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Synthesis of and NMR T_1 Relaxation in the Bimetallic Trihydride Complexes $Cp_2TaH_2(\mu\text{-}H)M(CO)_5$ (M = Cr, Mo, W)

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New bimetallic trihydrides $Cp_2TaH_2(\mu\text{-}H)M(CO)_5$ (M = Cr (**2**), Mo (**3**), W (**4**)) have been prepared by the room-temperature high-yield reaction between Cp_2TaH_3 (**1**) and $M(CO)_5$. The complexes have been characterized by elemental analyses and variable-temperature ^1H NMR and IR spectra. The structures and arrangements of the hydride ligands in complexes **2**−**4**, where the central hydride ligand is bound to M, have been determined from ^1H NMR and ^1H T_1 relaxation time data. It has been shown that structural interpretations of ^1H T_1 measurements, carried out for **1** and bimetallic systems below 295 K, can be made on the basis of the isotropic motion approach and of a model of uncoupled nuclei. The high-temperature saturation transfer experiments in the ^1H NMR spectra have shown complexes **2**−**4** to be stereochemically nonrigid demonstrating an H^X/H^A exchange on the T_1 NMR time scale. It has been established that the energy barrier of the hydride/hydride exchange is decreased in going from complex **1** to bimetallic systems **2**−**4**.

Introduction

The search for new heterobimetallic complexes with unusual stoichiometric or catalytic properties is currently under intensive investigation.[1] Among these systems, bimetallic polyhydrides are of special interest[2] because of the presence of terminal and bridging hydride ligands binding to different metal centers. In this work we describe the simple preparation and structures of new metallocenic trihydride compounds of the formula $Cp_2TaH_2(\mu\text{-}H)M(CO)_5$ [M = Cr **(2)**, Mo **(3)**, W **(4)**] where the central hydride ligand is bound to the second metal center. The structures of the bimetallic compounds have been established by variable-temperature ^1H NMR spectroscopy and from ^1H T_1 relaxation time data.

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere by standard techniques. Solvents were dried and deoxygenated by using conventional procedures.

IR spectra were recorded in solution on a Nicolet 205 instrument.

NMR data were obtained on Bruker AC 200 and AC 80 spectrometers. The conventional inversion-recovery method was used to determine T_1 relaxation times. The calculation of the relaxation times was made using the nonlinear three-parameter fitting routine of the spectrometers. In each experiment, the waiting period was 5 times the expected relaxation time and 16−20 variable delays were employed. The duration of the pulses were controlled at every studied temperature. The errors of such T_1 determinations were lower than 5%. The temperature was calibrated by ^1H NMR with a standard methanol sample. ^1H NMR saturation transfer experiments[3a] were performed by using the standard techniques of spectrometers. The rate constants of the H/H exchange (k) were calculated from the equation $I(S)/I(0) = 1/(1 + kT_1)$, where $I(S)$ and $I(0)$ correspond to the relative integral intensities of the H ligand signal with and without saturation.[3b] T_1 is the spin−lattice relaxation time of the nucleus.

The following compounds were prepared as described in the literature: Cp_2TaH_3,[4a] $Cr(CO)_5$,[4b] $Mo(CO)_5$,[4b] $W(CO)_5$.[4b]

Preparation of $Cp_2TaH_2(\mu\text{-}H)M(CO)_5$. A 1.2 equiv amount of $M(CO)_5$ was added to a red solution of Cp_2TaH_3 (0.5 g, 1.59 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred vigorously for 45 min to yield an orange solution, the solvent was removed under reduced pressure, and the residue was washed with 20 mL of pentane and dried. The remaining solid was dissolved in toluene and chromatographed on silica gel (70−230 mesh) using a mixture of toluene/pentane (5/1) as eluent.

$Cp_2TaH_2(\mu\text{-}H)Cr(CO)_5$ (an orange solid, yield 80%): Anal. Calcd for $C_{15}H_{13}CrO_5Ta$: C, 35.59; H, 2.59. Found: C, 35.59%; H, 2.31%. IR (THF): ν_{CO}, 2057, 1926, 1896 cm^{-1}. ^1H NMR (CD_3COCD_3, 294 K): δ 5.53 (s, Cp), −0.68 (d, J(HH) = 9.8 Hz, TaH_2), −18.10 (t, J(HH) = 9.8 Hz, TaHCr).

$Cp_2TaH_2(\mu\text{-}H)Mo(CO)_5$ (an orange solid, yield 72%): Anal. Calcd for $C_{15}H_{13}MoO_5Ta$: C, 32.75; H, 2.38. Found: C, 32.28; H, 2.43. IR (THF): ν_{CO}, 2067, 1933, 1890 cm^{-1}. ^1H NMR (CD_3COCD_3, 294 K): δ 5.46 (s, Cp), −1.63 (d, J(HH) = 10.4 Hz, TaH_2), −11.80 (t, J(HH) = 10.4Hz, TaHMo).

$Cp_2TaH_2(\mu\text{-}H)W(CO)_5$ (a yellow solid, yield 80%): Anal. Calcd for $C_{15}H_{13}WO_5Ta$: C, 28.24; H, 2.05. Found: C, 28.56; H, 2.09. IR (THF): ν_{CO}, 2061, 1922, 1891 cm^{-1}. ^1H NMR (CD_3COCD_3, 294 K): δ 5.54 (s, Cp), −1.40 (d, J(HH) = 9.8 Hz, TaH_2), −12.64 (t, J(HH) = 9.8 Hz, J(WH) = 36.5 Hz, TaHW).

Results and Discussion

Bimetallic complexes **2**−**4** were prepared in THF from trihydride **1** according to the room-temperature high-yield

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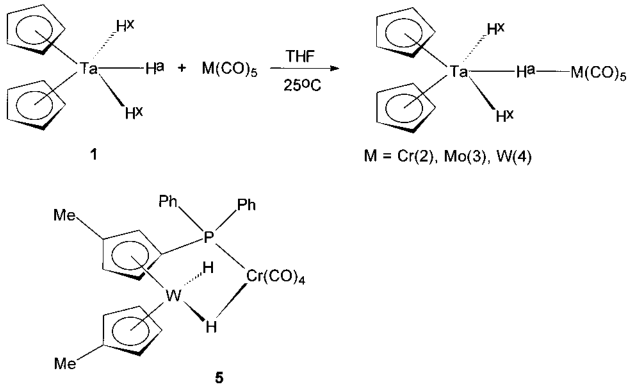
Scheme 1



reaction of Scheme 1. The complexes obtained were characterized by a correct elemental analysis, and their structures were assigned spectroscopically since it was not possible to grow crystals suitable for an X-ray crystal structure determination. Compounds **2**−**4** are quite stable in solution (THF, acetone, toluene) at $T < 294$ K.

The hydride regions of the room-temperature ^{1}H NMR spectra of **2**−**4** exhibit AX_2 patterns which remain unchanged on cooling in toluene-d_8 or acetone-d_6 up to 180 K. The H^A resonances in **2**−**4** are characterized by the high-field shifts of −18.10, −11.80, and −12.64 ppm, respectively, versus −1.70 ppm observed for H^A in **1** (toluene-d_8). It is remarkable that very similar δ values have been recently reported for the bridging hydride ligands in some W/Cr and W/W dihydrides[5] related to compound **5** (see Scheme 1). As follows from the ^{1}H NMR spectra, the H^X resonance undergoes an insignificant low-field displacement when **1** ($\delta(H^X) = -3.09$ ppm) transforms to the bimetallic complexes ($\delta(H^X) = -0.68$, −1.63, and −1.40 ppm in **2**−**4**, respectively). In the case of complex **4** the J(WH) constant of 36.5 Hz is observed only for the central hydride ligand. Finally, the IR spectra of **2**−**4** show the typical patterns of the $M(CO)_5$ fragments. Thus, the data allow formulation of the new bimetallic trihydrides as represented in Scheme 1 where the H^A ligand is bound to the second metal center M.

^{1}H T_1 relaxation time measurements have often been used in recent years to obtain quantitative structural information about transition metal hydride systems in solution.[6] Therefore in the absence of solid-state structural data, arrangement of the hydride ligands in **2**−**4** could be determined on the basis of comparison of T_1 data collected for these complexes and for complex **1**. Actually, all the proton−proton and Ta−proton distances in trihydride **1** are well-known from neutron diffraction data.[7]

Intramolecular proton−proton and proton−metal dipole−dipole interactions dominate the T_1 relaxation of hydride ligands in classical Re, Mn, Co, and Nb hydrides:[6a,c−e]

$$1/T_1^{\mathrm{obs}} = 1/T_1(\mathrm{H\cdots H}) + 1/T_1(\mathrm{M\cdots H}) \tag{1}$$

In terms of a model of uncoupled nuclei (see below) and isotropic molecular reorientations, the above relaxation contributions are described by eqs 2 and 3, respectively, where γ_H and γ_M are the ^{1}H and metal gyromagnetic ratios, ω_H and ω_M are Larmor frequencies, and τ_c is the correlation time for molecular reorientations.[8]

$$1/T_1(\mathrm{H\cdots H}) = 0.3\gamma_H^{\,4}h^2 r(\mathrm{H\cdots H})^{-6}(\tau_c/(1 + \omega_H^{\,2}\tau_c^{\,2}) + 4\tau_c/(1 + 4\omega_H^{\,2}\tau_c^{\,2})) \tag{2}$$

$$\tau_c = \tau_o \exp(E_a/RT)$$

$$1/T_1(\mathrm{M\cdots H}) = (2\gamma_H^{\,2}\gamma_M^{\,2}h^2 I(I + 1)/15r(\mathrm{M\cdots H})^6) \times (3\tau_c/(1 + \omega_H^{\,2}\tau_c^{\,2}) + 6\tau_c/(1 + (\omega_M + \omega_H)^2\tau_c^{\,2}) + \tau_c/(1 + (\omega_M - \omega_H)^2\tau_c^{\,2})) \tag{3}$$

On the conditions of the fast motion regime eq 2 takes the form of eq 4 (here and below T_1 units in s and r in Å).

$$1/T_1(\mathrm{H\cdots H}) = 8.55 \times 10^{11}\tau_c/r(\mathrm{H{-}H})^6 \tag{4}$$

According to the literature,[6c,e] among the metals in Scheme 1, only the tantalum can produce a noticeable contribution of metal−proton interactions (for example, the T_1 values were found to be very similar for the WH lines and for the ^{183}WH satellites of complex **4** showing tungsten−proton interactions to be insignificant). In the fast motion regime, this contribution is expressed as (5).

$$1/T_1(\mathrm{Ta\cdots H}) = 1.707 \times 10^{11}\tau_c/r(\mathrm{Ta{-}H})^6 \tag{5}$$

If T_1 times reaches a minimum, eqs 2 and 3 convert into eqs 6 and 7, respectively.

$$r(\mathrm{H\cdots H}) = 2.405(200T_{1\mathrm{min}}/\nu(\mathrm{MHz}))^{1/6} \tag{6}$$

$$r(\mathrm{Ta\cdots H}) = 2.001(200T_{1\mathrm{min}}/\nu(\mathrm{MHz}))^{1/6} \tag{7}$$

As mentioned above, eqs 2, 4, and 6 are valid for a model of a pair of uncoupled ^{1}H nuclei where the T_1 times are determined from monoexponential NMR decays in inversion-recovery experiments. Ernst et al.[9a] have found that use of strong nonselective 90° pulses for 180−τ−90 inversion-recovery relaxation time measurements in *strongly coupled* systems or in systems with *equivalent nuclei* leads to mixing of the eigenstate populations. Because of this phenomenon, the line intensities are dependent on populations of all the eigenstates of the spin systems and the decays become, in principle, multiexponential.[9] For example, in the case of an AX_2 system this results in faster relaxation of the central line of the A triplet with respect to the two outer lines.[9a]

In the relaxation experiments carried out for complexes **1**−**4** with 16−20 variable delays, the 1:2:1 equilibrium ratios of relative intensities of the A triplets were only minimally perturbed as the inverted AX_2 multiplets of the hydride ligands relaxed to equilibrium at low temperatures. In turn, the relaxations appeared to be monoexponential. Nonequilibrium relative intensities of the H^A triplets were observed only for bimetallic trihydrides **2**−**4** at room and higher temperatures. Figure 1 shows a series of partially relaxed ^{1}H spectra collected

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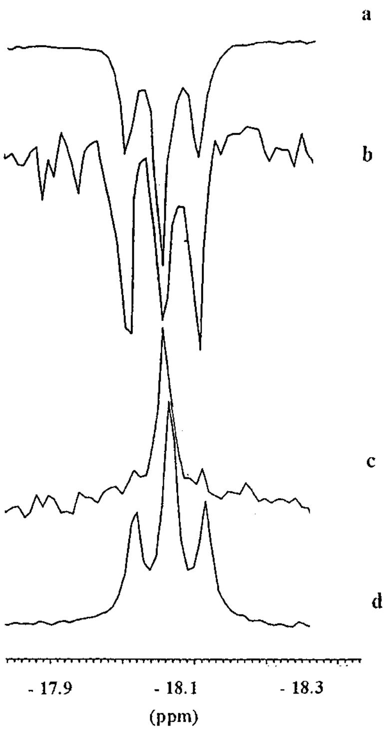

Figure 1. Room-temperature partially-relaxed ^{1}H NMR spectra of H^A collected in an inversion-recovery experiment at various times τ for a freshly-prepared acetone-d_6 solution of complex **2**: (a) $\tau = 0.1$ s; (b) $\tau = 0.6$ s; (c), $\tau = 1.1$ s; (d), $\tau = 20.1$ s.

Table 1. T_1 Data Collected for All the Resonances of the AX_2 Spin Systems of the Hydride Ligands (H^X and H^A) in Trihydrides **1** (Toluene-d_8) and **2**−**4** (Acetone-d_6)

complex	T_1(s)[a] H^X		H^A			T (K)
1	3.22	3.00	2.09	2.09	2.30	294[b]
1	3.32	3.43	2.49	2.44	2.45	303
1	4.04	4.07	3.33	3.13	3.30	320
2	2.49	2.45	2.33	1.68	2.16	294[c]
2	1.61	1.61	1.78	1.34	1.65	294[d]
3	2.88	2.88	1.75	1.41	1.66	294[e]
4	2.35	2.43	2.05	1.55	2.04	294

[a] Errors are less than 5%. [b] T_1(Cp) = 5.58 s. [c] T_1(Cp) = 8.80 s. [d] T_1(Cp) = 2.16 s. [e] T_1(Cp) = 6.62 s.

for a freshly-prepared acetone-d_6 solution of complex **2** in the inversion-recovery experiment at various times τ at 294 K. The spectra demonstrate a greater relaxation rate for the central line of the H^A triplet with respect to the outer resonances indicating the features of coupled relaxation. Similar behaviors have been observed for all the bimetallic trihydrides (Table 1), and in the case of complex **4** it was detected even for ^{183}WH satellites. Unfortunately, the spontaneous appearance of paramagnetic compounds of unknown structures at $T > 294$ K, resulting in shorter T_1 times of all the protons in **2**−**4** (it was manifested first of all for the Cp resonances (see Table 1)) makes studies of this phenomenon difficult. In contrast to bimetallic compounds **2**−**4**, all the lines of the H^A triplet in complex **1** relaxed identically at room temperature and on heating up to 320 K (Table 1). Thus in this work there is evidence that the relaxation of the hydride ligands in **1**−**4** (at $T < 294$ K) may be treated in terms of an uncoupled nuclei model.

It has been recently shown that in *mononuclear* hydride complexes T_1 relaxation of the hydride ligands can be successfully treated by assuming an isotropic motion.[6c,d] Table 2 lists the T_{1min} relaxation parameters calculated for the hydride ligands in trihydride **1** through eqs 6 and 7 by using the H···H and Ta···H distances taken from the neutron diffraction structure.[7] The calculations were made for the Cp conformations established in the solid state. According to the data, hydride−hydride interactions provide main contributions to the relaxation rates of the hydride ligands: 55 and 76% for H^X and H^A, respectively. Nevertheless, contributions caused by *Ta*/*H* and Cp*H*/Ta*H* interactions seem to be significant and they cannot be ruled out in quantitative T_1 interpretations. Such a situation could result in shorter hydride−hydride distances reported, for example, for the trihydride of the formula $(C_5H_4SiMe_3)_2TaH_3$ (**6**) (1.77 Å[9c] versus 1.85 Å in complex **1**[7]).

Table 2. Theoretical and Experimental T_1 (s) and T_1^{-1} (s^{-1}) Data for Hydride Ligands (H^X and H^A) in Trihydrides **1**−**4** and **6** at 200 MHz

complex	param	H^X	H^A
1	T_{1min}^{-1}(TaH···Cp)	1.90[a]	0.96[b]
1	T_{1min}^{-1}(Ta···H)	2.06[c]	2.06[c]
1	T_{1min}^{-1}(H^X···H^A)	4.81[d]	9.62[d]
1	T_{1min}(tot.)	0.114[e]	0.0794[e]
1	T_{1min}(exp) at 303 K	3.374[f]	2.462[f]
2	T_{1min}(exp) at 185 K	0.126[g]	0.0953[g]
3	T_1(exp) at 214 K	0.332[g]	0.242[g]
4	T_{1min}(exp) at 194 K	0.109[f]	0.0845[f]
6	T_{1min}(exp)[f]	0.157	0.102

[a] Calculated with r(H−H) = 2.426 Å.[7] [b] Calculated with r(H−H) = 2.744 Å.[7] [c] Calculated with r(Ta−H) = 1.774 Å.[7] [d] Calculated with r(H−H) = 1.851 Å.[7] [e] Calculated with eq 1. [f] In toluene-d_8. [g] In acetone-d_6.

Unfortunately, it was not possible to reach the minimal T_1 times in the variable-temperature ^{1}H NMR spectra of **1** at 200 MHz in toluene-d_8 because of the small moment of inertia of this molecule. Therefore, in order to be sure that the isotropic motion approach is actually valid in the case of **1**, we have calculated via eqs 4 and 5 the T_1 value expected for H^A using the $T_1(H^X)$ of 3.374 s observed in the experiment at 303 K (Table 2) and taking into account that 55% of the relaxation rate of H^X is caused by hydride−hydride interactions. Such a calculation gives a value of 2.517 s that corresponds well to the experimental value in Table 2.

The variable-temperature ^{1}H NMR relaxation data collected for **2** (acetone-d_6) and **4** (toluene-d_8) allowed determination of the T_{1min} values for the H^A and H^X ligands (Table 2). These complexes are binuclear, and therefore they seem to be "more anisotropic". Nevertheless a good agreement between the theoretical (the solid curve) and experimental data (Figure 2) obtained for the H^A ligand in **4** (toluene-d_8, 200 Mhz) shows that the isotropic motion model remains valid. It should be noted that the Ta/H contribution to the T_1 time of the H^A ligand in trihydride **1** is minimal (Table 2), and therefore, the above calculation was made taking into account only proton−proton dipole−dipole interactions in eq 2. In addition we have found that eq 2 also describes well the T_1 behaviors of the CH_3 protons and the hydride ligands even in the more anisotropic binuclear complex **5**[5] containing the bulky P ligands (Figure 2). It is important that the fitting procedures resulted in quite reasonable[6c,d] E_a (4.0 and 4.2 kcal/mol) and τ_o (0.2×10^{-13} and 0.5×10^{-13} s) values for solution molecular reorientations of **4** and **5**, respectively. It is also important that the calculation of the r(H···H) distance in the CH_3 groups of complex **5** from the T_{1min} value through eq 6 (taking into account the well-known very fast rotation of the methyl group) gives 1.72 Å which compare well with the value of 1.78 Å reported in the literature.[10] Thus we believe that the isotropic approach can

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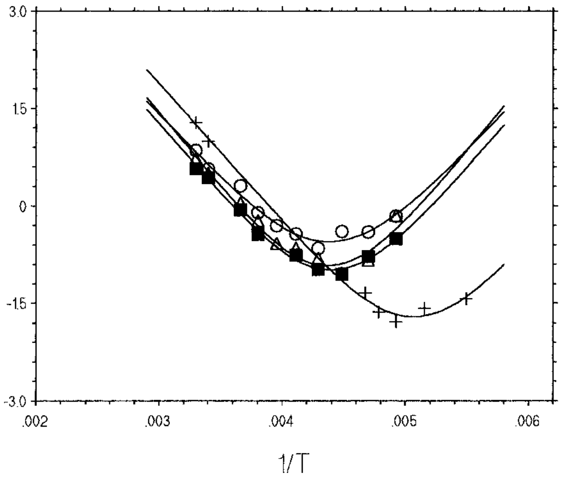


Figure 2. Variable-temperature T_1 data for trihydride **4** and dihydride **5** in toluene-d_8 solutions at 200 MHz: ○, CH_3 in complex **5** (taking into account interactions for a pair of protons); △ and ■, the hydride ligands in **5**; +, H^A in **4** (recalculated for a pair of the protons H^A and H^X).

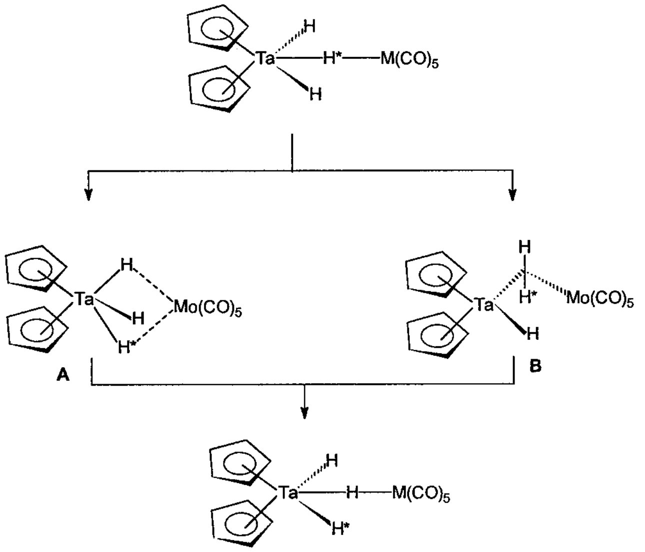
be used for quantitative interpretations of the T_1 data such as the ones obtained in this work for the bimetallic systems.

As seen from Table 2, Ta/W complex **4** shows the $T_{1\min}$ values which are very similar to the theoretical magnitudes calculated for trihydride **1**. The slightly increased $T_{1\min}$ times are observed for both H ligands in Ta/Cr complex **2**. However this increase seems to be insignificant because the $T_{1\min}$ values remain shorter than those reported for complex **6**.[9c] It is also important that the $T_{1\min}$ times of H^A in **2** and **4** (this central ligand interacts with two H^X ligands) are significantly longer than the value (0.0696 s, 200 MHz) reported for the classical dihydride *cis*-$(Cp_2TaH_2(P(OMe)_3))^+$ with an H···H separation of 1.67 Å.[11a] It should be noted that the above Ta complex shows exchange couplings[11] and, therefore, the distance of 1.67 Å seems to be quite realistic.

Taking into account all these data, one can conclude that the hydride arrangement in bimetallic systems such as **2** and **4** remains very similar to that in mononuclear complex **1** and, thus, three hydride atoms and the both metals of bimetallics **2**−**4** are located in the plane, with practically the same hydride−hydride and Ta−hydride distances as in the case of trihydride **1**. The similarity between values of the temperature-independent *J*(HH) constant observed for the trihydrides (9.3, 9.8, 10.0 and 9.8 Hz for **1**−**4**, respectively) supports the above conclusion. Unfortunately, precipitation at low temperatures prevents us determining a minimum of the ^1H T_1 times for Ta/Mo compound **3**. Nevertheless we believe that the above conclusion is also valid for this complex because the high-temperature T_1 behaviors of all the bimetallic molecules are practically identical.

In spite of the above structural similarity of the TaH_3 fragments in complexes **1**−**4**, the hydride resonances in the bimetallic systems show spectroscopic features. At low temperatures and on heating up to 320 K (toluene-d_6), trihydride **1** shows distinct T_1 values for the H^A and H^X hydrides indicating a lack of hydride exchange on the T_1 NMR time scale.[9c] In the absence of the exchange no saturation transfer[3] was observed in the ^1H NMR spectra of **1** even at 320 K with corresponding irradiation of the hydride resonances. In contrast to the mononuclear complex **1**, the high-temperature spectra of the bimetallic trihydrides **2**−**4** clearly revealed the stereochemical nonrigidity of the hydride ligands. For example, the H^X doublet of **4** loses 46% of its intensity on irradiation of the triplet of H^A in toluene-d_8 at 320 K. In turn, irradiation of H^X decreases intensity of the H^A triplet (60%), demonstrating an H^X/H^A exchange on the T_1 NMR time scale (Scheme 2). It is remarkable that the exchange remains slow in the T_2 NMR time scale because the hydride ligands display quite narrow resonances under these conditions. The saturation transfer experiments and T_1 measurements at 320 K allow us to estimate a rate constant (k^{exch}; see Experimental Section) of 0.73 s^{-1} for the H/H exchange in complex **4**. Less pronounced saturation transfer effects were detected for trihydrides **2**−**4** even at 303 K (80 MHz). The calculations of k^{exch} resulted in the magnitudes of 0.20, 0.15, and 0.27 s^{-1} for **4** (toluene-d_8), **3** (acetone-d_6), and **2** (acetone-d_6), respectively. Through the well-known Eyring's equation the above values corespond to $\Delta G^{\ddagger}(303\ K) = 18.7$, 18.9, and 18.5 kcal/mol.

Scheme 2



It seems to be obvious that the pairwise site exchange between the terminal and bridging hydride ligands in **2**−**4** requires an out-of-plane twist of two adjacent hydrogen atoms and their binding to both metal centers in a transition state (Scheme 2). This binding probably decreases the energy barrier of the exchange because complex **1** remains structurally rigid under the same conditions. According to theoretical studies of mononuclear trihydrides,[12] such an exchange can occur without or with the formation of an H−H bond. In the case of bimetallics **2**−**4** this corresponds to structure **A** or **B**. We have found for example that trihydride **4** loses dihydrogen after 1 h in an acetone-d_6 at 303 K: an H_2 signal with a T_1 time of 1.39 s (80 MHz) is clearly detected in the ^1H NMR spectrum under these conditions. We therefore propose that an exchange process occurs through the dihydrogen complex **B**, stabilized by two metal centers.[13] In this context, the structural rigidity of the Ta trihydride **1** can be explained in terms of a *high-lying* dihydrogen state as is found in theoretical calculations of the potential surface of this molecule.[12c]

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Conclusions

Bimetallic complexes **2−4** can be easily prepared by the room-temperature reaction between Cp_2TaH_3 and $M(CO)_5$, where M = Cr, Mo, and W. The structures of these bimetallic compounds with a central hydride ligand bound to M have been established spectroscopically. In the absence of solid-state structural data, the arrangement of the hydride ligands in complexes **2−4** has been determined from the ^1H T_1 relaxation time data on the basis of the isotropic motion approach and in terms of an uncoupled nuclei model. Good agreement between the theoretical and experimental T_1 data has shown that this simple approach can be successfully used for structural interpretations of ^1H T_1 measurements in the case of bimetallic systems **2−4**.

The high-temperature saturation transfer experiments have shown stereochemical nonrigidity of the hydride ligands in bimetallic trihydrides **2−4** demonstrating an H^X/H^A exchange on the T_1 NMR time scale. It is found that the energy barrier of the hydride/hydride exchange decreases in going from complex **1** to bimetallic systems **2−4**.

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