Dynamic Behavior in Solution of the *trans*-Hydridodihydrogen Complex $[OsHCl(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2]$: Ab Initio and NMR Studies

Vladimir I. Bakhmutov,* Juan Bertrán, Miguel A. Esteruelas, Agustí Lledós,* Feliu Maseras, Javier Modrego, Luis A. Oro,* and Eduardo Sola

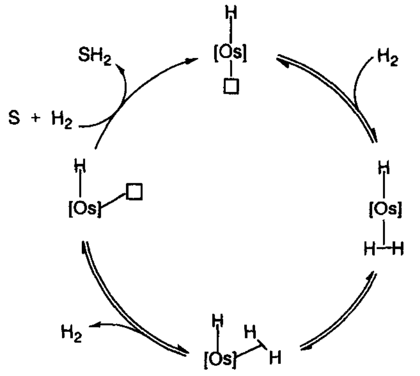
Abstract: Reaction of complex $[OsHCl(CO)(P\mathit{i}Pr_3)_2]$ (**1**) with hydrogen gives the *trans*-hydridodihydrogen complex $[OsHCl(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2]$ (**2**). The H–H distance in the dihydrogen ligand, determined by variable-temperature ^1H T_1 measurements, is 0.8 Å. The fast-spinning nature of the dihydrogen ligand of **2** has been deduced by evaluating the deuterium quadrupole coupling constant for the η^2-D_2 ligand of $[OsDCl(\eta^2\text{-}D_2)(CO)(P\mathit{i}Pr_3)_2]$ ($[D_3]$**2**). Measurements of the equilibrium constants for formation of **2** (K) give $\Delta H^\circ = -14.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^\circ = -30 \pm 1$ e.u. An equilibrium isotope effect K_d/K of 2.8 is found for this reaction. The activation parameters for the H_2 loss from **2** are $\Delta H^{\ddagger} = 14.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.9 \pm 0.5$ e.u. Hydrogen exchange between the hydrido and η^2-H_2 ligands of **2** takes place at a slow rate (k_2^{obs}) at high temperatures. Activation parameters $\Delta H^{\ddagger} = 17.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.3 \pm 1$ e.u., and a kinetic isotope effect (k_2^{obs}/k_{2d}^{obs}) of 4.6 at 333 K have been determined for this exchange. Ab initio calculations on the model system $[OsHCl(H_2)(CO)(PH_3)_2]$ confirm that the *trans*-hydridodihydrogen complex $[OsHCl(\eta^2\text{-}H_2)(CO)(PH_3)_2]$ (**4**) is the most stable species ($r_{HH} = 0.84$ Å). In addition, a *cis*-hydridodihydrogen complex **5**, with a relative energy of 13.8 kcal mol^{-1}, occupies a local minimum in the potential hypersurface. The energy of other possible trihydrido isomers have also been evaluated. On the basis of the thermodynamic and kinetic data, and the results of the ab initio calculations, the possible mechanism for the H/η^2-H_2 exchange is discussed.

Keywords
ab initio calculations · dihydrogen complexes · isotope effects · NMR spectroscopy · osmium complexes

Introduction

Dihydrogen complexes are important owing to their theoretical significance and potential importance in catalysis.[1] From a catalytic point of view, it has been proved that these types of compounds play a fundamental role in the homolytic[2] and heterolytic[3] hydrogen activation. Furthermore, the η^2-H_2 ligand can act as a good leaving group and stabilize unsaturated complexes in solution, without interfering with the coordination of substrates to the metal center.[4]

Several years ago, we reported the reaction of the five-coordinate complex $[OsHCl(CO)(P\mathit{i}Pr_3)_2]$ (**1**) with molecular hydrogen to afford *trans*-hydridodihydrogen $[OsHCl(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2]$ (**2**).[5] Furthermore, complex **1** was found to be a very active and highly selective catalyst for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one.[6] The mechanism (Scheme 1), deduced on the basis of kinetic results and spectroscopic observations, illustrates a new role for dihydrogen complexes in catalysis. Complex **1**, initially nonactive, is activated by the formation of **2**, which isomerizes to afford the *cis*-hydridodihydrogen complex; the latter subsequently dissociates to release the η^2-H_2 ligand.



Scheme 1. [Os]: $[OsCl(CO)(P\mathit{i}Pr_3)_2]$; S: $PhCH{=}CHC({=}O)CH_3$; SH_2: $PhCH_2\text{-}CH_2C({=}O)CH_3$; □: vacant coordination site.

In the context of these proposals, the main objective of this paper is the complete structural characterization of the *trans*-hydridodihydrogen complex **2**, and the study of its dynamic behavior in solution in the presence of dihydrogen. Detailed spectroscopic studies accompanied by theoretical calculations have been performed for this system. The results obtained for a deuterido analogue of **2** are also reported.

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Results

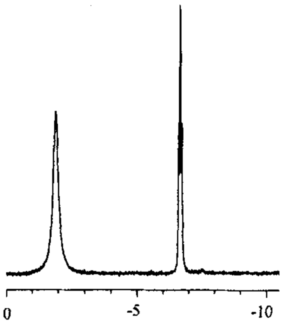


Fig. 1. High-field region of the ^{1}H NMR spectrum of **2** in [D$_8$]toluene at 240 K.

It has been previously reported that the *trans*-hydridodihydrogen complex **2** may be obtained from complex **1** in the presence of hydrogen.[5] The formation of **2** was found to be completely reversible under vacuum. Figure 1 shows the high-field region of the 300 MHz ^{1}H NMR spectrum of **2** in [D$_8$]toluene under a H_2 atmosphere at 240 K. A triplet at $\delta = -6.54$ ($J_{HP} = 18.6$ Hz) and a broad signal at $\delta = -1.8$ are observed, corresponding to the hydrido ligand and to the coordinated dihydrogen, respectively.

^{1}H and ^{2}H T_1 NMR relaxation studies on *trans*-[OsHCl(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$] (2) and *trans*-[OsDCl(η^2-D$_2$)(CO)(P*i*Pr$_3$)$_2$] ([D$_3$]2): Measurements of ^{1}H T_1 relaxation times have frequently been used to obtain quantitative information about the M–H and H–H bond lengths in transition metal hydrido complexes.[7] Figure 2 reports the ^{1}H T_1 data collected for the hydrido and dihydrogen signals of complex **2** at 300 MHz. The high-temperature sections in Figure 2, where the T_1 times of the H and η^2-H_2 ligands converge, clearly reflect the occurrence of a H/η^2-H_2 positional exchange (see below), whereas the sections below 283 K show the typical T_1 behavior caused by proton–proton dipole–dipole interactions.[8] This is supported by the variable-temperature ^{1}H T_1 data obtained for the hydrido ligand of the related complex [OsHCl(O$_2$)(CO)(P*i*Pr$_3$)$_2$] (**3**) (Fig. 2).

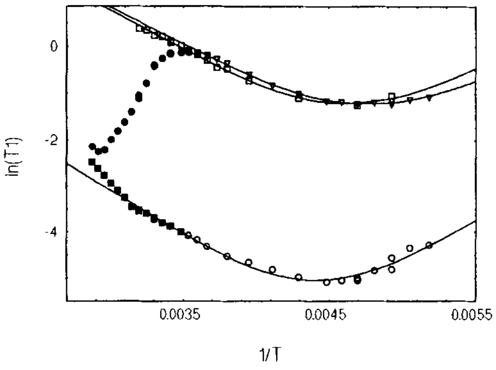


Fig. 2. Variable-temperature ^{1}H T_1 data (300 MHz, T_1 in s) for the [D$_8$]toluene solution of complex **2** (▾, ●: H–Os; ■, ○: (η^2-H$_2$)-Os) and complex **3** (□: H–Os).

It follows from Figure 2 that the T_1 time of the dihydrogen ligand of complex **2** reaches a minimum of 6.5 ms in the region of 227 K ($1/T = 0.0044$ K^{-1}). As in the case of the very similar *trans*-[IrHX$_2$(η^2-H$_2$)(P*i*Pr$_3$)$_2$],[9] the short value observed allows treatment of the variable-temperature T_1 data in terms of the dipole–dipole relaxation of a single pair of interacting protons [Eq. (1)],[8, 10] where γ_H is the ^{1}H giromagnetic ratio, τ_c is the correlation time for isotropic molecular reorientations, and ω_o is the Larmor frequency of ^{1}H. The plot of Figure 2 gives evidence for a good agreement between the theoretical and experimental lines.[11]

$$\frac{1}{T_1} = \frac{0.3\gamma_H^4 \hbar^2}{r_{HH}^6}\left\{\frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_o^2\tau_c^2}\right\} \qquad (1)$$

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

Figure 2 shows that the temperature dependence of T_1 for the hydrido and dihydrogen ligands of complex **2** reach minima at different temperatures. Very similar observations have been already noted for two nonequivalent hydrido ligands of [ReH$_2$(NO)(CO)(PO*i*Pr$_3$)$_2$] and attributed to the anisotropic character of molecular reorientations.[7e] This therefore appears to contradict the isotropic approach [Eq. (1)]; however, according to the recent quantitative analysis of these anisotropic effects,[7e] the isotropic-motion approach remains correct for the calculations of r_{HH} distances, producing quite small errors. Thus, the T_1 data collected in this investigation allow determination of the proton–proton distance in the dihydrogen ligand of **2** as 0.8 or 1.0 Å in the fast or slow η^2-H_2 rotation limits, respectively.[1d, f] In agreement with this range of H–H distances, the H–D coupling constant measured for the η^2-HD residual resonance of complex *trans*-[OsDCl(η^2-D$_2$)(CO)(P*i*Pr$_3$)$_2$] ([D$_3$]**2**) at 220 K is 30.5 Hz.[1d, f]

In order to eliminate the ambiguity connected with the well-known problem of the η^2-H_2 rotation limits, we used a new approach based on the estimation of the deuterium quadrupole coupling constant (DQCC) in the η^2-D_2 ligand of complex [D$_3$]**2**. It has recently been demonstrated that the DQCC for some transition metal deuterido compounds can be measured using ^{2}H T_1 relaxation times at low temperatures.[12]

T_1 relaxations of ^{2}H nuclei are completely dominated by quadrupole interactions,[8] and relaxation rates ($1/T_1$) are given by Equation (2), where ω_o is the Larmor frequency, I is the nuclear spin, $e^2q_{zz}Q/h$ is the static quadrupole coupling constant, η represents the asymmetry parameter of the electric field gradient, and τ_c corresponds to the isotropic molecular correlation time. In the case of ^{2}H nuclei $I = 1$ and ($e^2q_{zz}Q/h$) = DQCC.

$$\frac{1}{T_1} = \frac{3}{50}\pi^2\frac{2I+3}{I^2(2I-1)}\left\{\frac{e^2q_{zz}Q/h}{h}\right\}^2\left\{1+\frac{\eta^2}{3}\right\} \cdot \left\{\frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_o^2\tau_c^2}\right\} \qquad (2)$$

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

The 46.06 MHz low-temperature ^{2}H T_1 data collected for complex [D$_3$]**2** in toluene are reported in Figure 3, and show good agreement with the theoretical [Eq. (2)[13]] values.[14] As seen from Figure 3, the ^{2}H T_1 times reach minimum values of

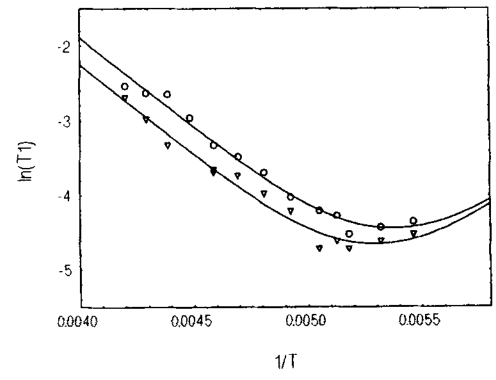


Fig. 3. Variable-temperature ^{2}H T_1 data (46.06 MHz, T_1 in s) for the toluene solution of [D$_3$]**2** (▾: D–Os; ○: (η^2-D$_2$)-Os).

9.0 and 11.0 ms for the D and η^2-D_2 ligands, respectively. According to ref. [13], the DQCC values can be calculated from Equation (3) (ν in MHz, T_1 in s) for the terminal D ligands when

$$\frac{e^2 q_{zz} Q}{h} = 10\left(\frac{0.6857\,\nu}{46.06\,T_{1\min}}\right)^{1/2} \tag{3}$$

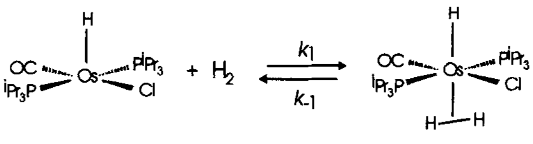
$\eta = 0$. The DQCC value of 87 kHz obtained for the deuterido ligand of [D_3]**2** is significantly higher than that found for deuterides of Zn, W,[15] Re, and Mn,[12] but is similar to that determined for [$OsD_4(PTol_3)_3$] (91 kHz).[12]

As mentioned above, Equation (3) is valid for terminal deuterides with the asymmetry parameter η equal to zero.[13] For the η^2-D_2 ligands this parameter should be expected to be non-zero;[15] however, to date no experimental information concerning possible magnitudes of η for the η^2-D_2 structural units has been given in the literature. Butler et al.[15] have studied the theoretical behavior of the DQCC and the asymmetry parameter η using the $[Rb-D_2]^+$ model system. Possible orientations of the major axis of the electric field gradient have also been determined. It was found that on decreasing the Rb–D_2 distance from 4.00 to 1.75 Å, when this system becomes a dihydrogen complex, the DQCC changes from 181.77 to 155.7 kHz, and the parameter η from 0.025 to the maximum limit of 0.62. In addition, it is important to mention that the DQCC in the HD molecule has been measured as 227 kHz,[16] and the solid-state ^{2}H NMR spectrum of the D_2 isotopomer of the dihydrogen complex [$W(\eta^2\text{-}H_2)(CO)_3(PiPr_3)_2$] gives a DQCC value of 124 kHz.[17]

For the η^2-D_2 ligand of complex [D_3]**2**, with the maximum η of 0.62 and $T_{1\min}$, a DQCC of 74 kHz is obtained, a value very similar to those reported for some Re(η^2-D_2) complexes, obtained by direct calculations of the DQCC's from $T_{1\min}$ data.[12] We believe that the 74 kHz, obtained for the *static* η^2-D_2 ligand, hardly contradicts the known experimental and theoretical data. Any disagreement can easily be explained if the η^2-D_2 ligand of [D_3]**2** is viewed as a *rapidly spinning* structural unit. In such case, a fourfold ($\eta = 0$) or 5.6-fold (at $\eta = 0.62$) difference between the observed and real $T_{1\min}$ times would be expected, resulting in a DQCC value of 155.8 or 174.5 kHz, respectively. This anisotropic approach[18] seems to be quite reasonable, because of the expected small angle between the D–D vector and the major axis of the electric field gradient (at least in the $[Rb-D_2]^+$ model system only a small change from 0.1 to 12.9° is observed when the Ru–D_2 distance decreases from 4 to 1.75 Å[15]).

Thus, the suggested approach using ^{2}H T_1 times allows the ambiguity of the η^2-D_2 rotation limits to be eliminated and the H–H distance in complex **2** to be determined as 0.8 Å (at least within the limits of the solution NMR method).

Thermodynamics and kinetics of formation of *trans*-[$OsHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$] (2) and *trans*-[$OsDCl(\eta^2\text{-}D_2)(CO)(PiPr_3)_2$] ([$D_3$]2): A correlation between the structural features of the dihydrogen ligands and the rates of H_2 loss has recently been reported for some dihydrogen complexes of iridium.[9] Hence, complex **2**, with a short H–H distance in the dihydrogen ligand, is expected to lose H_2 rapidly. Certainly, the variable-temperature spectra of solutions of **1** in [D_8]toluene under an atmosphere of H_2 display a full evolution from the slow to the fast exchange limits on the NMR timescale, according to the equilibrium in Scheme 2.



1 **2**

Scheme 2.

In the fast-exchange region, the equilibrium constants for the formation of complex **2** ($K = [\mathbf{2}]/[\mathbf{1}][H_2]$) were calculated using the chemical shifts of the exchange-averaged H_2/η^2-H_2 and HOs-**1**/HOs-**2** signals. The K values obtained are collected in Table 1. From the temperature dependence of K (Fig. 4), the values of $\Delta H^\circ = -14.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^\circ = -30 \pm 1$ e.u. were calculated for the formation of **2**. Similar calculations were performed based on the chemical shifts of the high-temperature ^{2}H NMR spectra of mixtures of complex [$OsDCl(CO)(PiPr_3)_2$] ([D]**1**) and [D_3]**2**. The corresponding K_d values are reported in Table 1 and shown in Figure 4. The data clearly manifest a well defined inverse thermodynamic isotope effect, with values of K_d/K of about 2.8.

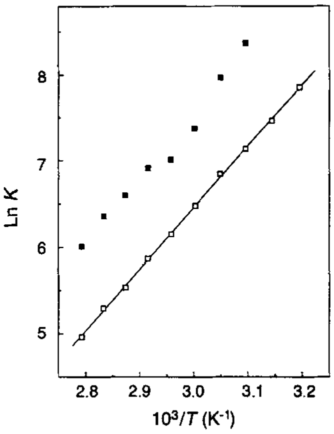


Fig. 4. Arrhenius plot of the equilibrium constants for formation of **2** (K, □) and [D_3]**2** (K_d, ■).

Table 1. Equilibrium constants for the formation of complexes **2** (K) and [D_3]**2** (K_d).

T/K	K/mol^{-1}	K_d/mol^{-1}	T/K	K/mol^{-1}	K_d/mol^{-1}
358	143	405	333	650	1600
353	200	579	328	937	2889
348	253	732	323	1253	4301
343	354	1000	318	1740	
338	468	1103	313	2572	

The variable-temperature ^{1}H NMR spectra of solutions of **1** under an atmosphere of H_2 also allow the rates of H_2 loss from complex **2** to be determined. Values of these rates (k_{-1}) calculated from lineshape analysis in the temperature range from 240 to 353 K are collected in Table 2. In order to expand the temperature region of the kinetic study, the relaxation approach[9, 19] was used. The T_1 measurements for the signal of free H_2 allow calculation of k_{-1} from Equation (4), where T_1^{obs}

$$1/T_1^{obs} = 1/T_1(H_2) + P/\{T_1(\eta^2\text{-}H_2) + \tau(\eta^2\text{-}H_2)\} \tag{4}$$

is the T_1 time measured for the free hydrogen signal, $T_1(H_2)$ and $T_1(\eta^2\text{-}H_2)$ are the relaxation times of free hydrogen[20] and the coordinated hydrogen of **2**, respectively, and $\tau(\eta^2\text{-}H_2)$ ($= 1/k_{-1}$) represents the lifetime of the dihydrogen ligand. The integration of the free-hydrogen and η^2-H_2 signals allows their relative populations P to be estimated. Equation (4) is valid from 198 to 223 K, when the equilibrium shown in Scheme 2 is slow on the NMR timescale. Values obtained by both of the above methods (Table 2 and Fig. 5) give the activation parameters for H_2 loss from **2**: $\Delta H^{\ddagger} = 14.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.9 \pm 0.5$ e.u..

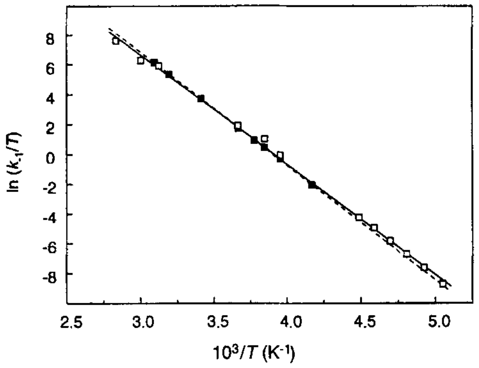


Fig. 5. Eyring plot of the rate constants for H_2 loss from **2** (k_{-1}, □, solid line) and for D_2 loss from [D_3]**2** (k_{-1d}, ■, dotted line).

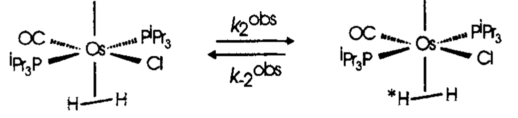
Table 2. Rates of H_2 loss from complex **2** (k_{-1}) and D_2 loss from complex [D_3]**2** (k_{-1d}).

T/K	k_{-1}/s^{-1}	k_{-1d}/s^{-1}	T/K	k_{-1}/s^{-1}	k_{-1d}/s^{-1}
353	710000 [a]		253	230 [a]	180 [b]
333	180000 [a]		240	30 [a]	30 [b]
323		150000 [b]	223	3.12 [c]	
320	120000 [a]		218	1.53 [c]	
313		67000 [b]	213	0.63 [c]	
293		12000 [b]	208	0.25 [c]	
273	1800 [a]	1500 [b]	203	0.10 [c]	
265		650 [b]	198	0.33 [c]	
260	700 [a]	400 [b]			

[a] From lineshape analysis of the ^{1}H NMR spectra. [b] From lineshape analysis of the ^{31}P NMR spectra. [c] From T_1 measurements of the ^{1}H NMR signal of dissolved H_2.

The corresponding rates of D_2 loss from complex [D_3]**2** (k_{-1d}) have been calculated by lineshape analysis of the variable-temperature ^{31}P NMR spectra of mixtures of [D]**1** and [D_3]**2** under a D_2 atmosphere in [D_8]toluene solutions. The data obtained between 240 and 323 K are shown in Table 2. The Eyring analysis of the k_{-1d} values (Fig. 5) gives the activation parameters $\Delta H^{\neq} = 15.2 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = 11.9 \pm 0.7$ e.u.

Kinetics of the H/η^2-H_2 and D/η^2-D_2 exchange in the complexes *trans*-[OsHCl(η^2-H_2)(CO)(P*i*Pr$_3$)$_2$] (2) and *trans*-[OsDCl(η^2-D_2)(CO)(P*i*Pr$_3$)$_2$] ([D_3]2): It has been reported that the room-temperature reaction between complex **1** and D_2 leads to the deuterated complex [D_3]**2**.[6] This reaction provides chemical evidence for an exchange process between the hydrido and dihydrogen ligands in **2** under an H_2 atmosphere (Scheme 3). This exchange is slow on the NMR timescale based on the spin saturation-transfer experiments[21] (see below) and the temperature dependence curves of the T_1 relaxation times in Figure 2.



Scheme 3.

In fact, above 270 K the observed T_1 values of the hydrido signal strongly differ from those calculated from Equation (1), decreasing as the temperature increases. Also, the T_1 values of the η^2-H_2 signal increase relative to the calculated values, moving close to the values for the hydride. This behavior indicates that an exchange between the hydrido and the dihydrogen ligand positions is taking place. Calculation of the exchange rates k_2^{obs} was possible by comparison of the experimental values for the hydrido T_1 (T_1^{obs}) with those predicted from Equation (1) (T_1^{calcd}, solid line in Fig. 2). At slow exchange rates these values are interconnected by Equation (5), where $\tau(\eta^2\text{-}H_2) = 1/k_{-2}^{obs}$.

$$1/T_1^{obs} = 1/T_1^{calcd} + 2/\{T_1(\eta^2\text{-}H_2) + \tau(\eta^2\text{-}H_2)\} \qquad (5)$$

The values of k_2^{obs} ($= 2k_{-2}^{obs}$) obtained by this method are reported in Table 3.

Spin saturation-transfer experiments, performed in a 30 K temperature range by saturating the η^2-H_2 ligand resonance and measuring the intensity of the hydrido signal, gave the exchange rates k_2^{obs} shown in Table 3. In the view of the good agreement between k_2^{obs} values obtained by both above methods, all the data were used to calculate the activation parameters. The values of $\Delta H^{\neq} = 17.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\neq} = 1.3 \pm 1$ e.u. were obtained from the linear least-squares fit in Figure 6.

Table 3. Rates of H/η^2-H_2 (or D/η^2-D_2) exchange for complex **2** (k_2^{obs}) and [D_3]**2** (k_{2d}^{obs}).

T/K	k_2^{obs}/s^{-1}	k_{2d}^{obs}/s^{-1}	T/K	k_2^{obs}/s^{-1}
358		130 [c]	313	10.7 [a], 9.4 [b]
353		80 [c]	308	5.8 [b]
348		54 [c]	303	3.9 [a], 3.0 [b]
343		34 [c]	298	2.3 [a], 1.8 [b]
333	64 [b]	14 [c]	293	1.3 [a], 1.4 [b]
328	38 [b]		288	0.8 [a], 0.6 [b]
318	13.5 [b]		283	0.5 [a]

[a] From spin saturation-transfer experiments in the ^{1}H NMR spectra. [b] From T_1 measurements of the ^{1}H NMR signal of the hydrido ligand. [c] From lineshape analysis of the ^{2}H NMR spectra.

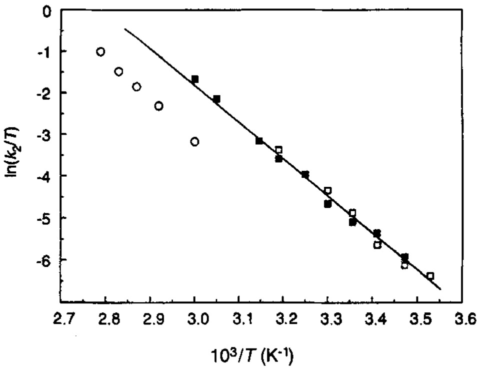


Fig. 6. Eyring plot of the rate constants for H/η^2-H_2 (and D/η^2-D_2) exchange in **2** (k_2^{obs} from spin saturation transfer: □; from T_1 measurements: ■) and [D_3]**2** (k_{2d}^{obs}: ○).

The high-temperature ^{2}H NMR spectra of [D_3]**2** in toluene (Fig. 7) also show the exchange between the deuterido and dideuterium ligands causing line-broadening effects above 333 K. Lineshape analysis of the spectra allow the calculation of the rate constants for this exchange (k_{2d}^{obs}) in a 25 K temperature range (Table 3, Fig. 6). Comparison of data at 333 K gives a first-order isotope effect $k_2^{obs}/k_{2d}^{obs} = 4.6$ for this exchange process.

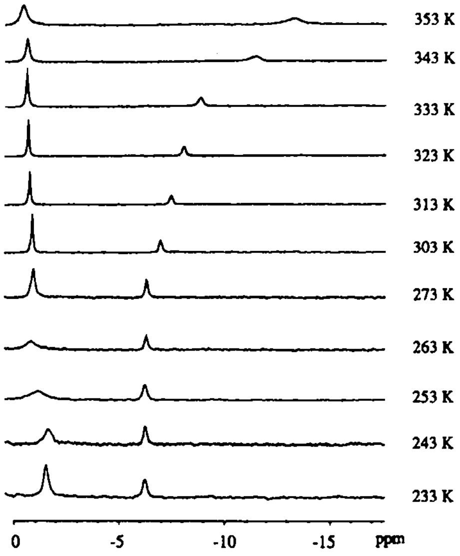
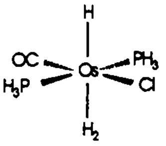


Fig. 7. High-field region of the variable-temperature ^2H NMR spectra of $[D_3]$**2** in toluene.

Theoretical studies: The experimental system is modeled by $[OsHCl(H_2)(CO)(PH_3)_2]$ in the calculations; that is, the experimental P*i*Pr$_3$ ligands are represented by PH_3 in the ab initio calculations, a common substitution. Because of the bulk of the experimental phosphines,[22] we have assumed the two phosphine ligands to be *trans*-disposed; this leaves only three possible stereochemistries for $[OsHCl(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2]$, namely, structures **4**, **5**, and **6**. Each of these structures was used as a starting point of an MP2 geometry optimization.



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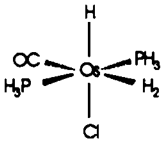

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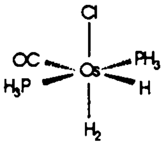

6

Only calculations based on isomers **4** and **5** produced local minima in the potential hypersurface for a complex of type $[OsHCl(\eta^2\text{-}H_2)(CO)(PH_3)_2]$; the final geometries are presented in Figure 8. The optimization of **6** led to a trihydrido complex $[OsH_3Cl(CO)(PH_3)_2]$, which will be discussed later. Isomer **4**, a *trans*-hydridodihydrogen complex, has the lowest energy. Calculations indicate that the reaction in Scheme 2 is exothermic by 11.3 kcal mol^{-1} at the MP2 level and 10.1 kcal mol^{-1} at the MP4 level, which is in good agreement with the above experimental data.

Complex **1** is known to be square-pyramidal, like the geometry of the corresponding fragment of **4**.[23] Complex **4** has C_s symmetry with the Os, Cl, and H(7) atoms in the symmetry plane (not a computational artifact, since no symmetry restrictions were introduced prior to the calculation). Compound **4** is essentially octahedral: the largest distortion from 90° is found for the H(7)-Os-P angles (82.7°). The H–H distance of 0.838 Å, which is in good agreement with that obtained from the NMR experiments, proves beyond doubt that **4** contains a dihydrogen ligand. The distance from the metal to each of the atoms of the dihydrogen unit (1.797 Å) is longer than the metal–hydride distance Os–H(7) (1.564 Å), a common feature in complexes containing both these ligands. The quality of the applied methodology can be tested by comparing the metal–ligand distances in **4** with those in other common osmium complexes.[24] $Os^{II}–PR_3$ bond lengths in complexes containing two mutually *trans* phosphine ligands are typically about 2.4 Å; $Os^{II}–CO$ bond lengths are typically about 1.90 Å. These values are in good agreement with the 2.405 Å for Os–P and 1.864 Å for Os–CO obtained in this calculation. The value for the Os–Cl distance (2.535 Å) also agrees well with those found for chloro–$Os^{II}(\eta^2\text{-}H_2)$ complexes by X-ray diffraction analysis.[25]

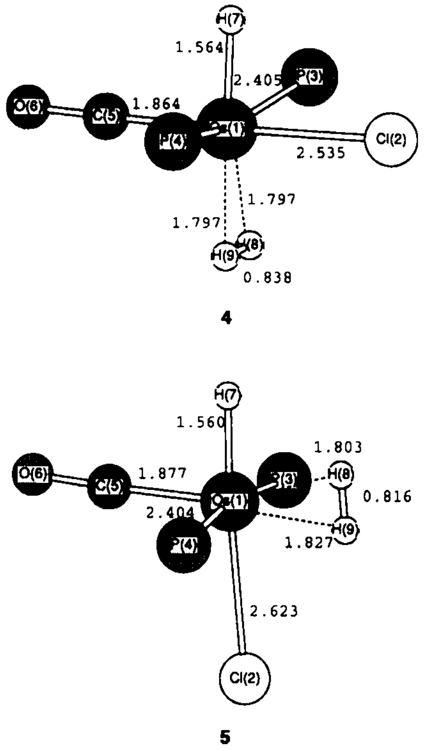

Fig. 8. MP2-optimized geometries of the dihydrogen complexes **4** and **5**. Some selected distances are given in Å. Hydrogen atoms of phosphine ligands are omitted for clarity.

The most noticeable geometric feature of **4** is the orientation of the H(8)–H(9) dihydrogen subunit, which lies in the plane of the P(3)-Os-P(4) moiety. The alignment of the dihydrogen ligand parallel to and of a carbonyl perpendicular to a P-M-P axis was also found in the first characterized dihydrogen complex $[W(\eta^2\text{-}H_2)(CO)_3(P\textit{i}Pr_3)_2]$.[26] The explanation for this arrangement is likewise the same,[27] namely, a strong π-acceptor such as a carbonyl ligand aligned with the dihydrogen ligand would strongly compete for electron backdonation from the metal to the σ* orbital of the dihydrogen molecule. In the context of the orientation of the coordinated dihydrogen, the question of its rotation was also examined. The geometry of the transition state, optimized at the MP2 level, corresponds to the alignment of the hydrogen molecule with the Cl-Os-C(5) axis, with an associated weakening of the metal–H_2 interaction (shortening of H(8)–H(9) to 0.781 Å and lengthening of Os–H(8) and Os–H(9) to ca. 1.94 Å). The energy barrier calculated for this process is 3.4 kcal mol^{-1} (both MP2 and MP4 levels), which is quite high with respect to the reported experimental data for this kind of process.[28]

The geometry of the other stable dihydrogen complex **5** is presented at the bottom of Figure 8; its energy with respect to **4** is 13.8 kcal mol^{-1} at the MP4 level (Table 4). This *cis*-hydridodihydrogen complex with *trans* disposition of the H_2 and CO

Table 4. The relative energies (ΔE, kcal mol^{-1}) of some selected species at the MP2 and MP4 levels. Geometries are optimized at the MP2 level [a].

	4	5	7	8	9	10
ΔE(MP2)	0.0	12.2	2.8	5.1	2.9	12.8
ΔE(MP4)	0.0	13.8	4.9	9.6	4.7	15.6

[a] Total energy of the reference species **4** is −235.53778 hartrees at the MP2 level and −235.61789 hartrees at the MP4 level.

ligands also has a C_s symmetry, with the symmetry plane defined here by Os, Cl, and C(5). Complex **5** is octahedral, with the largest distortion from 90° corresponding to the Cl-Os-C(5) angle (98.2°). The nature of **5** as a dihydrogen complex is also indisputable in view of the H(8)–H(9) distance of 0.816 Å. Complexes **4** and **5** display only small differences in the geometry of the Os, H(8), H(9) triangle, and therefore similar magnitudes for the metal–dihydrogen interaction. However, there is an energy gap of 13.8 kcal mol^{-1} between the two species. This difference in energy might be related to the different stabilities of the ML_5 fragments, which must obviously play a decisive role in the relative energies of [$ML_5(\eta^2\text{-}H_2)$] complexes, as recently discussed in detail in the literature.[29] The presence of a hydrido ligand *trans* to the chloro ligand must be an obvious destabilizing factor for **5**; the hydrido ligand in the ML_5 fragment of **4** is in the apical position.

In isomer **5**, the dihydrogen ligand lies in the symmetry plane of the molecule, parallel to the Cl-Os-H(7) axis and perpendicular to P(3)-Os-P(4). This arrangement was also observed in previously characterized complexes containing a hydrido ligand in the *cis* position. A further feature of this *cis* effect,[30] which has been shown to be a ligand-to-ligand interaction of electrostatic nature, is also present: the coordination of the dihydrogen ligand to the metal is asymmetric (Os–H(8) 1.803 vs. Os–H(9) 1.827 Å), skewed towards the hydride.

It is also worth mentioning the reasons for the nonexistence of complex **6**. The structural difference between **5** and **6** involves the exchange of positions between the carbonyl and chloride ligands. In the absence of substantial *cis* effects, which are not expected for such ligands, the main differences must come from *trans* effects, which are indeed very different. The strong π-electron withdrawing properties of the carbonyl ligand reduce the backdonation into the H_2 σ* orbital in **5**, and the dihydrogen complex is therefore favored over the corresponding dihydrido species. The opposite effect of the π-donor chloride ligand in **6** means that the trihydrido complex is the only stable form for this complex.

The possibility that trihydrido complexes [$OsH_3Cl(CO)(PiPr_3)_2$] exist as local minima in the potential hypersurface was examined, as part of our study into the H/η^2-H_2 exchange mechanism. Hence, the trihydrido complexes studied in detail were those directly related to the hydridodihydrogen compounds **4** and **5**. The results of the MP2 geometry optimizations are represented in Figure 9, and the relative energies are given in Table 4. Species **7**, derived from **4**, is a seven-coordinate pentagonal bipyramid (PBP) with the axial sites occupied by the carbonyl and chloride ligands. Although the H(8)-Os-H(9) angle of 56.3° falls short of the 72° expected for a regular PBP, this coordination polyhedron is clearly the one that best describes this species, from those available for coordination number 7.[31] The fact that this H-Os-H angle is smaller than the ideal value is hardly attributable to a chemical interaction between the two hydrogen atoms, which are separated by 1.503 Å, but seems rather to be related to the smaller electronic cloud of the hydrido ligand. Almost all of the above geometric considerations for **7** can be applied to **8**, also a PBP structure, but with the two phosphine ligands in the axial sites; the smallest bond angles are H(7)-Os-H(8) (55.5°) and H(8)-Os-H(9) (66.2°). Species **8** was also encontered during the failed optimization of the hypothetical hydridodihydrogen **6**.

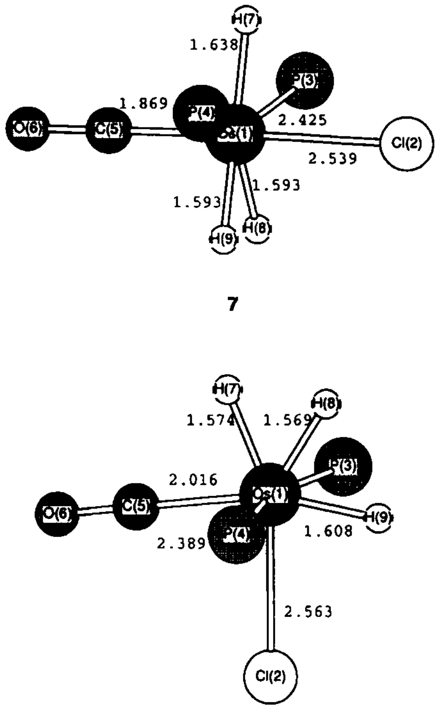

Fig. 9. MP2-optimized geometries of the trihydride complexes **7** and **8**. Some selected distances are given in Å. Hydrogen atoms of phosphine ligands are omitted for clarity.

More significant differences between **7** and **8** appear when their energies are considered with respect to the related dihydrogen complexes. While **7** is higher in energy than **4** (4.88 kcal mol^{-1}, MP4 level), **8** is lower in energy than **5** (by 4.1 kcal mol^{-1}, MP4 level). These differences become more apparent when the transition states **9** and **10** for the corresponding oxidative addition reactions are considered. The MP2 geometries, depicted in Figure 10, yield little of interest. They present intermediate values between those of the respective reactant and product complexes, and are always closer to the species of higher energy, as expected from Hammond's postulate. But the energies in Table 4 cast serious doubts on whether **7** is an authentic local minimum in the more accurate MP4 potential hypersurface. At least, both MP2 geometries for **7** and **9** cannot be accepted as MP4 stationary points, since the transition state **9** would have a lower energy (4.73 kcal mol^{-1}) than that of the product **7** (4.88 kcal mol^{-1}). An energy diagram describing the relative positions of all calculated structures is shown in Figure 11. Theoretical confirmation of the existence of the trihydrido complex **7** would require a computationally expensive geometry optimization at the MP4 level. This has not been carried out, because it does not seem particularly relevant to the problem under discussion. Even without giving a definitive answer on the real existence of a trihydrido complex **7** as a local minimum, the calculations presented here do demonstrate that a species of this geometry would have a low energy, even if it were a transition state. Moreover, despite this failure, the quality of the MP2 potential hypersurface appears acceptable: transition state **9** has an energy of only 0.07 kcal mol^{-1} above that of product **7** at the MP2 level.

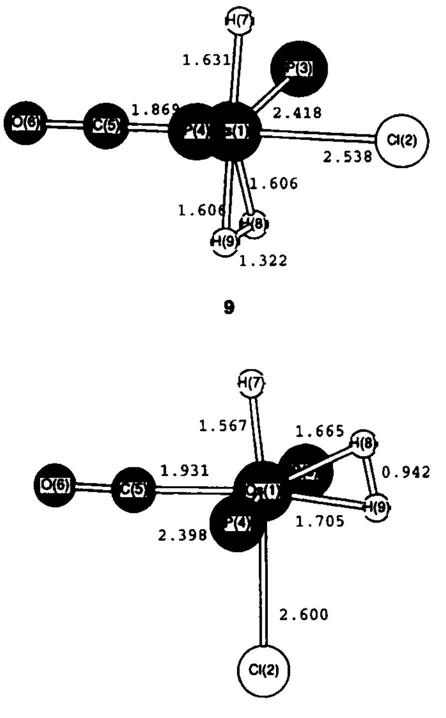

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Fig. 10. MP2-optimized geometry of the transition states **9** and **10**. Some selected distances are given in Å. Hydrogen atoms of phosphine ligands are omitted for clarity.

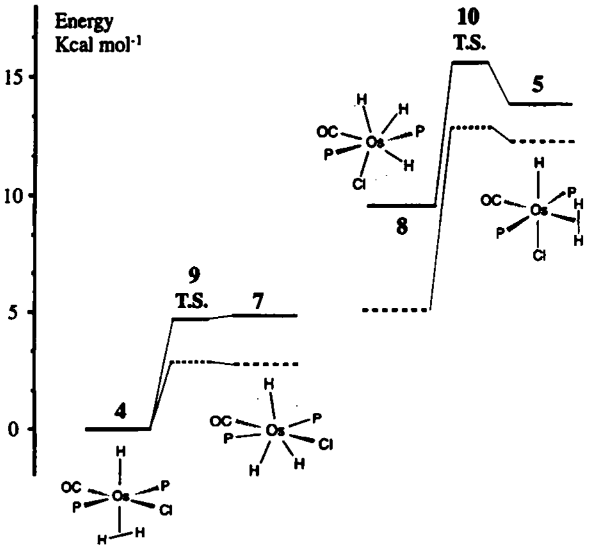


Fig. 11. Relative energies of the calculated structures (MP2, dotted line; MP4, solid line).

Finally, we should comment on the underlying assumption that the two phosphine ligands are *trans*, because of the bulk of the experimental phosphines $PiPr_3$.[22] Possibly, this could be seen as an artificial restriction in the ab initio calculations on the $[OsHCl(\eta^2\text{-}H_2)(CO)(PH_3)_2]$ model, for which these steric effects are conspicuously absent. If the phosphine ligands are allowed to be *cis* to one another, a lower energy species is indeed obtained. A PBP trihydrido complex, with the carbonyl and chloride ligands in axial positions. However, with a P-Os-P angle of 89.0°, this stabilization energy of 7.6 kcal mol^{-1} with respect to **4** would surely be outweighed by the steric repulsion between the two adjacent equatorial phosphine ligands. Therefore, such an arrangement has not been considered for the $[OsHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]$ system, although it could play an important role in experimental systems with less bulky phosphine ligands.

Discussion

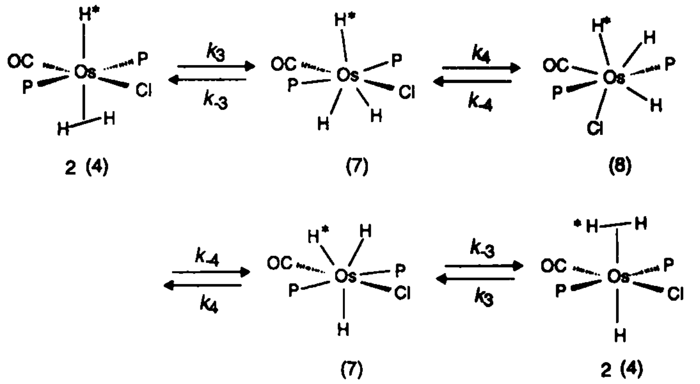
The reaction of complex **1** with H_2 gives the *trans*-hydridodihydrogen complex $[OsHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]$ (**2**) as the only reaction product detectable by NMR spectroscopy. The thermodynamic measurements for formation of **2** [Eq. (2)] give an equilibrium enthalpy of $\Delta H^\circ = -14.1 \pm 0.5$ kcal mol^{-1}, a value substantially higher than that reported for the ruthenium analogue $[RuHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]$ ($\Delta H^\circ = -7.7 \pm 0.2$ kcal mol^{-1} [32]). This result is in agreement with the general trend observed for all the previously reported dihydrogen complexes, namely, that the 5d derivatives always show greater thermodynamic stabilities than the 4d analogues.[1d] The decrease of entropy in this reaction, $\Delta S^\circ = -30 \pm 1$ e.u., is consistent with the expected loss of absolute entropy of free hydrogen (31.2 e.u.[33]). The measurements of the equilibrium constants for the formation of complex $[D_3]$**2** show that the dideuterium complex is more thermodynamically stable than the dihydrogen species.[34] Inverse thermodynamic isotope effects have also been found in the few examples of dihydrogen complexes that have been studied. K_D/K_H values of 2.7 and 2 were found at 260 K for the coordination of H_2 (D_2) to $[IrH_2Cl(PtBu_2Me)_2]$[35] and $[IrHCl_2(PCy_3)_2]$,[36] respectively. This inverse thermodynamic isotope effect is also a common feature for the oxidative addition of H_2/D_2.[37]

The kinetic analysis of the H_2 loss from **2** allows the reaction coordinate for formation of **2** to be determined. From the ΔH° and ΔH^{+} experimental values, an activation enthalpy of 0.5 ± 0.7 kcal mol^{-1} can be calculated for the H_2 binding to complex **1**. This low barrier is in good agreement with the formation of a *trans*-hydridodihydrogen complex, in the view of the square-pyramidal geometry of **1**[23] and the coordination vacancy *trans* to the hydrido ligand. Thus, coordination of H_2 is likely to occur in a one-step mechanism, in which the metallic fragment does not change its ground-state conformation. The activation enthalpy for coordination of H_2 is then in the range expected for a diffusion-controlled reaction. Such observations have also been made for a similar reaction in a dihydrogen–tungsten complex,[38] and for some oxidative addition reactions of H_2 to unsaturated complexes in solution[39] and in the gas phase.[40]

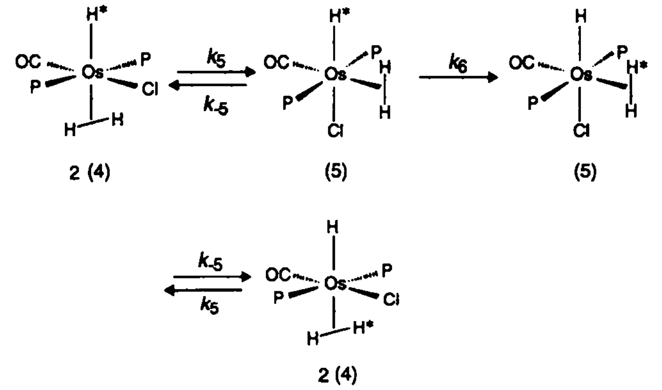
The Eyring analysis of the rate constants obtained for the D_2 loss from complex $[D_3]$**2** gives a positive enthalpy difference of 0.6 ± 0.5 kcal mol^{-1} between the transition states for dissociation of D_2 and H_2. This value, although in the range expected, lies outside the limits of experimental error for these determinations. Also, the k_{-1}/k_{-1d} ratio measured is close to unity in the temperature range studied (Fig. 5), most probably as a result of the opposite signs of ΔH^{+} and ΔS^{+} in the two dissociation reactions.[41] Hence, even though a kinetic isotope effect is expected because of the observed equilibrium isotope effect, and in view of the literature results,[41] we do not believe the experimental data to be fully conclusive.

The variable-temperature $^1H/^2H$ NMR spectra, ^1H T_1 measurements, and saturation-transfer experiments have shown complex **2** to be flexible, since the hydrido/dihydrogen ligand exchange occurs on the NMR timescale at high temperatures. It is remarkable that exchange between *trans*-H and η^2-H_2 ligands have been observed in positively charged complexes of Fe,[1d] Ru,[1d,43] and Os,[1d,44] whereas the neutral *trans*-hydridodihydrogen complexes $[IrHX_2(\eta^2\text{-}H_2)(PiPr_3)_2]$ (X = Cl,[9,29,36] Br[45]) have been reported to be rigid.

Two alternative mechanisms have been so far suggested for the $H/\eta^2\text{-}H_2$ exchange in complexes such as **2**, with reaction pathways through flexible seven-coordinate classical trihydrides[1d,44] (Scheme 4) and flexible *cis* structures[43,46] (Scheme 5). Both mechanisms seem to be reasonable because, according to our theoretical studies, the proposed intermediates correspond to local minima in the potential hypersurface (see structures **5**, **7**, and **8** in Fig. 8 and 9) with energies below the 17.4 kcal mol^{-1} experimental barrier found for the exchange.



Scheme 4.



Scheme 5.

Morris et al.[44] reported that the first step of Scheme 4 (k_3, k_{-3}), involving little heavy-ligand motion, is fast, whereas the second transformation, involving significant motion of these heavy groups (k_4, k_{-4}), is relatively slow. In full accord with this proposal it has been recently demonstrated that hydrido exchange in $[IrH_2Cl(\eta^2\text{-}H_2)(PiPr_3)_2]$, where the heavy-ligand skeleton is conserved, is rapid even in the solid state.[47] This is also in agreement with the low theoretical barrier calculated for the transformation between **4** and **7** (4.7 kcal mol^{-1}, Table 4). In terms of a formal approach and taking into account the above considerations, Scheme 4 leads to the rate law of Equation (6), where k_2^{obs} is the overall reaction rate determined from the NMR spectra. Clearly, no significant primary kinetic isotope effect (KIE) is expected for the second interconversion including the heavy-ligand movements (k_4). The practical absence of KIE was reported for the hydrido/hydrido exchange in octahedral *cis*-$[MH_2P_4]$ (M = Fe, Ru)[48] and *cis*-$[ReH_2(NO)(CO)(PR_3)_2]$.[50] It is also remarkable that a surprisingly small KIE ($k_H/k_D = 1.08$) has been found for the interconversion of the six-coordinate dihydrogen complex $[W(CO)_3(\eta^2\text{-}H_2)(PiPr_3)_2]$ to seven-coordinate $[W(CO)_3(H)_2(PiPr_3)_2]$.[38] Hence, Equation (7) allows the conclusion that the thermodynamic isotope effect (TIE) in the first interconversion could dictate the KIE (k_2^{obs}/k_{2d}^{obs}) for the $H/\eta^2\text{-}H_2$ exchange according to Scheme 4. This conclusion may well be extrapolated to any other mechanistic proposals involving exclusively seven-coordinate osmium(IV) intermediates.

$$\begin{aligned} d[\mathbf{2}]/dt &= -(k_3/k_{-3})k_4[\mathbf{2}] \\ k_2^{obs} &= (k_3/k_{-3})k_4 = K_3k_4 \end{aligned} \tag{6}$$

$$k_2^{obs}/k_{2d}^{obs} \approx K_3/K_{3d} \tag{7}$$

Several tautomeric equilibria have already been studied for transition metal dihydrogen complexes and their ^2H analogues.[1d] It has been found that these equilibria are weakly perturbed on going from ^1H to ^2H isotopes, showing TIE magnitudes between 1.2 (*trans*-$[OsH(\eta^2\text{-}H_2)(dppe)_2]BPh_4$, dppe = 1,2-bis(diphenylphosphino)ethane)[44] and 1.5 ($[ReH_2(\eta^2\text{-}H_2)(CO)(PR_3)_3]^+$)[50] at low temperatures. Taking into account Equation (7), it is now clear that similar values should be expected for the KIE when the $H/\eta^2\text{-}H_2$ exchange operates according to Scheme 4. In this context, it should be noted that the KIE reported by Morris et al. for the $H/\eta^2\text{-}H_2$ exchange in *trans*-$[OsH(\eta^2\text{-}H_2)(dppe)_2]BPh_4$ was 1.4 ± 0.2,[44] which can be compared with the TIE of 1.2 found for the corresponding tautomeric equilibrium.

The variable-temperature $^1H/^2H$ NMR studies of the hydrido/dihydrogen exchange in **2** and $[D_3]$**2** have shown an unusually large KIE (k_2^{obs}/k_{2d}^{obs}) of 4.6 at high temperatures. According to the above-mentioned literature data, this large KIE cannot be rationalized in terms of a mechanism involving only trihydridoosmium(IV) intermediates such as those shown in Scheme 4. Thus, let us formally consider the mechanism shown in Scheme 5.

Apart from the cationic complexes already mentioned, some neutral *trans*-hydridodihydrogen complexes of formula $[IrHX_2(\eta^2\text{-}H_2)(PiPr_3)_2]$[9,29,36,45] have been reported. They have rigid structures in solution, but the corresponding *cis*-hydridodihydrogen compounds of the same formula[29,45] give single averaged resonances in the hydrido region of the ^1H NMR spectra, due to the very fast $H/\eta^2\text{-}H_2$ exchange even at the lowest temperatures. The positively charged *cis*-$[OsH(\eta^2\text{-}H_2)(PP_3)]BPh_4$ ($PP_3 = P(CH_2CH_2PPh_2)_3$)[51] also shows fast $H/\eta^2\text{-}H_2$ exchange with a $\Delta H^{\neq}$ barrier of 7.6 kcal mol^{-1}. According to theoretical data, these low barriers can be attributed to the direct hydrogen transfer mechanism.[46] Our ab initio calculations of the model system $[OsH_3Cl(CO)(PiPr_3)_2]$ show that one of the local minima in the potential hypersurface is occupied by the *cis* compound **5**, with a relative energy of 13.8 kcal mol^{-1} (Table 4). As this energy lies well below the experimental energy barrier of 17.4 kcal mol^{-1} determined for $H/\eta^2\text{-}H_2$ exchange in *trans* complex **2**, the mechanism shown in Scheme 4 constitutes a feasible path for this exchange, at least from the energetic point of view.

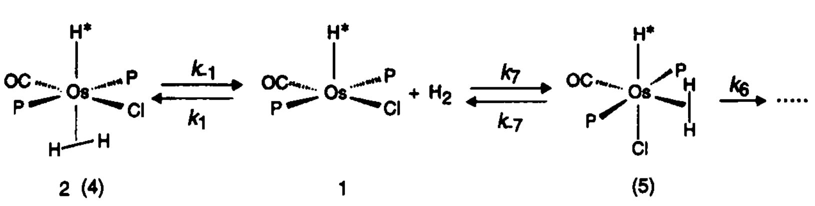
In addition, Scheme 5 resembles a previously reported sequence for the reaction of complex **1** with the alkyne $MeO_2CC{\equiv}CCO_2Me$.[5b] The initial product of the reaction is the *trans*-hydrido-η^2-alkyne, which slowly isomerizes to the detectable *cis*-hydrido-η^2-alkyne; this is followed by an insertion reaction to give a vinyl derivative.

The experimental and theoretical data collected in the present work allow us to postulate that the mechanism in Scheme 5 is a main pathway for the hydrido/dihydrogen exchange in complex **2**. In the absence of the direct detection of the postulated *cis* complex, because of its expected very small equilibrium concentration (see the relative energies of **4** and **5** in Table 4), and without the knowledge of how it forms, further discussion seems to be speculative. Nevertheless, we would like to give possible explanations for the above-mentioned large KIE, which cannot be ignored.

In view of the low energies involved in the exchange processes occurring in *cis*-hydridodihydrogen complexes, the expected slow step of the mechanism in Scheme 5 is likely to be the first, namely, the *trans–cis* isomerization. In related systems it has been proposed that direct reaction of five-coordinate species such as **1** with H_2 can also lead to *cis*-hydridodihydrogen complexes in spite of the *trans* disposition of the hydrido ligand relative to the vacant coordination site in the five-coordinate precursors.[29, 52] If we follow this line, irrespective of the concrete pathway of this reaction, the formal transformations shown in Scheme 6 should be considered as a possible reaction sequence, in view of the energy measured for the H_2 loss from **2**. Thus, an analysis of this mechanism assuming $k_6 \gg k_{-7}$ gives the rate law in Equation (8), and an expression for the KIE

$$k_2^{\text{obs}} = k_7(k_{-1}/k_1) = k_7/K$$
$$k_2^{\text{obs}}/k_{2d}^{\text{obs}} = (k_7/k_{7d})(K_d/K) \qquad (8)$$

which includes the TIE (K_d/K) for the formation of **2**. Consequently, relatively high values of KIE could be expected in view of the observed TIE values ($K_d/K \approx 2.8$). The ΔS^{+} value for the hydrido/dihydrogen exchange determined from NMR measurements has been found to be close to zero (1.3 ± 1 e.u.). In Scheme 6, this value could result from summation of the positive ΔS° found for the first equilibrium and a negative ΔS^{+} expected for the formation of *cis* complex **2**.



Scheme 6.

An alternative interpretation of the mechanism in Scheme 5, which cannot be excluded, is that the second step (k_6) has an energy barrier comparable to that of the *cis–trans* isomerization (k_{-5}). In this case $k_2^{\text{obs}} = k_5k_6/(k_{-5} + k_6)$. In such a mechanism the exchange step (k_6) could itself explain the KIE. The theoretical calculations on iron complexes have shown the direct hydrogen transfer mechanism[46] to be the most likely for the hydrogen exchange in *cis*-hydridodihydrogen complexes, where the calculated energies for this transformation are about 3 kcal mol^{-1}. The sum of this value and the energy calculated for formation of *cis* complex **5** (13.8 kcal mol^{-1}) is in good agreement with the experimental barrier measured for the exchange in complex **2**. In view of the characteristics of the direct hydrogen transfer mechanism, which involves a direct transfer of mass, a first-order KIE is expected for the step defined by the rate constant k_6, although there is no experimental data available at present.[53] In addition, because of the intramolecular character of this transformation, a value close to zero for ΔS^{+} is expected, in agreement with the experimental measurements.

Conclusion

This work provides experimental and theoretical evidence that the reaction of H_2 with complex **1** leads to *trans*-hydridodihydrogen complex **2** as the most stable product among all the possible hydridodihydrogen or trihydrido species. This complex contains a fast-spinning dihydrogen ligand with an H–H distance of 0.8 Å (within the limits of the T_1 NMR approach). The fast-spinning nature of the η^2-H_2 ligand in **2** has been established by estimating the deuterium quadrupole coupling constant (DQCC) in the η^2-D_2 ligand of complex [D_3]**2** (149 kHz). The thermodynamic measurements for formation of **2** [Eq. (2)] give values of $\Delta H^{\circ} = -14.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\circ} = -30 \pm 1$ e.u. and show an equilibrium isotope effect K_d/K of about 2.8 at 323 to 353 K. The kinetic analysis of the H_2 loss from **2** ($\Delta H^{+} = 14.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{+} = 9.9 \pm 0.5$ e.u.) allows an activation enthalpy of 0.5 ± 0.7 kcal mol^{-1} to be determined for the H_2 coordination to complex **1**. This low barrier corresponds to diffusion-controlled rates for coordination of H_2. The variable-temperature ^{1}H and ^{2}H NMR spectra, ^{1}H T_1 measurements, and saturation-transfer experiments have shown that hydrido/dihydrogen ligand exchange in complex **2** occurs on the NMR timescale at high temperatures ($\Delta H^{+} = 17.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{+} = 1.3 \pm 1$ e.u.). In order to rationalize the unusually large kinetic isotope effect ($k_2^{\text{obs}}/k_{2d}^{\text{obs}}$) of 4.6 observed at high temperature, an exchange mechanism via a nonclassical *cis*-hydridodihydrogen complex has been suggested. According to the ab initio calculations, one of the local minima in the potential hypersurface of the model system [$OsH_3Cl(CO)(PH_3)_2$] is actually occupied by the *cis* compound **5** with *trans* disposition of the CO and η^2-H_2 ligands.

Experimental Procedure

General Data: All manipulations were performed under H_2, D_2, or Ar atmosphere by standard techniques. NMR data were obtained on Varian UNITY 300 and Bruker ARX-300 spectrometers. Toluene and [D_8]toluene were dried over Na/K alloy and freshly distilled before use. The temperature of the NMR experiments was calibrated by ^{1}H NMR with a standard methanol sample. ^{1}H NMR chemical shifts were measured relative to the residual toluene methyl resonance ($\delta = 2.09$) and are reported relative to TMS. ^{2}H NMR chemical shifts were measured relative to the natural abundance toluene methyl resonance ($\delta = 2.1$). ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. Coupling constants are given in Hz. The relaxation times T_1 were obtained by a conventional inversion-recovery method. The calculations of the relaxation times and errors were performed using the fitting routine of the Varian UNITY 300 spectrometer. The mean values obtained are collected in Table 5. Adjustment of the experimental T_1 times to Equations (1) and (2) were performed using standard programs for nonlinear fittings. Complexes [$OsHCl(CO)(PiPr_3)_2$] (**1**) [22], [$OsDCl(CO)(PiPr_3)_2$] ([D]**1**) [5b], [$OsHCl(\eta^2$-$H_2)(CO)(PiPr_3)_2$] (**2**) [5b], [$OsDCl(\eta^2$-$D_2)(CO)(PiPr_3)_2$] ([D_3]**2**) [6], and [$OsHCl(O_2)(CO)(PiPr_3)_2$] (**3**) [5b] were prepared as described in the literature.

Measurements of the equilibrium constants *K* and *K*$_d$: Mixtures of complexes **1** and **2** (or mixtures of [D]**1** and [D_3]**2**) were prepared by bubbling H_2 (or D_2) into an NMR tube containing [D_8]toluene (or toluene) solutions of complex **1** (or [D]**1**) at ca. 310 K for 5 min. The solution was frozen and the tube sealed. The relative concentrations of H_2, **1**, and **2** were evaluated by ^{1}H NMR above the coalescence temperature to avoid the integration of strongly broadened lines. The [**2**]/[**1**] ratios were determined by means of the chemical shift of the exchange-averaged hydrido resonances [Eq. (9)]. It then follows that [**2**]/[**1**] = $x/(1-x)$. In addition, as **1** and **2**

$$\delta = x\delta(\text{HOs-}\mathbf{2}) + (1-x)\delta(\text{HOs-}\mathbf{1}) \qquad (9)$$

are the only metallic species present in solution: [**2**] + [**1**] = [**1**]$_0$, where [**1**]$_0$ is the initial concentration of **1** before addition of H_2. This allows the equilibrium concentrations [**2**] and [**1**] to be calculated at any temperature. The [**2**]/[H_2] ratios were given by the chemical shifts of the exchange-averaged dihydrogen resonances [Eq. (10)].

$$\delta' = y\delta(\eta^2\text{-}H_2) + (1-y)\delta(H_2) \qquad (10)$$

Table 5. Spin-lattice relaxation times (ms) of the hydrido (deuterido) and dihydrogen (dideuterium) ligands of complexes **2**, [D_3]**2**, and **3**.

	2		**3**	[D_3]**2**	
T/K	η^2-H_2	Os-H	Os-H	Os-D	η^2-D_2
183				11	13
188				10	12
193	14	346		9	11
198	13	327		9	15
203	9.5	310	354	15	18
208	7.9	307		19	25
213	6.5	296	286	24	31
218	6.4	301		25	36
223	6.2	319		26	52
228				36	71
233	6.8	370	335	51	72
238				68	79
243	8.1	443			
253	9.5	556	488		
263	11	708	620		
268	12	770	640		
273	13	820	748		
278	15	880	834		
283	17	886	918		
288	18	879	1018		
293	21	856	1100		
298	22	778	1231		
303	24	665	1258		
308	28	458	1419		
313	30	341	1453		
318	32	250			
323	39	202			
328	45	166			
333	53	138			
338	62	109			
343	72	105			
348	84	117			

Thus, the ratio [**2**]/[H_2] = $y/(1-y)$ permitted the free H_2 concentration to be calculated and the equilibrium constant K = [**2**]/[**1**][H_2].

The data shown in Table 1 were obtained from three samples containing different concentrations of dissolved hydrogen. Owing to the slow evolution of H_2 in solution, the spectra were recorded repeatedly until the chemical shifts of the signals remained constant. The chemical shifts of the nonaveraged signals were measured at 200 K (δ(HOs-**2**) = − 6.54; $\delta(\eta^2$-$H_2)$ = −1.79; δ(HOs-**1**) = − 32.50; $\delta(H_2)$ = 4.55). Similar calculations were carried out on the averaged ^{2}H NMR signals in the determination of K_d. ^{2}H NMR chemical shifts of the nonaveraged signals were also measured at 200 K (δ(DOs-**2**) = − 6.5; $\delta(\eta^2$-$D_2)$ = −1.8; δ(DOs-**1**) = − 32.0; $\delta(D_2)$ = 4.5).

ΔH° and ΔS° were calculated by least-squares fit of ln(K) vs. $1/T$. Error analysis assumes a 10% error in the equilibrium constant value and a 1 K error in temperature. Errors were computed by standard error propagation formulae for least-squares fitting [54].

Measurements of the dissociation rates k_{-1} and k_{-1d}: The Samples used were similar to those employed in the evaluation of equilibrium constants (see above). The rates of H_2 loss from **2** (k_{-1}) were measured by a conventional lineshape analysis of the ^{1}H NMR spectra using the DNMR6 program (QCPE, Indiana University). The values of T_2 for the hydrido signal of **1** were determined for all temperatures recorded in a sample of pure **1** in [D_8]toluene. The value of T_2 for the hydrido signal of **2** was taken from the 200 K spectrum, at which temperature the exchange was stopped. The T_2 for the η^2-H_2 and the free hydrogen signals were also measured at this temperature, but varied during the simulation to fit the experimental lines.

Rates of D_2 loss from [D_3]**2** were determined by lineshape analysis of the ^{31}P NMR spectra of mixtures of [D]**1** and [D_3]**2** in [D_8]toluene under D_2. Relaxation times T_2 and J_{PD} coupling constants were taken from the 200 K spectrum. The activation parameters, ΔH^* and ΔS^*, were obtained from a linear least-squares fit of ln(k/T) vs. $1/T$ (Eyring equation). Errors were computed by published methods [55] assuming a 10% error in the rate constants. The error in temperature was assumed to be 1 K.

Measurements of the exchange rates k_2^{obs} and k_{2d}^{obs}: The samples were prepared by bubbling H_2 (or D_2) into an NMR tube containing a [D_8]toluene (or toluene) solution of complex **1** (or [D]**1**) at 273 K until the solutions became colorless. Then the solution was frozen and the tube sealed. Spin saturation-transfer experiments were carried out according to the Forsén-Hoffman method [21]. Experiments were performed by saturating the resonance of the η^2-H_2 ligand and measuring the intensity of the hydrido resonance. The exchange rates k_2^{obs} were calculated from Equation (11) [56], where I' and I are the signal intensities of the terminal hydride

$$k = (1/T_1)((I/I') - 1) \tag{11}$$

with and without saturation of the η^2-H_2 resonance, respectively. T_1 is the spin-lattice relaxation time of the hydrido signal obtained by the inversion-recovery method in the presence of the saturating field at the η^2-H_2 ligand signal [57]. The ratio I'/I was calculated from the difference spectrum recorded by substracting the spectrum irradiated at the dihydrogen resonance from the nonirradiated spectrum. The activation parameters, ΔH^* and ΔS^*, were obtained from a linear least-squares fit of ln(k/T) vs. $1/T$ (Eyring equation). Errors were computed by published methods [55]. The error in temperature was assumed to be 1 K; the error in k_2 was estimated to be 10%.

Computational details: All calculations were performed with the GAUSSIAN 92 system of programs [58] with a molecular orbital ab initio method with introduction of correlation energy through the Moller-Plesset (MP) perturbation approach [59], excluding excitations concerning the lowest energy electrons (frozen-core approach). Effective core potentials (ECP) were used to represent the 60 innermost electrons of the osmium atoms [60], as well as the ten-electron core of each of the phosphorus and chlorine atoms [61]. The basis set used for the metal atom was that associated to the pseudopotential [60] with a (541/41/111) contraction [62], which is triple-ζ for the 5d shell. A somewhat extended 6-31G** basis set was used for the hydrogen atoms directly attached to it [63]. For the spectator ligands phosphine, chloride, and carbonyl, a valence double-ζ basis set was used. That associated to the ECP's in the case of the heavy atoms phosphorus and chlorine [61], and 3-21G for hydrogen, carbon and oxygen [64].

Geometry optimizations were carried out at the second level of the Moller-Plesset theory (MP2). All geometrical parameters were optimized except the dihedral angle of one of the hydrogen atoms of each phosphine, which was fixed to be oriented towards one of the hydrido substituents. This was done to avoid chemically meaningless rotations around the M-P angles. Single-point energy-only calculations were carried out at a higher computational level with the MP2 optimized geometries. This was the fourth level of the same perturbational theory (MP4), with consideration of single, double, triple, and quadruple excitations.

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[1] a) G. J. Kubas, *Comments Inorg. Chem.* **1988**, *7*, 17; b) G. J. Kubas, *Acc. Chem. Res.* **1988**, *21*, 120; c) R. H. Crabtree, *ibid.* **1990**, *23*, 95; d) P. G. Jessop, R. H. Morris, *Coord. Chem. Rev.* **1992**, *121*, 155; e) R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789; f) D. M. Heinekey, W. J. Oldham, *Chem. Rev.* **1993**, *93*, 913.

[2] C. Daniel, N. Koga, J. Han, X. Y. Fu, K. Morokuma, *J. Am. Chem. Soc.* **1988**, *110*, 3773.

[3] a) C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas, L. A. Oro, *Organometallics* **1992**, *11*, 138; b) M. A. Esteruelas, J. Herrero, A. M. López, L. A. Oro, M. Schulz, H. Werner, *Inorg. Chem.* **1992**, *31*, 4013.

[4] a) R. H. Crabtree, *Inorg. Chim. Acta.* **1986**, *125*, L7; b) D. E. Linn, J. Halpern, *J. Am. Chem. Soc.* **1987**, *109*, 2969; c) C. Hampton, W. R. Cullen, B. R. James, *ibid.* **1988**, *110*, 6918; d) E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein, K. G. Caulton, *ibid.* **1990**, *112*, 855; e) C. Bianchini, C. Bohanna, M. A. Esteruelas, P. Frediani, A. Meli, L. A. Oro, M. Peruzzini, *Organometallics* **1992**, *11*, 3873.

[5] a) M. A. Esteruelas, E. Sola, L. A. Oro, U. Meyer, H. Werner, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1563; b) A. Andriollo, M. A. Esteruelas, U. Meyer, L. A. Oro, R. A. Sánchez-Delgado, E. Sola, C. Valero, H. Werner, *J. Am. Chem. Soc.* **1989**, *111*, 7431.

[6] M. A. Esteruelas, L. A. Oro, C. Valero, *Organometallics* **1992**, *11*, 3362.

[7] a) M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. F. Schwitzer, A. Sella, *J. Am. Chem. Soc.* **1988**, *110*, 7031; b) P. J. Desrosiers, L. Cai, Z. Lin, R. Richards, J. Halpern, *ibid.* **1991**, *113*, 4173; c) X. Luo, H. Lui, R. H. Crabtree, *Inorg. Chem.* **1991**, *30*, 4740; d) D. G. Gusev, A. B. Vymenits, V. I. Bakhmutov, *Inorg. Chem.* **1991**, *30*, 3116; e) D. G. Gusev, D. Nietlispach, A. B. Vymenits, V. I. Bakhmutov, H. Berke, *ibid.* **1993**, *32*, 3270.

[8] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University, New York, 1971.

[9] V. I. Bakhmutov, E. V. Vorontsov, A. B. Vymenits, *Inorg. Chem.* **1995**, *34*, 214.

[10] The relaxation rate of the H_2 ligand can be described by Equation (12), where

$$1/T_{1\min}(\mathrm{obs}) = 1/T_{1\min}(\mathrm{H}\cdots\mathrm{H}) + 1/T_{1\min}(\mathrm{other}) \tag{12}$$

the contribution $1/T_{1\min}$(other) is caused by dipole–dipole interactions between the H_2 ligand and the phosphorus groups. In the case of the proton-rich PPh_3 ligands of complex $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$, the contribution of $1/T_{1\min}$(other) has been estimated to be between 7 and 12 s^{-1}. Thus, this contribution can be ignored when the T_1 times of the H_2 ligands are short. See: D. G. Gusev, A. B. Vymenits, V. I. Bakhmutov, *Inorg. Chim. Acta* **1991**, *179*, 195.

[11] The fitting procedure of the dihydrogen resonance experimental points to Equation (1) results in reasonable effective values of E_a (3.8 kcal mol^{-1}) and τ_0 (0.7 10^{-3} s), which compare well with the parameters obtained from the ^{1}H T_1 data collected for the hydrido ligands of complexes **2** and **3** ($E_a = 3.2$ and 3.3 kcal mol^{-1}, $\tau_0 = 1.7\ 10^{-3}$ and 1.4 10^{-3} s for **2** and **3**, respectively), and with those known for Re, Mn (ref. [7d]) and Os (ref. [7a,b]) hydrido complexes. The fitting of the T_1 data obtained for the hydrido ligands of complexes **2** and **3** to Equation (1) gives the effective, and meaningless, r_{HH} values equal to 1.84 Å.

[12] D. Nietlispach, V. I. Bakhmutov, H. Berke, *J. Am. Chem. Soc.* **1993**, *115*, 9191.

[13] The η value equal to 0 was used in fitting procedures, which is only valid for terminal hydrides. See: a) I. Y. Wei, B. M. Fung, *J. Chem Phys.* **1971**, *55*, 1486; b) W. L. Jarrett, R. D. Farlee, L. G. Butler, *Inorg. Chem.* **1987**, *26*, 1381.

[14] An E_a of 4.8 kcal mol^{-1} are found for both the D and η^2-D_2 ligands. This value seems to be significantly higher than those calculated for complex **2** from ^{1}H T_1 data (ref. [11]). The same effect has been noted earlier for toluene solutions of Re, W, and Mn deuterido complexes, and discussed in terms of solute/solvent interactions at low temperature (ref. [12]).

[15] H. Guo, W. L. Jarrett, L. G. Butler, *Inorg. Chem.* **1987**, *26*, 3001.

[16] J. A. S. Smith, *J. Chem. Educ.* **1971**, *48*, 39.

[17] G. J. Kubas, C. I. Unkefer, B. I. Swanson, E. Fukushima, *J. Am. Chem. Soc.* **1986**, *108*, 7000.

[18] a) D. E. Woessner, *J. Chem. Phys.* **1962**, *36*, 1; b) D. E. Woessner, B. S. Snowden Jr., G. H. Meyer, *ibid.* **1969**, *50*, 719.

[19] A. A. Vashman, I. S. Pronin, *Relaxation NMR Spectroscopy*; Moscow, **1986**, p. 178.

[20] Free hydrogen T_1 times were obtained from ref. [9].

[21] J. W. Faller in *Determination of Organic Structures by Physical Methods* (Eds.: F. C. Nachod, J. J. Zucherman), Academic Press, New York, **1973**.

[22] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.

[23] a) A. R. Rossi, R. Hoffmann, *Inorg. Chem.* **1975**, *14*, 365; b) I. E.-I. Rachidi, O. Eisenstein, Y. Jean, *New J. Chem.* **1990**, *14*, 671; c) M. A. Esteruelas, H. Werner, *J. Organomet. Chem.* **1986**, *303*, 221; d) J. T. Poulton, M. P. Sigalas, K. Folting, W. E. Streib, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1994**, *33*, 1476.

[24] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1.

[25] M. A. Esteruelas, F. J. Lahoz, L. A. Oro, E. Oñate, N. Ruiz, *Inorg. Chem.* **1994**, *33*, 787.

[26] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman, *J. Am. Chem. Soc.* **1984**, *106*, 451.

[27] a) Y. Jean, O. Eisenstein, F. Volatron, B. Maouche, F. Sefta, *J. Am. Chem. Soc.* **1986**, *108*, 6587; b) P. J. Hay, *ibid.* **1987**, *109*, 705.

[28] a) J. Eckert, A. Albinati, R. P. White, C. Bianchini, M. Peruzzini, *Inorg. Chem.* **1992**, *31*, 4241; b) G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson, O. Eisenstein, *J. Am. Chem. Soc.* **1993**, *115*, 569.

[29] A. Albinati, V. I. Bakhmutov, K. G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D. G. Gusev, V. V. Grushin, B. E. Hauger, W. T. Klooster, T. F. Koetzle, R. K. McMullan, T. J. O'Loughlin, M. Pélissier, J. S. Ricci, M. P. Sigalas, A. B. Vymenits, *J. Am. Chem. Soc.* **1993**, *115*, 7300.

[30] a) L. S. Van der Sluys, J. Eckert, O. Eisenstein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. F. Koetzle, G. J. Kubas, P. J. Vergamini, K. G. Caulton, *J. Am. Chem. Soc.* **1990**, *112*, 4831; b) F. Maseras, M. Durán, A. Lledós, J. Bertrán, *ibid.* **1991**, *113*, 2879; c) J. F. Riehl, M. Pélissier, O. Eisenstein, *Inorg. Chem.* **1992**, *31*, 3344.

[31] a) E. L. Muetterties, L. J. Guggenberger, *J. Am. Chem. Soc.* **1974**, *96*, 1748; b) M. G. B. Drew, *Prog. Inorg. Chem.* **1977**, *23*, 67; c) R. Hoffmann, B. G. Beier, E. L. Muetterties, A. R. Rossi, *ibid.* **1977**, *16*, 511.

[32] D. G. Gusev, A. B. Vymenits, V. I. Bakhmutov, *Inorg. Chem.* **1992**, *31*,1.

[33] *Handbook of Chemistry and Physics*, 66th ed., Chemical Rubber Co., **1985**.

[34] In view of the relatively large scattering of the experimental K_d points in Figure 4, we decided not to calculate the equilibrium parameters ΔH° and ΔS° for $[D_3]$**2**.

[35] B. E. Hauger, D. Gusev, K. G. Caulton, *J. Am. Chem. Soc.* **1994**, *116*, 208.

[36] D. Gusev, V. I. Bakhmutov, V. V. Grushin, M. E. Vol'pin, *Inorg. Chim. Acta* **1990**, *177*, 115.

[37] a) D. Rabinovich, G. Parkin, *J. Am. Chem. Soc.* **1993**, *115*, 353; b) M. J. Hostetler, R. G. Bergman, *ibid.* **1992**, *114*, 7629.

[38] K. Zhang, A. A. Gonzalez, C. D. Hoff, *J. Am. Chem. Soc.* **1989**, *111*, 3627.

[39] C. Hall, W. D. Jones, R. J. Mawby, R. Osman, R. N. Perutz, M. K. Whittlesey, *J. Am. Chem. Soc.* **1992**, *114*, 7425.

[40] E. P. Wasserman, C. B. Moore, R. G. Bergman, *Science* **1992**, *255*, 315.

[41] The different entropy changes at the transition state ΔS^* strongly influence the relative positions of the temperature dependence of $\ln k$ vs. $1/T$ (Eyring plots), and therefore the k_H/k_D ratio. Thus, values of 1.8 (ref. [35]), 5 (ref. [42]) or 7 (ref. [36]) have been found for k_H/k_D in reactions where H_2 dissociates from dihydrogen complexes, in spite of the similar, and always small, enthalpy difference between the transition states for H_2 and D_2.

[42] S. P. Church, F. W. Grevels, H. Hermann, K. Schaffner, *J. Chem. Soc. Chem. Commun.* **1985**, 30.

[43] M. Ogasawara, M. Saburi, *J. Organomet. Chem.* **1994**, *482*, 7.

[44] K. A. Earl, G. Jia, P. A. Maltby, R. H. Morris, *J. Am. Chem. Soc.* **1991**, *113*, 3027.

[45] V. I. Bakhmutov, A. B. Vymenits, V. V. Grushin, *Inorg. Chem.* **1994**, *33*, 4413.

[46] F. Maseras, M. Durán, A. Lledós, J. Bertran, *J. Am. Chem. Soc.* **1992**, *114*, 2922.

[47] L. L. Wisniewski, M. Mediati, M. C. Jensen, K. W. Zilm, *J. Am. Chem. Soc.* **1993**, *115*, 7533.

[48] P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, E. L. Muetterties, *J. Am. Chem. Soc.* **1970**, *92*, 3482.

[49] V. I. Bakhmutov, T. Bürgi, P. Burger, H. Ruppli, H. Berke, *Organometallics* **1994**, *13*, 4203.

[50] a) D. G. Gusev, D. Nietlishpach, I. Z. Eremenko, H. Berke, *Inorg. Chem.* **1993**, *32*, 3628; b) X. L. Luo, R. H. Crabtree, *J. Am. Chem. Soc.* **1990**, *112*, 6912.

[51] C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca, F. Zanobini, *Inorg. Chem.* **1993**, *32*, 2366.

[52] J. T. Poulton, M. P. Sigalas, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1993**, *32*, 5490.

[53] Only one case of KIE for hydrido/dihydrogen exchange has been previously reported. A KIE of 2 at 183 K has been found for the exchange in the dihydridodihydrogen complex $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_3)_3]^+$. However, a mechanism involving tetrahydrido intermediates has been proposed (ref. [50a]).

[54] P. R. Bevington, *Data reduction and Error Analysis for the Physiscal Sciences*, Mc Graw-Hill, New York, **1969**, Chapter 4.

[55] P. M. Morse, M. O. Spencer, S. R. Wilson, G. S. Girolami, *Organometallics* **1994**, *13*, 1646.

[56] J. K. M. Sanders, B. K. Hunter, *Modern NMR Spectroscopy, A Guide for Chemists*, 2nd ed., Oxford University Press, **1993**.

[57] B. E. Mann, *J. Magn. Res.* **1977**, *25*, 91.

[58] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, N. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andrés, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. De Frees, J. Baker, J. J. P. Stewart, J. A. Pople, GAUSSIAN 92 (Gaussian Inc., Pittsburg PA, 1992).

[59] C. Moller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.

[60] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[61] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284.

[62] Z. Lin, M. B. Hall, *J. Am. Chem. Soc.* **1992**, *114*, 2928.

[63] a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; b) P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213.

[64] J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939.

0947-6539/96/0207-0825 $ 15.00+.25/0