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Deuterium Quadrupole Coupling Constants and Ionic Bond Character in Transition Metal Hydride Complexes from ^{2}H NMR T_1 Relaxation Data in Solution

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Abstract: ^{2}H T_1 NMR relaxation times have been measured in solution for the D ligands of some transition metal hydride complexes and used for the calculation of deuterium quadrupole coupling constants (DQCC) and of the ionic contribution to the M–D bond. The DQCC values for the terminal hydride complexes $WD(CO)_2(NO)(PR_3)_2$ (R = CH_3, Ph), $MnD(NO)_2(PEt_3)_2$, $MnD(CO)_3(PEt_3)_2$, $ReD_2(CO)(NO)(PR_3)_2$ (R = CH_3, Cy, Pr^i, OPr^i), *cis*- and *trans*-$ReD(CO)(PMe_3)_4$, *cis,mer*-$ReD(CO)_2(PMe_3)_3$, *trans,mer*-$ReD(CO)_3(PMe_3)_2$, *fac*-$ReD(CO)_3(PMe_3)_2$, $OsD_4(PTol_3)_3$, $RhDCl_2(PPr^i{}_3)_2$, and $RhD_2Cl(PPr^i{}_3)_2$ cover a range from 55 to 158 kHz. Values of 148 and ≥120 kHz have been obtained for two nonclassical dihydrogen ligands of the complexes $ReD(D_2)(CO)(NO)(PMe_3)_2^+$ and $Re(D_2)(CO)(PMe_3)_4^+$, assuming their rapid rotation. The DQCC as well as the ionicity of the M–D bond is discussed in terms of structural parameters and substitution patterns of these complexes.

Introduction

The deuterium quadrupole coupling constant (DQCC) is a measure for the magnitude of the electric field gradient at the deuterium site and is therefore affected by the element-D bonding mode.[1] Thus, it represents an important parameter for the correlation of molecular structure and properties.

In this context it seemed of major interest to use the DQCC for the structural and electronic characterization of transition metal hydride complexes. However, up to now DQCC values were determined for only four transition metal deuteride complexes containing terminal M–D bonds (Cp_2MoD_2, 52 ± 3 kHz;[2a] Cp_2WD_2, 54 ± 4 kHz;[2a] $(CO)_5MnD$, 68.1 kHz;[2b] and Cp_2ZrD_2, 46.7 kHz[2c]) and for some bridging Cr and W hydrides.[1d] These constants were obtained by solid-state ^{2}H NMR spectra.

In this work we have tried to determine the DQCC by solution ^{2}H T_1 NMR techniques, and we wish to report in this paper the results of ^{2}H NMR studies of some terminal W, Mn, Re, Os, and Rh hydrides and two dihydrogen rhenium complexes. Earlier the solution NMR relaxation method was successfully applied for the determination of the DQCCs in organic compounds[2d] and of ^{11}B quadrupole coupling constants in *closo*-boranes and carboranes.[2e]

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere by standard techniques. Solvents (toluene-h_8 and CH_2Cl_2) were dried and freshly distilled before use. It should be noted that the freezing points of the studied solutions were, as a rule, lower than those of the pure solvent by 10–15°.

^{1}H, ^{2}H, ^{13}C, and ^{31}P NMR data were obtained on a Varian Gemini-300 spectrometer (300 MHz for ^{1}H nuclei). The inversion–recovery method (180–τ–90) was used to determine T_1 relaxation times. The calculations of the relaxation times were performed using the nonlinear three-parameter fitting routine of the spectrometer. The durations of the pulses were controlled at every studied temperature. The errors of such T_1 determinations were lower than 5%, and hence the relaxation appeared to be monoexponential. The temperature was calibrated by ^{1}H NMR with a standard methanol sample.

The following compounds were prepared as described in the literature: $WD(CO)_2(NO)(PR_3)_2$ (R = CH_3 (**1**), Ph (**2**)),[3a] $MnD(NO)_2(PEt_3)_2$ (**3**),[4a] $MnD(CO)_3(PEt_3)_2$ (**4**),[4a] $ReD_2(CO)(NO)(PR_3)_2$ (R = OPr^i (**5**), CH_3 (**6**), Cy (**7**), Pr^i (**8**))[3b] *cis*-$ReD(CO)(PMe_3)_4$ (**9**),[4a] *trans*-$ReD(CO)(PMe_3)_4$ (**10**),[4a] *cis,mer*-$ReD(CO)_2(PMe_3)_3$ (**11**),[4a] *trans,mer*-$ReD(CO)_3(PMe_3)_2$ (**12**),[4a] and *fac*-$ReD(CO)_3(PMe_3)_2$ (**13**).[4a] The complexes $ReD_2(CO)(NO)(PR_3)_2$ were prepared from the corresponding ReH_2 complexes (dissolved in toluene-h_8) by H/D exchange with CD_3OD at 50 °C as described in an earlier paper.[3a] The H/D exchanges were monitored by ^{1}H NMR, and after completion the solvent mixtures were evaporated in vacuo. The complexes $[ReD(D_2)(CO)(NO)(PMe_3)_2^+][CF_3COO^-]$ (**18**), $[Re(D_2)(CO)(PMe_3)_4^+][CF_3COO^-]$ (**19**), and $[ReD_2(CO)(PMe_3)_4^+][CF_3COO^-]$ (**14**) were obtained in situ by the protonation of the corresponding mono- and dihydrides with CF_3COOD[4b] in NMR tubes. All NMR parameters of **1–14** and **18, 19** are consistent with those reported earlier.[3,4]

Results and Discussion

T_1 relaxations of ^{2}H nuclei are completely dominated by quadrupole interactions.[5a] Quadrupole relaxation rates ($1/T_1$) are given by eq 1

$$1/T_1 = {}^3/_{50}\pi^2\frac{2I+3}{I^2(2I-1)}(e^2q_{zz}Q/h)^2(1+\eta^2/3)(\tau_c/(1+\tau_c{}^2\omega^2)+4\tau_c/(1+4\tau_c{}^2\omega^2)) \quad (1)$$

$$\tau_c = \tau_o \exp(E_{act}/RT)$$

where ω is the Larmor frequency, I is the nuclear spin, $e^2q_{zz}Q/h$ is the static quadrupole coupling constant, η represents the

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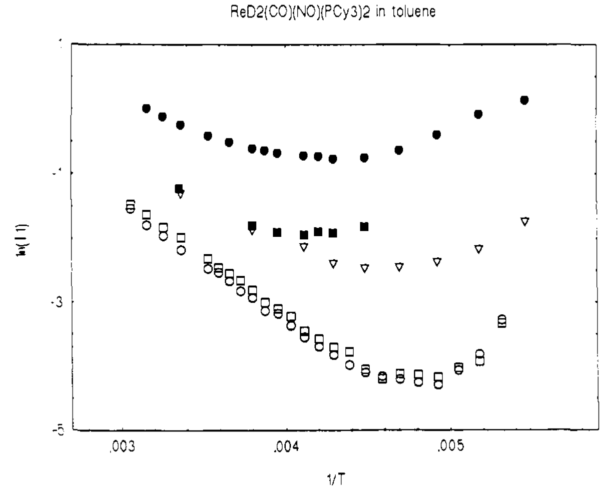

Figure 1. Variable-temperature T_1 data (T_1 in s) for the toluene solution of $ReD_2(CO)(NO)(PCy_3)_2$ (300 MHz for ^1H): ●, ^{31}P; ■, ^1H–Re (trans and cis to NO); ▽, $^{13}CH_2$; □, ^2H–Re (trans to CO); ○, ^2H–Re (trans to NO).

asymmetry parameter of the electric field gradient, and τ_c corresponds to the molecular rotational correlation time.

The minimum T_1 time is observed when $\omega\tau_c = 0.62$.[5a] Thus, the e^2qQ/h value can be calculated from eq 2

$$e^2qQ/h\ (\text{kHz}) = 10\left(\frac{0.6857}{46.06\ (\text{MHz})\ T_{1\text{min}}/\nu\ (\text{MHz})}\right)^{1/2} \quad (2)$$

where ν is the frequency in MHz. Equation 2 is valid for terminal hydrides with the asymmetry parameter η equal to 0, as it has been shown by solid-state ^2H NMR experiments.[2a–c]

The temperature-dependent part of eq 1 is the same as that in the case of ^1H homonuclear dipole–dipole relaxation.[6a] Hence both ^1H and ^2H $T_{1\text{min}}$ times are reached when $\omega\tau_c = 0.62$. Crabtree et al[6b] have shown that the H ligand $T_{1\text{min}}$ times can be detected in dilute solutions of mononuclear transition metal hydrides at low temperatures (usually from −70 to −90 °C) at 200–300 MHz. Later this was reported in many other studies.[6] Therefore the chance to observe the $T_{1\text{min}}$(M–D) times in such solutions seems to be quite low, because of the too large frequency difference between ^1H and ^2H nuclei and the too small activation energies of the molecular reorientations (2.5–3 kcal/mol[4a,6]). However, it should be possible to reach the temperature range of $T_{1\text{min}}$ in viscous media, in which a significant increase of τ_c and E_a can be expected.[5b] For this reason our investigations of complexes **1–14** and **18**, **19** were performed in concentrated solutions of toluene or CH_2Cl_2 (0.08–0.23 M).

Figure 1 shows the experimental temperature-dependent ^{31}P, ^2H-Re, ^1H-Re, and $^{13}CH_2$ T_1 data collected from a toluene-h_8 solution of complex **7**.[7a] Since it was required to carry out the determination of the ^1H T_1 times for the H ligands in $ReH_2(CO)(NO)(PCy_3)_2$ under exactly the same conditions, the solution of **7** was evaporated in vacuo, complex **7** was dissolved in toluene-d_8, and the hydride $ReH_2(CO)(NO)(PCy_3)_2$ was added to this solution.

All curves in Figure 1 go through broad minima showing individual values and temperature positions dependent on the type of observed nucleus. As mentioned above the ^1H and ^2H $T_{1\text{min}}$ time is reached when $\omega\tau_c = 0.62$. ^{13}C, ^1H heteronuclear dipole–dipole interactions[5a,6a] yield the $\omega\tau_c$ value equal to 0.792. In accord with the Arrhenius equation $\tau_c^{-1} = Ae^{-(E_a/RT)}$ used to describe the temperature dependence of τ_c for molecular reorientations of **7**, the linear plot of $-\ln(\tau_c)$ vs T^{-1} leads to an energy of activation of 4.6 kcal/mol. The ^{31}P T_1 data were excluded from this procedure, because of some uncertainty in the relaxation mechanisms.[6f]

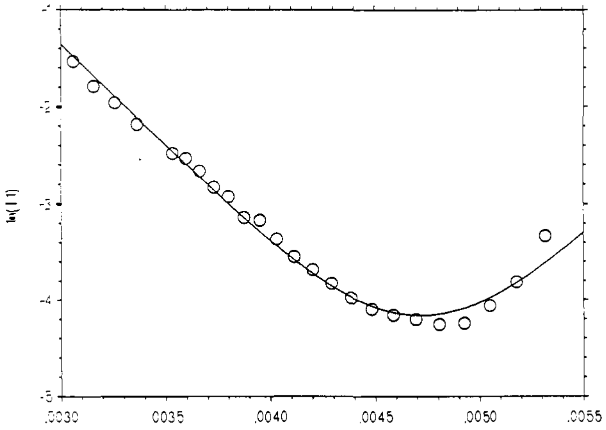

Figure 2. Variable-temperature T_1 data (T_1 in s) for the D ligand (trans to the NO group) of $ReD_2(CO)(NO)(PCy_3)_2$.

Figure 2 displays the experimental ^2H T_1 times for the D ligand (trans to the NO group) of complex **7** and the result of their nonlinear fittings to eq 1, respectively. If all temperature points are used, the theoretical and experimental data in the $T_{1\text{min}}$ range and in the low-temperature section of the curve do not match. In addition this treatment results in a smaller E_a value of 4.0 kcal/mol.

Equation 1 is only valid when the molecular reorientation can be characterized by a single correlation time (the case of isotropic molecular motion). It is also known that a reorientation motion of even small molecules (for example, toluene) can be anisotropic in the liquid phase.[5c] Thus, the observed discrepancy between theory and experiment could be caused by anisotropic motion of the dihydride **7**.

A recent analysis of anisotropic effects on the ^1H-ligand relaxation behavior of mononuclear transition metal hydride complexes containing two to four PR_3 ligands has shown that the ^1H–M $T_{1\text{min}}$ values are very reliable parameters for the determination of the force constants of proton–metal dipole–dipole interactions (the M–H distances). In addition the $T_{1\text{min}}$ values of such compounds were quite insensitive to those types of reorientational molecular motions.[4a]

In this work we observe the minimum relaxation time for the ^1H ligands in $H_2Re(CO)(NO)(PCy_3)_2$ at −30 °C (Figure 1). This is 40 °C higher than that in earlier work,[4a] where $H_2Re(CO)(NO)(PCy_3)_2$ has been investigated in dilute toluene-d_8 solution. However, in full accordance with the above-mentioned conclusion, the $T_{1\text{min}}$ value remains the same (144 ms at 300 MHz). Thus, we believe that the ^2H $T_{1\text{min}}$ parameter can be used equally well to calculate the quadrupole constants (DQCC) from eq 2. Very similar values were obtained for the D–Re $T_{1\text{min}}$ times in concentrated toluene-h_8 and CH_2Cl_2 solutions of complex **7**: $T_{1\text{min}}$ = 14.2 ms (D trans to NO) and $T_{1\text{min}}$ = 15.4 ms (D trans to CO) in toluene at −70 °C; $T_{1\text{min}}$ = 13.9 ms (D trans to NO) and $T_{1\text{min}}$ = 14.7 ms (D trans to CO) in CH_2Cl_2 at −90 °C. The latter also supports the reliability of the ^2H $T_{1\text{min}}$ parameter.

Figure 3 shows the ^2H T_1 data collected from the same toluene solution for the D ligand of complex **7** and for the aromatic deuterons of the toluene rings (at natural abundance). In addition the T_1 times of the aromatic deuterons of pure toluene at 46.06 (this work) and at 37.2 MHz[5d] are given.

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[7] (a) The temperature behavior of the T_1 times was the same for all CH_2 groups of **7**. Figure 1 shows one of them. (b) The T_1 time in eq 1 depends on the asymmetry parameter η. For the Rb–$(D_2)^+$ model the η value was calculated as 0.62.[12] In such a case the estimation of the DQCC for the (D_2) ligand of **18** yields 139 kHz.

Table I. DQCC Values, Effective Charges on the Metal (K(M)), an Ionicities of the M–D Bonds (i) for the Transition Metal Hydride Complexes Determined from the ^{2}H $T_{1\min}$ Measurements in Toluene-h_8 Solution

compound	$T_{1\min}$, ms (T, °C)	e^2qQ/h, KHz	r_{M-H}, Å	K(M), e	i
$WD(CO)_2(NO)(PMe_3)_2$ (**1**)	22.7 (–95)	55.0 ± 0.6	1.732[e]	+1.1	0.76
$WD(CO)_2(NO)(PPh_3)_2$ (**2**)	22.5 (–70)	55.2 ± 0.6	1.732[e]	+1.1	0.76
$MnD(NO)_2(PEt_3)_2$ (**3**)	21.5 (–87)	56.4 ± 0.6	1.59[f]	+0.91	0.75
$MnD(CO)_3(PEt_3)_2$ (**4**)	15.4 (–90)	66.7 ± 1.0	1.62[r]	+1.1	0.71
$ReD_2(CO)(NO)(POPr^i_3)_2$ (**5**)	14.5 (–80)[a]	68.8 ± 1.0	1.71[f]	+1.4	0.70
	15.6 (–80)	66.3 ± 1.0	1.71[f]	+1.3	0.71
$ReD_2(CO)(NO)(PMe_3)_2$ (**6**)	14.0 (–100)[a]	70.0 ± 1.0	1.72[f]	+1.4	0.69
	16.1 (–100)	65.3 ± 1.0	1.75[f]	+1.4	0.71
$ReD_2(CO)(NO)(PCy_3)_2$ (**7**)	14.2 (–70)[a]	69.5 ± 1.0	1.71[f]	+1.4	0.69
	15.4 (–70)	66.7 ± 1.0	1.74[f]	+1.4	0.71
$ReD_2(CO)(NO)(PPr^i_3)_2$ (**8**)	13.1 (–87)[a]	71.0 ± 1.0			0.69
	14.5 (–87)	68.8 ± 1.0			0.70
cis-$ReD(CO)(PMe_3)_4$ (**9**)	12.4 (–110)[b]	74.4 ± 1.0	1.69[f]	+1.4	0.67
trans-$ReD(CO)(PMe_3)_4$ (**10**)	15.3 (–110)[b]	66.8 ± 1.0	1.77[f]	+1.5	0.71
cis,mer-$ReD(CO)_2(PMe_3)_3$ (**11**)	17.0 (–87)	63.5 ± 1.0			0.72
trans,mer-$ReD(CO)_3(PMe_3)_2$ (**12**)	16.4 (–95)	64.7 ± 1.0			0.71
fac-$ReD(CO)_3(PMe_3)_2$ (**13**)	15.7 (–90)	66.1 ± 1.0			0.71
$ReD_2(CO)(PMe_3)_4$ (**14**)	12.2 (–115)[b]	74.9 ± 1.0			0.67
$OsD_4(PTol_3)_3$ (**15**)		91.0 ± 1.8[c]	1.659[e]	+1.7	0.60
$RhDCl_2(PPr^i_3)_2$ (**16**)		136 ± 5[d]	1.43[g]	+1.5	0.40
$RhD_2Cl(PPr^i_3)_2$ (**17**)		158 ± 6[d]	1.40[g]	+1.6	0.30
$ReD(D_2)(CO)(NO)(PMe_3)_2^+$ (**18**)	13.1 (–115)[b]	74.0			
	12.5 (calc)	148 ± 5			
$Re(D_2)(CO)(PMe_3)_4^+$ (**19**)	≤19.0 (–110)[b]	≥61			
		≥120			

[a] trans to the NO group. [b] In CH_2Cl_2. [c] Calculated from the $T_{1\min}$ value taken from ref 6a. [d] From the ^{2}H, ^{1}H T_1 data.[8] [e] Neutron diffraction data.[9] [f] Calculated in ref 4a from the ^{1}H T_1 data. [g] Neutron diffraction and three-dimensional single-crystal X-ray analysis of **16**[9a] and $RhH_2Cl(PBu^t_3)_2$.[10]

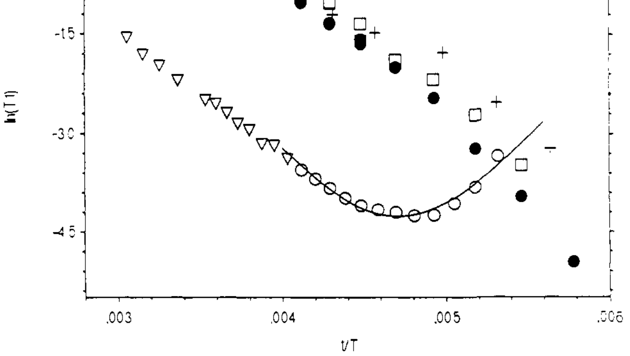

Figure 3. Variable-temperature T_1 data collected in the same solution for the D ligand (trans to the NO group) of $ReD_2(CO)(NO)(PCy_3)_2$ and for the C_6D_5 deuterons of toluene-h_8 (at natural abundance): ●, C_6D_5; ○ and ▽, D–Re. The T_1 times of the C_6D_5 ring of the pure toluene are represented by □ at 46.06 MHz and by + at 37.2 MHz.

The following main features are essential to Figure 3: (i) at temperatures above 240 K the T_1 times of pure toluene and toluene solution are very similar, (ii) below this temperature the T_1 times of pure toluene are markedly longer, (iii) below 240 K the relaxation rates of pure toluene are dependent on the Larmor frequency, (iv) below 250 K the Re–D T_1 times show a good fit with eq 1. This fitting leads to an E_a value of 4.8 kcal/mol, which was found above by applying the ^{1}H, ^{2}H, and ^{13}C $T_{1\min}$ approach; the points between –20 and +50 °C form approximately a straight line with a smaller slope (E_a = 3.5 kcal/mol). It should be noted that the latter was observed for all toluene solutions of the investigated complexes.

As denoted in (iii), the relaxation rates of the aromatic deuterons of pure toluene are different at 46.06 and 37.2 MHz below 240 K. A similar frequency dependence of the ^{2}H T_1 times has already been observed for small molecules (CD_2Cl_2, CD_3CN) at low temperatures in a viscous liquid phase with η between 22 and 316 c. It has been attributed to the appearance of locally ordered domains and slowly relaxing local structures.[5b] For the interpretation of the NMR relaxation behavior of a solute in solution, different physical models are generally applied. However all of them imply solute/solvent interactions and use relative solute/solvent size parameters.[5b] Following this logic, a "sticking" between molecules like that for complex **7** and toluene at low temperatures would result in an increase of the effective rotation correlation time τ_c and of the effective E_a value, respectively (see (iv)). It is obvious that such a phenomenon strongly complicates any calculation of the real correlation times from T_1 data (like in the case of anisotropic motions). However these effects seem to be insignificant when the quadrupole coupling constant is deduced from $T_{1\min}$ values according to eq 2. The small difference of the DQCC values found for substitutionally related Mn complexes in solution ($MnD(CO)_3(PEt_3)_2$, 66.7 kHz) and in the solid state ($MnD(CO)_5$, 68.1 kHz[2b]) can be considered as a support of the $T_{1\min}$ approach.

Table I lists the DQCC values of deuteride ligands determined by $T_{1\min}$ measurements in this work or calculated from literature ^{2}H T_1 data[6a,8] for transition metal hydrides containing phosphorus donors. The r(M–H) distances in Table I have been taken from neutron diffraction,[9] ^{1}H T_1 NMR,[4a] or three-dimensional X-ray[10] experiments.

Protonation of **6** and **9** with CF_3COOD[4b] results in the formation of nonclassical dihydrogen complexes **18** and **19**,

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respectively. The DQCC values for the (D_2) ligands are listed in Table I. The ^2H NMR spectra of **18** display an averaged signal of terminal D and (D_2) ligands due to a very fast positional exchange.[4b] The DQCC value for the (D_2) ligand of **18** (74 kHz at $T_{1\min} = 12.5$ ms in Table I) can be calculated by taking this exchange into account and by use of the corresponding averaged value of $T_{1\min}$ for the classical D ligands of **6**.

The values obtained (74 and ≥61 kHz for **18** and **19**, respectively) differ strongly from 124 kHz found in the solid-state ^2H NMR spectra of Kubas's dihydrogen complex[11] and from 155 kHz calculated for the $Rb-(D_2)^+$ model with $r(Rb-(D_2)) = 1.75$ Å.[12] However, this disaccord can be reconciled if the (D_2) ligands of **18** and **19** are viewed as rapidly spinning structural units ((H_2) rotation is well-known for such complexes[13a]). In this context a fourfold difference between the observed and real $T_{1\min}$ times is expected,[13b] which leads to DQCC values of 148[7b] and ≥120 kHz for **18** and **19**, respectively.

Thus, these data can be envisaged as independent evidence for the spinning nature of the (D_2) ligand. However they show that a dideuterium ligand (D_2) cannot unambiguously be distinguished from a dideuteride structural unit $(D)_2$ by an ^2H $T_{1\min}$ criterion.

The smallest known DQCC value of 33 kHz has been found for LiD.[14] The results in Table I show that among classical terminal transition metal deuterides the DQCC can vary from 55 to 158 kHz.

The DQCC may be used to characterize such molecules. The magnitude of the electric field gradient (eq_{zz}) on the deuterium site consists of a sum of nuclear and electronic terms.[1d] The latter is expressed as an expectation value of the electronic wave function ψ in eq 3

$$eq_{zz} = +\sum_n K_n \frac{3z_n^2 - r_n^2}{r_n^5} - e\left\langle \psi^* / \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} / \psi \right\rangle \quad (3)$$

where e is the electronic charge, n is the index over the other nuclei with the charge K_n, and i the index over the electrons. In order to represent the combined nuclear and electronic contributions from neighboring atoms, a point charge model can be used,[1d] which yields eq 4 in the case of the terminal M–H bond

$$e^2qQ/h = 2(e^2Q/h)K(M)\,r^{-3} \quad (4)$$

where r is the M–H bond length and $K(M)$ is an effective charge on the metal center. According to eq 4 the latter can be calculated if the M–H bond length and the sign of the DQCC are known. Assuming a positive sign for DQCC,[1a] the effective charge on the metal center was found to be between $+1.1e$ $(WD(CO)_2(NO)(PMe_3)_2)$ and $+1.7e$ $(OsD_4(PTol_3)_3)$ (see Table I). However the chemical meaning of this charge parameter is unclear. A rough tendency to go along with the oxidation state of the transition metal center may be derived, but there is no recognizable analytical relationship.

According to eq 4 the DQCC is strongly affected by the M–H bond length. Actually in this work the largest values of DQCC (136, 158 kHz)[8b] are found for the Rh hydrides with extremely short metal hydride distances.[9a,b] On the other hand, in deuterides of the alkali metals the DQCC value changes moderately (33–19.74 kHz[12]) in spite of a strong difference in the M–H distance (from 1.595 Å in LiD to 2.494 Å in CsD). As in the case of the point charge model, there is no obvious correlation of DQCCs with bond distances.

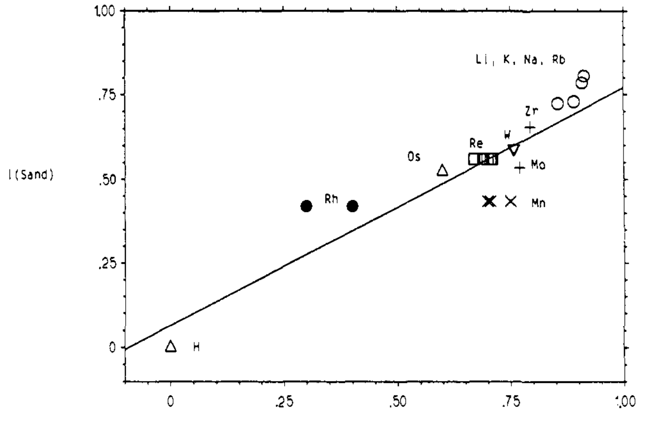

Figure 4. Plot of the ionic character of the M–D bonds calculated from eq 6 (i) versus the ionic character i(Sand) derived from Sanderson's electronegativities of the elements.

Following selected centers in a row of the PSE, a more drastic change of the DQCC is observed, for example on going from Rb to Rh deuterides RbD (19.74 kHz[12]) < Cp_2ZrD_2 (46.7 kHz[2c]) < Cp_2MoD_2 (52 kHz[2a]) < $RhD_2Cl(PPr^i_3)_2$ (158 kHz), suggesting a dependency on the M–H bond character. It is well-known that the quadrupole constants of ^{35}Cl nuclei derived from NQR measurements are affected by the ionic character of the element–chlorine bond.[15] The latter can be estimated from eq 5

$$(e^2qQ/h(X-Cl)) = (1 - S)(1 - i)(e^2qQ/h(Cl_2)) \quad (5)$$

relating the quadrupole constants of the Cl nuclei with the s orbital contribution $(1 - S)$ and the ionic character (i) of X–Cl bonds (it should be noted that eq 5 is a simplified interpretation of eq 3).

As mentioned already among metal deuterides, the smallest experimental DQCC value of 33 kHz is known for the LiD molecule,[14] getting close to the ionic limit of a M–D bond with a zero DQCC value. Theoretical calculations of DQCC for the other alkali metal hydrides led to values of 19.7–24.8 kHz.[12] On the other hand a DQCC value of 227 kHz has been measured for the HD molecule,[15b] representing the pure covalent end of the scale. A hydrogen atom is connected to other partner atoms by an s orbital only, and therefore eq 5 simplifies into eq 6.

$$i = 1 - \mathrm{DQCC}/227 \quad (6)$$

The DQCC (Table I and data obtained earlier from solid-state ^2H NMR) can directly provide chemically valuable information on the ionicity of the M–D bond in metal hydrides. Figure 4 shows the plot of the ionic character of the M–D bonds calculated from eq 6 (i) versus the ionic character i(Sand) found from corresponding Sanderson's electronegativities of the elements.[16] The relatively good agreement was quite surprising and seemed to give support to our approach. However it should be pointed out that the electronegativities of the metals depend on their ligand sphere and this may be the reason why significant deviations from a linear relationship are observed in Figure 4.

The M–H bond polarities of compounds **1**–**17** span a wide range covering prevailing ionicity in $WD(CO)_2(NO)L_2$ systems (L = phosphorus donor) to predominant covalency in $RhD_2Cl(PPr^i_3)_2$, which is in the latter case due to a very short Rh–D bond. Since the sign of DQCC cannot be determined from the $T_{1\min}$ measurements, we follow conclusions[17,18] derived earlier

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that all transition metal hydride complexes should display "hydridicity" in their bond polarizations. This was demonstrated to be the case even for such L_nM–H species which are capable of dissociating protons in polar solvents.

The strong polarities of the tungsten and manganese deuterium bonds in **1**, **2**, and **3**, which are approaching the up to now limiting case of hydridicity in transition metal hydride bond in Cp_2ZrD_2[2c] (i = 0.79), are reflected in their high propensity to undergo hydride-transfer reactions.[19,20] In addition it should be mentioned that the polar bond characters in **1** and **2** obviously give rise to intensive ν(W–H) IR absorptions.[3a] The enhanced ionic contribution to the M–H bond in **1**, **2**, and **3** may at least partly be attributed to the electronic effect of a nitrosyl ligand. From UPS measurements on cyclopentadienylnitrosyltungsten complexes, it is known that the nitrosyl moiety tends to put transition metal centers at lower first ionization potentials,[21] which consequently induce hydridicity in H or D substituents, respectively.

Table I shows a remarkable sensitivity of the DQCC and the M–D bond polarity to the trans influence of ligands in the Re complexes **5–8** and **10–13**. A difference in DQCC of the two deuterium ligands in complexes **5–8** (2.5–4.7 kHz) is paralleled by their chemical nonequivalency probably due to the different trans influence of the NO and CO group. The effect of a trans influence can also be seen from the difference in DQCC and bond ionicity of **9** and **10**, in which a PMe_3 or a CO ligand are located trans to the deuterium atom. Futhermore DQCCs of D ligands in Re complexes which are located trans to a CO group (**5–8** and **10–13**) fall into a quite narrow range between 63.5 and 68.8 kHz. However, it is obvious that these conclusions need to be supported in the future because of the limited set of the compounds in Table I.

Conclusion

This work shows that solution ^2H T_1 NMR measurements are well suited for the determination of the static DQCC in terminal transition metal deuteride complexes.

The DQCC values for a series of classical terminal W, Mn, Re, Os, and Rh deuterides were found to vary from 55 to 158 kHz. The largest constants are observed in Rh deuterides with extremely short M–H bond lengths. Values of 148 and 120 kHz are obtained for the dideuterium ligands of two nonclassical Re deuterides. The DQCC values of terminal deuteride complexes reflect the ionic M–D bond character. Thus, this study provides evidence for the use of DQCCs as important parameters of transition metal hydride systems.

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