First Observation in a Niobium Complex of the Rotation of a Coordinated H−D Molecule Blocked at the NMR Time Scale

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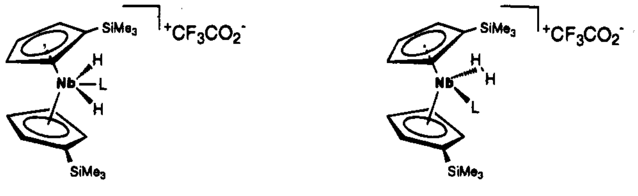
The discovery by Kubas[1] of dihydrogen coordination on a transition metal center has induced intense research activity in chemical, theoretical, and spectroscopic fields.[2] Dihydrogen has been reported to lead to stable complexes with group 5−10 metals. However, only one example of such a niobium complex, [Nb(η^5-C_5H_5)$(CO)_3(H_2)$], has been characterized by IR techniques in Xe(I).[3] Dihydrogen, when coordinated, exhibits several distinct spectroscopic features, for example, low T_1 minimum and high J_{HD} constants, which have helped to characterize the complexes and to estimate the H−H distance and hence get information on the amount of stretching of the H−H bond.[4,5] Evidence has been given that the rotation of coordinated dihydrogen can be blocked at the NMR time scale,[6] but no direct NMR observation of this phenomenon has been obtained, for example, no direct observation of the rotamers of coordinated H−D.

After the synthesis of the first thermally stable group 5 dihydrogen complex, $[Cp_2Ta(H_2)(CO)]BF_4$,[7] it was of interest to attempt the preparation of similar niobium derivatives. The niobium derivatives are of particular interest because niobium polyhydrides represent the first reported examples of complexes exhibiting anomalous NMR behavior[8] attributed to exchange couplings.[9] $[Cp_2Ta(H_2)(L)]BF_4$ (L = $P(OMe)_3$, PMe_2Ph) has also been shown to display such couplings,[10] a phenomenon related by some of us to the presence of a dihydrogen state.[11]

Scheme 1. Proposed Structures for **7a,b** and **9a,b**



Trans 7a,9a **Cis 7b,9b**

We report in this communication the protonation at low temperature of niobium monohydride complexes, the isolation of dihydrogen complexes, their characterization by spectroscopic methods, and the first observation that the rotation of a coordinated H−D molecule can be frozen at the NMR time scale.

The complexes $[Cp'_2NbHL]$ (Cp′ = η^5-$C_5H_4SiMe_3$; L = $P(OMe)_3$ **1**, $P(OEt)_3$ **2**, $P(OPh)_3$ **3**, PMe_2Ph **4**, CO **5**)[12] were synthesized by thermal reaction of $[Cp'_2NbH_3]$[8b] with the corresponding ligand (L) in THF. Protonation of **1−4** with $[PhNH_3]PF_6$ in THF allows the isolation of the corresponding transoid cationic niobocene dihydrides[12] *trans*-$[Cp'_2Nb(H)_2L]$-PF_6 (L = $P(OMe)_3$ **6**, $P(OEt)_3$ **7a**, $P(OPh)_3$ **8**, PMe_2Ph **9a**) whereas a similar protonation of **5** leads to decomposition materials. However, when HCF_3CO_2 is added to an acetone-d_6 solution of **2** and **4** at −90 °C in a NMR tube, the cisoid isomers *cis*-$[Cp'_2Nb(H_2)L]CF_3CO_2$ (L = $P(OEt)_3$ **7b**, PMe_2Ph **9b**) are formed[13] (see Scheme 1) according to the four different resonances observed for the cyclopentadienyl rings. When the temperature is raised, **7b** transforms into its transoid isomer **7a** through an irreversible process. Raising the temperature does not produce the transoid form of **9b** but its quantitative transformation at 20 °C into $[Cp'_2Nb(CF_3CO_2)(PMe_2Ph)]$, **10**.[12] The analogous $[Cp'_2Nb(CF_3CO_2)(CO)]$, **11**, is the only niobium compound observed at all temperatures when **5** is reacted under similar conditions with HCF_3CO_2,[12] probably because the large π-accepting property of the CO ligand prevents the stabilization of H_2 coordination.

The high-field ^1H NMR spectra of **7b** and **9b** show a doublet due to H−P coupling which broadens at very low temperature but does not show decoalescence. This coupling constant is found to be 26.4 Hz for **7b** and to vary between 24 Hz at 203 K and 27 Hz at 283 K for **9b**. The T_1 minima were found to be 24 ms at 188 K for **7b** and 19 ms at 196 K for **9b**. In the case of **7a**, the T_1 minimum is 450 ms at the same temperature,

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(13) ^1H NMR data for compounds **7b** and **9b** (300 MHz, acetone-d_6, 283 K, δ_{ppm}). **7b**: −5.23 (d, 2H, J_{PH} = 27.0, $Nb(H_2)$); 5.04, 5.35, 5.85, 6.24 (pt, 8H, C_5H_4); 0.25 (s, 18H, $SiMe_3$), 4.21 (m, 6H, J_{HP} = 14 Hz, CH_2−$P(OEt)_3$); 1.35 (t, 9H, J_{HH} = 7Hz, CH_3−$P(OEt)_3$). **9b**: −4.65 (d, 2H, J_{PH} = 24Hz, $Nb(H_2)$); 4.54, 5.17, 5.67, 6.18 (pt, 8 H, C_5H_4); 0.25 (s, 18H, $SiMe_3$); 2.06 (d, 6H, J_{HP} = 13.7 Hz, Me−PMe_2Ph); 7.7 (cm, 5H, Ph−PMe_2Ph. $^{31}P\{^1H\}$ NMR data for **7b** and **9b** (121.5 MHz, acetone-d_6, 283 K, δ_{ppm} (H_3PO_4 85%)). **7b**: 178.7 (bs). **9b**: 30.58 (bs).

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which allows us to calculate the H−H distance within the dihydrogen isomer **7b**. The observed relaxation R_{obs} for **7b** is the sum of that due to H−H dipole−dipole interaction (R_{H-H}) and that due to all other effects (Ro) which can be estimated using the observed relaxation for **7a** (R_{obs}(**7a**)); this includes the Nb−H dipole−dipole relaxation, which should even be slightly overestimated in the classical symmetrical dihydride due to an expected shorter Nb−H distance. Hence: R_{obs}(**7b**) = R_{H-H} + Ro; Ro = R_{obs}(**7a**); R_{H-H} = R_{obs}(**7b**) − R_{obs}(**7a**) = 39.45 s^{-1}.

Using Morris approximations[5b] we find d_{H-H} = 0.97 Å assuming rapid rotation of dihydrogen and d_{H-H} = 1.22 Å assuming a slow rotation. For **9b** we do not know the relaxation due to factors other than H−H distance, but using the relaxation found for **7a** as a reasonable indication of the niobium, phosphorus, and solvent contribution, we find d_{H-H} = 1.17 Å. These results are in agreement with an important stretching of the coordinated H−H bond since in our case the slow rotation approximation is most probably valid. However, it is not possible to exclude totally the existence of a dihydride/dihydrogen tautomeric equilibrium.[14]

The observation of a large J_{H-D} coupling constant is the most effective proof for the presence of a direct H−D bond[1] and hence for the existence of a dihydrogen complex. Therefore, the synthesis of the isotopomers *cis*-[$Cp'_2Nb(HD)L$]CF_3CO_2 (L = $P(OEt)_3$ **7b**-*d*, PMe_2Ph **9b**-*d*) was carried out in acetone-d_6 solution by reacting **2** or **4** with DCF_3CO_2. A J_{HD} constant of 18.2 Hz was measured for **7b**-*d*. This is in good agreement with the distance calculated from T_1 data and compares well with a J_{HD} constant of 21 Hz observed for [$Cp^*Ru(H_2)(dppm)$]$^+$ for which a H−H distance of 1.10 Å was determined by neutron diffraction and T_1 data.[6]

The most unusual result of this study is, however, observed with **9b**-*d* (see Figure 1). At 203 K two different rotamers, endo H **9b**-*d* and exo H **9b**-*d*,[15] can be observed by ^{1}H NMR (the experiments were carried out at 300 and 500 MHz; see Figure 1). Both isomers present a similar J_{HD} constant of ca. 15 Hz at 203 K but very different J_{HP} (50.5 Hz for endo H **9b**-*d* and <7 Hz for exo H **9b**-*d*); they were assigned by comparison with the corresponding *cis*-tantalum dihydrides in which the J_{H-P} values found for the hydrides cis and transoid to phosphorus are respectively 89.8 and 10.4 Hz.[16] The observation of large H−P couplings is unusual for a dihydrogen complex, but a precedent exists in the case of a stretched dihydrogen ligand.[5d,17] When the temperature is raised, the rotamers endo H **9b**-*d* and exo H **9b**-*d* interconvert by rotation of the HD molecule reaching coalescence at 233 K. At 273 K, a single resonance is observed for the HD fragment with J_{HD} = 16.0 Hz and J_{HP} = 26.4 Hz. This phenomenon is reversible since lowering the temperature leads to decoalescence and reappearance of the initial spectrum. This has allowed estimation of the free energy of activation at the coalescence temperature ($\Delta G^{\ddagger}_C$ = 46 kJ/mol). This is the first observation of a freezing of H−D rotation on a transition metal complex, and the value found here is very large for dihydrogen rotation. The barrier to rotation of coordinated dihydrogen has been previously measured by inelastic neutron scattering[18] but only for values <ca.15 kJ/mol. and estimated in complexes showing exchange couplings.[11b,18] This experiment shows in addition several unusual features. First, we do not observe the decoalescence for the dihydrogen isotopomer (down to 173 K); this could be due either to a very large kinetic isotope effect or to the presence of very large exchange couplings.[19] Second, we observe a slight increase in the J_{H-D} value after the coalescence.[6] This could result from H−D rotation during which, because less effective back-donation occurs, the $M-H_2$ distance should increase whereas the H−H should decrease.

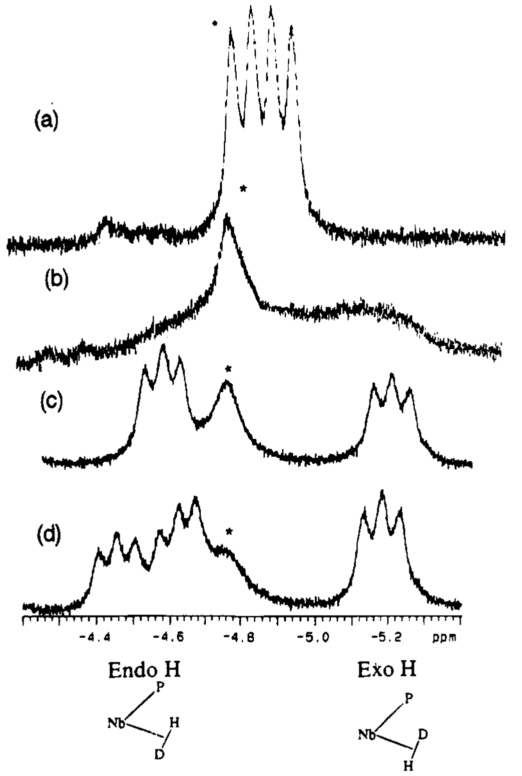

Figure 1. High-field $^1H\{^{31}P\}$ NMR spectrum (300 MHz) of [$Cp'_2Nb(HD)(PMe_2Ph)$]CF_3CO_2 (**9b**-*d*) at variable temperature: (a) 283 K; (b) 233 K (coalescence temperature); (c) 203 K; (d) ^{1}H NMR spectrum at 203 K. The asterisk denotes the presence of residual [$Cp'_2Nb(H_2)(PMe_2Ph)$]CF_3CO_2 (**9b**).

In conclusion, we describe in this paper the first niobocene dihydrogen complexes and, more importantly, the first NMR observed example of a slowly rotating HD molecule coordinated to a transition metal complex enabling the observation of two interconverting rotamers.

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Supporting Information Available: Full characterization of complexes and temperature dependence of T_1 in *cis*-[$Cp'_2Nb(H_2)(PMe_2Ph)$]CF_3CO_2 (**9b**) (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) The presence of large H−P coupling constants suggests an alternative explanation to the presence of a stretched dihydrogen molecule, namely, the existence of an equilibrium between dihydride and dihydrogen tautomers. In this case the small variation of J_{H-P} in **9b** could be indicative of an energy difference between the dihydrogen and the dihydride forms of ca. 2 kJ mol^{-1} whereas for **7b** the population of both tautomers would be equal. Calculated H−H distances from T_1 data for **7b** would be respectively 0.86 Å assuming rapid rotation of dihydrogen and 1.09 Å assuming a slow rotation, which is probably correct in our case. However, in the case of such an equilibrium a J_{H-D} value of ca. 33 Hz could be calculated for the nonclassical tautomer of **7b**, which seems too high compared to the H−H distance derived from T_1 measurements.

(15) Endo H and exo H refer to the hydrogen of the H−D molecule located respectively next or opposite to the phosphine ligand (see Figure 1). The signals are attributed using the H−P coupling constant shown in similar tantalum dihydride phosphine complexes to be large when the hydride and the phosphine are in a mutual cis position and low when they are in a transoid position (ref 16).

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