Metal−Hydride and Hydride−Hydride Distances from Measurements of Selective and Nonselective ^{1}H T_1 Relaxation Times of Hydride Ligands: Relaxation in $NbCp_2H_3$

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The detailed ^{1}H NMR relaxation study, performed for $Cp_2NbH^X{}_2H^A$ (**1**) and its partially-deuterated derivatives in toluene-d_8, has demonstrated how T_1 and T_{1sel} measurements can be used for accurate determination of the hydride−hydride and metal−hydride distances in Nb complexes. The T_{1sel} method was independently supported by the relaxation studies of the partially deuterated derivatives of **1**. The application of the T_{1sel} approach is limited by the presence in the H^X/H^A pair of the slow hydride/hydride site exchange characterized by saturation transfer experiments: $k^{296} = 1.34$ s^{-1}, $\Delta G^‡(298$ K$) = 17.3$ kcal/mol, $\Delta H^‡ = 13.1$ kcal/mol, and $\Delta S^‡ = -14.2$ eu. The exchange does not show a pronounced isotopic effect, and $k(H)/k(D) = 1.1$ at 295 K. It has been suggested that the T_{1sel} approach can be used for indication of slow hydride/hydride exchanges. The experimental estimations have shown Nb−H dipole−dipole interactions to be very important for the hydride relaxation in **1.** The Nb−H contribution shortens significantly the hydride T_1 times, providing, for example, up to 64% of the H^X relaxation rate. The relaxation $H^X−H^A$ and Nb−H distances have been discussed.

Introduction

After the discovery of dihydrogen coordination[1] and of the class of transition metal−hydride complexes in which the hydride ligands undergo quantum mechanical exchange coupling,[2] structural characterizations of the MeH_n fragments attracted increasing attention. It is well-known that the structural information about hydride ligands can be correctly obtained from neutron diffraction (ND) studies. However, the ND experiments are complicated and often unavailable. The X-ray method often gives unreliable hydride ligand positions, and, for example, the M−H distances determined by this technique are usually too short (by as much as 0.2−0.3 A [3]). Therefore the development of the NMR spin−lattice relaxation (T_1) approach[4] for structural characterizations of transition metal hydrides is of great interest.

In this paper we demonstrate how the M−H and H−H distances can be determined from measurements of selective and nonselective T_1 times of the hydride ligands in Nb complexes. We focus here on Cp_2NbH_3 (**1**) because this complex and its derivatives being classical trihydrides[5] often show proton−proton exchange couplings.[5b,6]

For the above complexes one should expect significant metal−hydride dipole−dipole interactions[7] which can lead to short relaxation times of the hydride ligands. Therefore the correct experimental estimation of the Nb−H relaxation contributions seems to be important for application of the well-known T_1 criterion.

Experimental Section

All NMR studies were carried out in NMR tubes sealed under vacuum using standard techniques. Toluene-d_8 was dried and deoxygenated by using conventional procedures.

NMR data were collected with Bruker AC 200 and AMX 400 spectrometers. The conventional inversion−recovery method (180°−τ−90°) was used to determine T_1. T_{1sel} relaxation times were measured by applying a selective 180° pulse provided by the decoupler AC 200 or by the decoupler system AMX 400. The duration and the power of the selective pulses were regulated to excite only one of the hydride resonances. The calculation of the relaxation times was made using the nonlinear three-parameter fitting routine of the spectrometers. In each experiment, the waiting period was 5 times larger than the expected relaxation time and 16−20 variable delays were employed. The duration of the pulses was controlled at every temperature. The errors in T_1 determinations were lower than 5% (this was checked with different samples).

^{1}H NMR saturation transfer experiments[8] were performed by using standard techniques of spectrometers. The rate constants of the H/H

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exchange (k) were calculated from the equation[8b] $I(S)/I(0) = 1/(1+kT_1)$, where $I(S)$ and I(0) correspond to the relative integral intensities of the H ligand signal with and without saturation; T_1 is the spin−lattice relaxation time of the nucleus.

Preparation of Cp_2NbH_3 (1). All manipulations were performed using conventional Schlenk techniques. Solvents were dried over sodium benzophenone ketyl. $LiAlH_4$ was purchased from Merk. Complex **1** was prepared according to the literature method[9a] using $LiAlH_4$ as the reducing agent and diethyl ether as a solvent. The product was multiply recrystallized from ether to give pale crystals with the NMR parameters corresponding to the literature data.[9b]

Preparation of the Deuterated Derivatives of Complex 1. A 0.102 g sample of Cp_2NbH_2Li[9c] was treated with D_2O in ether. The mixture was stirred until all Cp_2NbH_2Li dissolved. The organic phase was decanted and dried *in vacuo*. The product was multiply recrystallized from ether to give pale crystals. According to the ^1H NMR spectra collected with delays of 50 s, 26% of the H ligands in **1** have been replaced by D-ligands.

Results and Discussion

Relaxation Theory. Intramolecular proton−proton and proton−metal dipole−dipole interactions dominate the T_1 relaxation of hydride ligands in classical rhenium, Mn, Co and Nb hydrides.[7,10] Thus, the relaxation rate for the hydride ligands in **1** ($Cp_2NbH^X{}_2H^A$) can be described as follows:

$$1/T_1(H^A) = 1/T_1(Nb\cdots H^A) + 2/T_1(H^A\cdots H^X) + 1/T_1(Cp-H^A)$$

$$1/T_1(H^X) = 1/T_1(Nb\cdots H^X) + 1/T_1(H^A\cdots H^X) + 1/T_1(Cp-H^X) \quad (1)$$

In turn

$$1/T_1(Nb\cdots H) = 2\gamma_H{}^2\gamma_{Nb}{}^2h^2I(I+1)/15r(Nb\cdots H)^6 \times (3\tau_c/(1+\omega(H)^2\tau_c{}^2) + 6\tau_c/(1+(\omega(H)+\omega(Nb))^2\tau_c{}^2) + \tau_c/(1+(\omega(H)-\omega(Nb))^2\tau_c{}^2)) \quad (2)$$

$$1/T_1(H\cdots H) = 0.3\gamma_H{}^4h^2/r(H\cdots H)^6(\tau_c/(1+\omega(H)^2\tau_c{}^2) + 4\tau_c/(1+4\omega(H)^2\tau_c{}^2)) \quad (3)$$

where γ, h, I, and ω are well-known physical parameters and $\tau_c = \tau_0 \exp(E_a/RT)$.[11] When the T_1 time in eq 2 or 3 reaches a minimum, the corresponding internuclear distance can be calculated from eq 4 or 5 written in a convenient form (ν is the ^1H NMR resonance frequency in megahertz). Hence, isolating each relaxation contribution (eqs 1) provides an accurate structural characterization of the metal−hydride fragments when M and H have low vibrational amplitudes.

$$r(H\cdots H)(A) = 2.405(200T_{1min}(H-H)/\nu)^{1/6} \quad (4)$$

$$r(Nb\cdots H)(A) = 2.722(200T_{1min}(Nb-H)/\nu)^{1/6} \quad (5)$$

According to the recent NMR data, obtained for Mn and rhenium hydride complexes, the metal−proton relaxation contributions can be determined from measurements of selective (T_{1sel}) and nonselective (T_1) relaxation times of hydride ligands.[10b] On the basis of these data, the Nb−H distances in niobium hydrides can be expressed through T_{1min} by eq 6. In the equation, $k = (T_{1sel}/T_1 - 1)/(0.5 - T_{1sel}/3T_1)$ and the T_1, T_{1sel} times are measured at $\omega_H{}^2\tau_c{}^2 < 1$.

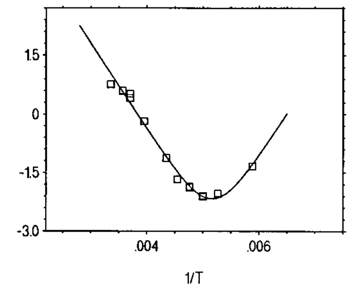

Figure 1. Variable-temperature ^1H T_1 data for the H^X resonance of **1** in toluene-d_8 at 400 MHz (the solid line corresponds to niobium−hydride dipole−dipole interactions in eq 2).

$$r(Nb\cdots H) = 5.109((1.4k + 4.47)T_{1min}/\nu)^{1/6} \quad (6)$$

Finally, in order to be sure that hydride relaxation in complex **1** by chemical shift anisotropy[11] is negligible, the hydride T_1 times were measured at 400 and 200 MHz between 295 and 318 K (when $\omega(H)^2\tau_c{}^2 << 1$). The T_1 values were the same for both frequencies.

NMR and T_1 NMR Data for Toluene-d_8 Solutions of 1 and Its Partially-Deuterated Derivatives. The variable-temperature ^1H NMR spectra of **1** have been previously reported by Curtis[9b] and Heinekey.[6a] According to Heinekey's analysis, the hydride ligands in **1** show an AX_2 spin system with quantum mechanical exchange coupling. In agreement with this analysis the H^A-H^X splitting of 22 Hz in the 400 MHz ^1H NMR spectrum of **1**, observed at 315 K, completely disappears in the ^2H NMR spectrum of the partially-deuterated derivatives of **1** (see Experimental Section). Indeed, similar isotopic effects have been reported earlier, for example, for some iridium trihydrides.[2d]

Ernst et al.[12a] have shown theoretically that nonselective 90° pulses in 180°−τ−90° inversion−recovery relaxation experiments can produce the *multiexponential* NMR decays in the case of AX_2 or strongly coupled spin systems. The complexity of T_1 time calculations from such decays is well-known.[12b] Therefore for a toluene-d_8 solution of **1** we have performed the 400 and 200 MHz relaxation experiments with 20 delays (τ), analyzing the region $T_1 < \tau < 3T_1$. In these experiments the relaxation has been found to be *monoexponential for all of the protons* in **1**, and thus the T_1 analysis is simple and correct.

As predicted by the relaxation theory, the temperature T_1 dependencies give "V-shaped" plots (Figure 1 shows one of them) reaching minimum values practically at the same temperature for all of the ligands of **1**. The T_{1min} values are collected in Table 1 in comparison with the theoretical values calculated with the account for all H···H and Nb···H contacts in the X-ray structure.[5a]

As it follows from the data, the theory well-reproduces the T_{1min} values for the cyclopentadienyl (Cp) ligands of **1** and predicts a significant effect of Nb−H dipole−dipole interactions. However, in spite of the excellent agreement between $T_{1min}{}^{exp}$ and $T_{1min}{}^{theor}$ for the Cp protons, the T_{1min} values measured for

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Table 1. Theoretical and Experimental Relaxation $T_{1\text{min}}$ Data for $(Cp)_2NbH^X{}_2H^A$ and Its Partially-Deuterated Derivatives (Toluene-d_8, 400 MHz)

$T_{1\text{min}}$ (s)	C_5H_5	H^A	H^X
$T_{1\text{min}}{}^{\text{theor}}$(tot.)	1.028	0.064	0.083
$T_{1\text{min}}{}^{\text{exp}}$(tot.)	1.025	0.099	0.122
		0.120[a]	0.124[b]
		0.145[c]	0.124[b]
$T_{1\text{min}}{}^{\text{theor}}$(Cp−H)		2.25	1.36
$T_{1\text{min}}{}^{\text{exp}}$(Cp−H)		2.08	
$T_{1\text{min}}{}^{\text{theor}}$($H^A\cdots H^X$)		0.154	0.308
$T_{1\text{min}}{}^{\text{exp}}$($H^A\cdots H^X$)		0.309	0.618
$T_{1\text{min}}{}^{\text{theor}}$($Nb\cdots H$)		0.117	0.117
$T_{1\text{min}}{}^{\text{exp}}$($Nb\cdots H$)		0.156	

[a] For $Cp_2Nb\mathit{H}^AH^XD^X$. [b] For the composite resonance of the H^X ligands in the isotopic mixture. [c] For $Cp_2Nb\mathit{H}^AD_2{}^X$.

H^A and H^X (0.099 and 0.122 s, respectively) differ remarkably from theoretical values. Nevertheless, the observed magnitudes are quite short and close to 0.080 and 0.11 s, reported for the hydride ligands in $(C_5H_4SiMe_3)_2NbH_3$ and $(C_5H_3(SiMe_3)_2\ )_2NbH_3$.[13] In this connection it was of great interest to estimate experimentally the relaxation contributions in eqs 1 (this could be used certainly in relaxation studies of related compounds). Therefore, we have here performed T_1 and $T_{1\text{sel}}$ measurements for the hydride ligands of **1** and its deuterated derivatives.

It follows from the theory[10b] that $T_{1\text{sel}} > T_1$ due to the absence of the hydride−hydride cross-relaxation. For trihydride **1** this is true at 230 K and 400 MHz: $T_{1\text{sel}}$ (H^X) = 0.462 s and T_1(H^X) = 0.406 s. However, increasing the temperature leads to a surprising phenomenon when $T_{1\text{sel}}(H^X) = T_1(H^X) = 1.05$ s at 260 K and $T_{1\text{sel}}(H^X)$ (1.67 s) < $T_1(H^X)$ (2.10 s) at 295 K. The latter effect was also examined at 200 MHz.

This surprising result can be rationalized only in terms of a slow H^A/H^X exchange in **1**. Note that this site exchange is often observed in trihydride complexes.[2d] Then it becomes obvious that the selective 180° pulses, operating in the region of the H^X resonance, lead to *different spin-temperatures*[14] of H^A and H^X. Hence "an additional relaxation rate" of H^X in the $180^\circ_{\text{sel}} - \tau - 90^\circ$ experiments could be caused by the exchange between H^X and the "colder" spin H^A.

To support this idea, we performed for the H^X/H^A pair in **1** the variable-temperature saturation transfer experiments[8] which have shown the transfer effects at 273 K and above. The collected data allowed the quantitative characterization of the site exchange: $k^{296} = 1.34\ s^{-1}$, $\Delta G^\ddagger(298\ K) = 17.3$ kcal/mol, $\Delta H^\ddagger = 13.1$ kcal/mol, and $\Delta S^\ddagger = -\ 14.2$ eu.

We have found here the important limitation in the application of the $T_{1\text{sel}}$ approach: this method can be used *only in the absence of hydride−hydride exchanges*. It is also important that the hydride−hydride exchange in **1** remains very slow on the T_2 NMR time scale between 273 and 318 K and that T_1(H^A) and T_1(H^X) are different up to 295 K in spite of the exchange. Hence, the above unusual $T_{1\text{sel}}$ behavior of the hydride ligands could be very useful for indication and studies of the positional exchange.

We have shown above that the quantum mechanical hydride exchange in **1** is quenched in the deuterated derivatives of **1**. In contrast to this, the classical H^A/H^X exchange *does not show* a pronounced isotopic effect and $k(H)/k(D) = 1.1$ (295 K, toluene-d_8; the k(D) value was measured for Cp_2NbH_2D). Note that similar results have been reported earlier for some iridium trihydride systems which also exhibited exchange couplings.[2d]

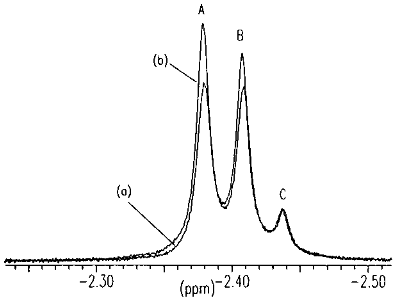

Figure 2. H^A region of the ^{1}H NMR spectrum of a toluene-d_8 solution of deuterated complex **1** without (a) and with (b) H^X irradiation at 220 K: A, $Cp_2NbH^X{}_2H^A$; B, $Cp_2NbH^XD^XH^A$; C, $Cp_2NbD^X{}_2H^A$.

Table 2. T_1 and $T_{1\text{sel}}$ Relaxation Data for the Hydride Ligands of $(Cp)_2NbH^X{}_2H^A$ and Its Deuterated Derivatives (Toluene-d_8, 400 MHz)

T_1 (s) (T (K))	H^A	H^X
$T_1{}^{\text{exp}}$(tot.) (220 K)	0.137	0.191[b]
	0.173[a]	
	0.241[c]	
$T_1{}^{\text{exp}}$(tot.) (230 K)	0.295[a]	0.406[d]
$T_{1\text{sel}}{}^{\text{exp}}$(tot.) (230 K)	0.365[a]	0.462[d]
$T_1{}^{\text{exp}}$(tot.) (230 K)	0.411[c]	
$T_{1\text{sel}}{}^{\text{exp}}$(tot.) (230 K)	0.444[c]	

[a] For $Cp_2Nb\mathit{H}^AH^XD^X$. [b] For the composite resonance of the H^X ligands in the isotopic mixture. [c] For $Cp_2Nb\mathit{H}^AD_2{}^X$. [d] For $Cp_2Nb\mathit{H}^XH^AD^X$.

Taking into account the limitation of the $T_{1\text{sel}}$ approach, the T_1 and $T_{1\text{sel}}$ data were collected for **1** and its partially deuterated derivatives at low temperatures.

Figure 2a demonstrates the H^A region in the 400 MHz ^{1}H NMR spectrum, recorded at 220 K, for a solution containing Cp_2NbH_3 (44%), Cp_2NbH_2D (43%) (**1a**), and Cp_2NbD_2H (13%) (**1b**). Here, the relative integral intensities of $Cp_2NbH^X{}_2\mathit{H}^A$, $Cp_2NbH^XD^X\mathit{H}^A$, and $Cp_2NbD^XD^X\mathit{H}^A$ are equal to 3.4, 3.3, and 1.0, respectively. The assignments in Figure 2a are well-confirmed by NOE[15] observed for the two strong H^A lines with irradiation of H^X (Figure 2b).

It follows from the spectrum that the D perturbation for H^A is the usual high-field isotope shift[16] of −0.029 ppm per D. Nevertheless the magnitude of this effect allows the correct relaxation studies for each isotopomer. Unfortunately, H^X do not show the pronounced isotope shift, and the H^X resonances of the isotopomers remain unresolved for substitution of H^A with D.

The isotopic ratio changes slowly according to the long-time ^{1}H NMR monitoring: the hydride resonances of **1** disappear completely in 2 weeks because of a slow H/D exchange with toluene-d_8. This solution, containing mainly Cp_2NbH_2D, was also used for the relaxation study.

All of the relaxation data, providing the full structural characterization of the NbH_3 fragment in complex **1**, are collected in Tables 1 and 2. The $T_{1\text{min}}{}^{\text{exp}}$($H^A-H^X$) value of 0.618 s, corresponding to hydride−hydride dipole−dipole interactions, is directly determined by comparing the $T_{1\text{min}}$ measurements for the H^A ligands in **1**, **1a**, and **1b**. The very

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small difference between T_1^{exp} and T_{1sel}^{exp} for the H^A ligand in twice deuterated complex **1b** (Table 2) corresponds to an insignificant (<7%) contribution $1/T_1(Cp-H^A)$ to the total H^A relaxation rate. Note that the $T_{1min}^{exp}(Cp-H^A)$ time equal to 2.08 s is well-predicted by the theory. Then the $T_{1min}^{exp}(Nb\cdots H^A)$ time is calculated from eq 1 as 0.156 s.

Thus, the hydride relaxation in **1** is >50% governed by Nb−H dipole−dipole interactions (64% in the case of H^X) which shorten T_1 significantly. For this reason one should be very careful with quantitative interpretation of the T_1 data in the case of niobium hydrides and niobium dihydrogen complexes. In the last case this is valid even if the dihydrogen ligand undergoes fast rotation,[17a] leading to reorientations of the Nb−H vector. Indeed, an analysis of this rotation according to Woessner[17b] (for simplicity in this consideration r(Nb−H) and r(H−H) can be taken as 1.8 and 1 Å, respectively) shows that the Nb−H dipole−dipole effect decreases due to the rotation by a factor of 0.78 ($T_1(Nb-H) = 0.78T_1^*(Nb-H)$ where $T_1^*(Nb-H)$ is the relaxation time of the spinning ligand) versus 0.25 in the case of proton−proton interactions in this ligand.[17a]

It is of great interest to consider the data reported for $[(C_5H_4SiMe_3)_2NbP(OEt)_3H^X{}_2]^+[CF_3COO]^-$ (**2**), where the hydride ligands showed the extremely long T_{1min} time of 0.600 s [18] (recalculated for 400 MHz). Even an unrealistic Nb−H distance of 2 Å could produce the T_1 value of 0.3 s (eq 5). Hence, the Nb−H dipole−dipole contribution is reduced significantly in **2**. The reason for this effect is not clear now. However, it seems to be obvious that this is connected with a relaxation behavior of ^{93}Nb in the positively charged complex.

The results of Curtis[9b] and our variable-temperature T_1 data allow us to estimate the ^{93}Nb T_1 time in complex **1** as 10^{-6} s at 192 K when the hydride T_1 time is minimal. This quite short time remains, however, much longer than the molecular motion correlation time τ_c (10^{-10} s, $\tau_c = 0.62/2\pi\nu$). This ratio provides the effective relaxation of the hydride ligands by Nb−hydride dipole−dipole interactions.

It becomes clear now that the ^{93}Nb T_1 values, close to τ_c, can decrease the effect of Nb−H dipole−dipole interactions, transforming the relaxation process to scalar relaxation of the second kind.[11] Note that the contribution of such relaxation to the total hydride T_1 time will be negligibly small under these conditions. Unfortunately there are no ^{93}Nb T_1 data in the literature for compounds related to complex **2**. This yields an additional complication in quantitative interpretations of T_1 data for niobium hydride complexes. However, we believe that the T_1 and T_{1sel} measurements can help in these cases (see the factor k in eq 6: $k \rightarrow 0$ when $T_{1sel} \rightarrow T_1$).

H−H and Nb−H Distances in Complex 1 from the Relaxation Data. The $T_{1min}^{exp}(Nb-H^A)$ time (Table 1) obtained from the T_1 experiments with **1** and partially-deuterated **1a** and **1b** gives the Nb−H^A bond distance of 1.78 Å through eq 5. Errors in such calculations are less than 4% according to the recent detailed analysis.[10b] A very close value (1.80 Å) can be obtained from eq 6 and the selective T_1 times collected in Table 2. Estimation of the Nb−H^X bond length from $T_{1min}^{exp}(Nb-H^X)$ (this contribution is easily determined from expression 7) gives 1.81 Å. In turn, the selective relaxation experiments (Table 2) give the Nb−H^X distance of 1.80 Å. Good agreement between two different NMR methods supports strongly the idea of using the T_{1sel} measurements for structural characterization of transition metal hydride systems. [10b]

$$1/T_{1min}^{exp}(Nb-H^X) = 1/T_{1min}^{exp}(tot.) - 1/T_{1min}^{theor}(Cp) - 1/T_{1min}^{exp}(H^A\cdots H^X) \quad (7)$$

According to the X-ray analysis,[5a] an averaged Nb−H bond length in **1** is estimated as 1.71 Å. This value is slightly shorter than the relaxation distances. A similar situation takes place when M−H bonds are analyzed by X-ray and ND methods.[3] A much larger difference is observed for the H^A-H^X distance. Indeed the $T_{1min}^{exp}(H^A\cdots H^X)$ value gives 1.98 versus 1.76 Å, found in the X-ray structure[5a] (the interligand angles are determined as 66 and 62°, respectively). Note, that this difference cannot be an artifact because it produces a *2-fold difference* between the experimental and theoretical $T_{1min}(H^A-H^X)$ times (Table 1), and therefore we believe that the relaxation H^A-H^X distance is more realistic. In this connection it is remarkable that the hydride ligands in **1** show quantum mechanical exchange couplings[6a] in spite of the quite large hydride−hydride distance. In good agreement with the current theoretical models[2b,d,e,f] this coupling in **1** is weak even at high temperature ($J(H^A-H^X) = 22$ Hz at 318 K) than that in the Ir[2d] and Os[18] complexes having more structurally-proximate (<1.7 Å) hydrides. The theoretical models show that the exchange coupling is greatly increased by increasing the amplitude of the vibration motion of the hydride ligands. This factor plays, perhaps, a main role in the spectral behavior of **1**. Indeed, Cp_2TaH_3, structurally close to **1** and having even more proximate hydride ligands (1.85 Å from the ND data[5a]), exhibits only magnetic proton−proton couplings.[6a]

Finally it should be noted that the Nb−H and H−H distances reported here were not corrected for the hydride librations. This task seems to be absolutely unrealistic in the absence of the neutron diffraction structure. Nevertheless one can expect that the T_1 relaxation distances can be slightly elongated (2−5% [19a,b]) due to these hydride librations.

Conclusions

The detailed NMR study of trihydride **1** has demonstrated how T_1 and T_{1sel} measurements can be used for determination of the hydride−hydride and metal−hydride distances in Nb complexes. The T_{1sel} method is independently supported by the relaxation studies of the partially deuterated derivatives of **1**. It has been found that the application of the T_{1sel} approach is limited by *the presence of the slow hydride/hydride site exchange* characterized quantitatively by saturation transfer experiments.

The correct experimental estimations have demonstrated Nb−H dipole−dipole interactions to be very important for the hydride relaxation in **1.** The Nb−H contribution shortens significantly the hydride T_1 times, providing, for example, up to 64% of the H^X relaxation rate.

The analysis of current T_1 data has shown that the effect of Nb−H dipole−dipole interactions decreases dramatically in some positively-charged niobium hydrides due to, probably, the fast ^{93}Nb spin−lattice relaxation. It is obvious that the presented data should be taken into account in quantitative interpretations of T_1 behavior of niobium hydrides and dihydrogen complexes.

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