Deuterium Quadrupolar Coupling Constants of Deuteride Bridging Ligands: A Study on Rhenium Hydrido Carbonyl Clusters

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Deuterium variable-temperature T_1 measurements have been performed for a series of rhenium carbonyl clusters containing doubly and triply bridging deuterides, namely $Re_2(\mu\text{-}D)_2(CO)_8$ (**1**), $Re_3(\mu\text{-}D)_3(CO)_{12}$ (**2**), $Re_4(\mu_3\text{-}D)_4(CO)_{12}$ (**3**), $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_{10}]$ (**4**), $[NEt_4][Re_3(\mu\text{-}D)_3(\mu\text{-}Cl)(CO)_{10}]$ (**5**), and $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_9]$ (**6**). The deuterium quadrupolar coupling constants (DQCC) of the deuteride ligands have been evaluated for compounds **1**–**5**, while the fluxionality of **6** hampered such a determination. The experimental DQCC of compound **3** (21.8 kHz) was, until now, the smallest found for organometallic compounds. Overall the DQCC values span a 4-fold range, and their fine-tuning depends on the bridging mode of the deuteride ligands (μ_3 vs μ), the local unsaturation degree of the Re atoms bridged by the deuteride, and the presence of other bridging ligands. The experimental DQCC's of rhenium derivatives and those of bridging deuterides in Cr, W, and Os clusters linearly correlate with the respective metal–hydrogen stretching frequencies.

Introduction

Spin–lattice relaxation time measurements of hydrogen isotopes provide a powerful tool for the investigation of structure and binding modes both in solution and in the solid state. Moreover, since different relaxation mechanisms for the two isotopes are operative, different site properties can be explored.

^1H relaxation basically depends on dipole–dipole interaction[1] and provides spatial relationship. In organometallic chemistry short relaxation times of hydrogens bound to a metal can be a signature of the occurrence of a nonclassical dihydrogen ligand[2] in the absence of a significant dipolar contribution of the metal itself.[3,4] Differential dipolar contributions to the hydrido ligand relaxation provided structural assignments,[5] distances in good agreement with the neutron diffraction data,[6] and proved the occurrence of hydrogen[7] or dihydrogen bond interactions in solution.[8]

In contrast, deuteron nuclei possess a nuclear quadrupole moment (Q) and their relaxation is controlled by quadrupole interactions of Q with the electric field gradient (EFG) at the nucleus.[1] The fundamental parameter that can be detected by measuring the relaxation times of ^2D nuclei is the deuterium quadrupole coupling constant, known as DQCC = $e^2q_{zz}Q/h$, where q_{zz} is the component on the z axis of the EFG. The electric field gradient is described by a second rank tensor and clearly depends on the distribution of charge around the nucleus. As pointed out by several authors, there are no effects of excited states in the determination of electric field gradients.[9] DQCC is then expected to depend on the specific structural and geometrical characters of the site of the deuterium atom. The use of DQCC to monitor the presence of hydrogen bonding has been reported in the literature.[10,11]

Organometallic complexes containing terminally bound deuterides and dideuterium have been recently studied. The DQCC values for the former were found to range between 36 and 158 kHz[12] and have been interpreted in terms of the ionicity of the M–D bond,[12,13] while for the latter DQCC's were found to be sensitive to the type of motion of the ligand.[14]

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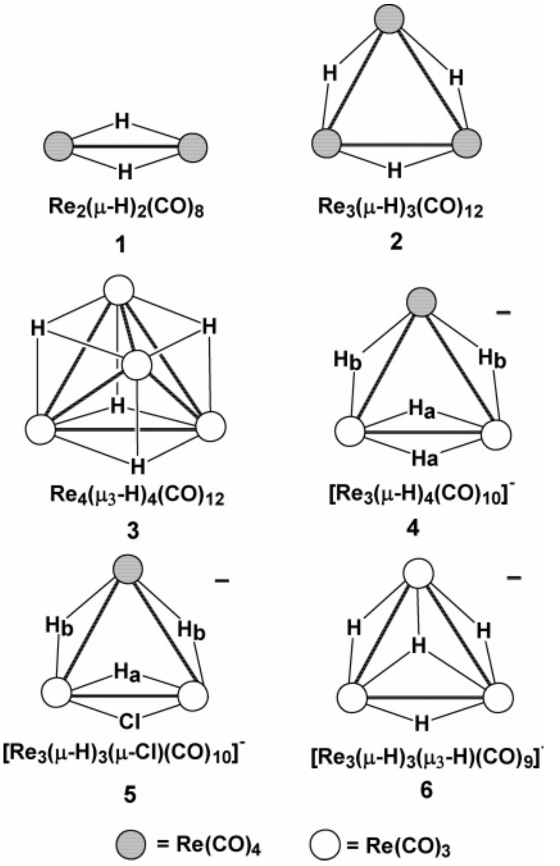
To the best of our knowledge, only three studies concerning compounds containing μ-bridging deuteride have been reported.[15–17] Actually there is still a need for a more specific spectroscopic investigation of metal deuterides in μ and μ_3 bonding modes in order to obtain, through their DQCC's, a better understanding of the metal–hydrogen interaction in transition-metal clusters.

For this reason, in the present paper, we report the results of the evaluation, by means of ^{2}D variable-temperature T_1 measurements, of the deuterium QCC's for deuteride ligands occupying bridging locations in a series of rhenium carbonyl clusters, namely $Re_2(\mu\text{-}D)_2(CO)_8$ (**1**),[18,19] $Re_3(\mu\text{-}D)_3(CO)_{12}$ (**2**),[19,20] $Re_4(\mu_3\text{-}D)_4(CO)_{12}$ (**3**),[21,22] $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_{10}]$ (**4**),[23] $[NEt_4][Re_3(\mu\text{-}D)_3(\mu\text{-}Cl)(CO)_{10}]$ (**5**),[24] and $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_9]$ (**6**)[25,26] (Chart 1). These clusters present different bridging modes, and four of them (**1**, **3**, **4**, and **6**) have electronic deficiencies which make them very reactive toward electron donors.[27–30] We will show that DQCC is a parameter very sensitive to electronic and structural effects and that their values correlate with the M–H stretching frequencies.

Chart 1. Schematic Structures of the Compounds Studied



Results and Discussion

The quadrupolar interaction can be measured directly using a number of experimental techniques including NMR and NQR spectroscopy.[31] Our approach is based on the measurement of the ^{2}D relaxation times at variable temperature in solution. This allows the estimate of the deuterium QCC by fitting the data to the following equation, which describes the quadrupolar contribution to T_1:[1]

$$\frac{1}{T_1^{\text{quadr}}} = \frac{3}{50}\pi^2\frac{2S_D+3}{S_D^{\,2}(2S_D-1)}(\text{DQCC})^2\left(1+\frac{\eta^2}{3}\right)\times\left(\frac{\tau_c}{1+\omega^2\tau_c^{\,2}}+\frac{4\tau_c}{1+4\omega^2\tau_c^{\,2}}\right)$$

where S_D is the deuterium spin quantum number, ω is the deuterium resonance frequency, η is the asymmetry factor ($0 \leq \eta \leq 1$), and τ_c is the molecular reorientational time, defined as $\tau_c = \tau_0 \exp(E_a/RT)$, E_a being the activation energy for the reorientation in solution. The asymmetry parameter for deuterium is usually quite small (≤ 0.2), and the $\eta^2/3$ term may often be neglected.[11]

The variable-temperature ^{2}D T_1 data of **1**–**6** were obtained at 7.05 and 14.1 T, and experimental results are available in Tables S1–S8 in the Supporting Information. To extract the DQCC values from these data, for each compound the reorientational motion parameters τ_0 and E_a are needed. They were derived from variable-temperature ^{1}H T_1 measurements on the proton-containing isotopomers of the studied compounds (Tables S9–S14 in the Supporting Information).[1] In these species the proton relaxation rate is determined by the H–H, Re–H, and D–H dipolar interaction and by the chemical shift anisotropy (CSA) of the hydrides under consideration:[32]

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$$\frac{1}{T_1} = \frac{1}{T_1^{\text{dipHH}}} + \frac{1}{T_1^{\text{dipHRe}}} + \frac{1}{T_1^{\text{dipHD}}} + \frac{1}{T_1^{\text{CSA}}}$$

Variable-field measurements (carried out at 14.05, 9.37, and 7.02 T) have shown that the hydride ^{1}H relaxation times do not depend on the field strength: i.e., chemical shift anisotropy does not contribute to T_1 (see for example Tables S10 and S11 in the Supporting Information). The D−H dipolar interaction also does not contribute to T_1, due to the low deuterium gyromagnetic ratio.

The equation which describes the proton relaxation for the various ^{1}H-containing isotopomers (and which has been used to fit the ^{1}H relaxation data) is then reduced as follows:[33]

$$\frac{1}{T_1} = n_{\text{Re}}\frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2 \gamma_{\text{H}}^2\, \gamma_{\text{Re}}^2 S_{\text{Re}}(S_{\text{Re}}+1)}{r_{\text{HRe}}^6} \times \left(\frac{3\tau_c}{1+\omega_{\text{H}}^2\,\tau_c^2} + \frac{\tau_c}{1+(\omega_{\text{H}}-\omega_{\text{Re}})^2\tau_c^2} + \frac{6\tau_c}{1+(\omega_{\text{H}}+\omega_{\text{Re}})^2\tau_c^2}\right) + \text{n}_{\text{H}}\frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_{\text{H}}^4}{r_{\text{HH}}^6} \times \left(\frac{\tau_c}{1+\omega_{\text{H}}^2\,\tau_c^2} + \frac{4\tau_c}{1+4\omega_{\text{H}}^2\tau_c^2}\right)$$

For compounds **1**−**5** the relaxation parameters τ_0 and E_a (from ^{1}H data) and DQCC's (from ^{2}D data) obtained accordingly are summarized in Table 1. Figure 1 shows the experimental relaxation rates for **1**−**4** together with their fitting curves. The asymmetry parameter has been neglected, since it is 0 for μ_3 sites, while for μ sites, even accounting for its maximal value, the DQCC reduction would amount to 20% without modifying the observed trends.

The experimental DQCC's span a wide range: the ratio between the extreme values is ca. 4, and the DQCC determined for **3** (21.8 kHz) is the lowest value reported up to now for organometallic deuterides. Such a low value can hardly be rationalized on the basis of ionicity of M−D bonds, since the known reactivity of **3** does not fit with a strong hydridic character. Indeed, **3** is known to behave as a Lewis acid[21a,28] or even a hydride acceptor[21a] rather than a hydride donor. The observed low DQCC value should therefore derive from other molecular features.[34,35]

Table 1. DQCC's and Relaxation Parameters Obtained for Compounds 1−5

compd	$10^{13}\tau_0$ (s)	E_a (J/mol)	DQCC (kHz)
1 ($\boldsymbol{\mu}$)	4.7	9450	48.9
2 ($\boldsymbol{\mu}$)	5.9	10100	80.1
3 ($\boldsymbol{\mu}_3$)	9.8	9150	21.8
4 ($\boldsymbol{\mu}_a$)	7.0	9830	43.5
4 ($\boldsymbol{\mu}_b$)			58.9
5 ($\boldsymbol{\mu}_a$)	4.9	9910	74.1
5 ($\boldsymbol{\mu}_b$)			86.2

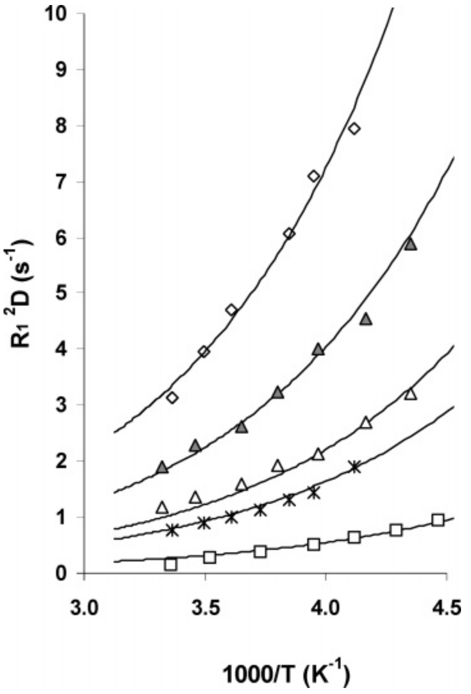

Figure 1. Variable-temperature ^{2}D T_1 data measured for the deuterides in compounds **1**−**4**: (*) $Re_2(\mu\text{-}D)_2(CO)_8$ (**1**); (◇) $Re_3(\mu\text{-}D)_3(CO)_{12}$ (**2**); (□) $Re_4(\mu_3\text{-}D)_4(CO)_{12}$ (**3**); (▲) D_b in $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_{10}]$ (**4**); (△) D_a in $[NEt_4][Re_3(\mu\text{-}D)_4(CO)_{10}]$ (**4**). The solid lines represent the best-fit curves for the various data sets, drawn according to the parameters reported in Table 1.

Some hints come from the comparison among compounds **1**−**3**. Actually, compound **3**, with the lowest DQCC value (21.8 kHz), is four electrons short with respect to a saturated tetrahedral cluster (i.e. has only 56 valence electrons (ve's)). Moreover in **3** each deuterium ligand bridges three Re atoms and each Re−Re interaction is spanned by two μ_3 ligands. On the other hand, the saturated triangular cluster **2** (48 ve's), with a single μ-bridging deuteride on each metal−metal interaction, shows one of the highest DQCC values in

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(32) The relevant equations for various mechanisms are

$$\frac{1}{T_1^{\text{dipHH}}} = n_{\text{H}}\frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_{\text{H}}^4}{r_{\text{HH}}^6}\left(\frac{\tau_c}{1+\omega_{\text{H}}^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_{\text{H}}^2\,\tau_c^2}\right)$$

$$\frac{1}{T_1^{\text{dipHX}}} = n_{\text{X}}\frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\,\gamma_{\text{H}}^2\gamma_{\text{X}}^2 S_{\text{X}}(S_{\text{X}}+1)}{r_{\text{HX}}^6} \times \left(\frac{3\tau_c}{1+\omega_{\text{H}}^2\,\tau_c^2} + \frac{\tau_c}{1+(\omega_{\text{H}}-\omega_{\text{X}})^2\tau_c^2} + \frac{6\tau_c}{1+(\omega_{\text{H}}+\omega_{\text{X}})^2\tau_c^2}\right)$$

$$\frac{1}{T_1^{\text{CSA}}} = \frac{1}{15}\gamma_{\text{H}}^2 B_0^2 \Delta\sigma^2\left(\frac{2\tau_c}{1+\omega_{\text{H}}^2\tau_c^2}\right)$$

where n_{H} and n_{X} are the number of proton and X (X = Re, D) nuclei which contribute to relaxation, γ_{X}, S_{X}, and ω_{X} are respectively the gyromagnetic ratio, the nuclear spin quantum number, and the resonance frequency of nucleus X, μ_0 is the magnetic susceptivity in the vacuum, r_{HX} is the distance between proton and nucleus X, B_0 is the magnetic field intensity, and $\Delta\sigma$ is the CSA value.

(33) For the H−Re interaction, the ^{187}Re parameters have been used: since the gyromagnetic ratio is very similar to that of ^{185}Re (and S is the same for both), this assumption does not introduce significant errors in the calculations.

(34) Also in the case of μ-deuterides, unreliable residual charges on the metals, K', have been obtained when we attempted their estimates through the point charge approximation scheme[15]

$$\frac{e^2 q_{zz} Q}{h} = \left(\frac{e^2 Q}{h}\right) 2K'\left(\frac{3z^2 - r^2}{r^5}\right) = \left(\frac{e^2 Q}{h}\right) 2K'\left(\frac{3\sin^2(\theta/2) - 1}{r^3}\right)$$

where z, the principal axis, is assumed along the M···M vector for the doubly bridging hydrides, r is the M−H bond length and θ the M−H−M bond angle, the geometric parameters being derived from the available X-ray and/or neutron diffraction structures.[19,35]

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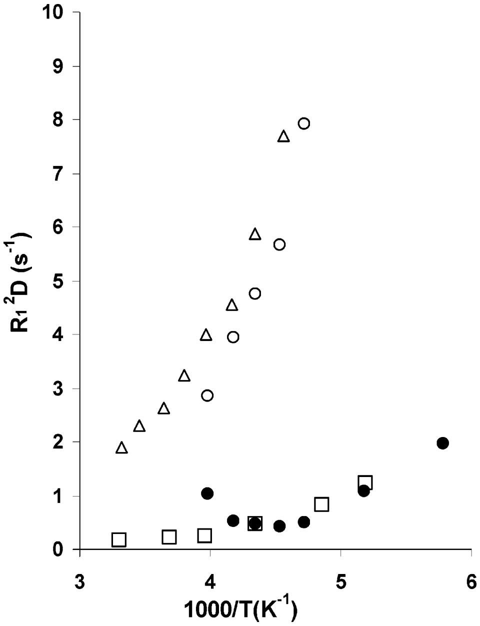

Figure 2. Variable-temperature ^{2}D relaxation rates (7 T) for compound **6** (○, μ-D; ●, μ_3-D). The relaxation rates for deuterides in compound **3** (□) and for D_b of compound **4** (△) are reported for comparison.

this series (80.1 kHz). An intermediate value (48.9 kHz) is found for the dimer **1**, which displays features intermediate between **2** and **3**: electronic unsaturation (32 ve's, 2 electrons short) but μ-coordination of the two deuterides bridging the Re–Re interaction.

These trends are confirmed by the values found for the anionic species **4**–**6**. Indeed, in the saturated compound **5** (48 ve's), both types of μ-bridging deuterides show DQCC values very similar to that of **2**. In contrast, the two types of μ-bridging deuteride ligands of the unsaturated triangular cluster **4** (46 ve's) show DQCC values quite close to that of the unsaturated dimer **1**. In particular, a smaller value is found for the H_a ligands of the basal Re(μ-H)$_2$Re fragment (a moiety similar to **1**), where the unsaturation is mainly localized, on the basis of the formal local electron count and the chemical reactivity.[29] Interestingly enough, the lower value of DQCC for the basal hydrides H_a, with respect to the hydrides H_b bridging the lateral edges, is accompanied by a higher hydridic character (it has been shown[23] that hydrides H_a interact with electrophiles, while H_b can be removed by OH^-). This suggests that the correlation between hydridic character and DQCC values might hold also for bridging hydrides, provided that all the other factors are constants.

The behavior of compound **6**, an unsaturated species (44 ve's) with both μ_3- and μ-hydrides, nicely fits in the above frame. Indeed, the relaxation rates of the μ_3 ligand closely follow those of compound **3**, while the behavior of the μ-deuterides is similar to that of **4** (Figure 2). Unfortunately this trend could be observed only at low temperatures, because **6** is fluxional and a dynamic process interchanges the hydrides,[25] leading to the progressive equalization of the relaxation rates at temperatures higher than 220 K. This process, being a 1:3 exchange, affects more remarkably the single μ_3-deuteride, the relaxation of which becomes faster on increasing the temperature, instead of slower, as expected for a simple temperature dependence (Figure 2). Therefore, we did not perform any fitting for the evaluation of the DQCCs, since too few low-temperature relaxation data could be reliably used.

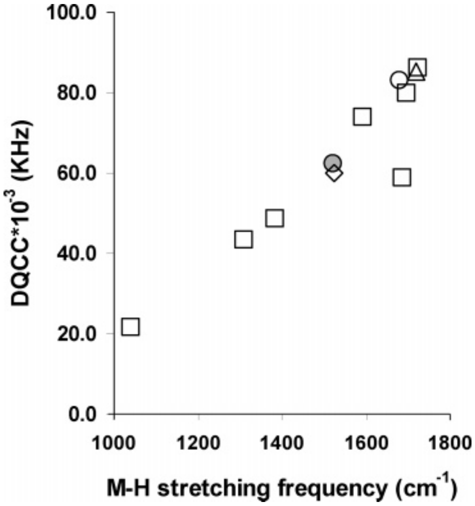

Figure 3. Correlation between the DQCCs of bridging deuterides and the M–H–M stretching frequencies reported in Table 2: (□) Re compounds; (○, △) the NEt_4 salts of $[W_2(\mu\text{-}H)(CO)_{10}]^-$ and $[Cr_2(\mu\text{-}H)(CO)_{10}]^-$, respectively; (●) PPN^+ salt of $[W_2(\mu\text{-}H)(CO)_{10}]^-$; (◇) $Os_3H(\mu\text{-}H)(CO)_{11}$.

On the basis of the above results, the DQCC values of the bridging ligands appear to be sensitive to (a) the unsaturation degree of the Re atoms bridged by the deuteride ligands, (b) the bridging mode (μ_3 vs μ), and (c) the number and the nature of the ligands bridging the same M–M interaction.

All of the observed differences in DQCC come from differences in the site symmetry and in the electron density available for each M–H interaction. Actually, correlations of DQCC with the X–H stretching frequencies[36] or force constants[37,38] were observed for terminally bound deuterons (including some transition-metal complexes),[37,38] and a decrease of DQCC values on going from terminal to bridging hydrides for the increase of M–H distance was predicted and observed.[38] Detailed vibrational studies[39] are available for some of the compounds investigated here, and we found a very good correlation between our experimental DQCCs and the highest energy stretching frequencies of the M–H–M bonds (Figure 3).[40]

Interestingly enough, in the approximation that the metal mass is infinitely large compared to the one of hydrogen, also the infrared data concerning the dimers[41] $[NEt_4][M_2(\mu\text{-}H)(CO)_{10}]$ (M = Cr, W), $[PPN][W_2(\mu\text{-}H)(CO)_{10}]$, and the bridging hydride[42] in $Os_3H(\mu\text{-}H)(CO)_{11}$

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[40] The only outliers are the data concerning the hydrides bridging the lateral edges of anion **4**.

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Table 2. Relevant M−H−M Stretching and DQCC Data for the Hydrido Carbonyl Complexes of Figure 3

compd	IR ν (cm^{-1})	DQCC (kHz)	ref[a]
1	1382	48.9	39a; this work
2	1697	80.1	39b; this work
3	1040	21.8	39d,e; this work
4 (H_a)	1309	43.5	39c; this work
4 (H_b)	1685	58.9	39c; this work
5 (H_a)	1590	74.1	39c; this work
5 (H_b)	1722	86.2	39c; this work
$[Cr_2(\mu\text{-}H)(CO)_{10}]^-$	1720	85.4	41 (NEt_4^+ salt); 15
$[W_2(\mu\text{-}H)(CO)_{10}]^-$	1680	83.0	41 (NEt_4^+ salt); 15
$[W_2(\mu\text{-}H)(CO)_{10}]^-$	1520	62.6	41 (PPN^+ salt); 15
$HOs_3(\mu\text{-}H)(CO)_{11}$	1525	60.1	42a,b; 7

[a] The first reference concerns the stretching data and the second one the DQCC data.

nicely fit in this correlation. On the basis of these results one can argue that, also in the absence of the deuterium NMR spectrum for a terminal or a bridging hydride site, an estimate of the deuterium quadrupolar coupling constant can be made from the M−H−M vibrational stretching frequencies. It is obvious that such a conclusion needs to be supported by further studies, due to the limited set of compounds presented in Table 2.

Conclusions

The results reported above show that in transition-metal complexes containing bridging deuterides DQCC is finely tuned by the electronic unsaturation, the bridging mode (μ_3 vs μ) of the deuteride ligands, and the presence of other bridging ligands. Even if the available series of compounds do not allow us to completely single out the effects of each different parameter, it is clear that electronic unsaturation and triple bridging coordination smooth the electric field gradient at the D atom and lead to low DQCC values. Therefore, DQCC's alone cannot be taken as indicative of the hydridic character, as has been suggested for terminal hydrides. Actually, the DQCC difference observed for two hydrides experimentally showing different polarizations (H_a and H_b in **4**) is much smaller (15 MHz) than the differences induced by the other aforementioned parameters.

Experimental Section

The deuteride derivatives **1** and **3** were prepared from $Re_2(CO)_{10}$ and D_2, according to literature procedures,[43,44] leading to mixtures of H_xD_y isotopomers. Partially deuterated samples of **2** were prepared by refluxing **1** in *n*-hexane;[19] the anion **6**, as the PPh_4^+ salt, was prepared from partially deuterated **3**;[28b] $[PPh_4]$**4** was obtained by reacting **6** with CO, and $[PPh_4]$**5** was obtained from the reaction of **4** with HCl.[24] Hydride ^1H chemical shift in CD_2Cl_2: **1**, −9.03 ppm; **2**, −17.12 ppm; **3**, −5.17 ppm; **4**, −8.67 (H_a) and −13.36 (H_b) ppm; **5**, −10.3 (H_a) and −13.9 (H_b) ppm; **6**, −5.96 (μ) and −8.14(μ_3) ppm.

T_1 measurements have been carried out on degassed samples by using the inversion recovery pulse sequence. Deuterium T_1 measurements have been performed in CH_2Cl_2 solutions on a Bruker Avance 600 instrument, operating at 92.10 MHz, in the 298−217 K temperature range and on a Bruker Avance 300 operating at 46.07 MHz, in the 298−173 K temperature range. ^1H T_1 measurements have been performed in CD_2Cl_2 solutions, in the 298−183 K temperature range, on Bruker Avance 300, JEOL EX-400 and Bruker Avance 600 instruments, operating at 300, 400, and 600 MHz respectively.

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Supporting Information Available: Experimental variable-temperature ^2D (Tables S1−S8) and ^1H (Tables S9−S14) relaxation data for compounds **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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