Articles

Theoretical Study of the Effect of a Lewis Acid on Hydrogen Exchange Coupling in a Trihydride Metallocene: The $Cp_2NbH_3{\cdot}AlH_3$ System

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In this paper the effect of a Lewis acid on the quantum exchange coupling of polyhydride transition metal complexes is analyzed. In particular, by means of the density functional methodology (DFT), we have calculated the different adducts and transition states that appear in the $Cp_2NbH_3{\cdot}AlH_3$ system. The quantum exchange coupling that arises when two hydrides interconvert has been evaluated through a one-dimensional tunneling model within a basis set formalism. We find that a Lewis acid of the AlH_3 type may increase the exchange couplings through formation of an adduct where the Lewis acid is only bonded to the outer hydride. In this structure, which is not the absolute minimum but that is close enough in energy to be significantly populated at the experimental range of temperatures, the two "free" hydrides come closer one to each other so that an incipient dihydrogen ligand that favors the exchange tends to be formed. This result can be explained by the reduction of the electronic density on niobium induced by the Lewis acid. Our results are in agreement with experimental data for the similar $Cp_2NbH_3{\cdot}AlEt_3$ system and recent ^1H NMR spectral analysis of the reaction of niobocene complexes with salts of the Lewis acidic cations Cu^+, Ag^+, or Au^+, though it is probable that, within the same general model found in the present work, the particular structure causing the exchange coupling will depend on each kind of Lewis acid.

Introduction

In recent years the extremely large and temperature-dependent H−H coupling constants exhibited by the proton NMR spectra of several transition metal polyhydride complexes have become a well-known phenomenon.[1−5] Although some of its aspects still remain under research, nowadays it is accepted that this spectroscopic property basically stems from the quantum mechanical exchange of a pair of hydrogens through an energy barrier.[6−8] The lower the energy barrier and shorter the tunneling path, the greater the exchange coupling turns out to be. In several papers we have theoretically shown that the exchange mechanism can take place through a dihydrogen-like transition state, in such a way that the stability of the η^2-H_2 structure relative to the minimum energy polyhydride would be the main parameter that governs the magnitude of the exchange coupling.[7] That is, the coupling is lower when the η^2-H_2 structures are less stable with respect to the polyhydride complex. On the other hand, this stability depends on the transition metal and the ligands attached to it that affect the subtle balance between donation and back-donation that rules the relative energies of dihydride and dihydrogen species.

It has been recently suggested that the formation of an adduct between some substituted niobocene trihydrides and a Lewis

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acid could stabilize the dihydrogen species upon reduction of electron density on niobium.[9] This argument has been used to explain the exchange couplings observed in Lewis acid adducts of niobocene trihydrides.[10] In effect, reaction of $Nb(C_5H_3\text{-}RR')_2H_3$ complexes with salts of the Lewis acidic cations Cu^+, Ag^+, or Au^+ yields 2:1 adducts whose ^1H NMR spectra display an AB_2 pattern for the hydrides at room temperature, which splits at low temperature into an ABC one in agreement with a fluxional behavior of the cation which binds to two hydrides of each niobium center.[10] The magnitude of exchange coupling in the niobocene trihydride complex is dramatically reduced upon interaction with a copper cation, is of the same order of magnitude upon interaction with a silver cation, and is greatly increased by addition of a gold cation.[10] A model has been proposed to explain these variations. It involves two isomeric structures that are close in energy, one containing two bridging and one terminal hydrides on niobium and one involving one bridging hydride and one dihydrogen molecule (this hydride dihydrogen structure would not necessarily be a minimum on the potential energy surface).[10c] On the other hand, our previous calculations indicate that BH_3, taken as the simplest model of a Lewis acid, is able to interact with a terminal hydride of the Cp_2NbH_3 trihydride complex leading to the formation of a stable dihydrogen complex, which can easily lose molecular hydrogen.[9]

To our knowledge, the ^1H NMR spectrum of the adduct $Cp_2NbH_3{\cdot}AlEt_3$ provided in the early 1970s the first experimental observation of an unusual effect of a Lewis acid on the NMR H−H coupling constants.[11] The spectra of the adducts $Cp_2MH_3{\cdot}AlEt_3$, where M = Ta and Nb, showed AB_2 patterns consistent with selective coordination of $AlEt_3$ to the central hydride,[12] but whereas the spectrum for the tantalum compound showed at room temperature a moderate coupling constant of 12.3 Hz, that for the niobium compound at 232 K turned out to be nearly 100 Hz.[11] It should be noted that more recent measurements by Heinekey provide values always below 20.4 Hz for the Cp_2NbH_3 complex in the temperature range 173−303 K.[2c]

The purpose of this work is to provide the first theoretical study of the effect of a Lewis acid on the exchange coupling constant of a polyhydride transition metal complex. To this aim we will analyze the different adducts that can be formed when the Cp_2NbH_3 complex interacts with AlH_3, taken as a realistic model of $AlEt_3$, and discuss why the exchange coupling reaches higher values when the Lewis acid is present.

Methodological Details

A. Calculations of Electronic Structure. All calculations are carried out with the Gaussian 94 series of programs.[13] Electronic structure calculations have been performed with the same methodology employed in a previous study of metallocene trihydride complexes $[Cp_2MH_3]^{n+}$ (M = Mo, W, $n = 1$; M = Nb, Ta, $n = 0$).[7c] Density functional theory (DFT) is applied.[14] The particular functional used is Becke's three-parameter hybrid method with the LYP correlation functional (Becke3LYP).[15]

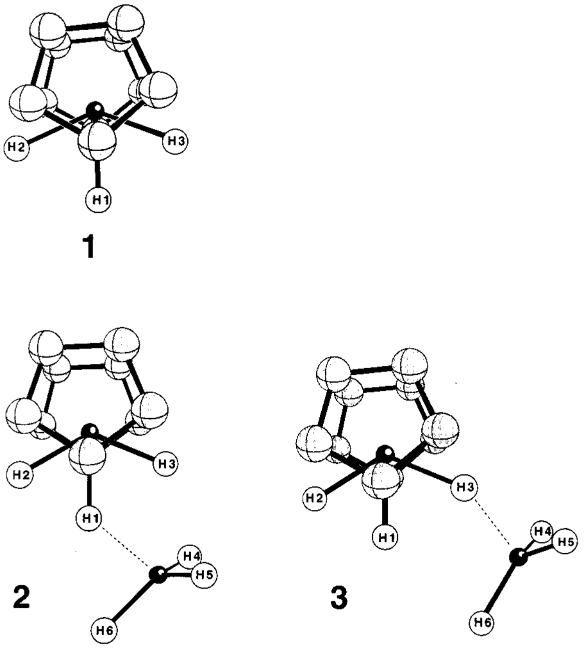

Figure 1. Geometries of the minimum energy structures **1**−**3**.

An effective core potential operator has been used to replace core electrons of niobium[16a] and aluminum[16b] atoms. The basis set for the niobium atom was that associated with the pseudopotential[16a] with a standard valence double-ζ LANL2DZ contraction.[13] The same basis set supplemented with a d polarization shell[17a] was taken for the aluminum atom.[16b] For the C and H atoms of the Cp ligand the valence double-ζ 6-31G basis set is used.[17b] A polarization p shell is added to the six hydrogen atoms directly attached to the niobium and aluminum atoms.[17b,c]

All along the exploratory process of the potential energy surface the Cp fragment is restricted to a local C_{5v} symmetry. The stationary points were located using the Schlegel gradient minimization algorithm.[18] If the approximate second derivative matrix is forced to contain zero or one single negative eigenvalue, the optimization locates a minimum or a transition state, respectively.

B. Tunneling Model. As it will be explained below, we have used the DFT results to calculate the quantum exchange coupling corresponding to the minimum energy structure in which the aluminum atom is bonded to one terminal hydride atom (structure **3** in Figure 1).

The first step to achieve this goal is to obtain a reasonable monodimensional tunneling path through the whole potential energy hypersurface. To do so, we have considered four internal coordinates

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as the only ones relevant to the rotation: the H_1-H_2 distance R_{HH}, the distance between Nb and the center of the H_1-H_2 bond R_{NbX}, the $XNbH_3$ angle (X stays at the midpoint of the H_1-H_2 segment), and the rotational angle θ of the H_1-H_2 bond in the plane orthogonal to the Nb−X direction.

The energy profile has been obtained by considering different values of the angle θ and optimizing the other three relevant geometrical parameters. The rest of the geometrical parameters are kept frozen at the values corresponding to **3**. The path length has been evaluated by obtaining the distance between two consecutive points in mass-weighted Cartesian coordinates. This implies that each point must be rotated and the center of mass of each pair of geometries must coincide in order to generate neither linear, nor angular momenta along the path.[19] In this manner we obtain a symmetric double-well profile with a maximum energy at $\theta = 90°$.

Then, a symmetric double well has been built by means of a cubic spline function which passes through each consecutive pair of points along the reaction coordinate. Because we are interested in the evaluation of the exchange coupling, we must obtain the vibrational states of the double well. For this purpose, we have used the basis set methodology by taking a set of localized Gaussian functions which have the form[20]

$$\chi_i = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left[\frac{-\alpha}{2}(s - s_i)^2\right]$$

where α is an optimizable parameter and s_i values are equally spaced points along the coordinate space. Then, a variational calculation by using *n* functions provides the lowest *n* eigenvalues and eigenfunctions of the one-dimensional system. In particular, we use 99 Gaussian functions throughout all the calculations. We have observed that a further increase in the number of basis functions does not appreciably modify the energies of the levels below the barrier.

This calculation provides the vibrational levels of the double well that appear in near-degenerate pairs. The difference in energy between the two levels of the lowest lying of these pairs provides the tunneling splitting at 0 K, which is a direct measure of the quantum exchange coupling in **3**. At higher temperatures, additional pairs of levels have to be considered. Since each consecutive pair is widely separated in energy, it can be safely assumed that the exchange process can be considered separately in each pair. Then a Boltzmann distribution over the thermally accessible energy levels has been used in order to obtain the exchange coupling at different temperatures.

Results and Discussion.

As explained in the Introduction, we will first analyze the adducts formed when the Lewis acid AlH_3 interacts with the niobocene Cp_2NbH_3 complex (**1**). Analysis of the corresponding potential energy surface has revealed the existence of two minimum energy structures (**2** and **3**) whose geometries are depicted in Figure 1. The more important geometrical parameters of these structures are given in Table 1. To analyze the effect of the Lewis acid on the niobocene complex, the minimum energy structure of **1**, which has been previously reported by us,[7c] is also given in Figure 1 and Table 1.

As seen in Figure 1, the two minima **2** and **3** correspond to the complex obtained through interaction of the aluminum with one of the hydrides of the complex. In **2** the Lewis acid is attached to the inner hydride (H_1), whereas in **3** the interaction is with one of the outer hydrides (H_3 in Figure 1; an equivalent structure **3′** would be obtained through interaction with H_2). As for the stability of the two minima, **2** corresponds to the more favorable interaction, **3** being higher in energy by 1.71 kcal/mol. The fact that the interaction with the central hydride is preferred agrees with the reported NMR spectra of Cp_2NbH_3 with $AlEt_3$ that indicated coordination of the Lewis acid to the central hydride of niobocene.[12]

Table 1. Geometrical Parameters of Structures **1**−**3**, **TS1**, and **TS2**, with Distances in Å and Angles in deg

param	**1**	**2**	**3**	**TS1**	**TS2**
$Nb-H_1$	1.750	1.791	1.746	1.789	2.084
$Nb-H_2$	1.734	1.730	1.722	1.730	2.084
$Nb-H_3$	1.734	1.735	1.804	1.730	1.780
$Nb-C^a$	2.466	2.457	2.434	2.456	2.463
$H_1\cdots H_2$	1.771	1.734	1.646	1.854	0.763
$H_1\cdots H_3$	1.771	1.968	1.955	1.854	2.721
$H_2\cdots H_3$	3.036	3.098	3.092	3.097	2.721
Nb−Al		3.338	3.469	3.627	3.531
$Al-H_1$		1.896	2.830	1.837	3.591
$Al-H_2$		3.619	4.407	3.249	3.591
$Al-H_3$		2.353	1.867	3.249	1.867
$Al-H_4$		1.605	1.607	1.604	1.607
$Al-H_5$		1.605	1.607	1.604	1.607
$Al-H_6$		1.606	1.608	1.600	1.595
$\angle X_{Cp}NbX'_{Cp}{}^b$	146.2	143.7	147.0	144.0	144.4
$\angle H_2NbH_1$	61.1	59.0	56.7	63.5	21.1
$\angle H_3NbH_1$	61.1	67.8	67.3	63.5	89.2

[a] Averaged. [b] X_{Cp} and X'_{Cp} represent the center point of each Cp.

The main geometrical parameters that disclose the kind of interaction of the Lewis acid with the complex involve the distances of the hydrides with the niobium and aluminum atoms. These distances, as seen in Table 1, indicate that in **2** the $Al-H_1$ interaction provokes a weakening of the $Nb-H_1$ bond (the $Nb-H_1$ distance increases from 1.750 to 1.791 Å). It is also noted that the aluminum is not centered with respect to the two outer hydrides. In fact, the $Al-H_3$ distance is relatively short (2.353 Å) though this does not appreciably affect the $Nb-H_3$ bond as the distance between both atoms remains almost invariant with respect to structure **1** where the Lewis acid is not present. The interaction between **1** and the Lewis acid can be estimated by the stabilization of **2** with respect to the separated fragments **1** + AlH_3. We obtain a value of 16.7 kcal/mol at our level of calculation. Since the basis set superposition error and the zero point energy have not been taken into account, this value represents a rough approach, but it already indicates a significant interaction between the two fragments, quite similar to the value previously reported for the interaction of **1** with BH_3.[9] Anyway, this interaction is weaker than the one found between Me_3N and $AlCl_3$ which has been reported to be 49.3 kcal/mol at the MP2 level[21a] (the experimental value is 47.5 kcal/mol).[21b]

A similar analysis can be done for the higher energy minimum **3**. Now the aluminum atom mainly interacts with the outer hydride H_3. This produces a lengthening of the $Nb-H_3$ distance from 1.734 Å in **1** to 1.780 Å. The other two Nb−H distances suffer a very minor diminution in accordance with the large Al−H distances that indicate a very small interaction. The geometry of **3** clearly precludes the existence of a direct interaction between the two metal centers as the distance Nb−Al is very large (3.469 Å). Another relevant geometrical parameter of **3** is the H_1-H_2 distance that clearly diminishes when the Lewis acid is present (from 1.771 in **1** to 1.646 Å in **3**). This diminution may be related to an incipient evolution toward the formation of a dihydrogen ligand which is expected to be favored due to the reduction of electronic density on the

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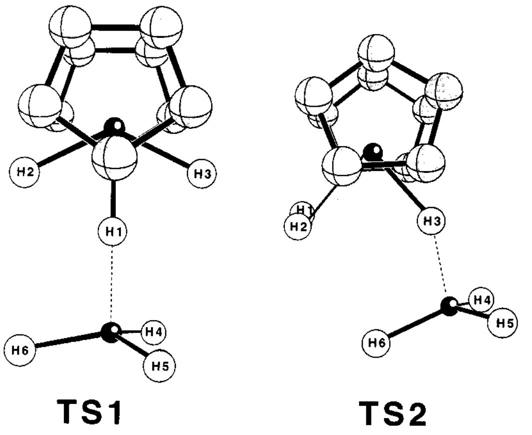

Figure 2. Geometries of the transition states **TS1** and **TS2**.

niobium by the Lewis acid. This result is also in accordance with the behavior of the Cp_2NbH_3 complex interacting with the stronger Lewis acid BH_3, where a clear dihydrogen complex is obtained when the BH_3 interacts with the outer hydride.[9] The diminution of the H−H distance upon interaction of a Lewis acid has also been recently seen in the X-ray structure of $\{[Nb(C_5H_3(SiMe_3)_2)H_3]_2Au\}^+$.[10c]

In the same way that structure **3** has an equivalent structure **3′**, structure **2** has an equivalent structure **2′** where the aluminum is closer to the outer hydride H_2 than to H_3. In all these minima (**2**, **2′**, **3**, **3′**) the three hydrides are not equivalent so that they would present an ABC pattern in the corresponding NMR spectra. The question that arises next is whether these structures can interconvert. Answering this requires an estimate of the energy barriers for the processes connecting the different structures. The direct location of the corresponding transition states is especially difficult because of the extreme flatness of the potential hypersurface and the impossibility of analytically computing the second derivatives with the program we were using. In any case, we were able to obtain an estimate of the magnitude of the energy barriers. In the first place, we considered the transformation **2** → **2′**. A stationary point was located by carrying out a geometry optimization within the restriction of a linear arrangement of the Nb, H_1, and Al atoms. This structure, which we name **TS1**, can be considered to be the transition state connecting the two equivalent minima **2** and **2′**. Its geometry can be seen in Figure 2. The main geometrical parameters are given in Table 1. This transition state implies only a very minor energy barrier of 1.18 kcal/mol above the absolute minimum **2**. This small energy barrier is consistent with the fact that the only difference between **2** and **TS1** is the disappearance in the latter of the very weak interaction between the AlH_3 fragment and the outer hydride H_3.

As for the interconversion between **2** and **3**, a transition state could not be located. We analyzed a reaction coordinate consisting of the motion of the AlH_3 fragment from the initial position of interaction with the inner hydride to one where the main interaction was with one of the outer hydrides. Calculations showed a continuous rise in energy from **2** to **3**. This can only mean that the transition state (that must exist because both **2** and **3** were located as local minima through the usual standard algorithm for energy minimization as implemented in the Gaussian 94 program) has to be very close to the less stable minimum **3**. Therefore it is safe to assume that the energy barrier from **2** is close to the value of 1.71 kcal/mol which corresponds to the difference in energy between both minima.

If our calculated energies are correct, the $Cp_2NbH_3 \cdot AlH_3$ complex would show a high degree of fluxionality so that at not very low temperatures the NMR spectrum of this complex would be an average over the temperature of the different spectra of the four minima **2**, **2′**, **3**, and **3′**. If this is the case, hydrides H_1 and H_3 become equivalent and the experimentally observed AB_2 pattern of the $Cp_2NbH_3 \cdot AlEt_3$ complex at 232 K is justified. This AB_2 pattern could also arise if the complex were rigid and the AlH_3 were binding to the central H ligand. However, our calculations indicate that this structure does not correspond to a minimum but to a transition state (**TS1**). Our calculations are also in agreement with the NMR analysis of the products of the reaction of $Nb(C_5H_3RR')_2H_3$ complexes with salts of the Lewis acidic cations Cu^+, Ag^+, or Au^+, where the hydrides showed an ABC pattern at low temperatures but an AB_2 one at room temperature.[10]

Next we shall study the quantum exchange coupling of the complex. It seems quite clear that the absolute minimum **2** has a negligible quantum exchange coupling, even at room temperature, as the interchange of the central hydride H_1 with one of the outer hydrides would imply a very high energy barrier because the interaction of the Lewis acid with H_1 would disappear during the exchange process. To keep the whole process low in energy the AlH_3 fragment would have to move along the interchange path. This would lead to a dramatic lengthening of the tunneling path so that, again, a near zero quantum exchange coupling is expected.

Things are different for the minimum **3** as here hydrogens H_1 and H_2 can interchange without the intrusion of the AlH_3 which is only interacting with H_3. We therefore considered the rotational process that interconverts H_1 and H_2 in **3**. We found a transition state for this process by a complete optimization of the geometry (as for **2** and **3**, the only restrictions apply to the Cp fragment which is restricted to a local C_{5v} symmetry) but constraining the H−H bond to remain 90° twisted with respect to the position of the minimum **3.** This structure, labeled as **TS2**, is shown in Figure 2. The main geometrical parameters are given in Table 1. Analysis of the geometry of this transition state shows that the H_1-H_2 distance has dramatically decreased to 0.763 Å and the $Nb-H_1$ and $Nb-H_2$ distances have clearly enlarged so that a dihydrogen complex has been formed. The structure of **TS2** is very similar to the transition state structure previously found for the dihydrogen rotational process in d^2-$[Nb(Cp)_2(L)(\eta^2\text{-}H_2)]^+$ complexes.[22] The large distance between dihydrogen and the metal center and the H−H bond length, similar to that of free dihydrogen, indicates a complete loss of π-back-donation in the transition state, what is the origin of the rotational energy barrier. As previously noted in this kind of complex, when the dihydrogen is rotated 90° the σ^* orbital of dihydrogen does not find any occupied d orbital in the metal to interact.[22]

The energy barrier of the interchange process through **TS2** is 15.85 kcal/mol above the minimum **3**, a relatively high value but of the same order of the theoretical energy barriers previously found in other complexes that are known to exhibit a measurable quantum exchange.[7] The very remarkable role of the Lewis acid in the hydrogen exchange process can now be clearly seen by a direct comparison of the energy barrier for the H−H exchange in our case (17.6 kcal/mol when considered from the absolute minimum **2**) and the value in **1** which has been previously reported to be 25.4 kcal/mol at the same level of calculation.[7c]

To obtain the tunneling splitting (i.e. the quantum exchange)

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[22] Antiñolo, A.; Carrillo-Hermosilla, F.; Fajardo, M.; Garcia-Yuste, S.; Otero, A.; Camanyes, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 6107.

Table 2. Vibrational Levels and Their Exchange Couplings for Structure **3**

energy (kcal/mol)	J_{exc} (Hz)	energy (kcal/mol)	J_{exc} (Hz)
0.681×10^0	0.254×10^0	6.391×10^0	0.749×10^5
2.068×10^0	0.651×10^1	7.861×10^0	0.102×10^7
3.489×10^0	0.207×10^3	9.336×10^0	0.116×10^8
4.931×10^0	0.449×10^4	1.081×10^1	0.114×10^9

Table 3. Total Exchange Couplings (Hz) at Different Temperatures

T (K)	$<J_{exc}>$(**3**)[a]	$<J_{exc}>_{complex}$[b]	$<J_{exc}>$(**1**)[c]	$<J_{exc}>_{complex}$/ $<J_{exc}>$(**1**)[d]
0	0.254×10^0	0.0	0.580×10^{-1}	0.0
50	0.254×10^0	0.865×10^{-8}	0.580×10^{-1}	0.149×10^{-6}
100	0.296×10^0	0.545×10^{-4}	0.580×10^{-1}	0.940×10^{-3}
150	0.333×10^0	0.107×10^{-2}	0.610×10^{-1}	0.176×10^{-1}
200	0.770×10^0	0.103×10^{-1}	0.800×10^{-1}	0.129×10^0
250	0.389×10^1	0.121×10^0	0.144×10^0	0.841×10^0
300	0.333×10^2	0.180×10^1	0.350×10^0	5.131×10^0
350	0.339×10^3	0.268×10^2	0.980×10^0	2.732×10^1
400	0.297×10^4	0.310×10^3	0.293×10^1	1.059×10^2

[a] Temperature-averaged exchange coupling from **3**. [b] Temperature-averaged couplings for the thermal equilibrium between **3**, **2**, **2′**, and **3′**. [c] Temperature-averaged exchange couplings from **1**. [d] Ratio of final exchange couplings with and without AlH_3.

it is now necessary to devise a tunneling path. We have evaluated it through calculation of different points along the rotation of the two hydrogen atoms as explained in the methodological section. This way a symmetrical double-well energy profile is obtained with a maximum energy point. Given the geometrical restrictions imposed along the rotation, the maximum energy point does not correspond to the true transition state but it is close: it is found 3.03 kcal/mol above the true transition state. This difference comes from a set of small changes in several geometrical parameters that are allowed to vary from **3** to **TS2** but that are kept frozen along the rotation path (for instance, the Nb−Al distance is restricted to remain 3.469 Å along the rotation but becomes 3.531 Å at the true transition state). Anyway, no important geometrical change is introduced by the restrictions. The effect on the tunneling splitting of such a higher energy is somewhat compensated by the shorter tunneling path which comes from the geometrical restrictions imposed along the path. It should be noted that the nuclear motion defining the tunneling path (mainly motion of exchanging hydrides) has nothing to do with the reaction path connecting the minima **2** and **3** (mainly motion of AlH_3).

Table 2 gives the tunneling splittings of the vibrational levels of this system (structure **3**) evaluated as indicated in the methodological section (J_{exc}). The first 8 levels, all below the energy barrier, are shown. The splitting of the lowest energy pair gives the quantum exchange coupling at 0 K. As the temperature increases, the higher pairs become populated. The temperature-averaged exchange coupling $<J_{exc}>$ can then be obtained through a population weighted average according to a Boltzmann distribution over the thermally accessible pairs of vibrational states. The second column of Table 3 gives the results obtained for temperatures up to 400 K. It is noteworthy that the very small values of $<J_{exc}>$ at low temperatures increase quickly as the temperature increases. This is because at higher temperatures the higher vibrational levels, whose splitting is considerably higher, become appreciably populated.

As explained before, the actual NMR spectrum in the hydride region shows an AB_2 pattern which results from the average of the two minima **2** and **3** (and their equivalent **2′** and **3′** forms). Therefore it can be safely assumed that the couplings can also be averaged over these structures taking into account the equilibrium thermal population. This has also been done, and the final Maxwell−Boltzmann averaged exchange couplings, $<J_{exc}>_{complex}$, are given in the third column of Table 3. These values provide our actual predictions for the observed NMR exchange couplings in this molecule as a function of temperature. For comparative reasons the fourth column of Table 3 gives the quantum exchange couplings of the niobocene complex Cp_2NbH_3 alone (structure **1**), obtained theoretically by using a methodology very similar to the one used here that was previously reported.[7c] Results of Table 3 clearly show that the exchange couplings that come from **3** are always higher than the values of **1**. This was to be expected given that in **3** the two hydrides not bonded to the Lewis acid come close one to each other and the exchange process becomes easier both energetically and geometrically. However, as stated above, the quantum exchange coupling in **2** has been assumed to be zero at all temperatures considered in this paper, so that the temperature-averaged $<J_{exc}>_{complex}$ of $Cp_2NbH_3{\cdot}AlH_3$ is zero at 0 K and very small at very low temperatures as the population of the higher energy structure **3** is not enough to appreciably contribute to the average. At these low temperatures the quantum exchanges in **1** are clearly higher. As the temperature is raised, the population of **3** increases so that it appreciably contributes to the total exchange. At sufficient high temperature the population of **3** is enough to lead $Cp_2NbH_3{\cdot}AlH_3$ to an exchange coupling higher than in Cp_2NbH_3 alone. The last column of Table 3, which gives the ratio of $<J_{exc}>_{complex}$ for the niobocene complex with and without AlH_3, clearly shows that between 250 and 300 K the exchange coupling in the Lewis acid adduct becomes higher than in the niobocene complex alone. A further increase in temperature quickly increases the differences between the two quantum exchanges so that the effect of the Lewis acid becomes more prominent.

Our results then correctly predict the increase of the exchange couplings in polyhydride niobocenes upon addition of a Lewis acid, an effect experimentally observed for the analogous $Cp_2NbH_3{\cdot}AlEt_3$ system[11] and, more recently, for niobocene complexes with Lewis acidic coinage cations.[10] For $Cp_2NbH_3{\cdot}AlEt_3$ a higher exchange coupling of ca. 100 Hz was obtained at the temperature of 232 K, a temperature still too low, within our results, to possess a measurable quantum exchange. This numerical discrepancy might be attributed to the oversimplification of the one-dimensional tunneling model which exaggerates the energy difference between the vibrational energy pairs. It has also to be remarked that the temperature-averaged exchange couplings are very sensitive to the energy difference between the two minimum structures **2** and **3** which are assumed to be in thermal equilibrium, so that very small energy differences may lead to very different quantitative values.

To summarize, our calculations clearly point out that Lewis acids of the AlH_3 type may increase the exchange couplings in polyhydride metal complexes through formation of adducts that favor the interchange of hydrogen atoms. In the structure that undergoes the quantum exchange coupling the Lewis acid is only bonded to an outer hydride, the other two hydrogen ligands still being hydrides, although their interatomic distance clearly diminishes showing an initial trend to form a dihydrogen ligand. The appearance of this structure, energetically close enough to the absolute minimum energy structure to be significantly populated at the range of temperatures corresponding to the NMR measures, arises from the reduction of the electronic density on niobium induced by the action of the Lewis acid.

Our results also provide theoretical ground for the model proposed by Antiñolo et al. to explain the exchange couplings observed in the adducts $[\{Nb(C_5H_3RR')_2H_3\}_2M]^+$, where M = Cu, Ag, and Au.[10c] As mentioned in the Introduction, their model involves two isomeric structures that are close in energy, one containing two bridging and one terminal hydrides on niobium and one involving one bridging hydride and one dihydrogen molecule. In this second structure the Lewis acidic metal cation would be bonded to both the hydride and the niobium atom. Our theoretical findings confirm the existence of an equilibrium between two structures close in energy, at least in the $Cp_2NbH_3{\cdot}AlH_3$ system: in one of them, the Lewis acid AlH_3 is attached to the central hydride, whereas in the other structure, which has a somewhat higher energy, the AlH_3 is only bonded to the terminal hydride. Anyway, it is probable that the concrete features of the structures mainly responsible of the quantum exchange coupling depend on the particular transition metal polyhydride complex considered and on each kind of Lewis acid. Since new, very recent, experimental works[23,24] are confirming the sensitivity of hydrogen exchange couplings to electronic effects induced by interaction with Lewis acids, additional theoretical calculations of other adducts with several Lewis acids would be desirable. Further theoretical work on this topic is presently in progress in our laboratory.

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