The Reversible Protonation of Rhenium(VII) Heptahydrides of Type $[ReH_7(PR_3)_2]$ to give η^2-Dihydrogen Complexes

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The first examples of the protonation of d^0 metal complexes of type $[ReH_7(PR_3)_2]$ [PR_3 = P(cyclohexyl)$_3$, PPh_3 or $PBu^t{}_2Me$], 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), [dppe = 1,2-bis(diphenylphosphino)ethane, cp = cyclopentadienyl, cy = cyclohexyl].

$$(d^2)\ [MoH_4(dppe\text{-}PP')_2] \xrightarrow{H^+} [MoH_4(\eta^2\text{-}H_2)(dppe\text{-}PP')_2]^{2+} \quad (1)^3$$

$$(d^4)\ [IrH_5(Pcy_3)_2] \xrightarrow{H^+} [IrH_2(\eta^2\text{-}H_2)_2(Pcy_3)_2]^+ \quad (2)^2$$

$$(d^6)\ [(cp)RuH(dppe\text{-}PP')] \xrightarrow{H^+} [(cp)RuH_2(dppe\text{-}PP')]^+ \text{ and } [(cp)Ru(\eta^2\text{-}H_2)(dppe\text{-}PP')]^+ \quad (3)^4$$

$$(d^8)\ [RhH\{P(CH_2CH_2PPh_2)_3\}] \xrightarrow{H^+} [Rh(\eta^2\text{-}H_2)\{P(CH_2CH_2PPh_2)_3\}]^+ \quad (4)^5$$

Such η^2-dihydrogen complex formation could go *via* a hydride, formed by protonation of a d-electron pair, *viz*. M–H → MH(H) → M(η^2-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, Henderson[3] reported the protonation of $[MoH_4(dppe\text{-}PP')_2]$ (d^2) to give a transient dihydrogen complex $[MoH_4(\eta^2\text{-}H_2)(dppe\text{-}PP')_2]^{2+}$ (lifetime 0.75 s) and suggested that an intermediate $[MoH_5(dppe\text{-}PP')_2]^+$ was in rapid equilibrium with $[MoH_3(\eta^2\text{-}H_2)(dppe\text{-}PP')_2]^+$.

We have now found that at or below −40 °C, on addition of $HBF_4{\cdot}Et_2O$, rhenium heptahydrides of the type $[ReH_7(PR_3)_2]$ (PR_3 = Pcy_3, PPh_3 or $PBu^t{}_2Me$) reversibly form species of composition $[ReH_8(PR_3)_2]^+$ which must be η^2-dihydrogen complexes. Thus, treatment of a dichloromethane–deuteriodichloromethane solution of the known heptahydride $[ReH_7(Pcy_3)_2]$[6] (n.m.r. data in Table 1) with > 1 mol. equiv. of $HBF_4{\cdot}Et_2O$ at −80 °C caused no evolution of gas and gave a new species showing a singlet $^{31}P\text{-}\{^1H\}$ resonance (δ_P 36.3 p.p.m.) and a broad ^1H resonance (δ_H −5.9, $w_{1/2} \simeq 20$ Hz) with no fine structure, in quantitative yield. Addition of an excess of NEt_3 gave back $[ReH_7(Pcy_3)_2]$ (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 $HBF_4{\cdot}Et_2O$ to $[ReH_7(Pcy_3)_2]$. Thus addition of 0.75 mol. equiv. at −80 °C

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

Complex	δ_P	δ_H	$^2J_{PH}$/Hz
$[ReH_7(Pcy_3)_2]$	47.6	−7.4	18.8
$[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$	36.3	−5.9	not resolved
$[ReH_7(PPh_3)_2]$	30.4	−5.0	18.5
$[ReH_{8-2x}(\eta^2-H_2)_x(PPh_3)_2]^+$	17.8	−4.6	4.2[c]
$[ReH_7(PBu^t_2Me)_2]$	50.2[d]	−6.65[e]	19.8[e]
$[ReH_{8-2x}(\eta^2-H_2)_x(PBu^t_2Me)_2]^+$	40.1[d]	−5.78[e]	6.1[e]

[a] Measured at 162 MHz and −80 °C in CD_2Cl_2, unless stated otherwise. [b] Measured at 400 MHz and −80 °C in CD_2Cl_2, unless stated otherwise. [c] Measured at −40 °C and 100 MHz. $^2J_{PH}$ was not resolved at −80 °C. [d] Measured at 40.3 MHz. [e] Measured at 100 MHz.

to a solution in CD_2Cl_2 showed a very small, broad peak at δ_H +11.7 ($w_{1/2} \simeq 50$ Hz) due to HBF_4, a well defined 1:2:1 triplet at −7.4, $^2J_{PH}$ 18 Hz, due to $[ReH_7(Pcy_3)_2]$, and a broad resonance at −5.9 ($w_{1/2} \simeq 20$ Hz) due to the protonated species $[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$, $x = 1, 2,$ or 3 (see below) (spectra measured at 400 MHz). The proportions of $[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$ and $[ReH_7(Pcy_3)_2]$ were ≃ 3:1. Similar results were obtained on protonation of $[ReH_7(PBu^t_2Me)_2]$ or $[ReH_7(PPh_3)_2]$[7] except that in these two cases $^2J_{PH}$ coupling in the η^2-dihydrogen complexes was resolved. Thus treatment of $ReH_7(PBu^t_2Me)_2$ with 0.75 mol. equiv. of $HBF_4 \cdot Et_2O$ at −80 °C in CD_2Cl_2 solution showed unchanged $[ReH_7(PBu^t_2Me)_2]$ (minor component) and the protonated species $[ReH_{8-2x}(\eta^2-H_2)_x(PBu^t_2Me)_2]^+$ (major component) (n.m.r. data in Table 1) and in this case no unreacted $HBF_4 \cdot Et_2O$ could be detected. The data for a similar experiment on the protonation of $[ReH_7(PPh_3)_2]$ giving $[ReH_{8-2x}(\eta^2-H_2)_x(PPh_3)_2]^+$, 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 $[ReH_7(Pcy_3)_2]$ and $[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$, present in the same CD_2Cl_2 solution prepared as above, and found for $[ReH_7(Pcy_3)_2]$ 0.12 s (−100 °C), 0.11 s (−70 °C), 0.13 s (−50 °C) and for $[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$ 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 $HBF_4 \cdot Et_2O$, which protonated all the $[ReH_7(Pcy_3)_2]$, we found at −90 °C that T_1 for $[ReH_{8-2x}(\eta^2-H_2)_x(Pcy_3)_2]^+$ 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 $[ReH_{8-2x}(\eta^2-H_2)_x(PPh_3)_2]^+$, *e.g.* 0.02 s at −100 °C.

We do not know the value of x in the protonated species $[ReH_{8-2x}(\eta^2-H_2)_x(PR_3)_2]^+$. The intramolecular exchange of hydride and η^2-H_2 was fast on the n.m.r. time scale even at −130 °C using $CD_2Cl_2/CHCl_2F$ mixtures as solvents to reach this temperature. It is possible that two or more of the species of type $[ReH_{8-2x}(\eta^2-H_2)_x(PR_3)_2]$ with $x = 1, 2, 3,$ or even 4 are in dynamic equilibrium.

It is also possible that complexes of the type $[ReH_7(PR_3)_2]$ are in dynamic equilibrium with $[ReH_5(\eta^2-H_2)(PR_3)_2]$ and this has been tentatively suggested by Crabtree[8] for $PR_3 = PPh_3$ or the $PPh_2CH_2PPh_2$ analogue: clearly, protonation might proceed *via* this η^2-dihydrogen complex.

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