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Combined single crystal neutron diffraction and solution NMR relaxation studies of mono- and bis(silyl) substituted niobocene hydrides with nonclassical interligand interactions

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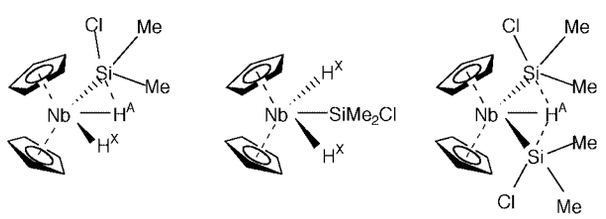
A neutron diffraction study of the bis(silyl) complex $Cp_2NbH(SiMe_2Cl)_2$ (**3**) provides unambiguous localization of the hydride ligand in a central position in the bisecting plane of the niobocene moiety, which is thus in accordance with the molecular symmetry group and the results of recent density functional theory (DFT) calculations. This result is compared with the quantitative localization of the hydride ligands in solutions of the isomeric mono(silyl) complexes $Cp_2NbH_2(SiMe_2Cl)$ (**1** and **2**) and the bis(silyl) complex **3** by means of T_{1min}, T_1, T_{1sel} and T_{1bis} NMR measurements. A good agreement between the solution and solid state structural data is observed. It is found that the presence of a neighbouring $SiMe_2Cl$ ligand increases the Nb–hydride bond length remarkably, probably through the mechanism of Si–H interligand hypervalent interaction (IHI). This effect is especially pronounced in the mono(hydride) complex **3** containing two Si groups, where the Nb–H distance is determined as 1.781(1) Å (NMR relaxation, solution) and 1.816(8) Å (neutron diffraction, solid state).

Recently reported X-ray structure determinations of mono- and bis(silyl) niobocene hydrides $Cp_2NbH(SiMe_2Cl)_2$[1] and $Cp_2NbH_2(SiMe_2Cl)$[2] suggest the presence of non-classical interligand hypervalent interactions Cl–Si···H (IHI) in the solid state. These interactions are different from those observed in silane σ-complexes (or η^2-Si–H complexes)[3] and are proposed to stem from the donation of electron density from the Nb–H bonding orbital into the Si–Cl antibonding orbital. The occurrence of IHI was inferred from the observation of relatively long Si–Cl bonds [2.163–2.170(1) Å], short Nb–Si bonds [2.579–2.597(1) Å] and a reduced Si–Nb–Si bond angle [104.27(5)°]. A similar interligand interaction of a Ta–H bond with a β-positioned Si–Cl bond (which can be called β-IHI) was observed in a tantalum half-sandwich complex.[4] Although short Si···H contacts (1.86–2.05 Å) were also observed, these parameters are less reliable due to the well-known foreshortening of M–H bonds caused by X-ray diffraction methods.[5] In particular, the question of whether the hydride ligand in the complex $Cp_2NbH(SiMe_2Cl)_2$ lies symmetrically between two silicon atoms or is shifted closer to one of them required further experimental elucidation. Thus, although the molecular symmetry group of complex $Cp_2NbH(SiMe_2Cl)_2$ (C_{2v}) observed in the X-ray structure requires the exact central positioning of the hydride in the bisecting plane of the Cp_2Nb moiety, the possibility of a disordered structure (C_s) with unequal Si–H contacts could not be ruled out.[6] In the present study this problem is unambiguously solved by a single crystal neutron diffraction experiment at 100 K.

Another question to be addressed here is whether these nonclassical interactions are retained in solution. Although reactivity studies and DFT calculations support the presence of nonclassical Si···H interactions,[2] quantitative experimental information is highly desirable. The NMR relaxation technique is a powerful method for the determination of metal–hydride and hydride–hydride distances in solutions of hydride complexes.[7,8] Here we report on the application of this technique in order to study the lateral (**1**) and central (**2**) isomers of the mono(silyl) complex $Cp_2NbH_2(SiMe_2Cl)$ (*lateral* and *central* correspond to the position of the silyl ligand in the bisecting plane of the niobocene moiety, see Scheme 1) and the bis(silyl)



1 **2** **3**

Scheme 1

complex $Cp_2NbH(SiMe_2Cl)_2$ (**3**). The data obtained from different experimental and computational methods are discussed.

Experimental

The preparation of complexes **1**, **2** and **3** has been reported previously.[2] Crystals of **3** suitable for a neutron diffraction study were grown from ether solution by keeping a saturated solution at −30 °C.

Neutron diffraction study of 3

A crystal of dimensions 2 × 2 × 1 mm^3 was used for the neutron diffraction experiment. Neutron diffraction data were collected

Table 1 Crystallographic data for the neutron diffraction study of **3**

Formula	$C_{14}H_{23}NbCl_2Si_2$
FW	411.32
T/°C	−173(1)
Space group	*Pnma*
Crystal system	Orthorhombic
Cell parameters/Å	a = 16.584(3) b = 13.214(3) c = 8.419(2)
Volume/Å^3	1844.9(6)
Z	4
ρ_{calcd}/g cm^{-3}	1.481
hkl ranges	0 to −28, 0 to −21, 0 to −14
Parameters	199 (All atoms refined with anisotropic atomic displacement parameters, including the hydrogen atoms)
Total number of observed reflections	8886
Int. merg. factor	0.0599
Merged reflections used in refinement	1537
S	1.185
R	0.062
Rw	0.098

on the SXD instrument at the ISIS spallation neutron source, using the time-of-flight Laue diffraction method.[9] In the present experiment, two position-sensitive scintillation detectors, each of 192 × 192 mm^2 active area, in 3 × 3 mm pixels, were used. These were situated with their centers at $2\theta = 54.5°$, about 168 mm from the sample (low angle detector), and $2\theta = 126°$, *ca.* 180 mm from the sample (high angle detector).

The crystal, sealed in Al foil for protection and attached to an aluminium pin by two thin aluminium adhesive strips, was mounted on a two circle goniometer (φ,χ) in a Displex closed cycle refrigerator (CCR) helium cryostat situated in a vacuum chamber. Data were collected at a temperature of 100 ± 1 K, the computer-controlled temperature being measured by a Rh–Fe thermocouple positioned around 10 mm from the sample at the CCR head.

Initially, 24 frames were collected at each detector for 550 μA h frame^{-1} (corresponding to around 3 h exposure), rotating χ in four steps and φ in six steps in the ranges $-2.5 > \chi > -80°$ and $0 < \varphi < 180°$. This was followed by a further 18 frames (275 μA h frame^{-1}) which interleaved with the initial 24 frames to ensure that all the Bragg intensities were measured more than once. Data collection times may be estimated by assuming an average ISIS beam current of *ca.* 165 μA.

The intensities were extracted and reduced to structure factors using standard SXD procedures.[9] A total of 8886 reflections were observed, reducing to a unique set of 1537 structure factors on merging ($R_{int} = 0.0599$). This structure factor set was used for structural refinement in CRYSTALS.[10] The non-hydrogen atom positions from the X-ray model were used as a starting point for the refinement. Hydrogen atom positions were located from subsequent difference neutron Fourier maps. All atoms were refined with anisotropic displacement parameters. Neutron scattering lengths were taken from the compilation of Sears.[11] Crystal data and a summary of the data collection and refinement parameters are given in Table 1.

NMR studies

All NMR studies were carried out in NMR tubes sealed under vacuum using standard techniques. Toluene-d_8 was dried and deoxygenated using conventional procedures.[2]

NMR data were collected with Bruker AC 200 and AMX 400 spectrometers. The conventional inversion–recovery method (180–τ–90)[12] was used to determine T_1. T_{1sel} and T_{1bis} relaxation times were measured by applying selective 180° pulses provided by the decoupler systems of the spectrometers. The duration and power of the 180° selective pulses (180_{sel}–τ–90) were regulated to excite only one or two NMR resonances. The calculation of relaxation times was carried out 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 pulses was controlled at every temperature. The errors in T_1 determinations were lower than 4%.

Relaxation theory

Intramolecular proton–proton and proton–metal dipole–dipole interactions dominate the T_1 relaxation of hydride ligands in classical Re, Mn, Co and Nb hydrides.[7,13] Thus, the total relaxation rate for the hydride ligands in, for example, the Nb dihydride complex **1** (see Scheme 1 for the notation of the hydride ligands) can be described as follows:

$$1/T_1(H^A) = 1/T_1(Nb\cdots H^A) + 1/T_1(H^A\cdots H^X) + 1/T_1(Cp\text{–}H^A) + 1/T_1(Me\text{–}H^A) \quad (1)$$

$$1/T_1(H^X) = 1/T_1(Nb\cdots H^X) + 1/T_1(H^A\cdots H^X) + 1/T_1(Cp\text{–}H^X) + 1/T_1(Me\text{–}H^X) \quad (2)$$

where $1/T_1$(Cp–H) and $1/T_1$(Me–H) are the relaxation contributions caused by dipole–dipole interactions between the hydride ligands and the protons of the Cp and CH_3 groups, respectively. In turn

$$1/T_1(H\cdots H) = 0.3\gamma_H{}^4h^2/r_{H\cdots H}{}^6[\tau_c/(1+\omega_H{}^2\tau_c{}^2) + 4\tau_c/(1+4\omega_H{}^2\tau_c{}^2)] \quad (3)$$

and

$$1/T_1(Nb\cdots H) = 2\gamma_H{}^2\gamma_{Nb}{}^2h^2\boldsymbol{I}(\boldsymbol{I}+1)/15r_{Nb\cdots H}{}^6\{3\tau_c/(1+\omega_H{}^2\tau_c{}^2) + 6\tau_c/[1+(\omega_H+\omega_{Nb})^2\tau_c{}^2] + \tau_c/[1+(\omega_H-\omega_{Nb})^2\tau_c{}^2]\} \quad (4)$$

where γ, h, $\boldsymbol{I}$ and ω have their usual meanings in this context and $\tau_c = \tau_o\exp(E_a/RT)$.[12] When the T_1 time in eqn. (3) or (4) reaches a minimum, the corresponding internuclear distance can be calculated from eqn. (5) or (6) written in a convenient form (ν is the ^{1}H NMR resonance frequency in MHz):

$$r_{H\cdots H}\,(Å) = 2.405[200T_{1min}(H\text{–}H)/\nu]^{1/6} \quad (5)$$

$$r_{Nb\cdots H}\,(Å) = 2.722[200T_{1min}(Nb\text{–}H)/\nu]^{1/6} \quad (6)$$

It is obvious that separation of the relaxation contributions in eqns. (1), (2) provides structural characterization of the metal–hydride fragment through eqns. (5), (6) when the hydride ligands have low vibrational amplitudes. A recent detailed analysis[13b] has shown that, even in the presence of anisotropic molecular motions, errors in the calculation of the M–H and H–H distances are minimal (≤5%), at least in the case of mononuclear complexes.

It has been found that the Nb–H distances in solutions of Nb hydrides can be determined reliably by measurement of selective (T_{1sel}), nonselective (T_1) and T_{1min} relaxation times of hydride ligands[8,13b] through eqn. (7):

$$r_{Nb\cdots H}\,(Å) = 5.109\,[(1.4k + 4.47)T_{1min}/\nu]^{1/6} \quad (7)$$

where $k = (T_{1sel}/T_1 - 1)/(0.5 - T_{1sel}/3T_1)$ and the T_1 and T_{1sel} times are measured at $\omega_H{}^2\tau_c{}^2 \ll 1$.

It follows from the theory that the Nb–H distance determined for complex **1** through eqn. (7) allows us to calculate the corresponding niobium–hydride contribution to eqns. (1), (2). Other relaxation contributions can be estimated from

Table 2 The spectral parameters [δ, T_{1min} (400 MHz)/s] for complexes **1**–**3** in toluene-d_8 at 295 K, unless otherwise stated

Complex	Cp	Me	H^X (J(Nb–H)/Hz)	H^A (J(Nb–H)/Hz)
1	4.894, 0.449 (220 K)	0.943, 0.365 (220 K)	−4.266 (46)	−4.470 (109)
2	4.817, 0.570 (220 K)	1.047, 0.357 (200 K)	−4.635 (72)	
3	4.739, 0.700 (200 K)	0.663, 0.523 (210 K)		−5.107 (125)

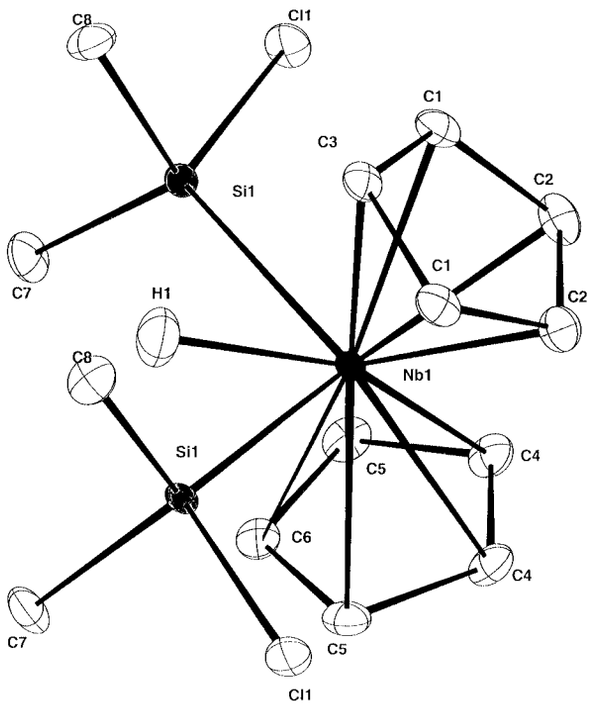


Fig. 1 Molecular structure of **3** determined from the ND experiment. Selected bond lengths (Å) and angles (°): Nb1–Si1 2.612(4), Cl1–Si1 2.166(4), Nb1–H1 1.816(8), Si1–C8 1.878(4), Si1–C7 1.879(4), Si1–H1 2.076(3); Nb1–Si1–Cl1 114.69(15), Si1–Nb1–H1 52.21(9), Si1–Nb1–Si1′ 104.42(18), Nb1–Si1–C8 116.38(18), Nb1–Si1–C7 117.07(19).

measurements of biselective T_1 times for the resonance pairs hydride–CH_3 and hydride–Cp(H). Actually, the parameters F(hydride) = [1/T_{1bis}(hydride) − 1/T_{1sel}(hydride)]/[1/T_1(hydride) − 1/T_{1sel}(hydride)] reflect *the fractional contributions* to the total relaxation rate of a hydride ligand *via* dipolar interactions with the corresponding protons.[14] All these data make it possible to determine the hydride–hydride distance in complex **1**. Finally, similar relaxation expressions can be used for characterization of the NbH fragments in complexes **2** and **3**.

Results and discussion

Neutron diffraction study of 3

Neutron diffraction is the most reliable method for accurate determination of hydrogen atom positions in the vicinity of heavy elements. Here this technique is applied to solve the structural dilemma of the complex $Cp_2Nb(SiClMe_2)_2H$ (**3**). The molecular structure of **3** determined from neutron diffraction (ND) is shown in Fig. 1, and the important bond lengths and angles are given in the figure caption. Overall, a good correspondence between the structural parameters of the ND ($\mathbf{3}_{ND}$) and X-ray ($\mathbf{3}_{X\text{-}ray}$) structures[1b] is observed. The Nb–Si bond lengths found in $\mathbf{3}_{ND}$ and $\mathbf{3}_{X\text{-}ray}$ are the same within the standard errors [2.612(4) *versus* 2.597(1) Å]. The Si–Cl bond distances in both structures are also in good agreement. The most important observation is that the hydride ligand in $\mathbf{3}_{ND}$ lies symmetrically between two silyl ligands, exactly on the crystallographically imposed mirror plane of symmetry, in good agreement with the molecular symmetry group and the results of recent DFT calculations.[2] As expected, the Nb–H bond, at 1.816(8) Å, is significantly longer than the corresponding value found for $\mathbf{3}_{X\text{-}ray}$ [1.74(7) Å]. This bond is also longer than the Ta–H bonds found from the ND determination of Cp_2TaH_3[15] [1.771(9) Å average] and $Cp_2TaH(SiMe_2H)_2$[16] [1.785(15) Å], but is in perfect agreement with the Nb–H bond length calculated for the model compound $Cp_2NbH(SiH_2Cl)_2$ (1.811 Å).[2] Note that longer Nb–H bonds allow better overlap between the Nb–H bonding and Si–Cl antibonding orbitals and also reflect an electron density transfer from the former onto the latter. Such an overlap was proposed to be the origin of interligand interactions in **3**.[1,2]

Elongation of the Nb–H bond in $\mathbf{3}_{ND}$ in comparison with $\mathbf{3}_{X\text{-}ray}$ only slightly changes the value for the Si···H contact [2.076(3) *versus* 2.056(5) Å]. In this regard, it is noteworthy that 2.0 Å is often cited as the maximum possible Si–H distance for the Si···H interaction in silane σ-complexes to be significant.[3a] We have argued previously that this criterion is based on incorrect assumptions and the range for the "maximum criterion" of interaction should be expanded.[2] One should also take into account that: firstly, the criteria for different types of interactions (*e.g.* IHI *versus* complexation of a σ-bond) can be different and, secondly, there is no strict border between "significant" and "not significant" interactions. For example, the potential energy curve for the Si···H interaction shows half the bond energy at a Si–H distance of *ca.* 2.20 Å.[17] Therefore, a "maximum bonding" criterion, if any, can only have the meaning of the "most likely" maximum value in a certain class of compounds. In this regard, note that the longest known Si···H contact found by X-ray crystallography for silane σ-complexes is 2.1 Å.[18]

To summarize this section, the neutron diffraction of **3** unequivocally establishes the central position of the hydride in the bisecting plane of the niobocene moiety. Moreover, it confirms the prediction of IHI theory that a Si···H interligand hypervalent interaction elongates the Nb–H bond of the "interacting" hydride. This important conclusion is further supported by the NMR studies.

NMR and T_1 NMR data for toluene-d_8 solutions of 1, 2 and 3

To gain an insight into the possible occurrence of interligand interactions in solutions of **1**, **2** and **3**, NMR relaxation studies were undertaken. A toluene-d_8 solution of the complex $Cp_2NbH_2(SiMe_2Cl)$ contains two isomeric compounds, having an outer (**1**) and a central (**2**) $SiMe_2Cl$ ligand, respectively ([**1**]:[**2**] = 1.3:1). Note that this isomeric ratio does not change with temperature. The hydride region of the room-temperature ^{1}H NMR spectrum of **1** (Table 2) shows two lines at −4.470 (H^A; for notation, see Scheme 1) and −4.266 ppm (H^X). The H^A resonance is significantly broadened due to pronounced scalar relaxation of the second kind,[12] as a result of coupling between the ^{1}H and ^{93}Nb nuclei. This effect has also been reported for the central hydride ligand in Cp_2NbH_3[19] and was used for the spectral assignments in Table 2. In agreement with the theory of scalar relaxation of the second kind,[12] lowering the temperature decreases this broadening and, for example, at 200 K the linewidths of both hydride resonances for **1** become practically identical (Fig. 2).

The equivalent H^X ligands in the isomeric complex **2** exhibit a single resonance at −4.635 ppm, which is slightly broadened at room temperature. A broader hydride signal is observed in the

^{1}H room-temperature spectrum of complex **3**, which supports the view that it is in a central position in the complex.

Table 3 shows the variable-temperature linewidth data ($\Delta\nu$) collected for the hydride resonances in complexes **1**–**3**. The widths of the observed signals ($\Delta\nu^{obs}$) are controlled by the natural linewidth ($\Delta\nu = 1/\pi T_2$, $T_2 = T_1$) and additional broadening ($\Delta\nu^{Nb-H}$) caused by the above mentioned scalar relaxation of the second kind. Note that $\Delta\nu^{Nb-H}$ can be estimated from $\Delta\nu^{Nb-H} = \Delta\nu^{obs} - \Delta\nu$, if the T_1 values are known. As can be seen from Table 3, $\Delta\nu^{Nb-H}$ increases significantly with temperature, in good agreement with the theory.[12] In turn, the $\Delta\nu^{Nb-H}$ values allow estimation of the J(Nb–H) coupling constant, if the T_1 time of ^{93}Nb is known:

$$\Delta\nu^{Nb-H} = (4/3)\pi J^2 \boldsymbol{I}(\boldsymbol{I}+1)T_1(\mathrm{Nb}) \qquad (8)$$

where $\boldsymbol{I} = 9/2$. A T_1(Nb) of 2×10^{-5} s was measured experimentally for Cp_2NbH_3 at room temperature which led to J(Nb–H) values of 40 and 100 Hz for H^X and H^A, respectively.[19] Similar magnitudes can be calculated for complexes **1**–**3** (Table 2), assuming the same T_1(Nb) value in eqn. (8).

Finally, it should be also emphasized that, in contrast to Cp_2NbH_3, complex **1** exhibits no visible hydride–hydride spin–spin splitting between 200 and 340 K. For example, the hydride region of the 200 K ^{1}H NMR spectrum of the isomeric complexes **1** (with the nonequivalent H ligands) and **2** (with the equivalent H ligands) shows resonances with the same linewidth (Fig. 2).

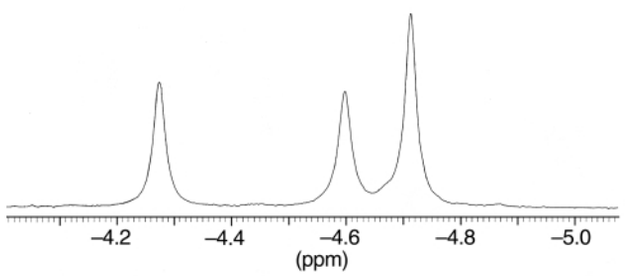


Fig. 2 The hydride region of the ^{1}H NMR spectrum of a mixture of complexes **1** and **2** at 200 K. The singlets at −4.266 and −4.470 ppm are due to the H^X and H^A protons of **1**, the singlet at −4.635 ppm is due to the H^X protons of **2**.

Table 3 The variable-temperature $\Delta\nu$ and T_1 data (400 MHz) for complexes **1**–**3**

	$\Delta\nu^{obs}$/Hz, $\Delta\nu^{Nb-H}$/Hz		T_1 (400 MHz)/s		
Complex	H^X	H^A	H^X	H^A	T/K
1	12.4	vb			340
	4.8, 4.4	25.0, 24.7	0.903	0.954	294
	4.4, 3.1	11.0, 9.8	0.241	0.269	240
	5.2, 2.4	7.0, 4.5	0.113	0.126	220
	4.2, 1.1	4.9, 2.2	0.102	0.118	200
2	26.0				340
	11.2, 10.9		1.368		294
	5.2, 4.2		1.368		240
	4.7, 2.9		0.178		220
	4.0, 1.4		0.125		200
3		32.6, 32.3		1.274	298
		23.6, 23.0		0.174	220

The T_{1min} time of 1.025 s was measured for the Cp rings of Cp_2NbH_3[8] in toluene-d_8. Considerably smaller values were determined for complexes **1**–**3** (Table 2), where there is an additional source for Cp relaxation through the protons of the bulky $SiMe_2Cl$ groups.

The results of the detailed relaxation measurements for the hydride ligands in complexes **1**–**3** are collected in Table 4 where the T_1, T_{1sel} and T_{1bis} values are represented as *averaged magnitudes* obtained in *5–7 different experiments* carried out at 295 K. A direct comparison of the T_{1min} values for the H^X and H^A ligands in **2** and **3**, respectively (in this case the hydride–hydride dipole–dipole interactions are absent) shows a slightly longer time in complex **3** in spite of the presence of two $SiMe_2Cl$ ligands in this molecule. Therefore, it would appear that the contributions $1/T_1$(Me–H^X) and $1/T_1$(Me–H^A) (caused by hydride–CH_3 interactions) to the total relaxation rate of the hydride ligands in complexes **2** and **3** are minimal. A similar conclusion can be deduced from the relaxation experiments carried out for complexes **1** and **2**. Actually, $T_{1sel} \approx T_{1bis}$ for the resonance pairs hydride–Me (Table 4). Measurements of selective and biselective T_1 times for the hydride–Cp resonances show that contributions to the total relaxation rates of the hydride ligands in **1** and **2** coming from the Cp-protons are also negligible. In good agreement with the relaxation experiments, we observed no NOE[20] effects for the hydride ligands in **1**–**3** on CH_3 or Cp irradiation. At the same time, a pronounced NOE enhancement of 0.21 (or of 0.17) is found for the Cp (or CH_3) resonance on CH_3 (or Cp) irradiation in the spectrum of monohydride **3** containing two $SiMe_2Cl$ ligands. Thus, all the presented data clearly show that the hydride relaxation in **2** and **3** is governed only by Nb–H dipole–dipole interactions, while in complex **1** there is a contribution caused by H^X–H^A dipole–dipole interactions. This follows from the fact that the T_{1min} times for the hydride ligands in **1** are slightly shorter than those in **2** and **3**.

Calculation of the H–H and Nb–H distances in complexes 1, 2 and 3 from the relaxation data

Calculation of the Nb–H^A distance in monohydride complex **3** on the basis of the $T_1/T_{1sel}/T_{1min}$ experiments, through eqn. (7), gives a value of 1.78(1) Å. This seems to be quite reasonable because direct calculation of this distance from eqn. (6) [using the T_{1min} (H^A) value only] leads to a value of 1.77(1) Å. For comparison, the Nb–H distance found in the solid state structure of **3** from the ND experiment (*vide supra*) is longer. A shorter Nb–H^X distance of 1.71(1) Å is calculated for the dihydride **2** through eqn. (6), where the hydride relaxation is governed by Nb–hydride dipolar interactions only. The relation $T_1(H^X) = T_{1sel}(H^X)$ observed for this dihydride (Table 4) supports this relaxation mechanism.

Comparison of the T_{1min} values for H^X (0.0921 s) and H^A (0.111 s) in dihydride **1** (here the hydride relaxation is governed by hydride–hydride and Nb–hydride dipole–dipole interactions) shows clearly that the Nb–H distance is longer in the case of the central hydride ligand. Calculation of the Nb–H^X bond length from the $T_1/T_{1sel}/T_{1min}$ measurements through

Table 4 The T_1 relaxation data for complexes **1**–**3** collected for the hydride ligands in toluene-d_8 solutions at 400 MHz[a]

	$T_{1min}^{210\ K}$/s		$T_{1sel}^{295\ K}$/s		$T_1^{295\ K}$/s		$T_{1bis}^{295\ K}$/s	
Complex	H^X	H^A	H^X	H^A	H^X	H^A	H^X–CH_3	H^X–Cp
1	0.0921	0.111	1.045		0.959	1.010	0.968	0.960
2	0.125		1.434		1.465		1.440	1.442
3		0.149		1.381		1.323		

[a] T_{1min}(Cp) = 0.449, 0.570 and 0.700 s, respectively.

Table 5 Comparison of metal–hydride distances (Å) obtained by different methods for **1**, **2** and **3**

Complex	Parameter	X-Ray	NMR relax. (210 K)	ND (100 K)	DFT[a]
1	$Nb–H^X$	1.76(6)[b]	1.68(1)		1.745
	$Nb–H^A$	1.67(9)[b]	1.74(1)		1.793
	$H^X–H^A$	1.92[b]	1.97(1)		1.688
2	$Nb–H^X$		1.71(1)		1.739
					1.774[c]
3	$Nb–H^A$	1.74(7)[d]	1.78(1)	1.816(8)	1.811[e]

[a] Ref. 2. [b] 193 K. [c] Two nonequivalent bond lengths calculated for the model complex $Cp_2Nb(SiH_2Cl)H_2$. [d] 173 K. [e] Calculated for the model complex $Cp_2Nb(SiH_2Cl)_2H$.

eqn. (7), gives a length of 1.68(1) Å. This value corresponds to a $1/T_{1min}(Nb–H^X)$ contribution of 9.209 s^{-1} (400 MHz) (eqn. (6)). In turn, this contribution allows us to calculate the $H^X–H^A$ distance as 1.97(1) Å through eqn. (5). Subtraction of the $H^X–H^A$ contribution from the total relaxation rate of the H^A ligand leads to an $Nb–H^A$ bond length of 1.74(1) Å (eqn. (6)). These bond lengths can be compared with the corresponding values found for the solid state structure from X-ray structure analysis,[2] 1.76(6) and 1.67(9) Å for the lateral and central hydrides, respectively. However, increasing the $Nb–H^A$ bond distance from 1.67 to 1.74 Å in **1** does not change the distance of the Si···H contact (1.86 Å). The metal–hydride distances in **1**, **2** and **3** obtained by different methods are summarized in Table 5. The NMR relaxation data are in a perfect agreement with the results of DFT calculations[2] which also show the elongation of the $Nb–H^A$ distances in comparison with the $Nb–H^X$ distances [1.793 Å ($Nb–H^A$) *versus* 1.745 Å ($Nb–H^X$) in **1** and 1.811 Å ($Nb–H^A$) in $Cp_2Nb(SiH_2Cl)_2H$ *versus* 1.756 Å (av. $Nb–H^X$) in $Cp_2NbH(SiH_2Cl)H$]. The lengthening of the $Nb–H^A$ distances can be attributed to an interaction between this hydride and the neighboring Lewis acid center $SiMe_2Cl$. This suggestion is in accord with the recent theoretical study of an interaction between Cp_2NbH_3 and AlH_3 which showed a substantial elongation of the Nb–H bond upon coordination of the Lewis acid.[21]

Finally, the Nb–H and H–H distances determined from the NMR relaxation study allow calculation of the $H^A–Nb–H^X$ interligand angle in **1** as 70.5°, which is in good agreement with the value obtained from the X-ray diffraction experiment (68.0°).[2] For comparison, a significantly smaller $H^A–Nb–H^X$ bond angle of 66.0° was found in the NMR relaxation study of Cp_2NbH_3. We believe that the above $H^X–H^A$ distance taken from this calculation reflects the actual situation because the hydride resonances of **1** show no quantum mechanical exchange coupling between 200 and 340 K which could elongate the hydride T_{1min} time.[22] Such an elongation effect is expected for Cp_2NbH_3, for example, which clearly shows exchange coupling.

Conclusions

A neutron diffraction study of **3** allowed us to unambiguously locate the hydride atom symmetrically between the two lateral silicon atoms. Concomitant NMR relaxation studies on **1**, **2** and **3**, together with the previously published X-ray crystal structure of **1**,[2] show a good agreement between the solid state and solution structures. In particular, good agreement between the $H^X–Nb–H^A$ bond angles and between the Si···H^A contacts (assuming the invariability of the Nb–Si bonds and $H^X–Nb–Si$ bond angles in both structures) was found. Both the ND and NMR relaxation values for the Nb–H distance in **3** are larger than the corresponding distance found from the X-ray structure.[1b] However, elongation of the Nb–H bond distance does not significantly change the H^A···Si contact length.

The relaxation localization of hydrides in the Nb complexes containing $SiMe_2Cl$ ligands leads to the following conclusions: (i) all the Nb–H distances seem to be quite reasonable according to the available ND (ref. 15 and the present study), theoretical[2,6] and NMR relaxation[8] data; (ii) the presence of a neighboring $SiMe_2Cl$ ligand increases the Nb–hydride bond length remarkably, probably through the mechanism of interligand hypervalent interaction (IHI); (iii) this effect is especially pronounced in the mono(hydride) **3** containing two Si groups; (iv) the presence of the $SiMe_2Cl$ group in complex **1** leads to an increase of the hydride–Nb–hydride interligand angle with respect to the Cp_2NbH_3 molecule, which also reflects an attraction between the H^A and Si ligands in the former.

All these observations are in good agreement with the proposed[2] nonclassical interligand hypervalent Si···H interactions in complexes **1** and **3**.

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