[1] The high selectivity is attributed to steric hindrance in the formation of an alkyl intermediate, which then undergoes oxidative addition of hydrogen followed by reductive elimination of alkane. This hindrance by bulky triphenylphosphine groups occurs when they are mutually *trans* and *cis* to the hydrido- or alkyl-groups.[2] This high selectivity is also found using $RhH(CO)(PPh_3)_3$ as catalyst.

We have now determined the crystal structure of the title compound. The molecule is monomeric with a highly distorted pentaco-ordination. We have located the position of the hydride hydrogen atom.

Hydridochlorotris(triphenylphosphine)ruthenium(II) crystallises from a supersaturated solution in benzene to give burgundy-red monoclinic prisms which are unstable in air. The unit-cell dimensions are $a = 19{\cdot}80$, $b = 14{\cdot}32$, $c = 20{\cdot}73$ Å, $\beta = 122{\cdot}34°$, $U = 4966$ Å^3. The crystals also contain solvated benzene; $Z = 4[RuClH(PPh_3)_3,C_6H_6]$, $D_m = 1{\cdot}33$, $D_c = 1{\cdot}341$ g. cm.$^{-3}$. The space group is $P2_1/c$.

Three-dimensional X-ray data were collected on a Siemens automatic four-circle diffractometer from a crystal sealed under nitrogen in a Lindemann tube. Using Cu-K_α radiation a total of 2770 independent reflections were measured (to $\theta = 40°$), of which 676 were judged to be unobserved. The structure was solved by standard methods and least-squares refinement has now reached R 0·058.

The molecular structure and the ruthenium co-ordination are shown in Figures 1 and 2 respectively. Of the pentaco-ordinate d^6 transition metal complexes $RhI_2Me(PPh_3)_2$[3] is square-pyramidal, $RuCl_2(PPh_3)_3$[4] is square-pyramidal but with an α-hydrogen of a phenyl group blocking the sixth octahedral position, while the title compound is much less easy to describe. The co-ordination can be visualised as being a considerably distorted trigonal bipyramid, where the two axial PPh_3 groups bend from the perpendicular position to accommodate the equatorial PPh_3 group, such that the P(2)–Ru–P(3) angle is 153·1° ($\sigma = 0{\cdot}2°$). The chlorine atom occupies the second equatorial position, and the angle Cl–Ru–P(1) is 121·4° ($\sigma = 0{\cdot}2°$). The hydride hydrogen atom, which is clearly apparent in a difference Fourier, cannot occupy its expected position in the equatorial plane [P(1)–Rh–H $\approx$ 120°] because of the proximity of a phenyl α-hydrogen almost in this plane at $2{\cdot}8_5$ Å from the ruthenium atom. The hydride

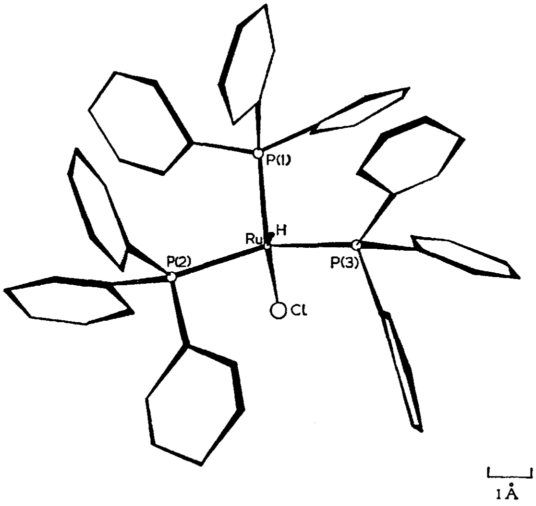

FIGURE 1. *Molecular structure of* $RuClH(PPh_3)_3$.

hydrogen is therefore displaced such that the P(1)–Ru–H angle is approximately 89°.

We estimate the Ru–H(hydride) distance to be $1{\cdot}7 \pm 0{\cdot}15$ Å, which is close to the sum of covalent radii. This may be compared to Rh–H of $1{\cdot}60 \pm 0{\cdot}12$ Å in $RhH(CO)(PPh_3)_3$,[5] and Re–H of $1{\cdot}68 \pm 0{\cdot}01$ Å (by neutron diffraction) in K_2ReH_9.[6]

The Ru–P distances are a little shorter than those found in $RuCl_2(PPh_3)_3$, but similarly we find one distance (2·206 Å, equatorial) considerably shorter than the other two (2·329 and 2·361 Å, axial). The Ru–Cl distance is slightly longer, 2·421 Å, as against 2·387 and 2·388 Å in $RuCl_2(PPh_3)_3$.

The chlorine atom has some close phenyl hydrogen neighbours. There are two intramolecular distances of $2{\cdot}4_4$ and $2{\cdot}6_8$ Å (based on calculated hydrogen positions), and one intermolecular distance of $2{\cdot}7_7$ Å. These are shorter than the sum of van der Waals' radii and might represent possible interactions.[7]

The benzene molecules are merely solvated and play no role in the co-ordination about the metal atom.

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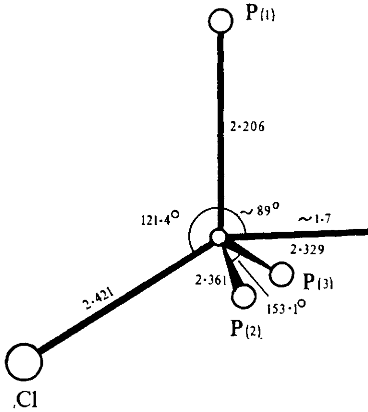

FIGURE 2. *Co-ordination about the ruthenium atom. Standard deviations*: Ru–P, 0·004 Å; Ru–Cl, 0·005 Å, P(1)–Ru–Cl, 0·2°; P(2)–Ru–P(3), 0·2°.

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