Characterisation and Properties of the Dinuclear Ruthenium Molecular Hydrogen Complex $[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$; dppb = $Ph_2P(CH_2)_4PPh_2$

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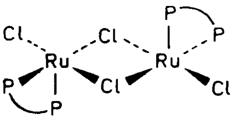
Dihydrogen adds reversibly to the dimeric Ru^{II} complex $[\{RuCl(dppb)(\mu\text{-}Cl)\}_2]$ (**1**), where dppb = 1,4-bis(diphenylphosphino)butane, to give the remarkably simple molecular hydrogen title complex (**2**) which is an effective catalyst for hydrogenations utilising H_2 and for transfer hydrogenations from propan-2-ol; the $\eta^2\text{-}H_2$ ligand (with an H–H distance of 0.86 Å as estimated by ^1H NMR T_1 data) is replaceable by other ligands including N_2.

Molecular dihydrogen complexes of transition metals continue to be of intense interest from both theoretical aspects and their potential role in catalytic hydrogenation and dehydrogenation of organic substrates.[1] Dinuclear $\eta^2\text{-}H_2$ complexes are rare; the four thus far reported all contain Ru–phosphine moieties, and also possess bridging as well as classical, terminal hydrides.[2] We now describe the title dinuclear $Ru(\eta^2\text{-}H_2)$ complex which is uniquely simple in having no other ancillary hydride ligands, and thus complicating H-exchange behaviour is absent.

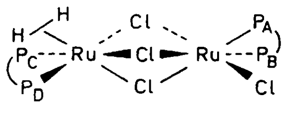
Interaction of $[\{RuCl(dppb)(\mu\text{-}Cl)\}_2]$, (**1**),[3] with 1 atm of H_2 in benzene or toluene at ambient temperature leads to the rapid, reversible *in situ* partial formation of the $\eta^2\text{-}H_2$ complex (**2**), equation (1). The ^1H NMR spectrum of (**2**) in $[^2H_8]$toluene shows a broad resonance ($w_{1/2}$ 30 Hz) at δ −11.02 with a typically short T_1 relaxation time of 14 ms at 292 K,† which is assigned to the $\eta^2\text{-}H_2$ ligand;[4,5] the resonance disappears if the H_2 atmosphere is removed under vacuum, or replaced by argon. The temperature dependence of T_1 is shown in Figure 1, the $\eta^2\text{-}H_2$ resonance also broadening with decrease in temperature. The V-shaped plot, as predicted by theory,[4] is observed only rarely, and certainly not with the other dinuclear $Ru(\eta^2\text{-}H_2)$ complexes,[2] because rapid exchange at higher temperatures among various hydrogens present results in an averaging of their T_1 values.

The $^{31}P\{^1H\}$ NMR spectrum of the same solution of (**1**) under H_2 shows, in addition to the single AB pattern of (**1**),[3] two other independent AB patterns of equal integrated

$$\underset{(1)}{[\{RuCl(dppb)(\mu\text{-}Cl)\}_2]} + H_2 \rightleftharpoons \underset{(2)}{[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3Ru(Cl)(dppb)]} \quad (1)$$



(**1**)



(**2**)

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† T_1 data were obtained by the inversion-recovery method[4] on a Varian XL (300 MHz) FT NMR spectrometer equipped with a variable temperature probe.

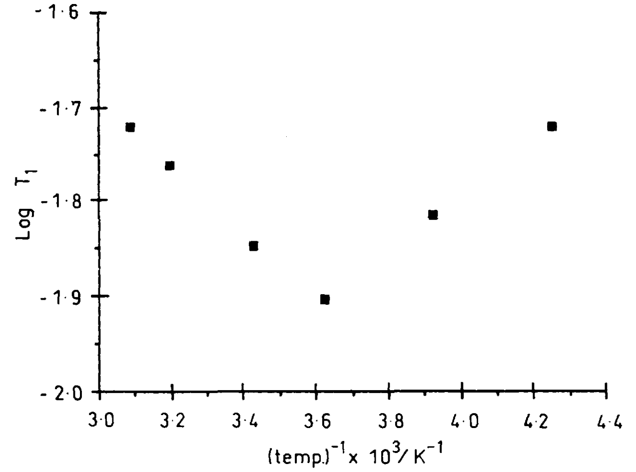

Figure 1. Plot of log T_1 *vs.* (temp.)$^{-1}$. Points (*T*/K, T_1/ms, $w_{1/2}$ Hz) correspond to: 324, 19 ± 2, 19; 313, 17 ± 1, 24; 292, 14 ± 1, 30; 276, 12 ± 1, 36; 255, 15 ± 2, 61; 235, 19 ± 2, 68.

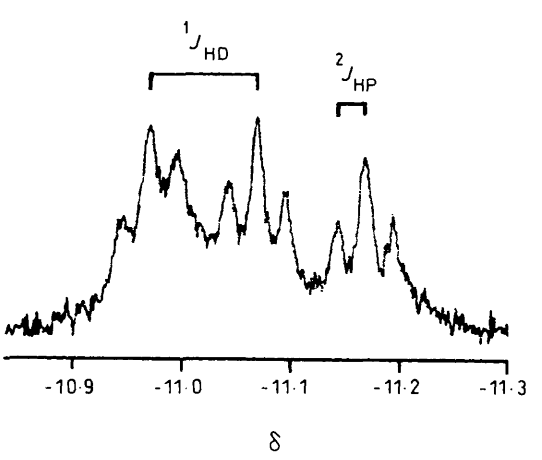

Figure 2. High-field ^1H NMR spectrum (300 MHz, C_6D_6, 20 °C) for the η^2-HD isotopomer of (**2**), formed *in situ* by leaving (**1**) overnight under 1.2 atm of H_2 and 1.8 atm of D_2.

intensity which are assigned to (**2**).‡ We have observed two very similar sets of $^{31}P\{^1H\}$ NMR patterns for other related and isolable, triply chloro-bridged complexes [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] [L = CO, (**3**); Me_2SO, (**4**); Me_2CO, (**5**)] also prepared from (**1**).‡ The ^{31}P spectrum indicates *ca.* 60% conversion of (**1**) to (**2**) with 1 atm of H_2. The existence of two relatively sharp, independent sets of ^{31}P signals for (**2**) means that exchange between bound and free H_2 is slow on the NMR time-scale and thus, in the absence of inter- or intra-molecular hydrogen exchange, the broadness of the η^2-H_2 resonance may be due to internal rotation of the η^2-H_2 ligand as suggested by others;[6] further broadening of the signal on cooling implies a slowing of the internal motion. From the minimum T_1 value of 12 ms, assuming a ±20% error (Figure 1), an internuclear H–H distance of 0.86 ± 0.02 Å may be calculated following the method described by Hamilton and Crabtree,[4] and using the correction factor suggested by Morris' group[7] for systems when the η^2-H_2 rotation is relatively rapid. The bond distance is comparable with that determined by *X*-ray crystallography, 0.80(6) Å, within one of the related dinuclear Ru species.[2]

Of particular interest, (**1**) catalyses, presumably *via* (**2**), isotope exchange between H_2 and D_2 to give HD and the η^2-HD isotopomer of (**2**) in C_6D_6 at 20 °C. The ^1H NMR signal of the HD ligand is a relatively narrow 1 : 1 : 1 triplet ($^1J_{HD}$ 29.4 Hz) of 1 : 2 : 1 triplets (*cis*, $^2J_{HP}$ 7.5 Hz) centred at δ −11.07 (Figure 2); the resonance due to dissolved HD appears as a 1 : 1 : 1 triplet ($^1J_{HD}$ 42.7 Hz) at δ 4.43. While $^1J_{HD}$ for the isotopomer is within the range 18—33 Hz reported for other η^2-HD complexes, resolution of further coupling to phosphorus ($^2J_{HP}$) or other nuclei is unusual.[6,8]

Complex (**1**) also reacts reversibly with 1 atm of N_2 to give a dinitrogen complex (**6**), with an equilibrium conversion of *ca.* 70% at 20 °C. The spectroscopic data‡ are consistent with a structure akin to (**2**) with the η^2-H_2 replaced by σ-N_2.

At 1.0 mM, (**1**) catalyses the H_2-hydrogenation of alkenes under mild conditions (1 atm H_2, 30 °C); for example, in *N,N*-dimethylacetamide solution, styrene (0.42 M) is completely reduced to ethylbenzene with an initial turn-over number of ~450 h^{-1} and (**1**) can then be recovered unchanged. Finally, (**1**) is also an effective catalyst for transfer hydrogenation of acetophenone; a turn-over frequency of 350 h^{-1} is realised at 50 °C using 2.25 mM of (**1**) with KOH (9 mM) in propan-2-ol containing ketone (1.5 M).

The kinetics and mechanisms of the catalytic hydrogenation reactions and the H/D exchange are amenable to detailed study, and it should be possible to evaluate the possible role played by the dinuclear η^2-H_2 species.

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‡ $^{31}P\{^1H\}$ *NMR data*: δ_A, δ_B p.p.m. (^2J Hz) relative to 85% H_3PO_4 (121.42 MHz, C_6D_6, 20 °C). For (**1**): 64.0, 54.9 (47.3). For (**2**): 53.7, 53.2 (44.4); 53.8, 38.3 (33.8). For (**3**) (ν_{CO} 1977 cm^{-1}, Nujol): 53.8, 53.3 (45.2); 46.9, 33.1 (29.6). For (**4**) (ν_{SO} 1090 cm^{-1}, Nujol): 53.6, 50.6 (43.8); 41.6, 28.9 (32.1). For (**5**) (ν_{CO} 1645 cm^{-1}, Nujol): 52.8, 51.5 (43.7); 50.1, 48.7 (38.4). For (**6**) (ν_{N_2} 2175 cm^{-1}, CH_2Cl_2): 54.4, 53.5 (45.1); 46.6, 36.8 (32.1). For (**2**)—(**6**), the relatively invariant lower field AB quartet and the more variable higher field quartet are assigned to P_A–P_B and P_C–P_D, respectively, of structures akin to (**2**) (see text). The geometrical arrangement of ligands within (**2**) is based on an *X*-ray crystallographic structure of (**4**), which shows the geometry drawn for (**2**) but with η^2-H_2 replaced by an S-bonded Me_2SO (to be published).