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$[Cp_2Ta(\eta^2\text{-}H_2)(CO)]BF_4$: The First Thermally Stable Group 5 Dihydrogen Complex

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The chemistry of dihydrogen complexes has developed very rapidly since the demonstration by Kubas in 1984 of dihydrogen coordination without dissociation.[2-5] Dihydrogen has been shown to give stable adducts with group 6–9 metal complexes whereas unstable dihydrogen adducts of groups 10, 11, and 5 were observed in a matrix.[5] In the latter case the group 5 derivatives $CpV(CO)_3(\eta^2\text{-}H_2)$[6a] and $CpNb(CO)_3(\eta^2\text{-}H_2)$[6b] were characterized whereas the corresponding tantalum complex was shown to be a classical dihydride.

A series of niobium trihydride[7] and cationic tantalum dihydrides[8] have been shown to exhibit quantum mechanical exchange couplings. We have shown that in all cases these complexes possessed a thermally accessible dihydrogen state and have proposed[9] that the existence of exchange couplings could be related to this dihydrogen state. We anticipated that a variation of the ligands could modify the equilibrium population of the dihydride and dihydrogen states by simply changing the phosphorus donor ligand by CO in $[Cp_2TaH_2L]^+$ derivatives. *trans*-$[Cp_2TaH_2(CO)]PF_6$ has previously been obtained by protonation of $Cp_2TaH(CO)$ (**1**) by aqueous HCl at room temperature.[10] However, precedents, in particular in ruthenium chemistry, have shown that low temperature protonation could lead to kinetic cis isomers.[11]

We describe in this communication the protonation of **1** at low temperature and the formation of the first thermally stable group 5 dihydrogen complexes.

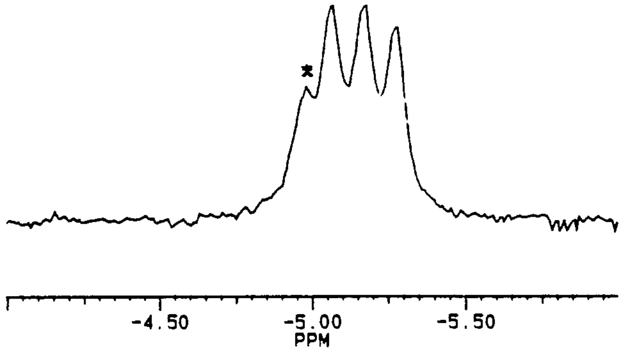
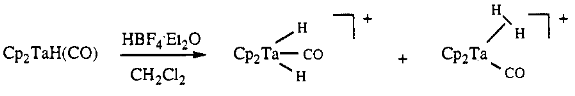


Figure 1. ^1H NMR spectrum in the hydride region of $[Cp_2Ta(\eta^2\text{-}HD)(CO)][BF_4]$, deuterated **3a** ($CD_2Cl_2$, 250 MHz); (*) residual nondeuterated **3a**.

Protonation of $Cp_2TaH(CO)$ ($Cp = C_5H_5$, **1a**;[12] $C_5H_4(^tBu)$, **1b**) by stoichiometric amounts of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at −78 °C affords rapidly $[Cp_2TaH_2(CO)]BF_4$ as two isomeric classes of compounds (eq 1). The minor isomers were identified by their



(1)

1a-b **2a-b** **3a-b**

spectroscopic properties as *trans*-$[Cp_2TaH_2(CO)]$ $[BF_4]$ (**2a,b**) similar to the complex previously characterized by some of us.[10] The major isomers (**3a,b**) display a resonance at δ −4.98 and −3.51 at 293 K which only broadens down to 178 K.[13] The ratios **2a**:**3a** and **2b**:**3b** are 1:17 and 1:7, respectively; they are found constant throughout the temperature range observed and even after keeping the samples for 3 h at room temperature. The relaxation time T_1 of the hydrides (250 MHz, CD_2Cl_2) shows a minimum of respectively 350 ms for **2a** and 9 ms for **3a** at 178 K and of 205 ms for **2b** and 12 ms for **3b** at 178 K. The relaxation of metal bound hydrides (R_T) is the sum of the relaxation due to hydride–hydride interaction (R_{H-H}) and that due to all other phenomena (R_O, relaxation due to dipole–dipole interactions with Cp, solvent, Ta, ...).[14] For **2a** R_{H-H} is negligible whereas R_O should be very similar or identical for **2a** and **3a**. Finally R_T(**2a**) and R_T(**3a**) are given by the measurements. Therefore the equations are R_T(**3a**) = R_{H-H}(**3a**) + R_O(**3a**) and R_T(**2a**) = R_O(**2a**) = R_O(**3a**); hence, R_{H-H}(**3a**) = R_T (**3a**) − R_T(**2a**). This is

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(13) ^1H NMR data for compounds **2a,b** and **3a,b** (250 MHz, CD_2Cl_2): **2a**, δ −1.50 (s, 2H, $Ta(H)_2$), 5.87 (s, 10H, C_5H_5); **3a**, δ −4.98 (s, 2H, $Ta(H_2)$), 5.68 (s, 10H, C_5H_5); **2b**, δ −1.68 (s, 2H, $Ta(H)_2$), 1.32 (s, 18H, *t*-Bu), 5.28 (pseudo-t, 4H, C_5H_4), 5.96 (pseudo-t, 4H, C_5H_4); **3b**, δ −3.51 (s, 2H, $Ta(H_2)$), 1.25 (s, 18H, *t*-Bu), 5.12 (m, 2H, C_5H_4), 5.61 (m, 2H, C_5H_4), 5.69 (m, 2H, C_5H_4), 5.78 (m, 2H, C_5H_4).

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(16) Pseudopotential parameters have been derived using the Durand and Barthelat method.[17] For C, O and Cl, standard values for the parameters have been used,[18] and for Ta, pseudopotential parameters have been determined in order to correctly reproduce the all-electron relativistic results for both $d^3s^2(^4F)$ and $d^4s^1(^6D)$ atomic states. The Gaussian basis set used was of double-ζ quality for C, O, Cl, and H and of triple-ζ quality for Ta. A p polarization function (exp 0.9) was added to the hydrogen basis set. Geometry optimizations and force constant calculations were carried out with the HONDO8 program.[19]

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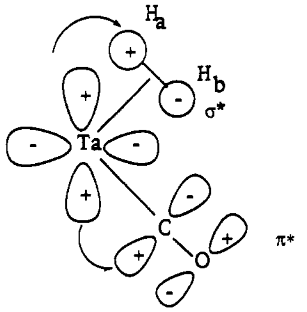
Table 1. Optimized Geometrical Parameters for *trans*-$[Cl_2TaH_2(CO)]^+$ and the Dihydrogen Complex $[Cl_2Ta(H_2)(CO)]^+$

geometrical parameters[a]	trans isomer **2** (C_{2v})	dihydrogen complex **3** (C_s)
Ta–H_a	1.716	1.950
Ta–H_b	1.716	1.961
H_a–H_b	3.099	0.814
Ta–C	2.411	2.279
C–O	1.119	1.120
Ta–Cl	2.255	2.303
H_aTaH_b	129.2	24.0
TaCO	180.0	178.4
ClTaCl	115.6	134.6

[a] Bond distances are in angstroms and bond angles in degrees. For the dihydrogen complex, H_a is the hydrogen atom located far from CO.

a rare case where the relaxation due to hydride–hydride interaction can be determined unambiguously. Since we know that the dihydrogen molecule is spinning as we observe a single line, Halpern's approximate equation[14] leads to a H–H distance of 0.84 ± 0.05 Å for **3a** and 0.89 ± 0.05 Å for **3b**. **3a** and **3b** are therefore the first thermally stable dihydrogen complexes of group 5 metals. It is interesting to note the variation of the relaxation time of the hydride signals of both isomers when substituting C_5H_5 by $C_5H_4(^tBu)$. This is due to the variation of the electronic properties of the Cp ligands: the more electron releasing ligand $C_5H_4(^tBu)$ induces a lengthening of the H–H bond. Upon carrying out the protonation of **1a** with $DBF_4{\cdot}D_2O$, the expected 1:1:1 triplet centered at δ −5.18 was observed for deuterated **3a**, namely, $[Cp_2Ta(\eta^2\text{-HD})(CO)][BF_4]$ (see Figure 1). The J_{H-D} value is 26.5 Hz, in agreement with an unstretched dihydrogen structure and the H–H distance calculated from T_1 measurements.

In order to understand the electronic structure of **3a,b** and the difference with the corresponding phosphine and phosphite adducts, ab initio calculations using a relativistic pseudopotential for tantalum were performed on the model cation $[Cl_2TaH_2(CO)]^+$.[15] Details of the calculation are available upon request.[16] Geometrical SCF optimizations followed by vibrational analyses allow identification of only two local minima on the singlet potential energy surface. The optimized structures are listed in Table 1. They correspond to a trans isomer of C_{2v} symmetry **2**, and a dihydrogen complex of C_s symmetry **3**, in agreement with the experimental results. Calculations beginning with a C_s cis structure did not produce another stationary point but instead the dihydrogen complex again. The energy separation between isomers **2** and **3** is found to be 9.1 kcal/mol in favor of the dihydrogen complex. However, calculations taking into account electron correlation effects[20] diminish this value to 1.1 kcal/mol, leading to a situation of quasi-degeneracy for the two structures. The dihydrogen complex is characterized by a bonding arrangement in which the H_2 and CO ligands located in the symmetry plane can compete as σ-donors and π-acceptors. The π-back-donation is illustrated in the following scheme:



It is well-known that CO is a better π-acceptor than H_2 in metal complexes. Therefore the back-donation does not populate too much of the σ^* orbital of H_2 preventing the breaking of the H–H bond. As a consequence a η^2-H_2 bonding is preferred to the formation of a classical *cis*-dihydride complex. The same situation occurs whenever a good π-acceptor ligand acts as a π-competitor with respect to H_2. In a parallel calculation[22] on the same cationic tantalum dihydride, but substituting CO by PF_3, which is known to be a π-acceptor of comparable strength,[23] we obtained the same result, i.e., the nonexistence of the *cis*-dihydride structure as a minimum on the singlet potential energy surface, whereas a *cis*-dihydride configuration was preferred when PH_3 was used.

In conclusion, we describe in this paper the first tantalum and more generally the first thermally stable group 5 dihydrogen complexes. These complexes are the kinetic isomers of the protonation reaction since only the *trans* dihydrides are obtained at room temperature in water. The presence of both isomers in the reaction products allows unambiguous calculation of the relaxation due to the hydrogen–hydrogen interaction within the dihydrogen molecule and hence calculation of the H–H distance (0.84 Å), which is in good agreement with the observed J_{H-D} value (26.5 Hz) and the optimized distance found by calculations (0.814 Å). These dihydrogen derivatives are electrophilic as deduced from the poor back-bonding observed on CO, which suggests a high acidity of the coordinated dihydrogen molecule. The reactivity of these species is being pursued.

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(20) Valence correlation energies have been calculated using the three-class version of the CIPSI algorithm.[21] The MOs of $[Cl_2TaH_2(CO)]^+$ have been localized by projection onto the two fragments $[TaH_2(CO)]^{3+}$ and Cl_2^{2-}, and the MOs corresponding to Cl_2^{2-} have been frozen in the process generating the excited determinants.

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