11602 J. Am. Chem. Soc. **1995,** *117,* 11602−11603

Upon the Chemical Origin of Exchange Couplings in d^2 Systems

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Received May 23, 1995

In the mid-1980s two major events renewed interest in the interaction between dihydrogen and transition metals. The most important was the discovery by Kubas that dihydrogen can coordinate to a transition metal without being dissociated.[1,2] Besides this major discovery, another new phenomenon was reported by two groups, namely, the existence of large, temperature-dependent H−H couplings in some transition metal polyhydrides.[3,4] The quantum mechanical origin of these couplings was independently recognized by Zilm[5] and Weitekamp.[6] However, the existence and magnitude of the couplings were shown to be favored by a reduction of the electronic density on the metal, as was the formation of the dihydrogen state, which indicated a link between these two phenomena.[3,7−9] Indeed, the two similar complexes Cp_2NbH_3 and Cp_2TaH_3 display very different spectroscopic properties. Calculations showed that the difference between their electronic structures was the existence of a low-lying dihydrogen state in the former.[8] Furthermore, the recent low-temperature NMR observation in a niobium complex of the two rotamers of a stretched H−D ligand[10] demonstrated the possibility for the dihydrogen rotation barrier to be higher than expected.

We now report the NMR behavior and the electronic structure of two tantalum derivatives and their isotopomers which are similar but display different ground states. Namely, $[Cp_2Ta(H_2)(CO)]^+$ (**1**) is a dihydrogen complex[11] whereas $\{Cp_2Ta(H)_2[P(OMe)_3]\}^+$ (**2**) displays exchange couplings.[3g] This study leads us to propose that the existence of a nonrotating dihydrogen ligand is the origin of the observation of exchange couplings in these d^2 systems.

$[Cp_2Ta(H_2)(CO)]^+$ (**1**) was previously shown, by both experimental observations and theoretical calculations, to be a dihydrogen complex.[11] $[Cp_2Ta(HD)(CO)]^+$ (**1-*d***) was prepared as previously reported and studied by ^1H NMR (CD_2Cl_2, 250 MHz). As shown in Figure 1, upon lowering of the temperature, the 1:1:1 triplet signal observed for the hydride coupled to the deuteride at δ −5.17 (J_{H-D} = 27.5 Hz) coalesced at 208 K and transformed into two triplets at δ −5.78 and δ −5.14 (J_{H-D} = 27.5 Hz for both) due to the nonrotating H−D molecule in which the hydrogen atom is located either next to CO or opposite to it. The energy of activation of the process was calculated by line-shape analysis to be 9.6 kcal·mol^{-1} (see Figure 1),[12] close to the value of 11.0 kcal·mol^{-1} found for the niobium complex $[Cp_2Nb(HD)(PMe_2Ph)]^+$ (**3**).[10] By contrast, no decoalescence is observed for **1**. This could arise from a large kinetic isotope effect or from the presence of large exchange couplings. Hence, in the latter case, the expected AB type spectrum would become a single line for J/δ ratios close to or higher than 10. The ^2H NMR spectra (CD_2Cl_2, 61.422 MHz) of a mixture of **1-*d*** and $[Cp_2Ta(D_2)(CO)]^+$ (**1-*d*₂**) show at 298 K the presence of a signal attributed to coordinated HD at −5.07 ppm (J_{H-D} = *ca.* 27.5 Hz) which splits at 183 K into signals at −5.10 and −5.75 ppm whereas another signal at −5.33 ppm (298 K) attributed to coordinated D_2 remains as a singlet down to 183 K (at −5.67 ppm). The presence of a single high-field line for **1** and **1-*d*₂** and of a decoalescence for **1-*d*** cannot be attributed to a kinetic HH/HD/DD isotope effect since **1-*d*₂** would be expected to show behavior similar to that of **1-*d*** but at higher temperature. We therefore prefer to propose the presence of large exchange coupling constants in the signals of **1** (J_{H-H} = *ca.* 1600 Hz or higher) and of **1-*d*₂** (J_{D-D} = *ca.* 250 Hz or higher), as resulting from the presence of a rigid H_2 (*viz.*, D_2) ligand on the NMR time scale.

For *cis*-$\{Cp_2Ta(H)(D)[P(OMe)_3]\}^+$ (**2-*d***)[13] two high-field signals are observed in the ^1H NMR at room temperature

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(12) The new compounds $[(C_5H_4SiMe_3)_2Ta(H_2)(CO)]^+$ (**1′**) and **1′-*d*** show similar behavior. The H−H distance was calculated to be 1.02 Å (slow rotation limit; see ref 11b) and the barrier to H−D rotation 9.4 kcal·mol^{-1}, in agreement with the electron-withdrawing properties of the $C_5H_4SiMe_3$ (Cp′) ligand. NMR data for **1′** and **1′-*d*** are given in the supporting information.

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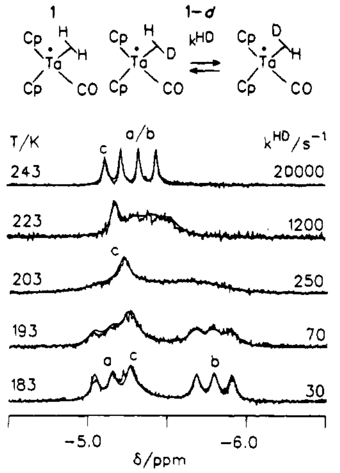

Figure 1. High-field ^1H NMR spectra of $[Cp_2Ta(HD)(CO)]^+$ (**1**-*d*) at various temperatures (250 MHz, CD_2Cl_2). Signal c represents the hydrides of **1**; signals a and b are for the endo and exo isomers of **1**-*d*.

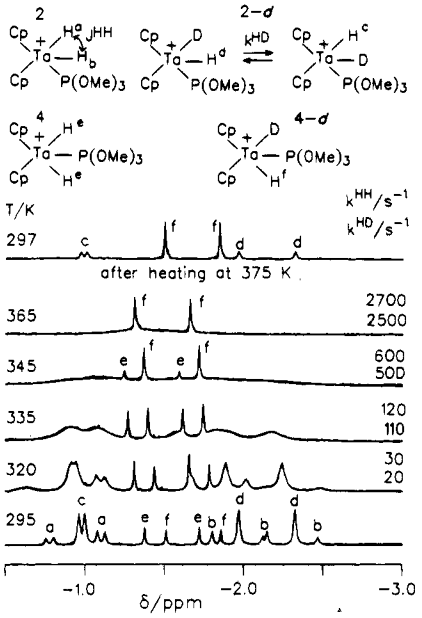

Figure 2. High-field ^1H NMR spectra of the mixture *cis*-$\{Cp_2Ta(H)_2[P(OMe)_3]\}^+$ (**2**), *cis*-$\{Cp_2Ta(H)(D)[P(OMe)_3]\}^+$ (**2**-*d*), *trans*-$\{Cp_2Ta(H)_2[P(OMe)_3]\}^+$ (**4**), and *trans*-$\{Cp_2Ta(H)(D)[P(OMe)_3]\}^+$ (**4**-*d*) at various temperatures (250 MHz, dioxane-d_8).

(dioxane-d_8, 250 MHz; see Figure 2) corresponding to the location of the hydride either next to the phosphite ligand or opposite to it respectively at δ −2.10 (J_{P-H} = 89.1 Hz) and −0.94 (J_{P-H} = 9.5 Hz). The J_{H-D} coupling constant was found to be *ca.* 1.5 Hz, in agreement with a classical dihydride formulation for *cis*-$\{Cp_2Ta(H)_2[P(OMe)_3]\}^+$ (**2**), for which a H−H separation of 1.67 Å[14] was calculated using T_1 min data (87 ms at 180 K, 250 MHz), close to the value calculated *ab initio* for *cis*-$[Cl_2Ta(H)_2(PH_3)]^+$ (1.57 Å, at the Hartree−Fock level). The signals for the hydrides of both isotopomers (**2** and **2**-*d*) coalesce at about 360 K (250 MHz, dioxane-d_8), indicating the absence of a kinetic HH/HD isotope effect on the dihydrogen rotation in **2**. The process is characterized by a barrier of about 16.6 kcal mol^{-1} as obtained by the line-shape analysis shown in Figure 2. The spectra also show a slow transformation of **2** into the *trans* form **4** especially at high temperatures, probably linked to H/D exchange with the solvent and D_2O present in the reaction mixture through deprotonation/protonation processes since, after heating to 375 K and cooling, **2**-*d* is the major isotopomer present in solution.

The electronic structures of **1** and **2** are very similar. The only difference is the larger electron-releasing effect of the phosphite ligand in **2**, which favors the classical tautomer. Calculations at the CI level including ZPE corrections[15] show that, whereas in the case of *cis*-$[Cl_2Ta(H_2)(CO)]^+$ the dihydrogen isomer is slightly more stable than the *trans*-dihydride by 0.5 kcal·mol^{-1} (the *cis*-dihydride isomer is not a minimum on the potential energy surface), in the case of *cis*-$[Cl_2Ta(H)_2(PH_3)]^+$ the dihydride isomer is more stable by 3.6 kcal·mol^{-1}. The barrier to rotation of dihydrogen in $[Cl_2Ta(H)_2(CO)]^+$ and *cis*-$[Cl_2Ta(H)_2(PH_3)]^+$ used as models for **1** and **2** can be calculated to be 9.7 and 11.3 kcal·mol^{-1}, respectively, in excellent agreement with the experimental value in the case of **1**.[16] The similarity of electronic structures between **1** and **2**, the absence of a kinetic isotope effect on the classical exchange process in **2** and **2**-*d* together with the existence of exchange couplings in **2**, and the experiments carried out on **1** and its isotopomers in ^1H and ^2H NMR, namely, the decoalescence of the signal for H−D in ^1H and ^2H NMR together with the apparent absence of decoalescence for the H_2 and the D_2 signals, allow us to exclude the existence of large, anomalous HH/HD/DD kinetic isotope effects but not the presence of large exchange couplings in **1** and **1**-d_2 below the decoalescence temperature of the H−D signal in **1**-*d*. The difference in magnitude between the exchange couplings observed in **1** and **2** could result either from a low population of the calculated low-lying dihydrogen state of **2**, if one assumes that rotational tunneling of coordinated dihydrogen is the origin of the phenomenon, or from the difference between their respective barriers to rotation.

In conclusion, we describe in this communication the second observation by ^1H NMR of a nonrotating coordinated H−D molecule. The experimental value of the barrier to rotation can be for the first time compared to a calculated value obtained by *ab initio* calculations. The two values found, respectively 9.6 and 9.7 kcal·mol^{-1}, agree remarkably well. The most important result of this study is the demonstration that no kinetic isotope effect is observed for the classical rotation of H_2 in those tantalum dihydride/dihydrogen complexes. This strongly suggests that rotational tunneling of a coordinated dihydrogen ligand, the classical rotation of which is blocked on the NMR time scale, is at the origin of the quantum mechanical exchange observed in d^2 transition metal polyhydrides in which only one orbital is available for back-donation. Finally, these labeling experiments can be used as a general method to detect the existence of otherwise unobservable, very large exchange couplings as previously proposed by Heinekey *et al.*[4b]

Acknowledgment. This work was supported by the European Union, Brussels, via the Human Capital & Mobility Network "Localization and Transfer of Hydrogen", the Deutsche Akademische Austauschdienst, Bonn-Bad Godesberg, within the program PROCOPE (H.-H.L., B.C.), the CNRS (B.C., S.S.-E.), and the Fonds der Chemischen Industrie, Frankfurt (S.U., H.-H.L.). The authors thank Madame Perret for technical assistance.

Supporting Information Available: NMR data for **1′** and parameters of the line-shape analysis of Figures 1 and 2 (3 pages). This material is contained in many 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.

JA951671D

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[14] Calculations were carried out using the relaxation found for the transoid isomer (T_1 min = 231 ms at 178 K, 250 MHz), as an indication of the contribution to relaxation of all factors but H−H dipole−dipole, and the equations developed for the nonrotating approximation by Morris (see ref 11b).

[15] Details of the calculation (pseudopotential parameters and Gaussian basis sets) are given in ref 11.

[16] The numbers given are obviously approximate because of the modeling of Cp by Cl; however, recent calculations performed on a similar compound (Cp_2NbH_3) show that the energy difference between the trihydride and the hydrido−dihydrogen isomers is very similar (at the Hartree−Fock and MP2 levels) when Cp is replaced by Cl. H. Abou el Makarim, J.-C. Barthelat, J.-P. Daudey, unpublished results.