

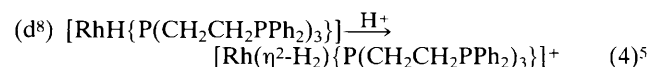
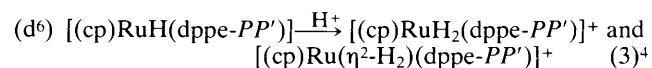
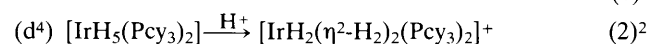
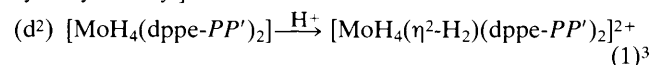
The Reversible Protonation of Rhenium(vii) Heptahydrides of Type $[\text{ReH}_7(\text{PR}_3)_2]$ to give η^2 -Dihydrogen Complexes

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The first examples of the protonation of d^0 metal complexes of type $[\text{ReH}_7(\text{PR}_3)_2]$ [$\text{PR}_3 = \text{P}(\text{cyclohexyl})_3, \text{PPh}_3$ or $\text{P}(\text{Bu}^t)_2\text{Me}$], to give η^2 - H_2 complexes, are described.

There is currently much interest in dihydrogen as a ligand, *i.e.* in η^2 - H_2 complexes, and in how such complexes relate to the isomeric dihydrido complexes.¹⁻⁵ Several such dihydrogen complexes have been prepared by protonation of hydrido-metal complexes, in which the metal atom has a d^2 , d^4 , d^6 , or d^8 electron configuration, *e.g.*, equations (1)–(4), [$\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane, $\text{cp} = \text{cyclopentadienyl}$, $\text{cy} = \text{cyclohexyl}$].



Such η^2 -dihydrogen complex formation could go *via* a hydride, formed by protonation of a d-electron pair, *viz.* $\text{M-H} \rightarrow \text{MH}(\text{H}) \rightarrow \text{M}(\eta^2\text{-H}_2)$. However, there is the possibility that a hydride ligand could be protonated directly without the intermediacy of a dihydrido species. We now report the first

examples of the protonation of d^0 metal complexes to give η^2 -dihydrogen complexes. Recently, Henderson³ reported the protonation of $[\text{MoH}_4(\text{dppe-PP}')_2]$ (d^2) to give a transient dihydrogen complex $[\text{MoH}_4(\eta^2\text{-H}_2)(\text{dppe-PP}')_2]^{2+}$ (lifetime 0.75 s) and suggested that an intermediate $[\text{MoH}_5(\text{dppe-PP}')_2]^+$ was in rapid equilibrium with $[\text{MoH}_3(\eta^2\text{-H}_2)(\text{dppe-PP}')_2]^+$.

We have now found that at or below -40°C , on addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, rhenium heptahydrides of the type $[\text{ReH}_7(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{Pcy}_3, \text{PPh}_3$ or $\text{P}(\text{Bu}^t)_2\text{Me}$) reversibly form species of composition $[\text{ReH}_8(\text{PR}_3)_2]^+$ which must be η^2 -dihydrogen complexes. Thus, treatment of a dichloromethane-deuterio-dichloromethane solution of the known heptahydride $[\text{ReH}_7(\text{Pcy}_3)_2]$ ⁶ (n.m.r. data in Table 1) with > 1 mol. equiv. of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at -80°C caused no evolution of gas and gave a new species showing a singlet ^{31}P - $\{^1\text{H}\}$ resonance ($\delta_{\text{P}} 36.3$ p.p.m.) and a broad ^1H resonance ($\delta_{\text{H}} -5.9$, $w_{1/2} \approx 20$ Hz) with no fine structure, in quantitative yield. Addition of an excess of NET_3 gave back $[\text{ReH}_7(\text{Pcy}_3)_2]$ (n.m.r. evidence) in quantitative yield. The protonated species evolved dihydrogen above -40°C . Particularly informative were experiments on the addition of less than 1 mol. equiv. of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to $[\text{ReH}_7(\text{Pcy}_3)_2]$. Thus addition of 0.75 mol. equiv. at -80°C

Table 1. ^{31}P - $\{^1\text{H}\}$ ^a and ^1H ^b n.m.r. data

Complex	δ_{P}	δ_{H}	$^2J_{\text{PH}}/\text{Hz}$
$[\text{ReH}_7(\text{Pcy}_3)_2]$	47.6	-7.4	18.8
$[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$	36.3	-5.9	not resolved
$[\text{ReH}_7(\text{PPh}_3)_2]$	30.4	-5.0	18.5
$[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{PPh}_3)_2]^+$	17.8	-4.6	4.2 ^c
$[\text{ReH}_7(\text{P}^i\text{Bu}_2\text{Me})_2]$	50.2 ^d	-6.65 ^e	19.8 ^e
$[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{P}^i\text{Bu}_2\text{Me})_2]^+$	40.1 ^d	-5.78 ^e	6.1 ^e

^aMeasured at 162 MHz and -80°C in CD_2Cl_2 , unless stated otherwise. ^bMeasured at 400 MHz and -80°C in CD_2Cl_2 , unless stated otherwise. ^cMeasured at -40°C and 100 MHz. ^d $^2J_{\text{PH}}$ was not resolved at -80°C . ^eMeasured at 40.3 MHz. ^fMeasured at 100 MHz.

to a solution in CD_2Cl_2 showed a very small, broad peak at $\delta_{\text{H}} + 11.7$ ($w_{1/2} \approx 50$ Hz) due to HBF_4 , a well defined 1:2:1 triplet at -7.4 , $^2J_{\text{PH}}$ 18 Hz, due to $[\text{ReH}_7(\text{Pcy}_3)_2]$, and a broad resonance at -5.9 ($w_{1/2} \approx 20$ Hz) due to the protonated species $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$, $x = 1, 2$, or 3 (see below) (spectra measured at 400 MHz). The proportions of $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$ and $[\text{ReH}_7(\text{Pcy}_3)_2]$ were $\approx 3:1$. Similar results were obtained on protonation of $[\text{ReH}_7(\text{P}^i\text{Bu}_2\text{Me})_2]$ or $[\text{ReH}_7(\text{PPh}_3)_2]$ ⁷ except that in these two cases $^2J_{\text{PH}}$ coupling in the η^2 -dihydrogen complexes was resolved. Thus treatment of $\text{ReH}_7(\text{P}^i\text{Bu}_2\text{Me})_2$ with 0.75 mol. equiv. of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at -80°C in CD_2Cl_2 solution showed unchanged $[\text{ReH}_7(\text{P}^i\text{Bu}_2\text{Me})_2]$ (minor component) and the protonated species $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{P}^i\text{Bu}_2\text{Me})_2]^+$ (major component) (n.m.r. data in Table 1) and in this case no unreacted $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ could be detected. The data for a similar experiment on the protonation of $[\text{ReH}_7(\text{PPh}_3)_2]$ giving $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{PPh}_3)_2]^+$, are also shown in Table 1.

We applied Crabtree's method of T_1 measurements to establish the presence of η^2 -dihydrogen ligands.^{2,8} Using the inversion recovery method we measured T_1 values at 400 MHz for both $[\text{ReH}_7(\text{Pcy}_3)_2]$ and $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$, present in the same CD_2Cl_2 solution prepared as above, and found for $[\text{ReH}_7(\text{Pcy}_3)_2]$ 0.12 s (-100°C), 0.11 s (-70°C), 0.13 s (-50°C) and for $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$ 0.03 s (-100°C), 0.03 s (-90°C), 0.05 s (-70°C), 0.09 s (-50°C).

With an excess (2 mol. equiv.) of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, which protonated all the $[\text{ReH}_7(\text{Pcy}_3)_2]$, we found at -90°C that T_1 for $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{Pcy}_3)_2]^+$ was 0.03 s, *i.e.* the same value as with a deficiency of acid. These values were reproducible and lie within the values suggested for η^2 -dihydrogen complexes. Similar small T_1 values were found for $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{PPh}_3)_2]^+$, *e.g.* 0.02 s at -100°C .

We do not know the value of x in the protonated species $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{PR}_3)_2]^+$. The intramolecular exchange of hydride and $\eta^2\text{-H}_2$ was fast on the n.m.r. time scale even at -130°C using $\text{CD}_2\text{Cl}_2/\text{CHCl}_2\text{F}$ mixtures as solvents to reach this temperature. It is possible that two or more of the species of type $[\text{ReH}_{8-2x}(\eta^2\text{-H}_2)_x(\text{PR}_3)_2]$ with $x = 1, 2, 3$, or even 4 are in dynamic equilibrium.

It is also possible that complexes of the type $[\text{ReH}_7(\text{PR}_3)_2]$ are in dynamic equilibrium with $[\text{ReH}_5(\eta^2\text{-H}_2)(\text{PR}_3)_2]$ and this has been tentatively suggested by Crabtree⁸ for $\text{PR}_3 = \text{PPh}_3$ or the $\text{PPh}_2\text{CH}_2\text{PPh}_2$ analogue: clearly, protonation might proceed *via* this η^2 -dihydrogen complex.

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References

- G. J. Kubas, R. R. Ryan, and D. A. Wroblewski, *J. Am. Chem. Soc.*, 1986, **108**, 1339.
- R. H. Crabtree, M. Lavin, and L. Bonneviot, *J. Am. Chem. Soc.*, 1986, **108**, 4032.
- R. A. Henderson, *J. Chem. Soc., Chem. Commun.*, 1987, 1670.
- F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1987, 1675.
- C. Bianchini, C. Mealli, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, 1987, **109**, 5548.
- E. H. Kelle Zeiher, D. G. DeWit, and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 7006.
- J. Chatt and R. S. Coffey, *J. Chem. Soc. (A)*, 1963, 1969.
- R. H. Crabtree. Verbally at the R.S.C. Dalton Division Third International Conference on The Chemistry of the Platinum Group Metals, Sheffield, July 1987.