

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

Stefano Antoniutti, Gabriele Albertin,\* Paola Amendola, and Emilio Bordignon\*

Dipartimento di Chimica dell'Università di Venezia, Calle Larga S. Marta 2137, 30123 Venice, Italy

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

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

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 100$  ms, and therefore the 125 ms  $T_1$  limit is no longer applicable to the distinction between classical and non-classical hydrides.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  $[MH(\eta^2-H_2)(P)_4]BPh_4$  (**1**) [ $M = Fe$  (**1a**);  $Ru$  (**1b**);  $Os$  (**1c**);  $(P) = PhP(OEt)_2$ ] were prepared by treating the dihydrides<sup>4</sup>  $MH_2(P)_4$  with an excess of  $HBPh_4 \cdot Et_2O$  at low temperature ( $-80^\circ C$ ) in ethanol. The pale-yellow solids, separated as  $BPh_4^-$  salts, are relatively air-stable and only by heating of their solutions to over  $70^\circ C$  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)[ $Fe(ArN_2)_2(P)_3$ ]-( $BPh_4$ )<sub>2</sub> and pentaco-ordinate monodiazeno [ $Ru(ArN=NH)(P)_4$ ]( $BPh_4$ )<sub>2</sub> 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  $-80^\circ C$  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 ( $\delta -3.8, -7.2$ ) with a very short apparent  $T_1$  value at  $-65^\circ C$  [4 ms for (**1a**), 7 ms for (**1b**), and 10 ms for (**1c**)] attributed to the  $\eta^2-H_2$  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<sup>2,3,5</sup> 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  $[RuH(\eta^2-HD)(P)_4]^+$ , which shows a characteristic 1:1:1 triplet at  $\delta -3.73$  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 <sup>a</sup>	Chem. shift, <sup>b</sup> $\delta$	$T_1$ , <sup>b,c</sup> ms	Assignment, H resonance
$[FeH(H_2)(P)_4]BPh_4$ ( <b>1a</b> )	-10.34m -7.2br	60 4	$H^-$ $\eta^2-H_2$
$[FeH_2(P)_4]^d$	-13.35m	64	$H^-$
$[FeH(CO)(P)_4]BPh_4^e$	-8.27qi	87	$H^-$
$[RuH(H_2)(P)_4]BPh_4$ ( <b>1b</b> )	-8.21m -3.8br	98 7	$H^-$ $\eta^2-H_2$
$[RuH(HD)(P)_4]BPh_4$	-8.19m -3.73t	98 25	$H^-$ $\eta^2-HD$
$[RuH_2(P)_4]$	-9.35m	81	$H^-$
$[RuH(CO)(P)_4]BPh_4^f$	-6.42qi	89	$H^-$
$[OsH(H_2)(P)_4]BPh_4$ ( <b>1c</b> )	-6.47m -6.9br	51 10	$H^-$ $\eta^2-H_2$
$[OsH_2(P)_4]$	-12.5m	66	$H^-$

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

of other monohydrides of known structure<sup>6</sup> 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  $\eta^2$ - $H_2$  protons is also low ( $T_1$  ratio  $H^-/\eta^2$ - $H_2$  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.<sup>†</sup>

The following example is typical: the reaction of the hydride<sup>7</sup>  $CoH(P)_4$  [ $(P) = PhP(OEt)_2$ ] with  $HBF_4 \cdot Et_2O$  in ethanol at  $-80^\circ C$  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  $-80^\circ C$  at about  $\delta -12.5$ , with a  $T_1$  value of 22 ms at  $-60^\circ C$ . On the basis of these data and the analytical results, formulation as a molecular hydrogen complex of the type  $[Co(\eta^2-H_2)(P)_4]BPh_4$  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  $\nu_{MH}$  band at  $1980\text{ cm}^{-1}$ , which disappears on deuteration, confirming the formulation as a dihydride species for the cobalt complex.

The financial support of the M.P.I. and the C.N.R., Rome, is gratefully acknowledged.

Received, 9th May 1988; Com. 8/01792A

## References

- 1 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
- 2 (a) M. Bautista, K. A. Earl, R. H. Morris, and A. Sella, *J. Am. Chem. Soc.*, 1987, **109**, 3780; (b) F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1987, 1675; (c) M. S. Chinn and D. M. Heinekey, *J. Am. Chem. Soc.*, 1987, **109**, 5865; (d) C. Bianchini, C. Mealli, M. Peruzzini, and F. Zanobini, *ibid.*, 1987, **109**, 5548; (e) G. J. Kubas, R. R. Ryan, and C. J. Unkefer, *ibid.*, 1987, **109**, 8113; (f) R. K. Upmacis, M. Poliakoff, and J. J. Turner, *ibid.*, 1986, **108**, 3645.
- 3 R. H. Crabtree and M. Lavin, *J. Chem. Soc., Chem. Commun.*, 1985, 1661.
- 4 P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.*, 1971, **93**, 4701; G. Albertin, S. Antoniutti, and E. Bordignon, unpublished work.
- 5 R. H. Crabtree, B. E. Segmuller, and R. J. Uriarte, *Inorg. Chem.*, 1985, **24**, 1949.
- 6 G. Albertin, S. Antoniutti, M. Lanfranchi, G. Pelizzi, and E. Bordignon, *Inorg. Chem.*, 1986, **25**, 950.
- 7 D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Commun.*, 1971, 322.

<sup>†</sup> 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.