X-Ray Crystal Structure of *trans*-Chlorohydridobis(diop)ruthenium(II); an Octahedral Complex with Inequivalent Phosphorus Atoms

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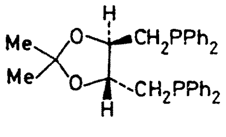
Summary The HRuCl(diop)$_2$ complex, although showing ^{31}P and high-field ^{1}H n.m.r. spectra typical of a *cis*-structure with inequivalent phosphorus atoms, has been shown by *X*-ray crystallography to have a distorted octahedron structure with the hydrogen *trans* to chlorine.

THE structure in solution of complexes of the type [HM{Ph$_2$P[CH$_2$]$_n$PPh$_2$}$_2$Cl]$^+$, M = Ir[1,2] or Rh,[3–5] or [HRuCl{Ph$_2$P[CH$_2$]$_n$PPh$_2$}$_2$][6] is commonly assigned using low temperature ^{31}P and high-field ^{1}H n.m.r. spectra. For example, a doublet of triplets in the low temperature {^{1}H}-^{31}P n.m.r. spectrum is interpreted in terms of a non-rigid structure with *cis*-geometry for the H and Cl atoms,[1,2] and we had similarly assigned[7] such a structure for the asymmetric hydrogenation catalyst HRuCl(diop)$_2$, where diop is the optically active chelating diphosphine 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane.[8] The crystal structure of the complex, however, is that of a distorted octahedron with the H atom *cis* to all four phosphorus atoms and *trans* to the chlorine atom.



(4*R*, 5*R*)-(−)diop

Crystal data: C$_{82}$H$_{85}$ClO$_4$P$_4$Ru, $a = 20{\cdot}506(3)$, $b = 16{\cdot}110(2)$, $c = 11{\cdot}085(1)$ Å, orthorhombic space group $P2_12_12$, $Z = 2$, $D_c = 1{\cdot}19$ g cm^{-3}; Mo-K_α radiation ($\lambda = 0{\cdot}71073$ Å), $\mu = 3{\cdot}81$ cm^{-1}. There were 9841 data measured out to $2\theta = 60°$, including 3928 Friedel pairs, on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by standard Patterson and Fourier techniques. A full-matrix least-squares refinement of 248 variables (those atoms not of the phenyl rings or the toluene solvate molecules were assigned anisotropic thermal parameters and the H atom contributions were included as fixed atoms) using 4103 unique reflections [$F^2 > 3\sigma(F^2)$] gave $R = 0{\cdot}048$.†

The molecular structure (Figure) has a crystallographic 2-fold axis of symmetry passing along the H–Ru–Cl bonds. The distortion from an octahedron consists of a bending of P(2) and P(2′) towards the hydrogen, and a bending of P(1) and P(1′) towards the chlorine. The hydrogen, located on a difference Fourier map, is 1·65 Å from the ruthenium, and this distance is similar to that found for ruthenium(II)–hydrogen bonds in related tertiary phosphine complexes.[9–11] The ruthenium–chlorine bond (2·548 Å) is considerably longer than those measured in HRuCl(PPh$_3$)$_3$, 2·421 Å[9] and in RuCl$_2$(PPh$_3$)$_3$, 2·387 Å;[12] this presumably reflects the *trans*-influence of the hydride ligand, and could account for some conductivity measured in nitromethane owing to partial loss of co-ordinated chloride.[7]

More detailed n.m.r. data can be interpreted assuming that the same structure pertains in solution with the in-

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† 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.

equivalence of the pairs of phosphorus atoms being maintained. In C_6D_6 at 28 °C, the $\{^{1}\text{H}\}$-^{31}P spectrum at 24·3 MHz consists of two triplets (J = 40 Hz) centred at 119·1 and 137·8 p.p.m. upfield from external trimethyl phosphite, each peak of the triplets showing a poorly resolved doublet.

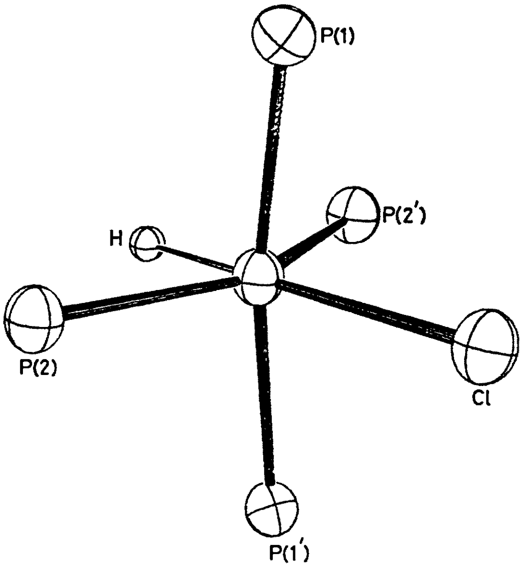

FIGURE. The co-ordination geometry of the HRuCl(diop)$_2$ complex. Bond lengths (Å) and bond angles (°) are: Ru–P(1), 2·393(1); Ru–P(2), 2·356(1); Ru–Cl, 2·548(2); and Ru–H, 1·65; ∠ P(1)–Ru–P(1'), 168·58(6); ∠ P(2)–Ru–P(2'), 149·52(7); and ∠ P(2)–Ru–Cl, 105·24(3). Atoms P(1) and P(2) are part of the same diop molecule. A prime superscript, *e.g.* P(1) and P(1'), indicates atoms related by the 2-fold axis.

Decoupling of all the protons except the co-ordinated hydride produced a further doubling of the 'triplets,' the low field one being split by 30 Hz and the upfield one by 13 Hz. The distorted septet observed[7] for the hydridic proton resonance centred at τ 28·7 results from the overlapping of the expected triplet of triplets. The n.m.r. data were essentially the same at −80 °C in $(CD_3)_2CO$.

The solid state structure of HRuCl(diop)$_2$ constitutes an AA'BB'X system, although the observed spectra are most simply interpreted as arising from an A_2B_2X system that is close to first order. The deceptively simple A_2B_2X spectra can occur for the AA'BB'X system when $J_{AB} = J_{AB'}$, or when the system is dominated by a large $J_{AA'}$ or $J_{BB'}$. Coupling between the phosphorus atoms of a chelated ligand may be regarded as a sum of terms transmitted through the ligand backbone and through the metal;[13] the backbone contribution will be negligible in this case since there are four carbon atoms between the phosphorus atoms, and thus the condition $J_{AB} =$ *ca.* $J_{AB'}$ is probably satisfied. $J_{AA'}$ and $J_{BB'}$ are also likely to be large since the couplings involve mutually ***trans*** phosphorus atoms. Successful computer simulation of all the spectra was achieved using $J_{AB} = J_{AB'} = J_{A'B'} = J_{A'B} = 40{\cdot}2$ Hz, $J_{AX} = J_{A'X} = 30{\cdot}5$ Hz, and $J_{BX'} = J_{B'X} = 13{\cdot}1$ Hz. (Values of $J_{AA'}$ and $J_{BB'}$ of *ca.* 200 Hz were used for the calculations but they are not well determined since the spectra are independent of these parameters when $J_{AB} = J_{AB'}$).

It is interesting to note that the HRuCl$\{Ph_2P[CH_2]_4PPh_2\}_2$ complex (comparable to the diop complex with four carbon atoms between the chelating diphenylphosphino groups) shows equivalent phosphines in the n.m.r. spectra under the same conditions at 28 °C[6] with the hydride appearing as a quintet at τ 28·8; C_{4v} symmetry is indicated. The dioxolan ring in the diop complex fixes the configuration of the seven-membered ruthenium-containing chelate ring and the geometry appears to distort to minimize phenyl–phenyl interactions; without the dioxolan ring the four-carbon backbone can twist and can lead to pseudo C_{4v} symmetry. The flexibility of the torsion angle between C-4 and C-5 is important in determining the extent of optical induction during asymmetric hydrogenation catalysed by such complexes.[14]

More caution is clearly necessary when assigning structures for octahedral bis(ditertiary-phosphine) complexes based on n.m.r. data.

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