^{1}H- and ^{2}H-T_1 Relaxation Behavior of the Rhodium Dihydrogen Complex [(Triphos)Rh(η^2-H_2)H_2]$^+$

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Protonation of the classical trihydride [(triphos)RhH_3] (**2**) at 210 K in either THF or CH_2Cl_2 by either HBF_4·OMe_2 or CF_3SO_2OH gives the nonclassical η^2-H_2 complex [(triphos)Rh(η^2-H_2)H_2]$^+$ (**1**) [triphos = MeC(CH_2PPh_2)$_3$]. Complex **1** is thermally unstable and highly fluxional in solution. In THF above 230 K, **1** transforms into the solvento dihydride complex [(triphos)Rh(η^1-THF-d_8)H_2]$^+$ (**5**) that, at room temperature, quickly converts to the stable dimer *trans*-[{(triphos)RhH}$_2$(μ-H)$_2$]$^{2+}$ (*trans*-**6**). In CH_2Cl_2, **1** is stable up to 240 K. Above this temperature, the η^2-H_2 complex begins to convert into a mixture of *trans*- and *cis*-**6**, which, in turn, transform into the bridging-chloride dimers *trans*- and *cis*-[{(triphos)RhH}$_2$(μ-Cl)$_2$]$^{2+}$ at room temperature. Complex **1** contains a fast-spinning H_2 ligand with a T_{1min} of 38.9 ms in CD_2Cl_2 (220 K, 400 MHz). An NMR analysis of the bis-deuterated isotopomer [(triphos)RhH_2D_2]$^+$ (**1**-d_2) did not provide a J(HD) value. At 190 K, the perdeuterated isotopomers [(triphos)-RhD_3] (**2**-d_3) and **1**-d_4 show T_{1min} values of 16.5 and 32.6 ms (76.753 MHz), respectively, for the rapidly exchanging deuterides. An analogous 2-fold elongation of T_{1min} is also observed on going from [(triphos)IrD_3] to [(triphos)-Ir(η^2-D_2)D_2]$^+$. A rationale for the elongation of T_{1min} in nonclassical polyhydrides is proposed on the basis of both the results obtained and recent literature reports.

Introduction

Kubas et al. first recognized in 1984 the existence of the η^2-H_2 ligand coordinated in the complexes M(η^2-H_2)(CO)$_3$(P^iPr_3)$_2$ (M = Mo, W).[1] Since then, more than 200 dihydrogen complexes have been prepared with metal ions from groups 4, 5, 6, 7, 8, 9, and 10.[2,3] However, only two authentic rhodium(III) derivatives are known, namely, the isolated complex [$Tp^{Me2}RhH_2$(η^2-H_2)] and the unstable derivative [$TpRhH_2$(η^2-H_2)] described by Venanzi et al. and by Heinekey et al., respectively [Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate; Tp = hydridotris(pyrazolyl)borate].[4−6] A third, highly fluxional, Rh(I) complex, [(PP_3)RhH_2]$^+$,[7] was postulated to contain a dihydrogen ligand in solution, but this formulation was later questioned on the basis of the absence of detectable J(HD) coupling in the deuterium-hydride isotopomer [PP_3 = P($CH_2CH_2PPh_2$)$_3$].[8,9]

The scarcity of rhodium dihydrogen complexes in the literature is highly intriguing, as rhodium is the essential ingredient in most homogeneous and heterogeneous hydrogenation catalysts. Moreover, several hydrogenation reactions have been postulated to involve the intermediacy of elusive η^2-H_2 Rh species.[10] Motivated by this evidence, we are presently trying to develop new spectroscopic techniques and theoretical models for the correct evaluation of H−H bonding interactions in polyhydrido metal complexes, especially in rhodium compounds, which are often thermally unstable and highly fluxional in solution. Indeed, low stability and/or high fluxionality may thwart, if not prevent, the measurement of either T_{1min} or J(HD) in polyhydride metal complexes.

In this work, we describe the synthesis and characterization of the new complex [(triphos)Rh(η^2-H_2)H_2]$^+$ (**1**), obtained by protonation of the trihydride [(triphos)RhH_3] (**2**) [triphos = MeC(CH_2PPh_2)$_3$] with different protic acids at low temperature in either CD_2Cl_2 or THF-d_8. To further support the nonclassical dihydrogen structure of the rhodium complex, we have carried out a detailed analysis of the ^{1}H- and ^{2}H-relaxation properties of **1**, of its perdeuterated isotopomer [(triphos)Rh(η^2-D_2)D_2]$^+$ (**1**-d_4), and of the authentic nonclassical iridium analogues [(triphos)Ir(η^2-H_2)H_2]$^+$ (**3**) and [(triphos)Ir(η^2-D_2)D_2]$^+$ (**3**-d_4).

Experimental Section

The NMR studies were carried out in standard 5-mm NMR tubes using CD_2Cl_2 or THF-d_8 as the solvent. All solvents were dried using conventional procedures and were then distilled under inert atmosphere prior to use. ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded on either a Bruker AMX 400 or an AVANCE DRX 500 spectrometer operating

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at 400.13 and 500.13 MHz (^1H) and at 162.04 and 202.52 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or against external 85% H_3PO_4 with downfield values taken as positive (^{31}P). The ^2H-NMR data were collected with either the Bruker AMX 400 spectrometer operating at 61.40 MHz or the Bruker DRX 500 instrument operating at 76.77 MHz. The conventional inversion−recovery method (180°−τ−90°) was used to determine the variable-temperature longitudinal-relaxation time T_1. 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 longer than the expected relaxation time, and 16−20 variable delays were employed. The duration of the pulses was controlled at each temperature. The errors in determinations of T_1 were lower than 5%. The high-pressure NMR (HPNMR) experiments were performed in 10-mm sapphire tubes (Saphikon Inc.) assembled with Ti-alloy pressure heads constructed at ISSECC-CNR.[11] The HPNMR spectra were recorded using a standard 10-mm probe tuned to ^{31}P and ^1H nuclei on a Bruker AC 200 spectrometer.

Caution: *All manipulations involving high pressures are potentially hazardous. Safety precautions must be taken at all stages of NMR studies involving high-pressure tubes.*[12]

The hydride [(triphos)RhH_3] (**2**) was prepared as described in the literature,[13] whereas [(triphos)IrH_3] (**4**) was synthesized via a procedure that was improved with respect to that reported in the literature.[14] The trideuterides [(triphos)RhD_3] (**2**-d_3) and [(triphos)IrD_3] (**4**-d_3) were prepared in 90% isotopic purity (^1H NMR) following the procedure reported for the protonated analogue by simply using deuterated solvents and reagents.

Preparation of [(Triphos)IrH_3] (4). A THF solution (20 mL) of $[IrCl(COE)_2]_2$[15] (500 mg, 0.74 mmol) (COE = cyclo-octene) was treated under nitrogen with 1 equiv of triphos. After gentle heating to 40 °C, a 10-fold excess of solid $LiAlH_4$ was added in small portions with stirring to give a slurry that was refluxed for 4 h. The resulting solution was cooled to room temperature, and the excess of $LiAlH_4$ was hydrolyzed with a THF/H_2O mixture (6 mL, 1:1, v/v). The solution was filtered through Celite and concentrated under vacuum to ∼10 mL before adding a 1:1 mixture of EtOH/*n*-hexane (10 mL). Slow concentration under a flow of nitrogen gave **4** as off-white microcrystals (65% yield). The product was authenticated by comparison with an authentic specimen prepared using the procedure reported by Venanzi et al.[14]

In Situ Protonation of [(Triphos)RhH_3] with $HBF_4 \cdot OMe_2$ in THF-d_8 (NMR Experiment). A 5-mm NMR tube was charged under nitrogen with 30 mg of **2** (0.041 mmol) and 1 mL of THF-d_8. Into this solution, cooled to 210 K with a liquid nitrogen/acetone bath, was added by syringe an excess of $HBF_4 \cdot OMe_2$ (20 μL, 0.16 mmol). The solution immediately turned pale yellow. The tube was inserted into the spectrometer, which was precooled at 210 K. ^1H- and $^{31}P\{^1H\}$-NMR spectra, immediately recorded at this temperature, revealed the formation of two compounds: the molecular hydrogen complex [(triphos)Rh(η^2-H_2)H_2]$^+$ (**1**) and the THF-d_8 adduct [(triphos)Rh(η^1-THF-d_8)H_2]$^+$ (**5**) in a 1:4 ratio.

Repeating the protonation reaction under 1 bar of H_2 did not significantly change the product composition.

NMR data for **1** in THF-d_8: $^{31}P\{^1H\}$ NMR δ 21.28 [3P, d, *J*(PRh) 96.7 Hz]; ^1H NMR δ −5.68 [4H, br qd, *J*(HP) 30 Hz, *J*(HRh) 15 Hz].

NMR data for **5** in THF-d_8: $^{31}P\{^1H\}$ NMR δ 53.18 [1P, dt, *J*(PRh) 138.9 Hz, *J*(PP) 22.3 Hz], δ 6.67 [2P, dd, *J*(PRh) 79.4 Hz, *J*(PP) 22.3 Hz]; ^1H NMR δ −6.53 [2H, dt, $J(HP_{trans})$ 164 Hz, $J(HP_{cis}) \approx J(HRh)$ 12.0 Hz].

In Situ Protonation of [(Triphos)RhH_3] with HBF_4 in THF-d_8 under a High Pressure of H_2. A 10-mm sapphire HPNMR tube was charged with 30 mg of **2** (0.041 mmol) and 2 mL of THF-d_8 that had been degassed under nitrogen. The tube was immersed, together with its safety apparatus, in a dry ice/acetone bath, and ∼20 μL of $HBF_4 \cdot OMe_2$ was added via syringe. Immediately after the introduction of the acid, the tube was pressurized with hydrogen to ∼30 bar and carefully shaken. The tube was then inserted into the spectrometer, which was precooled at 210 K. ^1H- and $^{31}P\{^1H\}$-NMR spectra, immediately recorded at this temperature, showed the formation of **1** and **5** in an approximately 1:1 ratio.

When the temperature was increased, the concentration of **5** increased steadily at the expense of that of **1** until above 240 K, at which point only **5** was visible in solution, together with traces of the tetrahydride dimer *trans*-[{(triphos)RhH}$_2$(μ-H)$_2$]$^{2+}$ (*trans*-**6**). At higher temperature, **5** rapidly transformed into *trans*-**6** (∼90%), together with other unknown products.[16]

In Situ Protonation of [(Triphos)RhH_3] with HBF_4 in CD_2Cl_2 under Nitrogen. Replacing THF-d_8 with CD_2Cl_2 in the in situ protonation of **2** at 210 K gave **1** in high yield (>90%), independent of either the acid (CF_3COOH, CF_3SO_2OH, or $HBF_4 \cdot OMe_2$) or the gaseous atmosphere (N_2 or H_2) employed. After standing at 240 K for 15 min, **1** converted to a 1:1.2 mixture of *cis*- and *trans*-[{(triphos)RhH}$_2$(μ-H)$_2$]$^{2+}$ (*cis*-**6** and *trans*-**6**). The formation of a 1:4 mixture of the known μ-chloride dimers *cis*- and *trans*-[{(triphos)RhH}$_2$(μ-Cl)$_2$]$^{2+}$ (*cis*-**7** and *trans*-**7**)[16] took place at room temperature within 1 h.

NMR data for **1** in CD_2Cl_2: $^{31}P\{^1H\}$ NMR δ 23.20 [3P, d, *J*(PRh) 96.6 Hz]; ^1H NMR δ −5.84 [4H, br qd, *J*(HP) 31 Hz, *J*(HRh) 15 Hz].

NMR data for *cis*-**6** in CD_2Cl_2: $^{31}P\{^1H\}$ NMR δ 17.15 [6P, d, *J*(PRh) 101.1 Hz]; ^1H NMR δ −10.53 [4H, qut, *J*(HP) 23.1 Hz, *J*(HRh) 4.8 Hz].

NMR data for *trans*-**6** in CD_2Cl_2: $^{31}P\{^1H\}$ NMR δ 25.23 [6P, d, *J*(PRh) 95.9 Hz]; ^1H NMR δ −7.86 [4H, qut, *J*(HP) 22.8 Hz, *J*(HRh) 14.0 Hz].

Results and Discussion

Synthesis and Characterization of [(Triphos)Rh(η^2-H_2)-H_2]$^+$. The synthesis and characterization of the octahedral Ir(III) nonclassical tetrahydride [(triphos)Ir(η^2-H_2)H_2]$^+$ (**3**) has recently been described.[17] This complex was obtained either by the solid-state hydrogenation of [(triphos)Ir(η^2-C_2H_4)H_2]BPh_4 at H_2 pressures higher than 5 bar or by the in situ protonation of the trihydride [(triphos)IrH_3] (**4**) with a slight excess of $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at low temperature. The latter procedure was employed to prepare a sample of **3** in THF-d_8 at 210 K that was studied, for comparative purposes, with the same NMR apparatus and in the same experimental conditions as those employed for the characterization of the new rhodium complex [(triphos)Rh(η^2-H_2)H_2]$^+$ (**1**).

Because of the presence of an excess of acid, **3** exhibits a single resonance for the four hydrogen atoms of the Ir(η^2-H_2)H_2 moiety, even at 210 K.[17] In these experimental conditions, the hydride signal shows a quite short T_1 time of 77 ms (500 MHz), much shorter than the relaxation time measured for **4** (560 ms at 210 K in THF-d_8). Above 230 K, the resonances of the free acid (δ 9.3) and the hydride ligands broaden, suggesting the occurrence of H^+/IrH_4 exchange on the NMR time scale. At higher temperature, **3** starts to decompose, yielding, first, the solvate adduct [(triphos)Ir(η^1-THF-d_8)H_2]$^+$ (**7**) and, then, the classical tetrahydride *trans*-[{(triphos)IrH}$_2$(μ-H)$_2$]$^{2+}$ (**8**).[17,18]

The η^2-H_2 rhodium complex **1** was similarly generated in solution by reacting the classical trihydride **2** in THF-d_8 at 210 K with 3 equiv of either HBF4$\cdot OMe_2$ or $HOSO_2CF_3$ (Scheme 1).

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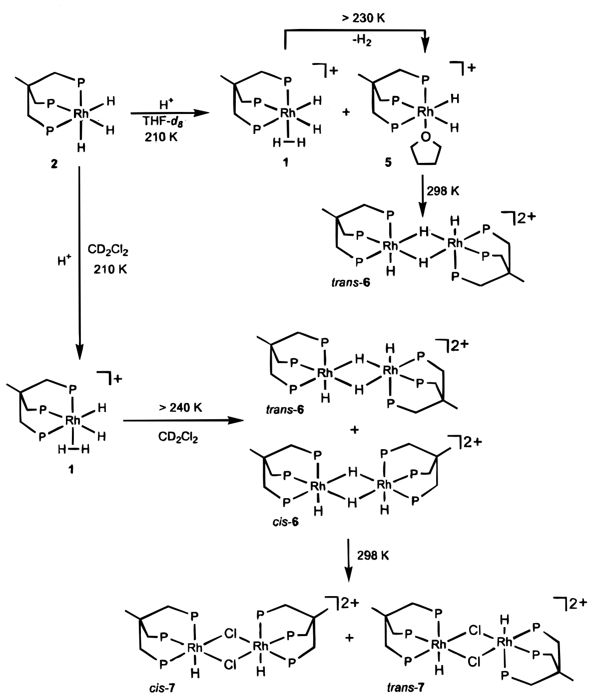
Scheme 1



The NMR parameters of **1** are quite similar to those of **3**. In the hydride region, the ^{1}H-NMR spectrum at 220 K contains a broad signal at −5.68 ppm that appears as a quartet of doublets with *J*(HP) = 30 Hz and *J*(HRh) = 15 Hz (Figure 1) in the spectrum obtained with resolution enhancement via Gaussian multiplication of the FID. Information about the ^{1}H−^{31}P coupling was provided by ^{1}H{^{31}P}-NMR experiments. The signal in these spectra corresponds to four hydrogen atoms (^{1}H-NMR integration with respect to the aliphatic resonances of the triphos ligands) and exhibits a very short T_1 time of 65.5 ms (500 MHz). Like the iridium analogue, **1** is thus very fluxional in solution, as shown also by the ^{31}P{^{1}H} spectrum, which consists of a single narrow doublet at 21.28 ppm with *J*(PRh) = 96.7 Hz. The experimental relaxation time of the resonance due to the four exchanging hydrides is close to the value found for the Ir derivative **3** and is much shorter than the value determined for the parent trihydride **2** (577 ms) under the same experimental conditions.

Complex **1** was not the sole product obtained upon protonation of **2** at 210 K. In fact, a compound that we assign as the THF adduct $[(triphos)Rh(\eta^1\text{-}THF\text{-}d_8)H_2]^+$ (**5**) was the major product (80%), because of competitive coordination of the solvent to the rhodium center (Scheme 1). In comparable reaction conditions, the Ir derivative $[(triphos)Ir(\eta^1\text{-}THF)H_2]BPh_4$ has also been isolated.[18]

The ratio of **1** to **5** did not change when the protonation reaction of **2** was performed under 1 bar of H_2. However, when the protonation was performed in a sapphire NMR tube at a H_2 pressure of 30 bar, **1** and **5** were formed in a 1:1 ratio.

The proton-NMR spectrum of the THF adduct **5** shows a hydride resonance at −6.53 ppm, which appears as a slightly perturbed doublet of triplets with a very long T_1 of 690 ms at 210 K (500 MHz). The ^{31}P{^{1}H}-NMR spectrum consists of an AM_2 spin system with δ 53.18 [1P, dt, *J*(PRh) 138.9 Hz, *J*(PP) 22.3 Hz] and δ 6.67 [2P, dd, *J*(PRh) 79.4 Hz, *J*(PP) 22.3 Hz]. The formation of **5** from **1** is accompanied by the appearance of the typical ^{1}H resonance at 4.53 ppm for free H_2.

The stability of **1** did not remarkably increase under 30 bar of H_2, as its irreversible transformation into **5** occurred already above 240 K. At room temperature, however, the THF adduct was unstable and slowly converted to the red-orange tetrahydride dimer *trans*-$[\{(triphos)RhH\}_2(\mu\text{-}H)_2]^{2+}$ (*trans*-**6**).[16] The formation of *trans*-**6**, which is scarcely soluble in THF and which may separate as red-orange crystals of the BF_4 salt depending on the concentration, is generally accompanied by the formation of other small impurities which, altogether, may sum up to ∼10%. A much more selective method for the synthesis of **1** in solution was provided by the reaction of **2** with a 3-fold excess of CF_3COOH in CD_2Cl_2 [RhH_4: δ −5.84, *J*(HP) 31 Hz, *J*(RhH) 15 Hz]. As in THF, **1** is highly fluxional in CD_2Cl_2, where the ^{31}P{^{1}H}-NMR spectrum consists of a temperature-invariant narrow doublet [δ 23.2, *J*(RhP) 96.6 Hz] down to 180 K. Above 240 K in CD_2Cl_2, **1** quickly loses H_2 to form a mixture of *cis*- and *trans*-**6** that irreversibly transformed into the double-bridging chloride dimers *cis*- and *trans*-**7** via H/Cl exchange (Scheme 1).[16]

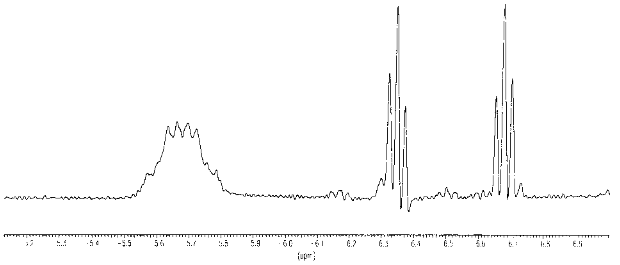


Figure 1. Hydride region of the ^{1}H-NMR spectrum (220 K, THF-d_8, 500 MHz) after protonation of **2** with $HBF_4\cdot OMe_2$ at low temperature.

^{1}H-Relaxation Study of $[(Triphos)Rh(\eta^2\text{-}H_2)(H)_2]^+$. The proton-relaxation data recorded at 500 MHz for the hydride ligands of **2** and **1** in THF-d_8 give a T_{1min} value of 311 ms at 260 K for the classical trihydride **2** and a value decreasing from 65.5 ms at 220 K to 46.0 ms at 235 K for **1**. These data allow one to suggest a nonclassical structure for **1**. Unfortunately, a direct T_{1min} measurement for **1** in THF-d_8 was not possible, because this complex is stable only at temperatures below 240 K. However, a T_{1min} value of 38.9 ms was observed at 220 K (400 MHz) in CD_2Cl_2. This value, scaled up to 500 MHz, corresponds to a T_{1min} of 48.6 ms. The absence of mixing of the T_1 times for the free acid and the hydride signal of **1** in the temperature range investigated eliminates the possibility of any H/H exchange between the RhH_4 moiety and the free acid and, therefore, indicates that the T_{1min} value measured in CD_2Cl_2 is absolutely correct.

A standard treatment of the ^{1}H-relaxation data in CD_2Cl_2 for **1** yields a r_{H-H} bond distance of either 0.91 or 1.14 Å, assuming the presence of either a fast-spinning or a slow-spinning dihydrogen ligand, respectively.[19,20] Inelastic neutron scattering studies recently performed on the complex $[Tp^{Me2}RhH_2(\eta^2\text{-}H_2)]$ are consistent with a very low rotational barrier ($E_a = 0.56$ kcal/mol) and a short r_{H-H} distance of 0.94 Å.[21] It has been proposed that *cis*-hydride/dihydrogen interactions can effectively lower the barrier to H_2 rotation.[22,23] On the basis of these arguments, it is most likely that the dihydrogen ligand in **1** is spinning very rapidly.[24]

^{1}H-NMR spin−lattice relaxation experiments are recognized as an important tool for elucidating the solution-phase structure of transition metal polyhydride complexes.[2,19,22] In particular, notwithstanding some criticism associated with the evaluation

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of this parameter,[25] the measurement of T_1 is particularly important when the complexes are thermally unstable and may exist only in solution and only at low temperature.[26] A more reliable diagnostic tool for assessing the nonclassical structure of a metal polyhydrido complex is provided by the measurement of the J(HD) coupling constant ($\geq$10 Hz) in the monodeuterated isotopomer.[2,27,28] In an attempt to synthesize **1**-d_1 for this kind of measurement, the trihydride **2** was protonated with CF_3COOD in CD_2Cl_2 at 210 K. Irrespective of the amount of acid employed (1−3 equiv), this reaction gave a largely predominant isotopomer that we assigned as [(triphos)RhH_2D_2] (**1**-d_2) on the basis of the relative integral intensities in the ^{1}H-NMR spectrum. Moreover, deuterium incorporation into **1** was evident by the appearance of free H_2 and HD. The hydride region in the ^{1}H-NMR spectrum of **1**-d_2, recorded with ^{31}P-decoupling at 230 K and 400 MHz, contains a broad doublet with J(RhH) = 15 Hz ($\Delta\nu = \sim$8−10 Hz) with no appreciable J(HD).

Complexes **1** and **1**-d_2 are highly fluxional, showing an averaged hydride resonance even at low temperature. This remarkable fluxionality should effectively reduce the J(HD) value in **1**-d_2 because of the different locations of deuterium in the complex. Indeed, unresolved J(HD) splitting in low-temperature NMR spectra has already been reported for other partially deuterated nonclassical polyhydrides, such as $RuH_2(H_2)(CO)(PPr^i_3)_2$.[29] It has been proposed that this phenomenon may be due to deuterium relaxation resulting in scalar relaxation of the second type for the proton coupled to deuterium.[30] A broad, featureless hydride resonance has also been observed for partially deuterated [$TpRhH_2(\eta^2\text{-}H_2)$].[4,5]

In the case of **1**-d_2, a simple calculation using the equation $1/T_2 = {}^8/_3\pi^2J^2(\mathrm{H{-}D})T_1(\mathrm{D})$,[29−32] where T_1(D) was measured for [(triphos)RhD_4]$^+$ (**1**-d_4) as 0.0385 s at 220 K (see below), shows that the expected line width of the hydride resonance ($\Delta\nu = 1/\pi T_2$) in **1**-d_2 might be ~8 Hz for a J(HD) value of ~5 Hz. It is therefore likely that both of these effects are responsible for the nondetection of the J(HD) constant in **1**-d_2.

To provide further support for the nonclassical structure of **1**, the relaxation behaviors of the perdeuterated isotopomers **2**-d_3 and **1**-d_4 have been studied by variable-temperature ^{2}H-T_1 measurements. For comparative purposes, these relaxation experiments were carried out for the Ir derivatives **4**-d_3 and **3**-d_4, the latter containing an intact D_2 ligand.[17]

Complex **1**-d_4 was readily prepared by protonation of **2**-d_3 with a 2-fold excess of CF_3SO_2OD in CH_2Cl_2 at 195 K. Upon acid addition, the deuteride resonance due to **2**-d_3 completely disappeared in the ^{2}H-NMR spectrum [δ −8.60, J(RhD) 3 Hz, $^2J(\mathrm{DP}) + 2 \times {}^2J(\mathrm{DP}') = 20$ Hz]. Formed in its place was a broad resonance at −5.70 ppm that could be ascribed to the four freely exchanging deuterides of **1**-d_4. Similar spectral changes were observed upon low-temperature protonation of **4**-d_3 with an excess of CF_3COOD in CH_2Cl_2: a single deuteride resonance was observed at −8.20 ppm for **3**-d_4 even at 170 K.

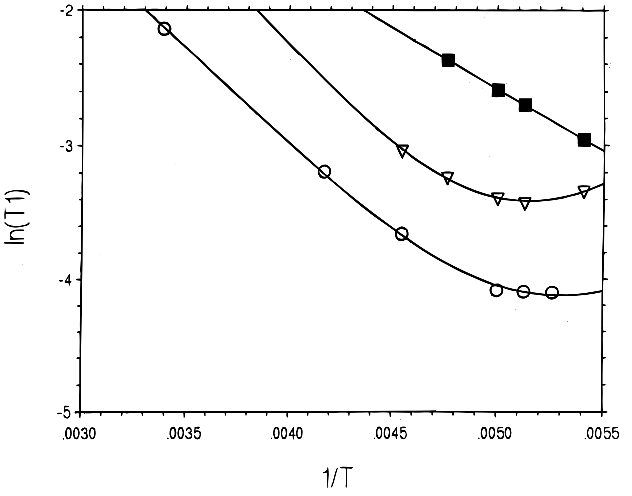

Figure 2. Plot of the ^{2}H-T_1 data collected at 76.75 MHz in CH_2Cl_2 for the OD resonance of the acid (■) and the RhD_4 resonance of **1**-d_4 (▽) and of **2**-d_3 (○).

Because the ^{2}H spin−lattice relaxation is dominated by quadrupolar interactions,[30] the deuterium quadrupole coupling constant (DQCC) is a relevant parameter for the characterization of polyhydride metal complexes (eq 1).[31−33]

$$1/T_1 = {}^3/_{50}\pi^2(2I+3)[I^2(2I-1)]^{-1}(e^2q_{ZZ}Q/h)^2(1+\eta^2/3) \\ [\tau_{\mathrm{mol}}/(1+\omega_D{}^2\tau_{\mathrm{mol}}{}^2) + 4\tau_{\mathrm{mol}}/(1+4\omega_D{}^2\tau_{\mathrm{mol}}{}^2)] \quad (1)$$

$$\tau_{\mathrm{mol}} = \tau_0 \exp(E_a/RT)$$

$$\eta = |q_{XX} - q_{YY}|/q_{ZZ}$$

In eq 1, I is the spin of deuterium, η the asymmetry parameter of the electric field gradient on D, τ_{mol} the correlation time of molecular reorientations with the activation energy E_a, and the term $e^2q_{ZZ}Q/h$ the DQCC on the nucleus D.[32]

When the T_1 time reaches a minimum, the DQCC value can be calculated by means of eq 2.

$$\mathrm{DQCC} = 1.2201(1+\eta^2/3)^{-1/2}(\nu/T_{1\mathrm{min}})^{1/2} \qquad (2)$$

where DQCC, ν, and $T_{1\mathrm{min}}$ are measured in kilohertz, megahertz, and second, respectively.[31−33] According to recent molecular orbital calculations,[32] the asymmetry parameter η can be taken as 0 and 0.62 for classical hydrides and dihydrogen complexes, respectively.

Figure 2 compares the ^{2}H-T_1 data for the RhD_4 resonance in **1**-d_4 at 76.753 MHz at different temperatures with the OD signal of the acid and with the deuteride resonance of **2**-d_3. Complexes **2**-d_3 and **1**-d_4 show $T_{1\mathrm{min}}$ values of 16.5 and 32.6 ms, respectively, at ~190 K. Given that the η parameter is approximately 0 in terminal deuterides,[34−36] eq 2 gives a very reasonable DQCC value of 83.2 kHz for **2**-d_3.[32] The $T_{1\mathrm{min}}$ time for the classical ligands in **4**-d_3 is also quite short and is measured as

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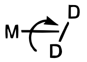
10.1 ms at 190 K (61.402 MHz), corresponding to a DQCC value of 95.0 kHz.

It follows from the ^{2}H-relaxation data that the value of $T_{1\text{min}}$ for the η^2-D_2 complex **1**-d_4 is significantly longer than that for the classical trihydride **2**-d_3 (32.6 vs 16.5 ms, 76.753 MHz). This $T_{1\text{min}}$ elongation in the nonclassical η^2-D_2 complex **1**-d_4 might be associated with the occurrence of slow D^+/D_2 exchange between the D_2 ligand and the free acid, which actually exhibits a quite long T_1 time. This type of exchange on the NMR time scale has been detected by ^{1}H-NMR spectroscopy for the iridium derivative **3** in THF-d_8 at temperatures ≥230 K,[17] but the ^{1}H-NMR spectra of the rhodium derivative **1** in either CD_2Cl_2 or THF-d_8 did not reveal this process in the temperature range investigated. On the other hand, the absence of D^+/D_2 exchange in CH_2Cl_2 solutions of **1**-d_4 was evident also from an analysis of the ^{2}H-NMR data. Indeed, the standard calculations of the $\ln(T_1)$ vs $1/T$ relaxation curves using eq 1 (solid lines in Figure 2) provide the same E_a value of 2.7 kcal/mol for the molecular reorientations of **2**-d_3 and **1**-d_4, whereas the activation energy calculated for the acid is significantly lower (1.8 kcal/mol). All of the curves in Figure 2 are thus independent from the relaxation viewpoint, showing the absence of D^+/D_2 exchange on the T_1 NMR time scale.

A recent analysis of the ^{2}H-$T_{1\text{min}}$ behavior for a series of dideuterium complexes has shown that a significant elongation of T_1 takes place when the D_2 ligand undergoes a fast intramolecular rotation (or fast libration) around the axis perpendicular to the D−D bond with the correlation time $\tau_{\text{rot}} \ll \tau_{\text{mol}}$.[32,33]



For example, when the angle α between the rotation axis and the direction of the main axis of the electric field gradient is equal to 90° and, thus, the main axis is aligned with the D−D bond, a fast rotation has been found to cause a 4-fold elongation of $T_{1\text{min}}$.[37] In general, the DQCC value for a spinning D_2 ligand can be calculated with eq 3, showing that a maximal elongation of $T_{1\text{min}}$ should be expected when α is close to the magic angle (∼54°) and $T_{1\text{min}} \rightarrow \infty$.

$$\text{DQCC} = 2.4402(1 + \eta^2/3)^{-1/2}[\nu/T_{1\text{min}}(3\cos^2\alpha - 1)^2]^{1/2} \quad (3)$$

Complex **1**-d_4 undergoes a fast deuteride/dideuterium exchange, and therefore $T_{1\text{min}}$ for its D_2 ligand [$T_{1\text{min}}(D_2)$] can be calculated as 1.34 s (±5%) from $T_{1\text{min}}{}^{\text{obs}}$ (0.0326 s) using eq 4,[38] where the value of $T_{1\text{min}}(D)$ for the deuteride ligands in **2**-d_3 is 0.0165 s.

$$1/T_{1\text{min}}{}^{\text{obs}} = 0.5/T_{1\text{min}}(D) + 0.5/T_{1\text{min}}(D_2) \quad (4)$$

The $T_{1\text{min}}$ time thus undergoes approximately an *80-fold increase* on going from the classical deuteride ligand to the intact D_2 ligand. A related effect has been observed for the complex $[\text{RuD}(D_2)(\text{dppe})_2]^+$, for which the minimum T_1 value of the D_2 ligand is 12 times greater than that of the terminal deuteride ligand (dppe = diphenylphosphinoethane).[33]

A perusal of eq 4 shows that $T_{1\text{min}}{}^{\text{obs}} = 2T_{1\text{min}}(D)$ when $T_{1\text{min}}(D_2) \rightarrow \infty$. According to our ^{2}H-relaxation measurements, the ratio $T_{1\text{min}}$(**1**-d_4)/$T_{1\text{min}}$(**2**-d_3) is 1.98, which is close to the maximum elongation of the relaxation time on going from a classical hydride complex to a very fluxional nonclassical tetrahydride. In conclusion, **1**-d_4 can be formulated as a dihydrogen complex that contains a D_2 ligand undergoing a fast rotation with the angle α close to the magic angle.

For comparative purposes, a ^{2}H-relaxation study has also been performed for the iridium η^2-D_2 complex **3**-d_4 prepared by protonation of the trihydride **4**-d_3 with CF_3COOD in CH_2Cl_2.[17] Interestingly, for the averaged resonance of **3**-d_4, a value of 20.1 ms (61.402 MHz) was experimentally measured at 170 K when no $D^+/(D_2)$ exchange occurs as the minimum value from the temperature dependence of T_1. Like the Rh analogues, the transformation of the classical trihydride **4**-d_3 into the nonclassical tetrahydride **3**-d_4 causes a *2-fold increase* in $T_{1\text{min}}{}^{\text{obs}}$.

On the basis of the preceding results, one may conclude that the dihydrogen ligands in both **3**-d_4 and **1**-d_4 are spinning very rapidly and that the direction of the main axis of the electric field gradient shows an α value close to the magic angle. A similar α value (52.5° or 49.7°) for the D_2 ligand in $[\text{Os}(D_2)\text{Cl}_2(\text{CO})(\text{PPr}^i{}_3)_2]$ has recently been inferred from variable-temperature solid-state ^{2}H-NMR measurements.[33] These data somewhat contrast with recent molecular orbital calculations on several Os, W, and Ru dihydrogen complexes, according to which the main axis of the electric-field gradient lies along the D−D vector and α takes values between 72° and 84°.[32]

Variable-temperature ^{1}H-NMR spectra of solid $\text{IrH}_2(\text{H}_2)(\text{Cl})(\text{PPr}^i{}_3)_2$ have revealed a surprising hydride scrambling (eq 5) with an energy barrier lower than 3 kcal/mol.[39]

$$\text{IrH}_2(\text{H*}_2)(\text{Cl})(\text{PPr}^i{}_3)_2 \rightleftarrows \text{IrH*}_2(\text{H}_2)(\text{Cl})(\text{PPr}^i{}_3)_2 \quad (5)$$

A standard treatment of the relaxation data in terms of eq 1 has shown that the molecular reorientations in the rhodium complexes **1**, **1**-d_4, **2**, and **2**-d_3 in THF or CH_2Cl_2 require activation energies ($E_{\text{act}}{}^{\text{mol}}$) ranging between 2.8 and 3.6 kcal/mol, which is consistent with the variable-temperature ^{1}H- and ^{2}H-NMR spectra of **1** and **1**-d_4. Accordingly, one may expect that $E_{\text{act}}{}^{\text{exch}} < E_{\text{act}}{}^{\text{mol}}$ and hence that $\tau_{\text{mol}} > \tau_{\text{exch}}$. The ^{2}H relaxation is caused by reorientations of the main axis of the electric-field gradient at D, generally as a result of molecular motions with the correlation time τ_{mol}. This is absolutely valid for the classical deuteride ligands in **1**-d_4 or **3**-d_4, whereas additional reorientations of the gradient, attributable to rapid intramolecular rotation with $\tau_{\text{rot}} < \tau_{\text{mol}}$, are apparently operative for the D_2 ligands. This rotation leads to the elongation of the relaxation for processes in which the rotation and the hydride/dihydrogen exchange are independent. However, when $\tau_{\text{rot}} \sim \tau_{\text{exch}}$, the two processes may couple with each other. In this eventuality, during τ_{mol}, the main axis of the electric-field gradient on the classical D ligands in **1**-d_4 and **3**-d_4 might also undergo additional reorientations as an effect of motion transfer. Intuitively, this effect might contribute to the elongation of $T_{1\text{min}}{}^{\text{obs}}$ in nonclassical D_2 complexes. In the absence of further experimental data, however, the effect of motion transfer remains an intriguing working hypothesis.

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Conclusions

In addition to reporting a new example of a rhodium η^2-H_2 complex, this work describes the ^{2}H variable-temperature spin–lattice relaxation behavior of two structurally related dihydrogen complexes of rhodium and iridium in solution. It has been shown that deuterium-relaxation studies are extremely useful for the characterization of polyhydride metal complexes, especially when the complexes are thermally unstable and/or highly fluxional in solution and the measurement of their T_{1min} values and/or J(HD) parameters is prevented. On the basis of the experimental data obtained in this work, it is confirmed that the ^{2}H-T_{1min} time *elongates significantly* in going from classical to nonclassical structures of polydeuterido metal complexes.

Acknowledgment. Thanks are given to NATO (Contract "^{2}H-Relaxation as a Tool To Study Hydrogen Transfer Reactions", Grant HTECH-CRG 972135) and the CNR/RAS cooperation bilateral agreement for financial support. Thanks are also given to Prof. R. H. Morris for disclosing some unpublished results to us.

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