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A Molecular Dihydrogen Moiety within Dimeric Chlorohydrido(tertiary phosphine)ruthenium Complexes

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Three years ago in the centennial issue of *Inorganica Chimica Acta*, ongoing work from this Department was reported on chlorohydridoruthenium(II) complexes containing two tertiary phosphines per Ru. These are key species within hydrogenation systems catalyzed by, for example, $RuHCl(PPh_3)_3$ [1]. The dimeric complexes $[RuH_2XL_2]_2$ (X = Cl, Br; L = PPh_3, $AsPh_3$ and $Ptol_3$, where tol = *p*-tolyl), were synthesized and 'fully characterized' by elemental analyses, ^1H and $^{31}P\{^1H\}$ NMR, a range of chemical reactions and, in the case of $[RuH_2Cl(Ptol_3)_2]_2$ (**1**), a crystal structure determination.

The crystallographic analysis did not locate the hydrogen ligands, but based on the structural data and the NMR data, especially three high-field ^1H signals measured in CD_2Cl_2 at −95 °C, the positions of the hydrogens were shown as in Fig. 1 [1]: a bridging hydride H(1), one terminal hydride H(3) on one Ru, and two terminal hydrides H(2) on the other Ru. Relaxation measurements (T_1) on this complex now show that the H(2) atoms are in fact a coordinated η^2-H_2 moiety, and the species is a further example within a growing series of molecular hydrogen complexes [2], these being first reported in 1984 [3].

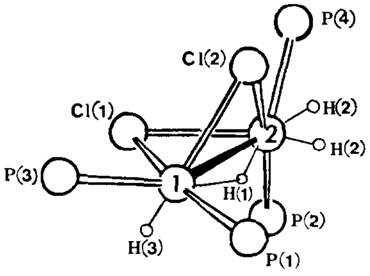

Fig. 1. Diagrammatic crystal structure of $[RuH_2Cl(Ptol_3)_2]_2$ (**1**) as given in ref. 1; the H(2) atoms are now shown to be a coordinated η^2-H_2.

The upfield resonances of **1** at −95 °C, of relative intensities 1:2:1, seen at δ −9.27 (dd, 72 Hz, 4 Hz), −11.65 ($\nu_{1/2}$ = 120 Hz) and −19.15 (t, 28 Hz), are assigned, as discussed previously [1], to H(1), H(2) and H(3), respectively (Fig. 2). Application of the inversion recovery method, as described by Crabtree *et al.* [2], to CD_2Cl_2 solutions of **1** using a Varian 300 MHz instrument provides data of the kind shown in Fig. 3. The T_1 values at −95 °C are 123(±11), 44(±2) and 350(±40) ms, respectively, for H(1), H(2) and H(3). The short relaxation time measured for H(2) is typical of that found for η^2-H_2 [2]. Warming the solution reveals the usual exchange [2] between the classical hydrides and the η^2-hydrogens (above −40 °C, a weighted average single resonance is observed [1]); at −64 °C, the T_1 values (ms) become comparable: δ −9.2 (41 ± 1), −11.7 (40.0 ± 0.5), −19.0 (47 ± 2). The exchange process, discussed in the earlier paper (eqn. 17 in ref. 1), is pictured much as before but with η^2-H_2 forming alternately at Ru(1) and Ru(2).

Correspondence in ^1H and ^{31}P NMR data (but more limited because of solubility problems) implies η^2-H_2 moieties within the other $[RuH_2XL_2]_2$ compounds (X = Cl, Br; L = PPh_3, $AsPh_3$). The reactions of $[RuH_2XL_2]_2$ with L, CO, and dipy, to give $RuHXL_3$, $RuHCl(CO)_2L_2$ and $RuHCl(dipy)L_2$, respectively, in each case with liberation of 1 mole H_2 per

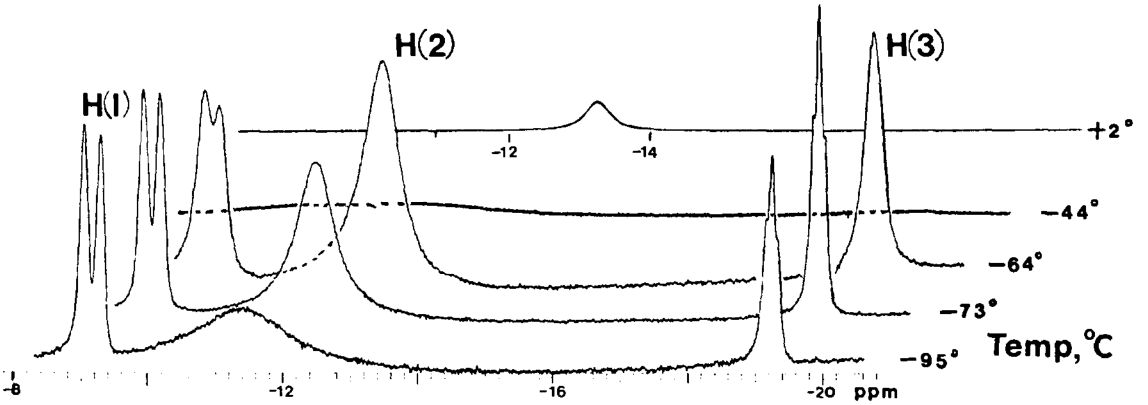

Fig. 2. High-field region ^1H NMR spectrum (300 MHz) of complex **1** in CD_2Cl_2 at various temperatures (expanded H(1) and H(3) resonances at −95 °C are shown in Fig. 5 of ref. 1).

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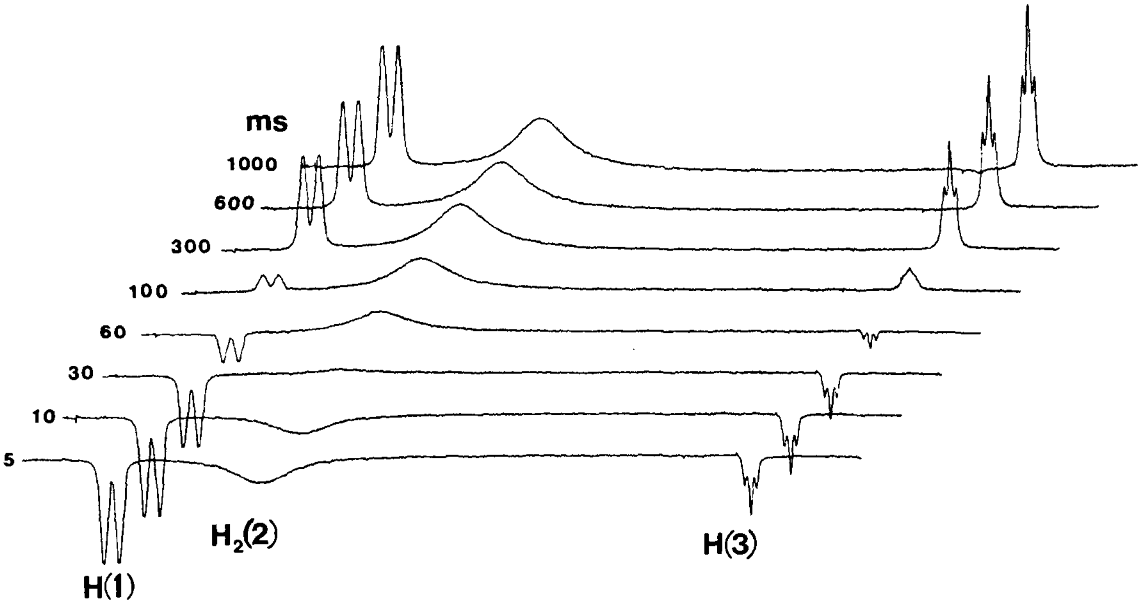

Fig. 3. Inversion–recovery spectra (high-field ^1H NMR, 300 MHz) of complex 1 in CD_2Cl_2 at −84 °C (*cf.* Fig. 2). The η^2-H_2 hydrogens are seen to relax more quickly than the terminal and bridging hydrides.

reactant dimer, presumably proceed via predissociation of the η^2-H_2; similar dissociation has been invoked for reactions of $Ru(H)_2(\eta^2\text{-}H_2)(PPh_3)_3$ [2, 4]. Kinetic data on the reaction of $Ptol_3$ with complex **1**, which showed a direct inverse dependence on H_2, yielded information on the equilibrium constant for the predissociation [1]. **1** is stable in solution under 1 atm H_2, but loses H_2 slowly under, for example, an argon atmosphere. The lability of the η^2-H_2 seems comparable to that of the η^2-H_2 in $RuH(\eta^2\text{-}H_2)[Ph_2P(CH_2)_2PPh_2]_2^+$ [5].

It is worth noting that on subjecting $RuHCl(Ptol_3)_3$ to 1 atm H_2 in toluene-d_8, the high-field ^1H NMR quartet (δ −16.8, $J(PH) = 26$ Hz) of the hydride is broadened and is accompanied by development of a weak broad signal at δ −12.8 that corresponds to the averaged ambient temperature high-field signal of complex **1**. Similar broadening of the quartet hydride signal of $RuHCl(PPh_3)_3$ has been noted by others [6] and ourselves, but there is no observable, averaged signal of $Ru_2H_4Cl_2(PPh_3)_4$, the triphenylphosphine analogue of **1**; it may just be too weak to be detected. The dinuclear η^2-H_2 species could play a role in the extremely rapid H_2/D_2 exchange process observed in the presence of $RuHCl(PPh_3)_3$, and in the exchange process that leads to broadening of the high-field quartets [6].

In conclusion, the complex $[RuH_2Cl(Ptol_3)_2]_2$ is now reformulated as $(Ptol_3)_2RuH(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(\eta^2\text{-}H_2)(Ptol_3)_2$, and to our knowledge is the first dinuclear species reported to contain a molecular dihydrogen ligand [7]*. We await more definitive structural data regarding the nature of the metal–metal interaction, and the formal oxidation states of the metals.

Acknowledgements

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*A complex analogous to 1 but with the bridging chlorines replaced by hydrogens has recently been synthesized.