T_1 Values in Hydride and New Molecular Hydrogen Phosphite Complexes of Comparable Structure

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The molecular hydrogen complexes $\{MH(\eta^2\text{-}H_2)[PhP(OEt)_2]_4\}BPh_4$ (M = Fe, Ru, Os) and dihydride species $\{CoH_2[PhP(OEt)_2]_4\}BPh_4$ have been prepared and T_1 measurements for H^- and η^2-H_2 resonances give T_1 <100 ms for all complexes at 80 MHz.

Since their discovery,[1] new examples of molecular hydrogen complexes continue to be reported[2] and their characterization as η^2-H_2 derivatives is often based on the T_1 criterion.[3] T_1 values below 125 ms are considered characteristic of H_2 ligands, while T_1 >300 ms are attributed to hydride ligands.[2c]

In the course of our studies on the first molecular hydrogen complexes containing phosphite ligands, we have found a number of hydride derivatives with T_1 <100 ms, and therefore the 125 ms T_1 limit is no longer applicable to the distinction between classical and non-classical hydrides.

The complexes $[MH(\eta^2\text{-}H_2)(P)_4]BPh_4$ (**1**) [M = Fe (**1a**); Ru (**1b**); Os (**1c**); (P) = $PhP(OEt)_2$] were prepared by treating the dihydrides[4] $MH_2(P)_4$ with an excess of $HBF_4 \cdot Et_2O$ at low temperature (−80 °C) in ethanol. The pale-yellow solids, separated as BPh_4^- salts, are relatively air-stable and only by heating of their solutions to over 70 °C was a slow loss of H_2 detected. Substitution reactions with CO, RCN, RNC, and PR_3 ligands to give $[MHL(P)_4]BPh_4$ compounds are easy for (**1a**) and (**1b**), while reflux conditions are required for (**1c**). Furthermore, the reaction of (**1**) with aryldiazonium cations affords respectively bis(aryldiazenido)$[Fe(ArN_2)_2(P)_3](BPh_4)_2$ and pentaco-ordinate monodiazene $[Ru(ArN{=}NH)(P)_4](BPh_4)_2$ complexes with (**1a**) and (**1b**), whereas (**1c**) is unreactive.

Analytical and spectroscopic data confirm the proposed formulation. The $^{31}P\{^1H\}$ n.m.r. spectra of (**1**) at −80 °C in each case show a multiplet, suggesting *cis*-geometry for the complexes. In the high-field region of the ^1H n.m.r. spectra each complex shows a broad singlet (δ −3.8, −7.2) with a very short apparent T_1 value at −65 °C [4 ms for (**1a**), 7 ms for (**1b**), and 10 ms for (**1c**)] attributed to the η^2-H_2 ligand, and a multiplet with a much longer T_1 value [60 ms for (**1a**), 98 ms for (**1b**), and 51 ms for (**1c**)] attributed to the hydride ligand.

These T_1 values are unexpectedly low, especially for the hydride resonance, because all previously reported hydride complexes[2,3,5] show H^- resonances with T_1 >200 ms, while our data with T_1 <100 ms, fall in the range generally attributed to non-classical hydrides. However, the difference between the T_1 values of the broad singlet and the sharp multiplet is as expected (a factor of *ca.* 10), and the ^1H n.m.r. spectrum of the isotopomer $[RuH(\eta^2\text{-}HD)(P)_4]^+$, which shows a characteristic 1 : 1 : 1 triplet at δ −3.73 with J_{HD} 34 Hz, fully supports the proposed formulation.

In order to clarify these unusual T_1 values, we first measured the relaxation time of the dihydride precursors and

Table 1. Apparent T_1 values for selected complexes.

Compound[a]	Chem. shift,[b] δ	T_1,[b,c] ms	Assignment, H resonance
$[FeH(H_2)(P)_4]BPh_4$ (**1a**)	−10.34m	60	H^-
	−7.2br	4	η^2-$_2$
$[FeH_2(P)_4]$[d]	−13.35m	64	H^-
$[FeH(CO)(P)_4]BPh_4$[e]	−8.27qi	87	H^-
$[RuH(H_2)(P)_4]BPh_4$ (**1b**)	−8.21m	98	H^-
	−3.8br	7	η^2-H_2
$[RuH(HD)(P)_4]BPh_4$	−8.19m	98	H^-
	−3.73t	25	η^2-HD
$[RuH_2(P)_4]$	−9.35m	81	H^-
$[RuH(CO)(P)_4]BPh_4$[f]	−6.42qi	89	H^-
$[OsH(H_2)(P)_4]BPh_4$ (**1c**)	−6.47m	51	H^-
	−6.9br	10	η^2-H_2
$[OsH_2(P)_4]$	−12.5m	66	H^-

[a] (P) = $PhP(OEt)_2$. [b] In CD_2Cl_2 at −65 °C; qi = quintet. [c] Determined by the inversion-recovery method at 80 MHz on a Varian FT-80A spectrometer; T_1 values are accurate to ±10%. [d] Measured for *cis*-isomer. For the *trans*-isomer δ −10.9 qi and T_1 about 60 ms. [e] $\ln T_1 = 10.28 - 1214/T$ between 203 and 303 K. [f] $\ln T_1 = 9.94 - 1135/T$ between 203 and 303 K.

of other monohydrides of known structure[6] containing the same phosphite ligands. Furthermore, the temperature dependences of T_1 for these resonances in the range 203—303 K were also determined; the results are reported in Table 1. These data show that the hydrides containing ethoxy phosphite ligands relax faster (T_1 <100 ms) than all those reported so far, and that, for the same central metal, similar T_1 values for H^- are found for both mono-, di-hydride, and hydrogen–hydride complexes. However, in the last derivatives, the relaxation of the η^2-H_2 protons is also low (T_1 ratio H^-/η^2-H_2 *ca.* 10:1). Therefore, the T_1 criterion discerning between a classical and a non-classical hydride can still be used; however, in the absence of definitive terms of reference, which may be provided by hydride resonances of the metal complexes containing the same ligands, reliance cannot be placed on absolute T_1 values only.†

The following example is typical: the reaction of the hydride[7] $CoH(P)_4$ [(P) = $PhP(OEt)_2$] with $HBF_4\cdot Et_2O$ in ethanol at −80 °C leads to the separation of a white solid, (**2**), which is diamagnetic and a 1:1 electrolyte, as its BPh_4^- salt. Its high-field ^1H n.m.r. spectrum shows a broad signal between +30 and −80 °C at about δ −12.5, with a T_1 value of 22 ms at −60 °C. On the basis of these data and the analytical results, formulation as a molecular hydrogen complex of the type $[Co(\eta^2\text{-}H_2)(P)_4]BPh_4$ may seem at first plausible. However, under the same conditions, the $CoH(P)_4$ precursor shows a T_1 value of 21 ms (ln T_1 = 9.35 − 1280/T between 203 and 303 K) for the hydride resonance, and therefore a classical structure $[CoH_2(P)_4]^+$ for the cation can be proposed. The i.r. spectrum shows a medium-intensity ν_{MH} band at 1980 cm^{-1}, which disappears on deuteriation, confirming the formulation as a dihydride species for the cobalt complex.

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† Measurements of ln T_1 *vs.* $1/T$ at 200 MHz for $[FeH(CO)P_4]BPh_4$ as suggested by a referee revealed a T_1 minimum of 190 ms at 231 K.

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