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Formation of $ReCl(H_2)(PMePh_2)_4$; a Complex containing an η^2-H_2 Ligand

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Reducing $ReCl_5$ with Na/Hg in the presence of $PMePh_2$ yields $ReCl(\eta^2$-$H_2)(PMePh_2)_4$, which has been characterized spectroscopically and crystallographically.

There have been many reports describing dihydrogen as a side-bonded (η^2-H_2) ligand.[1] Of particular interest are the circumstances (steric and electronic) that allow this form of bonding to exist; such information would be of great value in the synthesis of these complexes. A reasonable hypothesis, based on the available evidence, was that if $\nu(N_2)$ in $M(L)_n(N_2)$ is in the range 2060—2150 cm^{-1} then it is likely that the analogous dihydrogen complex $M(L)_n(H_2)$ contained an (η^2-H_2) ligand.[2] Thus the dihydride analogue of $ReCl(N_2)(PMePh_2)_4$[3] [$\nu(N_2)$ = 1925 cm^{-1}] was not expected to contain a nonclassical[1] dihydride ligand.

The complex $ReCl(H_2)(PMePh_2)_4$ (**1**) is formed in one step by the sodium amalgam reduction of $ReCl_5$ in the presence of $PMePh_2$ in tetrahydrofuran (THF) under H_2. Crystals suitable for *X*-ray diffraction were obtained by the slow diffusion of methanol into a THF solution of (**1**). The *X*-ray structural determination† of (**1**) done at −80 °C was not successful in locating the metal-bonded hydrogen atoms. The molecular geometry of (**1**) is shown in Figure 1 and can best be described as distorted octahedral, with one pair of *trans* phosphorus atoms lying above, and the other below the equatorial plane. This sort of geometry is also observed in the closely related $ReCl(N_2)(PMe_2Ph)_4$ (**2**)[4] as well as in $ReH(N_2)(PEt_2Ph)_4$ (**3**)[5] and $Mo(N_2)_2(PMePh_2)_4$ (**4**).[6] The Re–Cl distance of 2.541(2) Å in (**1**) is slightly longer than that in (**2**) [2.521(4) Å], and although the average Re–P distance of (**1**), 2.423(4) Å, is similar to the average in (**2**), 2.422(7) Å, a greater range of Re–P distances is found in (**1**) as opposed to (**2**) [compare 2.396(2)—2.452(2) Å in (**1**) with 2.413(4)—2.435(3) Å in (**2**)].

The $^{31}P\{^1H\}$ and ^1H n.m.r. spectra‡ of (**1**) are indicative of an octahedral geometry in solution and a fast atom bombardment (f.a.b.) m.s. study‡ determined that the number of

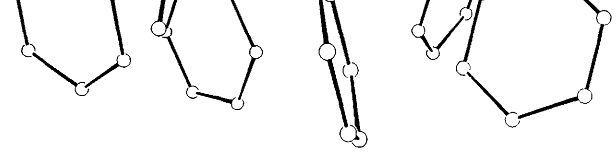

Figure 1. ORTEP drawing of $ReCl(H_2)(PMePh_2)_4$ (**1**) showing the vacant co-ordination site *trans* to the chloride ligand. Some important distances (Å) and angles (°): Re(1)–Cl(1), 2.541(2); Re(1)–P(1), 2.406(2); Re(1)–P(2), 2.439(2); Re(1)–P(3), 2.396(2); Re(1)–P(4), 2.452(2); Cl(1)–Re(1)–P(1), 91.33(6); Cl(1)–Re(1)–P(2), 83.96(6); Cl(1)–Re(1)–P(3), 99.67(6); Cl(1)–Re(1)–P(4), 81.41(7); P(1)–Re(1)–P(2), 93.06(6); P(1)–Re(1)–P(3), 168.85(6); P(1)–Re(1)–P(4), 92.41(6); P(2)–Re(1)–P(3), 89.90(7); P(2)–Re(1)–P(4), 164.50(5); P(3)–Re(1)–P(4), 87.50(7).

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† *Crystal data* for (**1**): $C_{52}H_{54}ReClP_4 \cdot 2C_4H_8O$, M = 1168.8, triclinic, space group $P\bar{1}$, a = 12.210(4), b = 19.269(9), c = 12.138(4) Å, α = 101.10(3), β = 103.98(2), γ = 104.13(3)°, U = 2589.5(7) Å, Z = 2, D_c = 1.495 g cm^{-3}, μ(Mo-K_α) = 25.9 cm^{-1}, crystal dimensions 0.1 × 0.2 × 0.4 mm. Intensity data in the range $0 \leqslant 2\theta \leqslant 50$ were collected by the ω scan technique at −80 °C using an Enraf–Nonius CAD4 diffractometer. The positions of nearly all the non-hydrogen atoms were obtained from a three-dimensional Patterson map and then refined by full-matrix least-squares calculations using the SDP/V, V3.0 package. The rest were found in a series of alternating refinements and difference maps. Subsequent refinement was performed with the SHELX-76 package of programs. Final refinement converged to R = 0.0405 (R_w = 0.0506) for 476 parameters and 7334 unique reflections with $F_o > 3\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *Selected spectroscopic data:* ^1H N.m.r. (C_6D_6, 293 K, 200 MHz) δ −8.6 (q, 2 H, $^3J_{PH}$ 19 Hz, η^2-H_2–Re), 2.0 (br., 12 H, CH_3Ph_2P–Re), 6.3—8.0 [m, 40 H, $(C_6H_5)_2MeP$–Re]; $^{31}P\{^1H\}$ n.m.r. (toluene, 352 K, ref. H_3PO_4, 81 MHz): δ −17.9 (s, 4 P). The positive ion f.a.b.m.s. measurement was made using a VG Analytical 70S high resolution double focusing magnetic sector mass spectrometer in a *m*-nitrobenzyl alcohol matrix (Aldrich, 98%) without any unusual handling precautions and without any further purification of the matrix. The spectrum contained a molecular ion corresponding to $[ReCl(H_2)(PMePh_2)_4-H]^+$ m/z 1025.

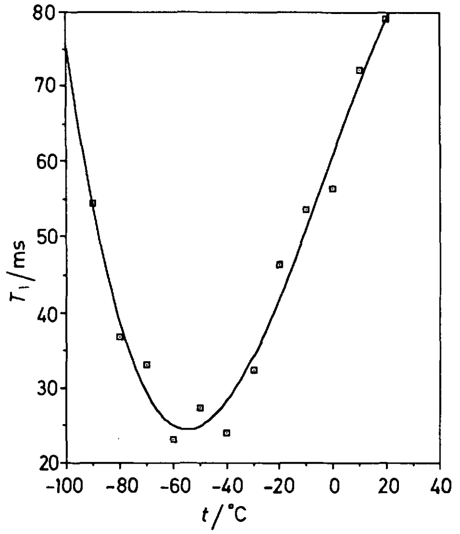

Figure 2. T_1 *vs.* temperature for complex (**1**) in CD_2Cl_2 at 200 MHz.

hydrogen atoms attached to the metal was 2. The low T_1 relaxation time values (*e.g.* 70 ms, 22 °C) for the H_2 ligand of (**1**) (measured by the inversion recovery method[7]) provided evidence of the H–H bond, Figure 2. It has been suggested that the minimum T_1 value can be used to estimate the H–H distance.[1] For (**1**), T_1 reaches a minimum of 25 ms at −50 °C which can be used to calculate an H–H distance of 1.03 Å. This calculation takes into account relaxation contributions *via* rotation of the η^2-H_2 ligand and thus can be regarded as a lower limit for the H–H distance.[8] This molecular hydrogen ligand can exist in the pocket created by the five phenyl groups that point downwards, Figure 1. This type of steric protection may explain why (**1**) exists as a molecular hydrogen complex and not as a classical dihydride. It is also possible that the dihydrogen ligand may be bonded in an end-on η^1-H_2 fashion. It is notable that this arrangement of phenyl groups contrasts sharply with that in (**4**) where the phenyl moieties on adjacent phosphorus atoms are arranged parallel to one another, alternating above and below the equatorial plane.

The HD analogue is obtained by heating benzene solutions of (**1**) under an HD atmosphere, but owing to exchange with the *ortho* protons on the phenyl groups of co-ordinated tertiary phosphine ligands (as evidenced in the ^2H n.m.r. spectra),§ a clean exchange cannot be accomplished. No H–D coupling is resolved in the $^1H\{^{31}P\}$ spectrum at 20 °C.[9] The known dinitrogen product $ReCl(N_2)(PMePh_2)_4$[3] is produced (albeit in low yields) when solutions of (**1**) are placed under a dinitrogen atmosphere. However, under CO, the new complex $ReCl(CO)_3(PMePh_2)_2$ is formed.¶

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§ ^2H N.m.r. (CH_2Cl_2, 293 K, 31 MHz): δ −8.8 (br., η^2-HD- or η^2-D_2-Re), 7.0—8.0 (br., *o*-Ph_2MeP-Re).

¶ ν(CO) (Nujol) 2060, 1950, 1900 cm^{-1}; ^1H n.m.r. (C_6D_6, 293 K, 200 MHz): δ 2.2 (t, 6 H, $^2J_{HP}$ 3.7 Hz, CH_3Ph_2P-Re), 6.7—7.8 [m, 20 H, $(C_6H_5)_2MeP$-Re]; $^{31}P\{^1H\}$ n.m.r. (toluene, 352 K, reference to H_3PO_4, 81 MHz): δ −8.9 (s, 2 P). For details of the f.a.b.m.s. experiment see footnote ‡. A molecular ion assigned as $[ReCl(CO)_3(PMePh_2)_2]^+$ (*m/z* 706) was observed.