J. Am. Chem. Soc. **1997,** *119,* 6107−6114

6107

Synthesis and Spectroscopic Properties of Dihydrogen Isocyanide Niobocene [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-H$_2$)(CNR)]$^+$ Complexes. Experimental and Theoretical Study of the Blocked Rotation of a Coordinated Dihydrogen

Antonio Antiñolo,[†] Fernando Carrillo-Hermosilla,[†] Mariano Fajardo,[‡] Santiago Garcia-Yuste,[†] Antonio Otero,*,[†] Santiago Camanyes,[§] Feliu Maseras,[||] Miquel Moreno,[§] Agustí Lledós,*,[§] and José M. Lluch*,[§]

Contribution from the Departamento de Química Inorgánica y Bioquímica, Universidad de Castilla-La Mancha, Campus Universitario de Ciudad Real, 13071 Ciudad Real, Spain, Departamento de Química Inorgánica, Universidad de Alcalá, 28871 Alcalá de Henares, Spain, Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Laboratoire de Structure et Dynamique des Systèmes Moleculaires et Solides, U.M.R. 5636, Université de Montpellier II, 34095 Montpellier Cedex 5, France

Abstract: Synthesis of stable hydride isocyanide derivatives Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)(CNR) has been achieved through the formation of coordinatively unsaturated 16-electron species Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$H by thermolytic loss of H$_2$ followed by the coordination of an isocyanide ligand. Low-temperature protonation with a slight excess of CF$_3$COOH leads to the η^2-dihydrogen complexes [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-H$_2$)(CNR)]$^+$. NMR spectra of these H−H complexes and their monodeuterated H−D isotopomers present a single high-field resonance at room temperature. By lowering the temperature to 178 K, decoalescence of the signal was observed for the H−D complexes but not for the H−H ones. By combining DFT electronic structure calculations with a monodimensional rotational tunneling model, it has been shown that the absence of decoalescence of the H−H signal is due to the existence of a very large exchange coupling. Conversely, for the H−D isotopomer, the difference in zero point energy corresponding to two nonequivalent (H−D and D-H) positions leads to a slight asymmetry which dramatically reduces the exchange coupling, allowing decoalescence to be observed. Therefore, the H−D classical rotation and the quantum exchange processes will not be practically observed for this complex, whereas only the classical process for the H−H species is quenched out on the NMR time scale.

1. Introduction

Since the discovery of the first η^2-dihydrogen complex by Kubas,[1] several transition-metal complexes containing dihydrogen as a ligand have been described for a wide variety of metals.[2] Until the seminal discovery by Kubas, the only way in which hydrogen was known to coordinate to a wide range of metals was in the polyhydride form.[3] Both types of complexes present very interesting spectroscopic properties. Many dihydrogen complexes exhibit the phenomenon of rotational tunneling splitting, which is observed by inelastic neutron scattering in the microwave zone of the electromagnetic spectrum.[4] On the other hand, the proton NMR spectra of several polyhydride complexes exhibit extremely large and temperature-dependent scalar couplings, the isotope dependence of these couplings also

being unusual.[5] Although the two types of phenomena appear to be very different, they actually both come from the same origin: the exchange of a pair of hydrogens through an energy barrier. Apart from the length of the tunneling path, the difference between the two processes is the different magnitude of the energy barrier through which tunneling takes place: less than 3.5 kcal/mol for the dihydrogen rotational process[4,6] and more than 10 kcal/mol for the hydride exchange.[7,8]

Recently the first thermally stable group 5 dihydrogen complexes were described. Chaudret and co-workers[9] reported the tantalocene complex [Ta(η^5-C$_5$H$_5$)$_2$(η^2-H$_2$)(CO)]$^+$ and some of us[10] the niobocene complexes [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984,** *106,* 451.
(2) (a) Kubas, G. J. *Acc. Chem. Res.* **1988,** *21,* 120. (b) Crabtree, R. H. *Acc. Chem. Rev.* **1990,** *23,* 95. (c) Jessop, P. J.; Morris, R. H. *Coord. Chem. Rev.* **1992,** *121,* 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993,** *93,* 913. (e) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 789.
(3) (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985,** *65,* 1. (b) Dedieu, A. *Transition Metal Hydrides*; VCH: Weinheim, Germany, 1991. (c) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994,** *135,* 845.
(4) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993,** *97,* 2378 and references therein.

(5) (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990,** *112,* 909. (b) Antiñolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalón, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988,** 1210. (c) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994,** *116,* 2685. (d) Chaudret, B.; Limbach, H. H.; Moise, C. *C. R. Hebd. Séances Acad. Sci.* **1992,** *315-II,* 533.
(6) (a) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C. Vergamini, P. J.; Unkefer, C. J.; Khalser, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am Chem. Soc.* **1993,** *115,* 569. (b) Eckert, J.; Jensen, C. M.; Jones, G.; Clot, E.; Eisenstein, O. *J. Am Chem. Soc.* **1993,** *115,* 11056. (c) Li, J.; Ziegler, T. *Organometallics* **1996,** *15,* 3844.
(7) (a) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1993,** *115,* 5861. (b) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1995,** *117,* 1069.
(8) (a) Barthelat, J. C.; Chaudret, B.; Daudey, J. P.; DeLoth, P.; Poilblanc, R. *J. Am. Chem. Soc.* **1991,** *113,* 9896. (b) Limbach, H. H.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1369. (c) Clot, E.; Leforestier, C.; Eisenstein, O.; Pélissier, M. *J. Am. Chem. Soc.* **1995,** *117,* 1797.

$H_2)L]^+$, (L = P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$, PMe$_2$Ph) by protonation at low temperature of the corresponding neutral hydride niobium(III) complex. One of the interesting points of these dihydrogen complexes lies in the fact that the activation barriers for the rotation are surprisingly high (ca. 10 kcal/mol), therefore providing an intermediate case between the normal dihydrogen complexes and the polyhydride ones. As a consequence of the high barrier, rotation of the dihydrogen molecule seems to be blocked at the NMR time scale.[9b,10] For these complexes a single resonance is obtained for the NMR spectrum at high temperatures. When the temperature is lowered, decoalescence is not observed for the nonisotopically substituted H$_2$ isomer, but it is observed for the partially deuterated HD species. This has allowed estimation of the activation barriers for these complexes. This surprising result has been explained through the postulation of a large exchange coupling in the H$_2$ case. It is known[9b] that for $J/\Delta\delta$ ratios higher than 10 the expected AB-type spectrum becomes a single line. Although it is expected that H−H and H−D have very similar barriers for the rotation, there is no direct experimental evidence of the H−H rotation being also practically blocked. From a theoretical point of view, the rotational barrier for the H−H rotation has been calculated for the simplified model complexes [Cl$_2$Ta(η^2-H$_2$)CO]$^+$ and [Cl$_2$Ta(η^2-H$_2$)(PH$_3$)]$^+$ to be 9.7 and 11.3 kcal/mol, respectively.[9b]

The purpose of this paper is twofold: first, to obtain a new experimental example of a nonrotating coordinated H−D molecule and, second, to analyze its structure and the hydrogen exchange process to obtain theoretical evidence that for the corresponding H−H molecule this process is also classically blocked at the NMR time scale and to estimate the order of magnitude of the exchange coupling. To this aim we decided to explore the reactivity of the Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)$_3$ toward isocyanides, which has allowed the preparation of stable hydride−isocyanide derivatives, Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)(CNR), as well as their protonation process to give [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$-(η^2-H$_2$)(CNR)]$^+$, a new niobocene containing dihydrogen as a ligand that is likely to have the dihydrogen rotation practically blocked.

Isocyanide complexes of a wide variety of transition metals are known, although insertion reactions of this ligand into transition-metal−carbon, −hydride, −halide, −nitrogen, −sulfur, and −oxygen bonds are found to readily occur in organometallic chemistry.[11] In particular, the insertion process into metal−hydride bonds to give stable iminoacyls (−CHN) is specially noteworthy.[12] In this field, early transition metallocenes containing isocyanides as ligands have been extensively studied[11] and some stable group 5 metallocenes with halide and alkyl as ancillary ligands were reported.[13] However, because of the aforementioned easy insertion of isocyanides into the metal−hydride bond, only one hydride−isocyanide metallocene species has been described,[14] [Mo(η^5-C$_5$H$_5$)$_2$(H)(CNMe)]$^+$I$^-$, which was prepared by the reaction of Mo(η^5-C$_5$H$_5$)$_2$HI with CNMe, which did not undergo insertion even under refluxing

(9) (a) Sabo-Etienne, S.; Chaudret, B.; Abou el Makarim, H.; Barthelat, J-C.; Daudey, J.-P.; Moïse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9335. (b) Sabo-Etienne, S.; Chaudret, B.; Abou el Makarim, H.; Barthelat, J.-C.; Daudey, J.-P.; Ulrich, S.; Limbach, H. H.; Moïse, C. *J. Am. Chem. Soc.* **1995**, *117*, 11602.

(10) Jalón, F.; Otero, A.; Manzano; B.; Villaseñor, E.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 10123.

(11) (a) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209; (b) Treichel, P. M. *Adv. Organomet. Chem.* **1983**, *11*, 21.

(12) Durfee, L. D.; Rothwell, I. A. *Chem. Rev.* **1988**, *88*, 1059.

(13) (a) Serrano, R.; Royo, P. *J. Organomet. Chem.* **1983**, *247*, 33. (b) Klazinga, A. H.; Teuben, J. *J. Organomet. Chem.* **1980**, *192*, 75. (c) Martinez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1988**, *340*, 187.

(14) Calhorda, M. J.; Dias, A. R.; Duarte, M. T.; Martins, A. M.; Matias, P. M.; Romao, C. C. *J. Organomet. Chem.* **1992**, *440*, 119.

Table 1. IR Data (cm^{-1}) for Complexes **2**−**4** in Comparison with the Corresponding Free Ligand

complex	ν(NbH) (cm^{-1})	ν(CN) (cm^{-1})	ν(CN) (cm^{-1}) (free ligand)
2	1717	2077; 1825	2129
3	1715	2254; 1813	2138
4	1676	2000	2113

THF. In addition, Bercaw and co-workers[15] have suggested the formation of an undetected intermediate Nb(η^5-C$_5$H$_5$)$_2$(H)-(CNMe) in the synthesis of an amide−isocyanide derivative. Taking all of this into account, the synthesis of the Nb(η^5-C$_5$H$_5$)$_2$(H)(CNR) complexes is an additional challenge we will consider in this work.

2. Results and Discussion

Preparation of Hydride−Isocyanide Niobocene Complexes. The complexes Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)(CNR) (R = ^{t}Bu, **2**; Cy, **3**; 2,6-Me$_2$C$_6$H$_3$=Xylyl, **4**) are readily prepared in high yields (95%) by thermal treatment in THF of Nb(η^5-C$_5$H$_4$-SiMe$_3$)$_2$(H)$_3$ (**1**) in the presence of the corresponding isocyanide (eq 1). In the preparation of hydride−isocyanide complexes,

R = ^{t}Bu **2**; Cy **3**; 2,6-Me$_2$C$_5$H$_3$=Xylyl **4**
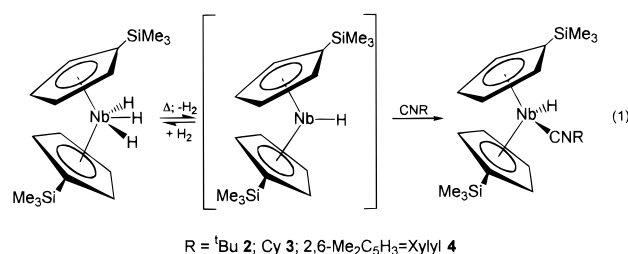
the initial step would be the formation of the coordinatively unsaturated 16-electron species Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$H by thermolytic loss of H$_2$ followed by the coordination of isocyanide ligand (eq 1). The reaction is similar to that previously reported[16] for the preparation of several families of niobocene complexes, Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)(L) (L = π-acid ligand). The complexes were isolated as air-sensitive red oily materials of spectroscopic purity. It is noteworthy that no subsequent insertion process was observed even when the process was carried out with an excess of ligand in refluxing THF for a long time. This surprising behavior has been previously reported[14] for the complex [Mo(η^5-C$_5$H$_5$)$_2$(H)(CNMe)]$^+$, where the insertion was not observed either under similar reaction conditions. This behavior contrasts with the one found for hydride group 4 metallocenes where the insertion process to give iminoacyl derivatives is especially favored.[17]

Spectroscopic Properties of Hydride−Isocyanide Niobocene Complexes. A terminal hydride stretching mode, ν(Nb−H), is detected by infrared spectroscopy for the complexes **2**−**4** at ca. 1700 cm^{-1} (Table 1). However the most significant IR band corresponds to isocyanide stretching mode, ν(CN) at ca. 2000 cm^{-1}. In addition, a band in the spectra of **2** and **3** at ca. 1800 cm^{-1} could be a combination band (Table 1). The data agree with the presence of a linear isocyanide ligand.

^{1}H NMR spectra show a high-field resonance at ca. −6.0 ppm for hydride ligands and four multiplets, corresponding to

(15) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

(16) (a) Antiñolo, A.; Fajardo, M.; Jalón, F.; López-Mardomingo, C.; Otero, A.; Sanz-Bernabé, C. *J. Organomet. Chem.* **1989**, *369*, 187. (b) Antiñolo, A.; Carrillo, F.; Fajardo, M.; Garcia-Yuste, S.; Otero, A. *J. Organomet. Chem.* **1994**, *482*, 93. (c) Antiñolo, A.; Carrillo, F.; Garcia-Yuste, S.; Otero, A. *Organometallics* **1994**, *13*, 2761.
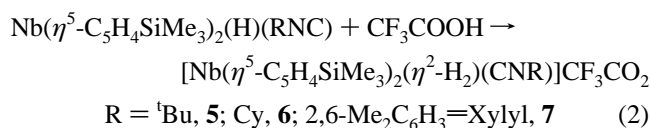
(17) See, for example: Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450.

an AA′BB′ spin system, for the cyclopentadienyl rings in accordance with an asymmetrical environment for the niobium center (see Experimental Section).

In the ^{13}C NMR spectra (see Experimental Section), the most interesting feature is the extremely low-field resonance which has been observed for the carbon of isocyanide bonded to the niobium center, at δ 267.0, 263.0, and 240.0 ppm for **2**−**4**, respectively, far from the δ values (154−165 ppm) obtained in the free isocyanides. This resonance, which should appear as an 1:1:1 triplet from ^{13}C−^{14}N spin coupling, is usually observed[11a] as a broad singlet, like in the present case, or a triplet with a more intense central peak due to the quadrupolar relaxation of the coupling.

Preparation and Spectroscopic and Theoretical Characterization of η^2-Dihydrogen Complexes. Low-temperature protonation of neutral hydride complexes to give cationic dihydrogen species was reported for the first time by Crabtree *et al.* in 1985.[18] Following this method, several cationic dihydrogen complexes have been prepared for group 8 metals and iridium in the last years.[19,20]

Complexes **2**−**4** were easily protonated at low temperature to give the corresponding dihydrogen-containing complexes according to eq 2. These processes were carried out by adding

$$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{H})(\text{RNC}) + \text{CF}_3\text{COOH} \rightarrow$$

$$[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\eta^2\text{-H}_2)(\text{CNR})]\text{CF}_3\text{CO}_2$$

$$\text{R} = {}^t\text{Bu}, \textbf{5}; \text{Cy}, \textbf{6}; 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{=Xylyl}, \textbf{7} \qquad (2)$$

a little excess of CH$_3$COOH to an acetone-d_6 solution of these complexes at 183 K in a NMR tube.

The dihydrogen complexes **5**−**7** constitute, as far as we know, the third example of dihydrogen−isocyanide complexes. Simpson and co-workers[20] prepared the first complex, [Ru(η^5-C$_5$H$_5$)(PPh$_3$)(CN^{t}Bu)(η^2-H$_2$)]$^+$PF$_6^-$, by protonation of the corresponding neutral hydride isocyanide species. Recently, Heinekey *et al.*[21] also obtained several rhenium complexes by using the same procedure.

The ^{1}H NMR spectra show a broad dihydrogen resonance at 213 K at ca. −7.0 ppm and a large line width, 60 Hz, explained by the rapid dipolar relaxation of these nuclei. At low-temperature decoalescence was not observed, and at 178 K, a single high-field resonance was present. When the temperature is raised near 283 K, decomposition of the dihydrogen complexes **5** and **6** takes place to give a complex mixture and H$_2$. Nevertheless, **7** evolves with elimination of H$_2$ and formation of the neutral complex Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(OOCCF$_3$)(CNXylyl) (**8**).[22]

The monodeuterated complexes **5**−**7**-d_1 have been prepared by adding CF$_3$COOD to an acetone-d_6 solution of **2**−**4** at 183 K in a NMR tube. ^{1}H NMR spectra show an 1:1:1 triplet which broadens at low temperature (with cooling). Couplings

Table 2. Observed $J_{\text{H−D}}$ and Activation Parameter for Complexes **5**−**7**-d_1, Observed Minimum T_1 Values for the Dihydrogen Ligand in Complexes **5**−**7**, and Estimated $r_{\text{H−H}}$ Distances, Assuming Slow H$_2$ Spinning

complex	$J_{\text{H−D}}$ (Hz)	T_c (K)	ΔG (kcal/mol)	T_1 (ms)	$r_{\text{H−H}}$ (Å)
5	30	193	8.9	9.4 (203 K)	1.01
6	30	198	9.1	7.9 (193 K)	1.03
7	30	183^a	8.4^a	10.8 (204 K)	1.06

^{a} See text.

$^1J(\text{H−D}) = 30$ Hz (at 243 K) (Table 2) verify the presence of an H−D bond and are an effective proof of the presence of a dihydrogen complex.[2] Moreover, the observation of low longitudinal relaxation times, T_1, is particularly useful to diagnose the presence of dihydrogen ligand in fluxional polyhydrides.[23] The T_1 values of the dihydrogen nuclei, $T_1(\text{H}_2)$, of **5**−**7** and the hydride ligand, $T_1(\text{H})$, of **4** were determined over the temperature range 178−273 K in acetone-d_6 (Table 2). The $T_1(\text{min})$ were found to be 9.4 ms at 193 K for **5**, 7.9 ms at 198 K for **6**, 10.8 ms at 204 K for **7**, and 500 ms at 154 K for **4**. In accordance with the Crabtree's proposal,[23] the H−H distance $r_{\text{H−H}}$ in the coordinated H$_2$ ligand can be determined from the T_1 measurements, but although the H−H dipole interaction is the most important factor in the relaxation mechanism, we have considered that additional contributions must be introduced. Thus, the observed relaxation (R_{obs}) for **5**−**7** was considered as the sum of what is due to H−H dipole interaction ($R_{\text{H−H}}$) and what is due to all other effects (R_o). The value of R_o was approximated as the relaxation observed for **4**, as a reasonable indication of the niobium and solvent contributions. Then, the following equation is obtained:

$$R_{\text{obs}}(\textbf{5−7}) = R_{\text{H−H}} + R_o; \quad R_o = R_{\text{obs}}(\textbf{4})$$

From this equation we have calculated $R_{\text{H−H}}$ values of 104.38, 124.58, and 90.59 (μs)$^{-1}$, for complexes **5**−**7**, respectively. $r_{\text{H−H}}$ values between 1.01 and 1.06 Å were found in accordance with the Morris approximations assuming slow H$_2$ spinning (Table 2).[24]

The calculated J_{HD} of 30 Hz for **5**−**7**-d_1 agree very well with the presence of an unstretched dihydrogen ligand (as a comparison, the value of J_{HD} in the HD gas molecule is 43.2 Hz[25]), and it is comparable with the value of $J_{\text{HD}} = 27.5$ Hz found previously in [Ta(η^5-C$_5$H$_5$)$_2$(η^2-HD)(CO)]$^+$. The data are indicative of a similarity in the back-donation of both metal centers to the σ^* orbital of HD, in accordance with a comparable behavior as π-acid ligands of both carbonyl and isocyanide ligands. In contrast, in the analogous niobocene complexes[10] [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-HD)(L)]$^+$ (L = P(OEt)$_3$, PMe$_2$Ph), the reported $J_{\text{H−D}}$ values (18.2 and 15.0 Hz, respectively) indicate the presence of a stretched H−D ligand. This is due to the fact that a more effective back-donation on the σ^* orbital of HD may occur in the presence of the less π-acceptors phosphite or phosphine ligands.

Experimental characterization of species **5**−**7** as dihydrogen complexes is only spectroscopical. X-ray or neutron diffraction experiments have not been feasible for any dihydrogen metallocene complex of group 5 metal, nor for any dihydrogen complex having an isocyanide ligand. At this point, ab initio calculations have proven to be very useful providing quite

(18) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.

(19) Some selected references: (a) Morris, R. M.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Chinn, M. S.; Heinekey, D. M. *J. Am Chem. Soc.* **1987**, *109*, 5865. (c) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am Chem. Soc.* **1989**, *111*, 2072. (d) Chinn, M. S.; Heinekey, D. M.; Paune, N. E.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (e) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignan, E. *J. Chem. Soc., Chem.Commun.* **1989**, 229. (f) Chinn, M. S.; Heinekey, D. M. *J. Am Chem. Soc.* **1990**, *112*, 5166.

(20) Conroy-Lewis, F. M.; Simpson, S. O. *J. Chem. Soc., Chem. Commun.* **1986**, 506.

(21) Heinekey, D. M.; Voges, M. M.; Barnhart, D. M. *J. Am Chem. Soc.* **1996**, *118*, 10792.

(22) Antiñolo, A.; Carrillo-Hermosilla, F.; Fajardo, M.; Freitas, M.; García-Yuste, S.; Otero, A.; Prashar, S.; Villaseñor, E. *Inorg. Chim. Acta*, in press.

(23) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(24) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

(25) Bloyce, P. E.; Rest, A. J.; Whitwell, L.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1985**, 846.

Table 3. Main Geometrical Parameters^a of Structures **9**–**11**

geometrical parameters	dihydrogen complex **9**	trans complex **10**	rotational transition structure **11**
Nb–H$_1$	1.853	1.739	2.093
Nb–H$_2$	1.880	1.739	2.092
H$_1$···H$_2$	0.871	3.166	0.765
Nb–C$_1$	2.149	2.192	2.134
C$_1$–N	1.178	1.172	1.181
Nb···X$_{Cp}$	2.135	2.135	2.127
∠H$_1$NbH$_2$	27.0	131.1	21.1
∠NbC$_1$N	179.5	180.0	178.4
∠X$_{Cp}$NbX$_{Cp}$	139.3	139.4	138.5
∠H$_1$NbC$_1$	101.0	65.5	86.6
∠C$_1$NC$_2$	178.6	179.8	179.9

^{a} Distances in angstroms and angles in degrees.

accurate data in both classical polyhydride[3c,26] and nonclassical dihydrogen complexes.[27] Up to now, the only theoretical calculations of a group 5 metal dihydrogen complexes are restricted to very simplified models: [Cl$_2$Ta(H$_2$)CO]$^+$ and *cis*-[Cl$_2$Ta(H$_2$)(PH$_3$)]$^+$.[9b] We have performed, for the first time, such a study for the [Nb(η^5-C$_5$H$_5$)$_2$(η^2-H$_2$)(CNCH$_3$)]$^+$ complex **9**, which is a realistic model of the **5**–**7** complexes where the SiMe$_3$ group of the C$_5$H$_4$SiMe$_3$ ligand has been substituted by a hydrogen atom and the R group of the isocyanide ligand is a methyl group.

Density functional theory (DFT) calculations lead to the characterization of **9** as a minimum energy structure. Its main geometrical parameters are shown in the second column of Table 3, whereas Figure 1a depicts the geometry and the numeration used in Table 3 to label the atoms. It can be clearly seen that a dihydrogen ligand is present. The H–H distance of 0.871 Å is smaller than the values obtained from NMR relaxation times assuming a slow rotation (see Table 2). However, it is well-known that the T_1 method give ambiguous values of H–H distances which depend on the interpretation of the motion of the H$_2$ ligand.[28] The best estimate of r_{H-H} in solution for a dihydrogen complex when J_{H-D} is known is provided by an equation obtained by Morris and co-workers.[28] According to that equation, a value of J_{H-D} of 30 Hz for **5**–**7**-d_1 corresponds to a distance of 0.919 Å. In a previous study of compounds very similar to the ones considered here, the direct protonation leads to a dihydride transoid structure instead of the dihydrogen complexes **5**–**7** obtained when a little excess of CF$_3$COOH is added.[10] Therefore, we have also calculated the dihydride transoid **10** structure which is also shown in Table 3 (third column) and Figure 1b. **10** is also a minimum energy structure, and it is slightly more stable (0.30 kcal/mol) than the dihydrogen one at our level of calculation. This very small difference explains the fact that slight modifications of the experimental conditions can lead to different tautomers. It is quite clear that **10** possesses two hydride ligands. Nb–H distances are, as expected, shorter for the dihydride **10** structure; these distances are also very similar to the equivalent Nb–H distances in the trihydride Nb(η^5-C$_5$H$_5$)$_2$(H)$_3$ complex which has been previously reported.[26d,29] The fact that in **10** the hydride ligands are more

strongly bonded to the metal than the dihydrogen ligand in **9** provokes a weakening of the Nb–CNR bond which clearly enlarges when going from the dihydrogen **9** to the dihydride **10** structures.

Rotational Process. In metallocene complexes **5**–**7** with two different substituents, namely isocyanide and dihydrogen ligands, the two hydrogen atoms might be observed as chemically inequivalent if rotation could be frozen out[30] or decoalescence might occur if intramolecular rotation of the η^2-dihydrogen ligand could be slowed to a rate comparable to the chemical shift difference (estimated at ca. 0.2 ppm at 183 K for **5**–**7**) between the two ends of the H$_2$ ligand. Upon lowering of the temperature (Figure 2), the experiments were carried out at 300 MHz in acetone-d_6 as solvent and the triplet signals observed in **5**-d_1 and **6**-d_1 decoalesced below 193 and 198 K, respectively, and were transformed in two unresolved broad singlets (line width of 100 Hz) which are due to the nonrotating H–D molecule in the two different rotamers *endo* H **5**-d_1 and **6**-d_1 and *exo* H **5**-d_1 and **6**-d_1, with the H atom located either next or opposite to the isocyanide ligand, respectively. For complex **7**-d_1 the triplet signal coalesced at 183 K, but the splitting in two signals corresponding to the two rotamers was not observed in the range of temperatures used (293–178 K). The processes were reversible; thus, when the temperature was raised, the rotamers *endo* H **5**-d_1 and **6**-d_1 and *exo* H **5**-d_1 and **6**-d_1 were interconverted by rotation of the H–D molecule.

A similar behavior, which involves a slowly rotating HD molecule coordinated to a metal center, has been recently described for the first time for the [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2–HD)-(PMe$_2$Ph)]CF$_3$CO$_2$[10] and [Ta(η^5-C$_5$H$_5$)$_2$(η^2–HD)(CO)]BF$_4$[9b] complexes. Inelastic neutron scattering studies have been carried out on several dihydrogen complexes, such as W(CO)$_3$(η^2-H$_2$)-(PCy$_3$)$_2$,[31a] IrClH$_2$(η^2-H$_2$)(P^{i}Pr$_3$)$_2$,[6b] MoCO(η^2-H$_2$)(dppe)$_2$,[6a] [FeH-(η^2-H$_2$)(dppe)$_2$]$^+$,[31b] and Tp^{Me2}Rh(η^2-H$_2$)H$_2$.[31c] Rotational energy barriers below 3.5 kcal/mol were found in all cases.[4,6,31] Free energy of activation of our processes was found to be ca. 8.4–9.1 kcal/mol (Table 2) from a line-shape analysis, although we have not clearly observed the exchange limit of the resonances of both rotamers in the NMR spectra.[32] These values are close to the 11.0 and 9.6 kcal/mol free energies of activation obtained respectively for the aforementioned niobocene[10] and tantalocene[9b] complexes. Although decoalescence for **7**-d_1 was not observed, taking into account a similar line separation as for **5**-d_1 and **6**-d_1, a free energy of activation of 8.4 kcal/mol for the process can be estimated. Moreover, the single high-field resonance observed for **5**–**7** at low temperature could be attributed to either a kinetic isotope effect or a very large exchange coupling. For complex [Ta(η^5-C$_5$H$_5$)$_2$(η^2-H$_2$)(CO)]-BF$_4$, no kinetic isotope effect was observed for the classical rotation of the dihydrogen molecule and the presence of a large exchange coupling constant in the signal was proposed.[9b]

To theoretically evaluate the energy barrier for the rotational process, we have located the transition state for the rotation. It has been calculated by a complete optimization of the geometry (as for **9** and **10**, the only restriction applies to the internal C$_5$H$_5$ coordinates which are restricted to a local C_{5v} symmetry; see Details of the DFT Calculations). However, now, the H–H

(26) (a) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 2569. (b) Esteruelas, M. A.; Jean, Y.; Lledós, A.; Oro, L. A.; Ruiz, N.; Volatron, F. *Inorg. Chem.* **1994**, *33*, 3609. (c) Buil, M. L.; Espinet, P.; Esteruelas, M. A.; Lahoz, F. J.; Lledós, A.; Martínez-Ilarduya, J. M.; Maseras, F.; Modrego, J.; Oñate, E.; Oro, L. A.; Sola, E.; Valero, C. *Inorg. Chem.* **1996**, *35*, 1250. (d) Camanyes, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1996**, *118*, 4617.

(27) (a) Dapprich, S.; Frenking, G *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 354. (b) Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. M. *Organometallics* **1996**, *15*, 2947.

(28) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.
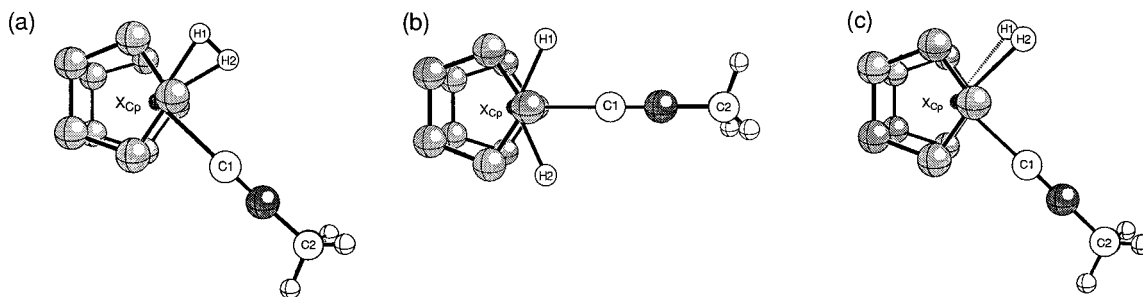
(29) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, Å.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(30) Only for the rotamer with the η^2-dihydrogen ligand perpendicular to the molecular symmetry plane, the two hydrogen atoms would be equivalents even in the absence of rotation.

(31) (a) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324. (b) Eckert, J.; Blank, H.; Bautista, M. T.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 747. (c) Eckert, J.; Albinati, A.; Bucher, U. E.; Venanzi, L. M. *Inorg. Chem.* **1996**, *35*, 1292.

(32) The maximum separation found was used in the calculation.

Figure 1. Structures corresponding to (a) **9**, (b) **10**, and (c) **11**.
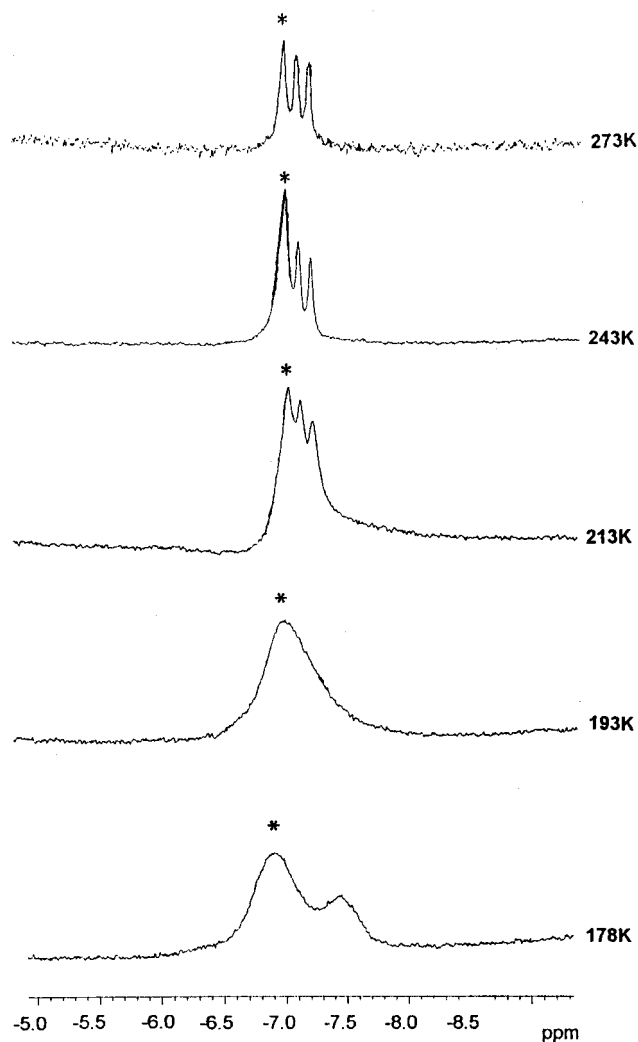
Figure 2. Variable-temperature 300 MHz ^{1}H NMR spectra in the high-field region of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-HD)(CN^{t}Bu)](CF$_3$COO)(**5**-d_1) in acetone-d_6. The asterisk denotes the presence of residual [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-H$_2$)(CN^{t}Bu)](CF$_3$COO).

bond is twisted 90° with respect to the position in the minimum **9**. In this way structure **11** is found. Figure 1c and the last column of Table 3 give, respectively, the geometry and the most relevant parameters of this transition state. It is worthwhile to note a diminution of the H$_1$−H$_2$ bond as compared to the minimum dihydrogen **9** structure which is accompanied by a clear increase of Nb−H distances. The values of 0.765 Å for the H−H distance and ca. 2.09 Å for Nb−H distances are very close to the values previously reported by some of us[26d] for the transition state corresponding to the exchange of two hydrides in the Nb(η^5-C$_5$H$_5$)$_2$(H)$_3$ system. This similarity validates the mechanism proposed for the hydrogen exchange in trihydrides which also involved a twisted dihydrogen structure as a

transition state. The energy barrier of the rotational process is 10.85 kcal/mol at our level of calculation. This value compares well with the free energy barriers obtained from the analysis of NMR spectra at different temperatures for **5**−**7** complexes (see Table 2). These high barriers to rotation of coordinated dihydrogen contrast with other complexes previously studied where the rotational barriers obtained were always below 3.5 kcal/mol.[4,6,31]

The high rotational barrier can be explained through molecular orbital analysis. The occupied d orbital in a d^2 [Nb(η^5-C$_5$H$_5$)$_2$(L)] fragment lies in a plane that contains the Nb−L bond and is perpendicular to the straight line joining the two Cp centers.[33] This orbital can back-donate to the σ^* of the H$_2$ fragment when the dihydrogen is placed in that plane. This is the case of minimum **9**. However, when the H$_2$ is rotated 90°, the σ^* orbital does not find any occupied d orbital in the metal to interact so that the back-donation is completely lost in transition state **11**, which therefore has a remarkably high energy. The energy of the rotational barrier can be attributed then to the complete loss of back-donation in the transition state. In this way, the contribution of backdonation to the binding energy of the H$_2$ to the [Nb(η^5-C$_5$H$_5$)$_2$(CNCH$_3$)]$^+$ fragment is 10.85 kcal/mol. We have also calculated this binding energy: its value is 20.7 kcal/mol, indicating a strong bonding of H$_2$ to the fragment, comparable to the values experimentally determined[34] and theoretically predicted[27a] by high-level calculations in complexes M(CO)$_5$(η^2-H$_2$), (M = Cr, Mo, W). The difference (9.8 kcal/mol) between the binding energy and the rotational barrier can be taken as an approximate value of the $\sigma_{H_2} \rightarrow$ Nb donation contribution to the metal H−H bond energy.

Rotational Tunneling. A very interesting feature of compounds **5**−**7** is the non-decoalescence of the NMR signal of the dihydrogen upon lowering the temperature. In a similar case, [Ta(η^5-C$_5$H$_5$)$_2$(η^2-H$_2$)(CO)]$^+$, the presence of a very large exchange coupling ($J/\Delta\delta$ > 10) has been tentatively proposed.[9b] In this subsection, we will use the DFT results to analyze the rotational tunneling of the dihydrogen ligand which will allow us to obtain the order of magnitude of the exchange coupling in complex **9**.
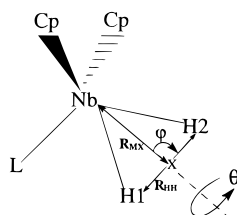
The first step to achieve this goal is to obtain a reasonable monodimensional tunneling path through the whole potential energy hypersurface. To do so, we have considered four internal coordinates as the only ones relevant to the rotation: the H$_1$−H$_2$ distance R_{HH}, the distance between the Nb and the center of the H$_1$−H$_2$ bond R_{MX}, the angle between the H$_1$−H$_2$ bond and the Nb−X vector φ, and the rotational angle θ of the H$_1$−H$_2$ bond (see Scheme 1).

The energy profile has been obtained by considering different values of the angle θ and optimizing the other relevant geometrical parameters. The rest of the parameters are kept

(33) Lauer, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.
(34) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

6112   *J. Am. Chem. Soc., Vol. 119, No. 26, 1997*

Antiñolo et al.

Scheme 1

Table 4. Calculated Exchange Couplings at Various Temperatures for the Different Isotopomers

T (K)	$J_{\text{H–H}}$ (Hz)	$J_{\text{D–D}}$ (Hz)	$J_{\text{T–T}}$ (Hz)
0	9.9×10^5	2.7×10^2	2.3×10^0
50	9.9×10^5	2.7×10^2	2.3×10^0
100	9.9×10^5	2.8×10^2	2.3×10^0
150	1.0×10^6	4.3×10^2	3.9×10^0
200	1.2×10^6	2.1×10^3	1.4×10^2

frozen at the minimum energy values. The path length is 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.[35] In this manner, we obtain a symmetric double-well profile with a maximum energy at $\theta = 90°$. The energy barrier, 11.02 kcal/mol, is only slightly above the 10.85 kcal/mol of transition state **11** found in the previous subsection. This validates the election of the geometrical parameters used to analyze the rotational process.

It has to be remarked that the hydrogen exchange in a η^2-dihydrogen complex involves a shorter tunneling path than in a polyhydride complex. In effect, the exchange of two hydrides takes place through the formation of a hydrogen molecule bonded to the transition metal, which is already able to rotate. The evolution from the dihydride structure to the hydrogen molecule originates a long tunneling path. On the contrary, the hydrogen molecule already exists in a η^2-dihydrogen complex, in such a way that the tunneling path length in this case is essentially determined by the rotation motion.

Once the energy profile was obtained by DFT calculations, a symmetric double well was 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 a basis set methodology by taking a set of localized Gaussian functions which have the form[36]

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

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 have used 99 Gaussian functions throughout 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 energy of each pair of near-degenerate levels. The difference in energy between the two levels of the lowest lying of this pairs provides the tunneling splitting at 0 K which is a direct measure of the quantum exchange coupling. 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 and a Boltzmann distribution over the thermally accessible energy levels has been performed in order to obtain the exchange coupling at different temperatures. Results are summarized in Table 4.

The second column in Table 4 shows the exchange coupling for the original, nonisotopically substituted complex **9**. The value of the exchange at the usual experimental temperatures (ca. 200 K) is on the order of 10^6 Hz. This high value would clearly indicate that decoalescence cannot occur for the H–H complex. Even at 0 K the exchange would still be too fast to be observed by NMR experiments as seen in Table 4. Therefore, the classical H–H rotation is dramatically slowed down for compound **9** but a significant quantum exchange (i.e., tunneling) still occurs.

A very different matter happens for the monodeuterated H–D isotopomer. In this case, given the different isotopic substitution of both hydrogens, the double-well energy profile for the rotational process is not symmetric. We have evaluated the asymmetry by assuming that it comes only from the different contribution to the zero point energy of the H–H/H–D stretching frequency. To achieve that, given the high frequency of the hydrogen stretching, we have considered that the rest of the motions in the molecule do not noticeably affect H–H frequency. Therefore, a numerical evaluation of the second derivatives of the energy through small displacements of the Cartesian coordinates restricted to the two hydrogen atoms has been carried out. The 6×6 matrix obtained is then diagonalized and the highest eigenvalue assigned to H–H stretching. In this manner we have evaluated H–H stretching in **9** to be 2592 cm^{-1}. This value is clearly smaller than the one for the free dihydrogen (4470 cm^{-1} at our level of calculation), indicating a considerable degree of cleavage for the H–H bond in the complex. This frequency depends on the mass of the atoms. Upon deuteration of one of the hydrogens, the system is no longer symmetric and two different frequencies can be found for the H–D isotopomer. This difference in frequency is very small and implies a difference of zero point energy of only 0.037 kcal/mol. However, it is known that only a very small difference in energy between the two wells breaks the symmetry of the system and the tunneling dramatically decreases.[37] A new calculation of the energy levels of the double well by introducing this very small asymmetry shows that tunneling is totally quenched. Then, the presence of nonidentical particles, H and D, prevents permutational symmetry on the wave function, in such a way that, for the H–D isotopomer, the quantum exchange is not possible and decoalescence should be obtained as it is observed experimentally.

A different behavior is predicted for the D–D and T–T isotopomers respectively shown in the third and fourth column of Table 4. In these cases, the symmetry of the energy profile is preserved so that quantum exchange is not quenched. The main difference from the initial H–H complex comes now from the different mass of the rotating atoms which greatly increases the tunneling path which is measured in mass-weighted Cartesian coordinates. Therefore, the quantum exchange is smaller for the D–D isotopomer. Anyway, the values, even at very low temperatures, are still very large compared with the NMR displacements of the deuterium so that, in this case, decoales-

(35) (a) Miller, W. H.; Ruf, B. A.; Chang, Y. *J. Chem. Phys.* **1988**, *89*, 6298. (b) Bosch, E.; Moreno, M.; Lluch, J. M. *J. Am Chem. Soc.* **1992**, *114*, 2072.

(36) (a) Hamilton, I. P.; Light, J. *J. Chem. Phys.* **1986**, *84*, 306. (b) Makri, N.; Miller, W. H. *J. Chem. Phys.* **1987**, *86*, 1451.

(37) Gelabert, R.; Moreno, M.; Lluch, J. M. *J. Comput. Chem.* **1994**, *15*, 125.

cence should not be observed either. This fact has been experimentally observed for the [Cp$_2$Ta(D$_2$)(CO)]$^+$ complex.[9b] Finally, for the T−T complex, the additional diminution of the quantum exchange down to values lower than 4 Hz at 150 K indicates that this hypothetical species should show decoalescence. In other words, at very low temperature, the classical rotation as well as the quantum exchange of the T−T species seem to be blocked at the NMR time scale.

3. Concluding Remarks

In this paper, we have prepared stable hydride isocyanide derivatives Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)(CNR) through formation of coordinatively unsaturated 16-electron species Nb(η^5-C$_5$H$_4$-SiMe$_3$)$_2$H by thermolytic loss of H$_2$ followed by the coordination of isocyanide ligand. Contrary to the behavior observed in other hydride−isocyanide metallocenes, no evidence of isocyanide insertion on the niobium−hydride bond is found. Low-temperature protonation with a little excess of HCF$_3$CO$_2$ leads to the η^2-dihydrogen complexes [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(η^2-H$_2$)-(CNR)]$^+$.

These H−H complexes and their monodeuterated H−D isotopomers show very interesting spectroscopic properties. Their NMR spectra present a single high-field resonance at room temperature. By lowering the temperature to 178 K, decoalescence of the signal was observed for the H−D complexes but not for the H−H ones. The temperature of decoalescence has allowed the estimation of free energy of activation of the dihydrogen internal rotation which ranges between 8.4 and 9.1 kcal/mol. A similar behavior had been previously observed for related complexes. Non-decoalescence of the H−H signal was there tentatively attributed to a large exchange coupling.

In this paper, for the first time, we have theoretically demonstrated the existence of exchange coupling in the [Nb(η^5-C$_5$H$_5$)$_2$-(η^2-H$_2$)(CNCH$_3$)]$^+$ complex that is a realistic model of the experimental cases. This has been achieved by first determining the structure of the minima and the transition state for the dihydrogen rotation. The energy barrier obtained from these DFT calculations compares very well with the experimental estimations. The magnitude of the rotational tunneling of the dihydrogen ligand has been evaluated by obtaining the vibrational quantum states of a monodimensional double-well energy profile for the H−H rotation.

We have obtained exchange couplings of ca. 10^6 Hz for the H−H case even at 0 K, so that decoalescence should not be observed. Conversely, for the H−D isotopomer, the difference in zero point energy corresponding to two nonequivalent (H−D and D−H) positions leads to a slight asymmetry which dramatically reduces the coupling, allowing decoalescence to be observed. Therefore, for this complex, the H−D classical rotation and the quantum exchange processes will not be practically observed, whereas for the H−H isomer, only the classical process is quenched out on the NMR time scale. Additionally, our theoretical results also predict that the D−D isotopomer would not show decoalescence, whereas for the T−T isotopomer decoalescence could be seen.

The complex studied here is then an intermediate case between the hydrogen rotation of dihydrogen complexes and the exchange of a pair of hydrides in polyhydride complexes. The former implies the exchange of hydrogens through a low barrier and a relatively short tunneling path, leading to a splitting of the energy levels for the double-well potential which can be found by inelastic neutron scattering in the microwave zone of the electromagnetic spectrum (frequencies on the order of ca. 10^{10} Hz). On the other hand, for polyhydrides, the exchange implies a high energy barrier and a very long tunneling path;

both factors diminish the splitting, so these processes can be observed in the radiofrequency zone of the electromagnetic spectrum, around 10^3 Hz. For the case studied here, the energy barrier is high but the tunneling path is short so that exchange couplings are on the order of 10^6 Hz. These couplings are detected in the NMR spectra, preventing the decoalescence of the H$_2$ signal. A similar effect would occur if a case of low barrier but long tunneling path for the H−H exchange could be found. Additional theoretical research on this field is now in progress.

4. Experimental Section

Oxygen and water were excluded by the use of vacuum lines supplied with purified N$_2$. Tetrahydrofuran (THF) was dried over and distilled from sodium−benzophenone. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. Isocyanide ligands were used as purchased from Aldrich. NMR spectra were recorded on a Varian Unity 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) spectrometer. Chemical shifts were measured related to partially deuterated solvent peaks and reported relative to TMS. T_1 measurements were made at 300 MHz using the inversion recovery method, and probe temperatures were calibrated by comparison to the observed chemical shifts differences in the spectrum of pure methanol with use of data reported by Van Geet.[38] IR spectra were recorded on a Perkin Elmer 883 spectrometer in Nujol mulls over CsI windows. Complex Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)$_3$ was prepared as described in the literature.[5b]

Preparation of [Nb(C$_5$H$_4$SiMe$_3$)$_2$(H)(CN^{t}Bu)] (2). Nb(C$_5$H$_4$SiMe$_3$)$_2$-(H)$_3$ (**1**) (0.300 g, 0.800 mmol) was dissolved in 40 mL of THF to form a tan solution. To this solution was added 0.091 mL (0.067 g, 0.800 mmol) of CN^{t}Bu by syringe.

The mixture was stirred at 343 K for 2 h. The resulting red-brown solution was filtered and evaporated to dryness. Complex **2** was isolated as a red oily material after maintaining it under vacuum for a lengthy period (yield: 95%). ^{1}H-NMR (300 MHz, C$_6$D$_6$, δ): −5.94 (s, 1H, Nb-H), 0.22 (s, 18H, SiMe$_3$), 1.20 (s, 9H, CN(C(CH$_3$)$_3$)), 4.30 (m, 2H), 4.50 (m, 2H), 4.90 (m, 2H), 5.20 (m, 2H) (AA'BB', C$_5$H$_4$, exact assignment not possible). ^{13}C-NMR (75 MHz, C$_6$D$_6$, δ): 0.7 (SiMe$_3$), 30.5 (CN(C(CH$_3$)$_3$)), 58.0 (CN(C(CH$_3$)$_3$)), 88.2, 91.2, 91.8, 92.6 (C^2−C^5, C$_5$H$_4$), 94.6 (C^1, C$_5$H$_4$), 267.0 (CN^{t}Bu). IR (Nujol, cm^{-1}): 1717 (Nb-H), 2077, 1825 (C≡N, see the text), 1245 (SiMe$_3$).

Preparation of [Nb(C$_5$H$_4$SiMe$_3$)$_2$(H)(CNCy)] (3) and [Nb-(C$_5$H$_4$SiMe$_3$)$_2$(H)(CN-2,3-Me$_2$C$_5$H$_3$)] (4). Complexes **3** and **4** were isolated as red oily materials in a manner similar to that for **2**, in 95% yield.

3: ^{1}H-NMR (300 MHz, C$_6$D$_6$, δ): −5.94 (s, 1H, Nb-H), 0.22 (s, 18H, SiMe$_3$), 1−1.95 (m, CNC$_6$H$_{11}$), 4.30 (m, 2H), 4.50 (m, 2H), 4.90 (m, 2H), 5.20 (m, 2H) (AA'BB', C$_5$H$_4$, exact assignment not possible). ^{13}C-NMR (75 MHz, C$_6$D$_6$, δ): 0.7 (SiMe$_3$), 24.6, 25.8, 34.0 (Cy), 91.6, 91.7, 92.2, 93.9 (C^2−C^5, C$_5$H$_4$), 87.8 (C^1, C$_5$H$_4$), 263.0 (CNCy). IR (Nujol, cm^{-1}): 1715 (Nb−H), 2254, 1813 (C≡N, see the text), 1246 (SiMe$_3$).

4: ^{1}H-NMR (300 MHz, C$_6$D$_6$, δ): −6.20 (s, 1H, Nb-H), 0.63 (s, 18H, SiMe$_3$), 2.65 (s, 6H, CH$_3$), 4.82 (m, 2H), 4.94 (m, 2H), 5.36 (m, 2H), 5.60 (m, 2H) (AA'BB', C$_5$H$_4$, exact assignment not possible), 7.13−7.14 (m, 3H, C$_6$H$_3$). ^{13}C-NMR (75 MHz, C$_6$D$_6$, δ): 0.4 (SiMe$_3$), 19.6 (CH$_3$), 86.7, 91.6, 91.7 (C$_5$H$_4$), 124.8, 127.8, 128.2, 130.6 (CN(2,6-Me$_2$C$_6$H$_3$)), 240.0 (CN(2,6-Me$_2$C$_6$H$_3$)). IR (Nujol, cm^{-1}): 1676 (Nb−H), 2000 (C≡N, see the text), 1245 (SiMe$_3$).

Protonation of 2−4. CF$_3$COOH, or CF$_3$COOD, was added to an acetone-d^6 solution of **2**, **3**, or **4**, in a 5 mm NMR tube at 183 K, to give the dihydrogen complexes [Nb(C$_5$H$_4$SiMe$_3$)$_2$(H$_2$)(CNR)]$^+$(CF$_3$CO$_2$)$^-$ (**5−7**) and their (HD) isotopomers (**5**-d_1, **6**-d_1, and **7**-d_1).

Details of the DFT Calculations. All calculations have been carried out with the GAUSSIAN 94[39] series of programs. Electronic structure calculations have been performed with the same methodology employed in the previous study of metallocene trihydride complexes [Nb(η^5-C$_5$H$_5$)$_2$(H)$_3$]$^{n+}$ (M = Mo, W, n = 1; M = Nb, Ta, n = 0).[26d] The

---

(38) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

Density functional theory (DFT)[40] was applied. The particular functional used was the Becke's three-parameter hybrid method[41a] using the LYP correlation functional (Becke3LYP).[41b]

An effective core potential operator has been used to replace core electrons of metal atom.[42] This involved 28 electrons. The basis set used for the metal was that associated with the pseudopotential[42] with a standard valence double-ζ LANL2DZ contraction.[39] For the N, C,

and H atoms of the isocyanide ligand, the valence double-ζ 6-31G basis set was used.[43a] A polarization p shell was added to the two hydrogen atoms directly attached to the metal.[43]

All along the exploratory process of the potential energy surface, the (C_5H_5) fragments were restricted to a local C_{5v} symmetry.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stevanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(40) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(41) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(42) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.

(43) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.