^{2}H-T_1 Relaxation and Deuterium Quadrupole Coupling Constants in Transition Metal η^2-D_2 Complexes

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Abstract: ^{2}H-$T_{1\,min}$ values of the classical D and non-classical D_2 ligands in the complexes pp_3RuD_2 ($[D_2]$**1**), pp_3OsD_2 ($[D_2]$**2**), $[pp_3RuD(D_2)]^+$ ($[D_3]$**3**), and $[pp_3OsD(D_2)]^+$ ($[D_3]$**4**) ($pp_3 = P(CH_2CH_2PPh_2)_3$) have been measured by variable-temperature ^{2}H NMR spectroscopy in CH_2Cl_2. The deuterium quadrupole coupling constants (DQCCs) for the dihydrogen ligands in $[D_3]$**3**, $[D_3]$**4**, $[OsD(D_2)Cl(CO)[P(iPr)_3]_2]$ ($[D_3]$**8**) and $[Re(PMe_3)_4CO(D_2)]^+$ ($[D_2]$**10**) have been derived from the ^{2}H-$T_{1\,min}$ data assuming four different models of internal D_2 motion. By estimating the angle α between the direction of the electric field gradient and the motion axis, and the asymmetry parameter η, from MO calculations, we showed that the model adopted can influence the calculation of the DQCC. The DQCCs in the dideuterium complexes ranged between 47 and 86 kHz (or between 56 and 101 kHz when α was close to the magic angle), demonstrating clearly that the DQCC in a D_2 ligand is lower than that in comparable, classical deuteride systems. This conclusion was supported by independent ^{2}H-$T_{1\,min}$ experiments carried out on both $[Cp^*Ru(D_2)(dppm)]^+$ (dppm = $PPh_2CH_2PPh_2$) containing a D_2 ligand that was quite rigid (on the T_1 NMR time scale) and its classical analogue $[Cp^*Ru(D)_2(dppm)]^+$. The results can be interpreted in terms of direct back-bonding interactions between M and H in an $M-H_2$ *triangulo* system.

Keywords: deuterium · NMR spectroscopy · osmium · ruthenium

Introduction

Since the discovery of transition metal–dihydrogen complexes,[1] ^{1}H-T_1 NMR relaxation has become an important diagnostic method (the T_1 criterion) for assessing the presence of intact dihydrogen ligands in polyhydrido metal complexes. In η^2-H_2 complexes the $^{1}H-^{1}H$ dipole–dipole interactions can effectively shorten the longitudinal relaxation times T_1 to less than 0.03 s (250 MHz), whereas values higher than 0.3 s are observed for classical dihydride systems.[2]

Besides the determination of J(H,D) coupling constants in the monodeuterated η^2-HD derivatives,[1b,c] a physical parameter that may be very relevant to the structural characterisation of polyhydrido metal complexes in solution is the deuterium quadrupole coupling constant (DQCC). The formation of a chemical bond creates a strong non-homogeneous electric field along its direction (the z axis). A measure of this field is the magnitude of the electric field gradient,[3a] $q_{zz} = \partial^2 V/\partial^2 z$, where V is the electrostatic potential at the atomic nucleus. The electric field gradient at deuterium, expressed as the DQCC, is affected by the element–deuterium (X–D; $X \neq M$) bonding interaction,[3] and by other well-known factors;[3a] in particular, the DQCC depends on the nuclear charge of the atom X, and rises as the X–D bond length decreases. Recently it has been suggested that the DQCC also reflects the ionicity of the metal–deuterium bond in classical perdeuterated polyhydrido complexes.[4] For all of these reasons, DQCC measurements may be extremely important to studies of the nature of $M(H_2)$ bonding.

Both theoretical and experimental methods have been developed recently to determine the DQCC of deuterium in a metal complex.[3, 5a,b]

Molecular orbital (MO) calculations on a $[Rb-D_2]^+$ model compound[3c] have predicted that the DQCC may vary from approximately 15 to 155 kHz when the rubidium dihydride species is transformed into the η^2-H_2 derivative (in the free HD molecule, a DQCC of 227 kHz has been measured).[3a]

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The electric field gradient is the sum of nuclear and electronic terms (Equation (1), where e is the electronic charge, n is the index of the other nuclei with charge K_n and i is the index of the electrons of the molecule).[3]

$$eq_{zz} = \sum_{n} K_n(3z_n^2 - r_n^2)/r_n^5 - e\langle \psi^* \,|\, \sum_{i} (3z_i^2 - r_i^2)/r_i^5 \,|\, \psi \rangle \tag{1}$$

For the free HD molecule, this equation leads to a nuclear contribution (to the total DQCC) of 404 kHz ($r = 0.79$ Å).[3a] When the H–H distance is 0.85 Å, this contribution is reduced to 312 kHz. Since dihydrogen coordination to a transition metal centre results in an elongation of the H–H bond,[1] the DQCC value of 155 kHz obtained from theoretical calculations for the $[Rb-D_2]^+$ model[3c] seems to be quite reasonable.

An experimental method for calculating the DQCC is based on determination of the quadrupole splitting ($\Delta\nu_q$) of deuterium from solid-state ^{2}H NMR spectra [5a,b] (Equation (2), in which α is the angle between the direction of the

$$\Delta\nu_q = 0.75\,\mathrm{DQCC}\cdot 0.5\,(3\cos\alpha^2 - 1) \tag{2}$$

electric field gradient and the motion axis with an order of symmetry greater than 2).[5b]

This method, however, cannot be applied universally as the calculation of DQCC from $\Delta\nu_q$ depends strongly on internal D_2 motion. Equation (2) transforms into Equation (2a) in the

$$\Delta\nu_q = 0.75\,\mathrm{DQCC} \tag{2a}$$

absence of motion. For example, experimental data for the complex $[W(D_2)(CO)_3\{P(i\mathrm{Pr})_3\}_2]$show a resonance with a quadrupole splitting ($\Delta\nu_q$) of 62 kHz in the solid-state ^{2}H NMR spectrum.[5a] If fast D_2 rotational diffusion (Figure 1a) with $\alpha = 90°$ (the major axis of the electric field lies along the D–D bond) is assumed, a $\Delta\nu_q$ value of 62 kHz gives DQCC = 165 kHz. In the absence of intensive D_2 motion [Eq. (2a)], 62 kHz would give a DQCC value of 82.7 kHz. According to the ^{1}H NMR spectra, the H_2 ligand in solid $[W(H_2)(CO)_3\{P(i\mathrm{Pr})_3\}_2]$ undergoes a zero-point libration in a twofold well with an averaged libration angle ϕ of 16° (Figure 1b).[5c] In this case, Equation (2) is not valid and thus the DQCC value in the complex may assume values between 83 and 165 kHz.

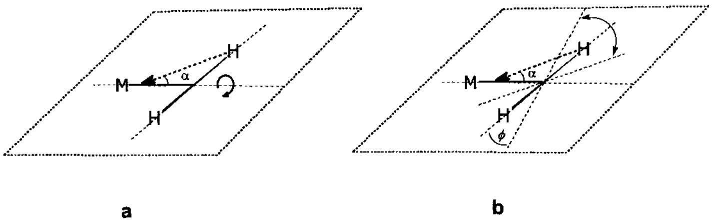
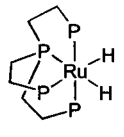


Figure 1. Motion of the H_2 ligand: a) rotational, b) librational.

We show here that variable-temperature ^{2}H-T_1 relaxation experiments in solution may indeed provide an alternative, valid method for the determination of DQCC in non-classical dideuterium–metal complexes.[4] The classical or non-classical polyhydrido structures of all the compounds investigated (**1**–**11**) have been determined unambiguously by a variety of solid-state and solution techniques.[6b, 7, 8b, 9a]



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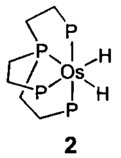

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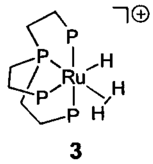

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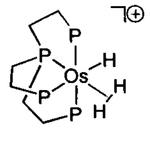

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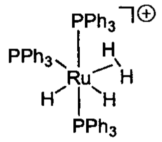

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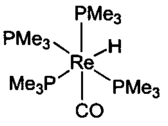

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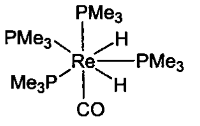

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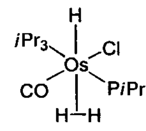

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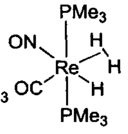

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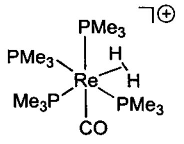

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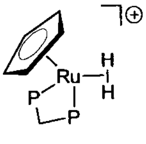

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Results and Discussion

DQCCs from MO calculations: A theoretical study of a simple $[Rb-D_2]^+$ model[3c] has recently shown that the transformation of the Rb dideuteride species into the dideuterium isomer is accompanied by both a change in DQCC from approximately 15 to 155 kHz and an increase in the asymmetry parameter η ($\eta = |q_{xx} - q_{yy}|/q_{zz}$) from 0.025 to 0.62. It has also been reported that the orientation of the main axis of the electric field gradient, which is aligned with the D–D bond in the dideuterium molecule, rotates towards the M–D bond as the D–D bond is broken. According to the calculations, the angle α (Figure 1a) in the dihydrogen ligand assumes a value of 77°.

For the transition metal complexes that we investigated, our calculations have revealed a similar tendency (Table 1). In particular, the α and η values for the D_2 ligands are in the

Table 1. Electric field gradients (q_{ZZ}), asymmetry parameters (η), DQCC and α values calculated for some perdeuterated molecular hydrogen complexes.

Complex	q_{ZZ} [au]	η	DQCC[a] [kHz]	α [°]
$[W(D_2)(CO)_3(PH_3)_2]$	– 0.1767	0.64	119	84
$[WD(NO)(CO)_2(PH_3)_2]$	– 0.1044	0.078	70.2	–
$[Os\mathbf{D}(D_2)(CO)Cl(PH_3)_2]$	– 0.1830	0.085	123	–
$[OsD(\mathbf{D}_2)(CO)Cl(PH_3)_2]$	– 0.1919	0.481	129	84
$[P(CH_2CH_2PH_2)_3Ru(D_2)\mathbf{D}]^+$	– 0.1314	0.056	88	–
$[P(CH_2CH_2PH_2)_3Ru(\mathbf{D}_2)D]^+$	– 0.2231	0.45	150	84
	– 0.2141	0.49	144	83
$[P(CH_2CH_2PH_2)_3Os(D_2)\mathbf{D}]^+$	– 0.1490	0.053	100	–
$[P(CH_2CH_2PH_2)_3Os(\mathbf{D}_2)D]^+$	– 0.1601	0.83	108	74
	– 0.1530	0.87	103	72

[a] The DQCC values has been calculated from the equation: DQCC = 672 q_{zz} where 672 is the conversion factor for the deuteron [kHz au^{-1}] (see reference [3a]).

range 73–84° and 0.45–0.87, respectively. The DQCC values increase on going from the classical deuteride ligands to the non-classical deuterium ones. Interestingly, this effect is very weak for $[pp_3Os(D_2)D]^+$ ($[D_3]$**4**) and $[OsD(D_2)(CO)Cl(PH_3)_2]$ ($[D_3]$**8**) as the calculated DQCC values for the D and D_2 ligands are practically identical, indicating that the DQCC difference for classical and non-classical deuteride ligands depends on the nature of the transition metal. The D_2 ligands in complexes $[D_3]$**3** and $[D_3]$**4** have two inequivalent deuterium atoms arising from the difference in their interactions with the terminal deuterium ligand.[10] It is noteworthy that the η values calculated for the classical deuteride ligands are very close to 0, in excellent agreement with the solid-state ^{2}H NMR spectra of metal complexes containing terminal deuterides.[3]

The DQCC values in Table 1 range between 103 and 150 kHz and, as expected, are remarkably lower than that measured for free HD (227 kHz).[3a] Nevertheless, these constants may be overestimated because the DQCCs for the CD_2 groups proximal to the phosphorus donors in $[P(CH_2CH_2PH_2)_3Ru(D_2)D]^+$ and $[P(CH_2CH_2PH_2)_3Os(D_2)D]^+$ (models for $[D_3]$**3** and $[D_3]$**4**, respectively) are 201–204 kHz (calculated) and 167 kHz (determined by solid-state ^{2}H NMR experiments on aliphatic C–D groups).[5b] Moreover, for the classical deuteride ligands in $[WD(NO)(CO)_2(PH_3)_2]$ and $[OsD(D_2)(CO)Cl(PH_3)_2]$, the calculations give DQCCs of 70.2 and 123 kHz, respectively, whereas much lower values were found experimentally (55.2 and 87.3 kHz for $[WD(NO)(CO)_2(PMe_3)_2]$[4] and $[OsD(D_2)(CO)Cl\{P(i\text{-}Pr)_3\}_2]$,[9a] respectively).

The computed ab initio values of DQCC do not show good quantitative agreement with experimental data,[11] and, in general, give DQCCs for dideuterium which are not much higher than those of the classical dideuteride ligands. Nonetheless, the calculations have provided more reliable α and η values for the D_2 ligands than those obtainable from equations containing additional parameters to be determined experimentally.[3b]

^{2}H relaxation theory and the influence of internal D_2 motion on DQCC values: ^{2}H spin–lattice relaxation in solution is dominated by quadrupole interactions (Equation (3), where I

$$1/T_1 = 0.06\pi^2(2I+3)(I^2(2I-1))^{-1}(e^2q_{zz}Q/h)^2(1+\eta^2/3)$$
$$(\tau_{mol}/(1+\omega_D{}^2\tau_{mol}{}^2)+4\tau_{mol}/(1+4\omega_D{}^2\tau_{mol}{}^2))$$

$$\tau_{mol} = \tau_0\exp(E_{act}/RT) \tag{3}$$

$$\eta = |q_{xx}-q_{yy}|/q_{zz}$$

is the spin of D, η represents the asymmetry parameter of the electric field gradient on D, $(e^2q_{zz}Q/h)$ is the DQCC reflecting the electric field gradient on D and τ_{mol} is the correlation time of isotropic molecular re-orientations).[6a]

The isotropic approximation in quantitative interpretations of $T_{1\,min}$ relaxation data is valid in spite of the anisotropic character of the molecular motion of transition metal hydride complexes.[6b,c] When T_1 reaches a minimum ($T_{1\,min}$), the DQCC value can be calculated readily by means of Equation (4), where DQCC, ν and $T_{1\,min}$ are measured in kHz, MHz and s, respectively.[4]

$$DQCC = 1.2201(1+\eta^2/3)^{-1/2}(\nu/T_{1\,min})^{1/2} \tag{4}$$

Accordingly, the observation of ^{2}H-$T_{1\,min}$ provides a simple and reliable method for the determination of the DQCC in non-classical D_2 metal complexes if the η values are known and the deuterium ligands are relatively immobile (that is, the correlation time of any internal motion of the D_2 ligand must be much greater than τ_{mol}).

According to theoretical and experimental data,[3a,c] the asymmetry parameter η is close to 0 in terminal deuterides and in free D_2, but is expected to be non-zero in non-classical D_2 ligands. It can reach 0.85 in transition metal–dihydrogen complexes (Table 1). A simple estimate shows that even in this case the magnitude $(1+\eta^2/3)^{1/2}$ in Equation (4) gives a value of only 1.1. On this basis it is evident that the effect of η on the calculation of the DQCC is not dramatic, although some ambiguity may always be present.

Fast intramolecular rotation of the D_2 ligand around the axis perpendicular to the D–D bond with the correlation time $\tau D_2 \ll \tau_{mol}$ may generate strong effects on the DQCC calculation, however (Figure 1a). The influence of this rotation on the ^{1}H relaxation properties of dihydrogen complexes has been analysed thoroughly by Morris and Wittebort.[12a] The same approach (in terms of Woessner's equations[12b]) gives Equation (5), where α is the angle between the rotation axis and the direction of the main axis of the electric field gradient (Figure 1a).

$$DQCC = 2.4402(1+\eta^2/3)^{-1/2}[\nu/T_{1\,min}\cdot(3\cos^2\alpha-1)^2]^{1/2} \tag{5}$$

From an analysis of this expression, it is readily evident that the fast D_2 rotation with $\alpha = 90°$ results in a two-fold increase in the DQCC calculated from $T_{1\,min.}$ According to the theoretical calculations, α may assume values ranging from of 83 to 73° in the transition metal–dihydrogen complexes investigated (Table 1) and 77° in $[RbD_2]^+$. This situation generates a stronger effect which, however, can be estimated using Equation (5). Interestingly, the fast D_2 rotation leads to a remarkable elongation of ^{2}H-$T_{1\,min}$ relative to the relaxation time of an immobile D_2 ligand.

Figure 1b illustrates a D_2 ligand undergoing the above-mentioned librational motion in a two-fold potential well when the barrier to rotation is quite high ($E_{rot} > E_{act}$ in Equation (3)). The ^{1}H-T_1 relaxation behaviour of such complexes was analysed by Morris and Wittebort.[12a] The deuterium relaxation can be treated in a similar manner on the basis of Woessner's functions of spectral density.[12b] For a fast-spinning D_2 ligand, these functions take the form of Equations (6a) and (6b), where $\tau_c = [1/\tau_{mol} + 1/\tau D_2]^{-1}$, τ_{mol} is the correlation time of molecular re-orientations, τD_2 is the correlation time for the D_2 motion and α is the angle between the motion axis and the electric field gradient vector.

$$J(\omega) = 0.25(3\cos^2\alpha-1)^2(\tau_{mol}/(1+\omega^2\tau_{mol}{}^2)$$
$$+0.75\sin^2 2\alpha(\tau_c/(1+\omega^2\tau_c{}^2)+0.75\sin^4\alpha(\tau_c/(1+\omega^2\tau_c{}^2) \tag{6a}$$

$$J(2\omega) = 0.25(3\cos^2\alpha-1)^2(\tau_{mol}/(1+4\omega^2\tau_{mol}{}^2)$$
$$+0.75\sin^2 2\alpha(\tau_c/(1+4\omega^2\tau_c{}^2)+0.75\sin^4\alpha(\tau_c/(1+4\omega^2\tau_c{}^2) \tag{6b}$$

For a fast-spinning D_2 ligand with $1/\tau D_2 \gg 1/\tau_{mol}$ the maximum of the $[J(\omega) + 4J(2\omega)]$ function gives Equation (5), and a slow D_2 motion ($1/\tau_{mol} \gg 1/\tau D_2$) corresponds to Equation (4).

Taking the dihydrogen libration into account, Equations (6a) and (6b) can be written as Equations (7a) and (7b), where ϕ is the libration angle [radians].[12a]

$$J(\omega) = 0.25\,(3\cos^2\alpha - 1)^2 (\tau_{mol}/(1+\omega^2\tau_{mol}{}^2)) + 0.75\,(\sin^2 2\alpha + \sin^4\alpha)\,(1 - 4\,\langle\phi\rangle^2)\,(\tau_{mol}/(1+\omega^2\tau_{mol}{}^2)) \quad (7a)$$

$$J(2\omega) = 0.25\,(3\cos^2\alpha - 1)^2 (\tau_{mol}/(1+4\omega^2\tau_{mol}{}^2)) + 0.75\,(\sin^2 2\alpha + \sin^4\alpha)(1 - 4\,\langle\phi\rangle^2)\,(\tau_{mol}/(1+4\omega^2\tau_{mol}{}^2)) \quad (7b)$$

Thus, when $\phi = 0$, the maximum of the $[J(\omega) + 4J(2\omega)]$ function corresponds to Equation (4) describing a slow-spinning D_2 ligand.

The effect of the librational motion (causing the elongation of the ^2H-$T_{1\,min}$ with respect to the relaxation time of the slow-spinning D_2 ligand) can be estimated quantitatively for different ϕ (or α) values as factor F in Equation (8), where J^{max}_{slow} and J^{max}_{libr} are maxima of the $[J(\omega) + 4J(2\omega)]$ functions calculated for the slow and librational motion, respectively.

$$\mathrm{DQCC} = 1.2201\,(1 + \eta^2/3)^{-1/2}[\nu/(T_{1\,min}F)]^{1/2} \qquad F = (J^{max}_{slow}/J^{max}_{libr})^{-1} \quad (8)$$

The J_{max} magnitudes can be calculated easily by standard computer programs.

Table 2 lists the F factors obtained for complexes [D_3]**3**, [D_3]**4**, [D_3]**8** and $[Re(PMe_3)_4CO(D_2)]^+$ ([D_2]**10**), when their D_2 ligands undergo librational motion, with the ϕ values calculated on the basis of the ^1H-$T_{1\,min}$ studies.[12a] For simplicity, these factors were obtained by assuming that in all complexes α is 77° and η is 0.62. In turn, these values were averaged magnitudes obtained from the above MO calculations. As previously shown, the maximal influence of the librational motion is reasonably expected for complex [D_3]**4**, where ϕ is maximum.

Table 2. F values for the complexes [D_3]**3**, [D_3]**4**, [D_3]**8** and [D_2]**10** assuming that the dideuterium ligands undergo librational motions with a libration angle ϕ.

Complex	ϕ [°]	Factor F
[D_3]**3**	13	0.83113
[D_3]**4**	23	0.47186
[D_3]**8**	16	0.74445
[D_2]**10**	19	0.63966

According to the F and DQCC values obtained for the D_2 ligand in [D_3]**4** (Table 3), the compound undergoes libration motion ($\phi = 23°$) with variation of α (the angle between the direction of the electric field gradient and the motion axis). As a consequence, the maximum effect (corresponding to the minimum F value in Table 3) is observed when α is close to the magic angle. Accordingly, the theoretical analysis of [D_3]**4** shows that an ambiguity in α can produce a 17% underestimation of the DQCC calculated from the $T_{1\,min}$ data.

Table 3. F factor and DQCC value[a] in [D_3]**4** ($\phi = 23°$) calculated with various α values.

α	Factor	DQCC [kHz]
90	0.51705	60.3
77	0.47186	63.1
67	0.4031	68.3
57	0.3580	72.5
47	0.3813	70.2
37	0.4903	61.9

[a] Calculated with $\eta = 0.62$ and ^2H-$T_{1\,min} = 0.0431$ s (see Table 4).

^2H NMR spectra and relaxation data: ^2H-$T_{1\,min}$ data obtained for the molecular deuterium complexes studied in this work are collected in Table 4 with relevant data from the literature.

Complexes [D_3]**3** and [D_3]**4** were prepared directly in the NMR tubes by protonation of [D_2]**1** and [D_2]**2** dissolved in CH_2Cl_2 with a five-fold excess of CF_3COOD.

Table 4. ^1H- and ^2H-$T_{1\,min}$ data for the H_2 and D_2 ligands in the dihydrogen and dideuterium complexes (the ^2H relaxation measurements were carried out in CH_2Cl_2 or [H_8]toluene solutions).

Complex	^1H-$T_{1\,min}$ [s][a] (at 400 MHz)	^2H-$T_{1\,min}$ [s] (at 61.402 MHz)	r(H–H)[b] [Å]	J(H,D)[c] [Hz]
3	0.008	0.0434	0.92	29.7
4	0.0293	0.0431	1.04	22.5
5	0.0111	0.0237	–	< 10
8	0.00844[9a]	0.0147[9a]	0.91	30.5
9	0.0065	0.0164[4]	0.90[9b]	–
10	0.012	0.0253[4]	0.96	27.7

[a] Taken from reference [12a] and recalculated for 400 MHz. [b] Calculated from the J(H,D)/r(H–H) correlation (see reference [12a]). [c] Taken from reference [12a].

In good agreement with the ^1H NMR data,[7a,b] the room-temperature ^2H NMR spectra of [D_2]**1** and [D_2]**2** in CH_2Cl_2 showed fast D/D exchange. The deuteride scrambling was slowed below 230 K for [D_2]**1**, so that we could measure the ^2H-$T_{1\,min}$ and then calculate the DQCC for both D ligands, using Equation (4) with $\eta = 0$ (Table 5). Unfortunately, the exchange process in [D_2]**2** was fast on the NMR time scale even at 180 K, so the $T_{1\,min}$ and the DQCC values could be evaluated only for the averaged ^2H resonance.

Table 5. ^2H-$T_{1\,min}$ data and DQCC values for classical deuteride complexes.

Complex	$T_{1\,min}$ [s] (at 61.402 MHz)	Solvent	DQCC [kHz]
$[pp_3RuD_2]$ ([D_2]**1**)	0.017[a]	CH_2Cl_2	73.3
	0.0158[b]		76.1
$[pp_3OsD_2]$ ([D_2]**2**)	0.0144	CH_2Cl_2	79.7
$[pp_3Ru(D_2)\mathbf{D}]^+$ ([D_3]**3**)	0.0118	CH_2Cl_2	88.0
cis-$[ReD(PMe_3)_4CO]$ ([D_1]**6**)	0.0165[4]	CH_2Cl_2	74.4
$[Os\mathbf{D}(D_2)(CO)Cl(P\mathit{i}Pr_3)_2]$([$D_3$]**8**)	0.012[9a]	toluene	87.3
$[ReD_2(PMe_3)_4CO]^+$ ([D_2]**7**)	0.0163[4]	CH_2Cl_2	74.9

[a] Low-field resonance. [b] High-field resonance.

It has been reported recently that DQCC values are related to the ionicity of the metal–deuterium bond.[4] We can calculate the ionicity of the Ru–D bonds in [D_2]**1** (0.66 and 0.68) and the Os–D bonds in [D_2]**2** (0.65). These values are quite reasonable in view of the strong donor properties of the pp_3 ligand, which makes the protonation reaction a very simple process capable of generating the corresponding dideuterium complexes $[D_3]$**3** and $[D_3]$**4**.

Due to the fast D/D_2 exchange,[7b] the dihydrogen complex $[D_3]$**4** displays a single resonance in its ^{2}H NMR spectra, even at the lowest temperature investigated in CH_2Cl_2 ($T_{1\,min}$ = 0.0259 s), and therefore no direct $T_{1\,min}$ measurement for the D and D_2 ligands in $[D_3]$**4** could be made. Accordingly, the D_2-$T_{1\,min}$ for the osmium complex (Table 4) was calculated using the value of 0.0144 s measured for the D ligands in $[D_2]$**2**. In keeping with the reported ^{1}H NMR data,[7a] the D/D_2 exchange in $[D_3]$**3** was frozen below 230 K and the $T_{1\,min}$ for the D and D_2 ligands in the ruthenium derivative (Tables 4 and 5) were measured separately.

As the deuterium relaxation experiments on $[D_3]$**3** and $[D_3]$**4** were carried out in the presence of an excess of CF_3COOD, a slow CF_3COO*D*/M*D*$_2$ exchange, operating on the T_1 time scale, might have affected the relaxation measurements. However, comparison of the T_1 values for the CF_3COOD and D_2 resonances in CF_3COOD and $[D_3]$**3** allowed us to rule out this possibility and also supported our measurements (Table 6).

Table 6. Variable-temperature ^{2}H-T_1 data (61.402 MHz) for the OD and D_2 resonances in a solution of $[D_3]$**3** and CF_3COOD in CH_2Cl_2.

T [K]	T_1 [ms] CF_3COOD	 D_2
180	5.7	58.8
190	6.5	43.4
200	11. 4	78.3
210	15.1	79.4

A DQCC of 68.7 kHz was calculated for $[Ru(PPh_3)_3D_2(D_2)]$ ($[D_4]$**5**)[8a] on the basis of variable-temperature T_1 measurements for an averaged Ru–^{2}H resonance (in this case also, the D/D_2 exchange was fast in $[H_8]$toluene, even at the lowest temperature investigated) and for C–D resonances of the phenyl rings at a ^{2}D frequency of 30.701 MHz. According to Equation (4), a DQCC of 68.7 kHz corresponds to $T_{1\,min}$ = 0.0194 s at 61.402 MHz. Interestingly, this value scaled up to 30.701 MHz (0.0097 s) is very close to the experimental T_1 value (0.011 s) measured for a solution of $[D_4]$**5** in $[H_8]$toluene at 190 K.[8a] To characterise the D_2 ligand in $[D_4]$**5**, we used the above value, $T_{1\,min}$ = 0.0194 s for the averaged D resonance, and $T_{1\,min}$ = 0.0164 s measured for the classical D ligands in $[D_2]$**1** (see Table 5). With this approach, a value of 0.0237 s was obtained for ^{2}H-$T_{1\,min}$ (Table 4).

It is well known that the deuterium relaxation is governed by quadrupole interactions[6a] and therefore the contribution to the relaxation of deuterium caused by deuterium–proton dipole–dipole interactions (protons from solvents or ancillary ligands) is small and may be neglected. To verify this hypothesis, we looked at the deuterium spectra of $[D_3]$**3** and of its monodeuterated isotopomer $[pp_3Ru(HD)D]^+$ ($[D_2]$**3**), which was prepared in situ in an NMR tube by adding a sixfold excess of $(CF_3)_2CHOH$ to $[D_2]$**1** in CH_2Cl_2. In agreement with the literature data,[7a] the hydride region of the ^{2}H NMR spectrum of $[D_2]$**3** (200 K) included the D–H resonance as a broad doublet at $\delta = -3.6$ (J(H–D) = 30 Hz) accompanied by a broad singlet at $\delta = -8.9$ due to the classic deuteride ligand. In a $^2H\{^1H\}$ experiment the doublet transformed into a narrow singlet. Comparison of the ^{2}H-T_1 values for $[D_3]$**3** and $[D_2]$**3** (Table 7) demonstrated clearly that the ^{1}H nucleus in the (H–D) ligand makes no contribution to the relaxation rate of deuterium in spite of the very short D–H distance (0.92 Å).[10c]

Table 7. ^{2}H-T_1 data for $[D_3]$**3** and its monoprotiated isotopomer ($[D_2]$**3**) in CH_2Cl_2.

Complex	T_1 [s] Ru(D_2) or Ru(H-D)	 RuD	T [K]
$[D_3]$**3**	0.0586	0.0165	180
$[D_2]$**3**	0.0545	0.0145	180
$[D_3]$**3**	0.0780	0.0158	200
$[D_2]$**3**	0.0815	0.0168	200

Four of the six dihydrogen compounds reported in Table 4 are positively charged. The influence of the charge on $T_{1\,min}$ and DQCC can be deduced from studies of classical M–D systems as the simple determination of DQCC from $T_{1\,min}$ became accessible with Equation (4). In this case $\eta = 0$ and the D ligands undergo motion with the correlation time τ_{mol}. Comparison between *cis*-$[DRe(PMe_3)_4CO]$ ($[D_4]$**6**) and $[D_2Re(PMe_3)_4CO]^+$ ($[D_2]$**7**) or, especially, between $[pp_3RuD_2]$ ($[D_2]$**1**) and $[pp_3Ru(D_2)D]^+$ ($[D_3]$**3**) (Table 5) suggests that a decrease in ^{2}H-$T_{1\,min}$ (or, *mutatis mutandis*, an increase in DQCC) occurs when the complex bears a positive charge. In terms of a point-charge model[3a] this effect is reasonable, because an increase in a point charge on the metal centre causes development of an additional electric field gradient along the metal–D bond.[3]

From Table 4 it appears that the ^{2}H-$T_{1\,min}$ values for the D_2 ligands of complexes **3**–**10**, ranging from 0.014 to 0.044 s, do not correlate simply with the structural parameters r(H–H) or J(H–D) and there is a lack of any correlation between the ^{1}H and ^{2}H relaxation properties of the complexes. However, the ^{2}H-$T_{1\,min}$ value, although dependent mainly on the electric field gradient at the deuterium nucleus, depends also on the chemical properties of the D_2 ligand. As an example, whereas the Os complex **8** is characterised by fast and reversible H_2 dissociation in solution,[9a] the dihydrogen ligand in the Os complex **4** is very stable in solution and does not undergo H/D exchange when exposed to a D_2 atmosphere for 12 h.[7b] In agreement with this dichotomy in their macroscopic properties, the ^{2}H-$T_{1\,min}$ value in $[D_3]$**8** is significantly shorter than in $[D_3]$**4**. Similar effects hold also for the Ru complexes **5** and **3**: H_2 dissociates reversibly from **5**,[8a] whereas the H_2 ligand in **3** is quite robust.[7a] Similarly, the Re complex *cis*-$[ReH(H_2)(NO)(CO)(PMe_3)_2](CF_3COO)$ (**9**), readily undergoes H_2 displacement by trifluoroacetate above −70 °C in CD_2Cl_2,[4, 8b] whereas the related complex $[Re(H_2)(PMe_3)_4(CO)](CF_3COO)$ (**10**) is transformed irreversibly into the classical dihydride $[ReH_2(PMe_3)_4(CO)](CF_3COO)$ above −30 °C.[8b]

MO calculations have shown that DQCCs in the dideuterium ligand may vary from 103 kHz in the model [Os(P(CH$_2$-

$CH_2PH_2)_3)(D)(D_2)]^+$ to 155 kHz in $[Rb(D_2)]^+$. For immobile D_2 ligands, the corresponding ^2H-$T_{1\,min}$ values are calculated by Equation (4) to be very short: 0.0076 and 0.0034 s, respectively (61.402 MHz, $\eta = 0.62$). In general, MO calculations predict a decrease in $T_{1\,min}$ on going from a classical hydride ligand to its dihydrogen tautomer. This phenomenon is not observed in the relaxation experiments summarised in Tables 4 and 5, however. In contrast, the ^2H-$T_{1\,min}$ times listed in Table 4 are quite long and, in going from classical to non-classical ligands, an opposite effect, a prolongation of ^2H-$T_{1\,min}$, is evident. This effect is still reduced for the neutral Os complex $[D_3]$**8** (0.012 s for OsD and 0.0147 s for $Os(D_2)$), but it is very pronounced for the cationic complexes $[D_3]$**3** and $[D_3]$**4** (see Tables 4 and 5).

The discrepancy between the experimental ^2H-$T_{1\,min}$ and the values expected on the basis of the MO-calculated DQCC values is probably related to intrinsic problems in the MO calculations.[11] However, the ^2H-$T_{1\,min}$ values in Table 4 can be affected by fast internal D_2 motion (which leads to prolongation of $T_{1\,min}$, relative to that of an immobile-H_2 ligand).

From the theoretical analysis, the rationalisation of ^2H-$T_{1\,min}$ in terms of internal D_2 motion is evidently difficult, as the α and η values corresponding to a dihydrogen ligand are generally both unknown. Although the uncertainty in η is not dramatic (see the section on relaxation theory), the ambiguity in the character of internal (D_2) motion and in α may be quite critical, as it may be responsible for significant errors in the DQCC value calculated from the $T_{1\,min}$ data (see, for example, Table 3). We have calculated the DQCCs for the D_2 ligands in **3**–**10** (Table 8), assuming that one of the following modes of motion may take place in the non-classical D_2 complexes: i) a slow D_2 rotation (SR); ii) a fast D_2 rotation with $\alpha = 90°$ ($FR^{(90°)}$); iii) a fast D_2 rotation with $\alpha = 77°$ ($FR^{(77°)}$); iv) a D_2 libration with $\alpha = 77°$ (L). Within the limits of the libration-motion model, the libration angles (ϕ) derived from the ^1H relaxation studies of complexes **3**, **4**, **8** and **10** have been used.[12a]

Table 8. DQCC values for the D_2 ligands in complexes **3**–**5** and **8**–**10** assuming various models for the dideuterium motion.[a]

Complex	ϕ	DQCC[b] [kHz]				
		SR	$FR^{(90°)}$	$FR^{(77°)}$	L	C
$[D_3]$**3** (Ru)	13	43.2	86.4	101.9 93[d] (147)[c]	47.4	88.0 (88)[c]
$[D_3]$**4** (Os)	23	43.4	86.8	102.2 111[d] (105)[c]	63.1	79.7 (100)[c]
$[D_4]$**5** (Ru)	–	58.5	117.0	137.9	–	–
$[D_3]$**8** (Os)	16	74.2	148.5	175 (129)[c]	86.0	87.3
$[D_3]$**9** (Re)	–	70.3	140.6	165.7	–	67.5
$[D_2]$**10** (Re)	19	56.6	113.2	133.4	70.8	74.4

[a] For simplicity, an η value of 0.62 has been assumed for all the dihydrogen ligands. [b] C = calculated for the classical deuteride ligand assuming $\eta = 0$; other abbreviations are defined in the text. [c] Determined from the molecular orbital calculations. [d] Calculated from the $T_{1\,min}$ value on the basis of α and η values resulting from the quantum chemical calculations.

The data obtained show clearly that the experimental DQCC values are in fairly good agreement with the MO calculations for complexes **3**, **4** and **8** if a free-spinning D_2 ligand motion (FR model) is assumed. As a consequence, the DQCCs of the D_2 ligands are higher than those found for the classical hydrides and lower than that (227 kHz) found for the free HD molecule.[3a] This model, however, may be questionable because, according to recent data for the protiated isotopomers,[12a] the dihydrogen ligands in **3**, **4**, **8** and **10** undergo a librational motion in solution. The same type of motion was detected even in the solid state for $[W(H_2)(CO)_3\{(P(iPr)_3)\}_2]$.[5c]

Detailed IR, Raman and INS (inelastic neutron scattering) studies have shown that the Kubas complex $[W(H_2)(CO)_3(PCy_3)_2]$ (Cy = cyclohexyl) exhibits low-frequency torsional modes (associated with the librational motion depicted in Figure 1b) which are even more populated in the D_2 isotopomer at 300 K.[13] Considering this important result and the ^1H relaxation data reported above, we conclude that the L model is the most probable one. The D_2 rotation with a frequency near the Larmor NMR frequency[12a] can be ruled out because no distortions[12a] from the usual V-shape of the $\ln(^2H$-$T_1)$ versus $1/T$ plots were observed for **3** and **8** in solution.[9a]

Hence, an important conclusion may be drawn from these ^2H-relaxation studies: the DQCCs in the perdeuterated isotopomers of dihydrogen ligands (reflecting the electric field gradient on the D atoms) can be significantly lower than those measured for classical deuterides. A paradigmatic example is the Ru complex $[D_3]$**3**, in which the D_2 and D ligands exhibit DQCCs of 47 kHz and 88 kHz, respectively. Moreover, this conclusion remains valid in spite of the uncertainty affecting the DQCC values, which can be underestimated by as much as 17% because of the ambiguity in evaluating α (47 kHz became 58 kHz as α approached the magic angle). To support this conclusion further, we studied the ^2H relaxation of the complex $[Cp^*Ru(D_2)(dppm)]BF_4$ ($[D_2]$**11**). The protiated isotopomer of **11** was studied in detail.[14] Inter alia, it was demonstrated that the H_2 ligand in **11** does not undergo any librational motion and also has a high rotational barrier,[12a] computed to be 4.2 kcal mol^{-1}.[12c]

The DQCC value for the D_2 ligand in this complex was determined directly from the ^2H-$T_{1\,min}$ measurements. In excellent agreement with the data reported by Morris et al.,[14] the ^2H NMR spectrum of complex $[D_2]$**11** in CH_2Cl_2 shows the presence of both classical and non-classical tautomers with NMR parameters close to those given in the literature. Morris and co-workers have shown that the H/H exchange between classical and non-classical isomers is already frozen out on the ^1H-T_1 NMR time scale at 250 K (at 400 MHz). In keeping with the literature data, we have measured different ^2H-T_1 relaxation times for the classical (37.9 ms) and the non-classical (49.4 ms) tautomers of $[D_2]$**11** at 230 K (at 76.75 MHz for deuterium, 500 MHz for ^1H). The $T_{1\,min}$ values for the two tautomers, determined at 185–190 K to be 17.0 and 24.3 ms respectively, demonstrate clearly that the ^2H relaxation time increases on going from the classical Ru–D ligand to the non-classical Ru–D_2 ligand. These values correspond to DQCCs of 82 and 64.6 kHz, respectively, using Equation (4) and asymmetry parameters of 0 and 0.62 for the two cases. The two positively charged complexes $[D_3]$**3** and $[D_2]$**11** exhibit similar DQCC values (88 and 82 kHz, respectively) for the classical deuteride ligand.

Our DQCC results allow us to make some interesting observations on the oxidative addition of H_2 to a transition metal centre. Along the reaction coordinate leading to the formation of a molecular hydrogen complex and then to the classical dihydride, we observe an initial decrease in the DQCC from 227 kHz (as in the free dideuterium) when the dideuterium complex forms, followed by an increase when the classical dideuteride forms. For the $[pp_3Ru]$ derivative (Figure 2, curve 1), the bond ionicity (i), calculated from the DQCC,[4] increases from 0 in the free dihydrogen ($i = 1 - DQCC/227$) to 0.79 as soon as the D_2 ligand in $[D_3]$**3** forms, then decreases to 0.61 for the D ligand in $[D_3]$**3** or to 0.66 and 0.68 for the classical deuteride complex $[D_2]$**1**.

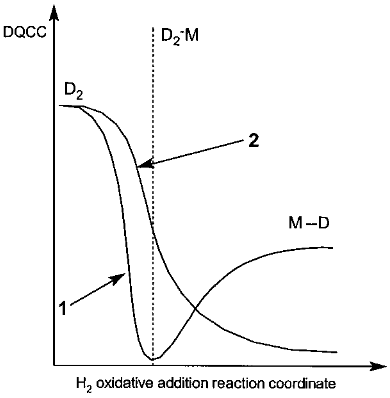
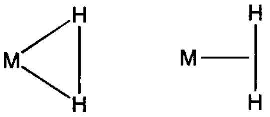


Figure 2. Variation of DQCC versus the reaction coordinate along the oxidative addition of D_2 for the systems $M + D_2$ (**1**) and $Rb^+ + D_2$ (**2**), (M = transition metal fragment).

Detailed vibrational data and theoretical calculations for $[W(H_2)(CO)_3(PCy_3)_2]$ have shown that the $W-H_2$ fragment is better described as a *triangulo* system with a direct back-bonding interaction between M and H rather than as a pure T-shaped system[13] (Scheme 1). Such a formulation of dihydrogen complexes can provide a better explanation of our DQQC data for complexes $[D_3]$**3** and $[D_3]$**4** and points to an increasing role of the nuclear (metal centre) contribution to the electric field gradient experienced by the deuterium atom(s) in the non-classical ligand [see Eq. (1)].



Scheme 1.

Figure 2 (curve 2) represents schematically the DQCC changes along the reaction coordinate describing H_2 addition to an Rb^+ centre acting as a Lewis acid.[3c] In the absence of any back-bonding interaction, the DQCC value quickly decreases with the lengthening of the D–D bond to give two distinct Rb–D bonds, calculated[4] from DQCC = 15 kHz[3c] to have a very high ionicity (0.93). With the considerations described above, this result is reasonable.

The increase in $T_{1\,min}$ in Table 4 (reflected by the decrease in DQCC in Table 8) in the pairs **4**–**8**, **9**–**10** and **3**–**5** corresponds to an increase in the *triangulo* character of the bonding mode within the MH_2 assembly, with proportional reduction in the trend towards H_2 dissociation.

Conclusion

^2H-$T_{1\,min}$ values of both D and D_2 ligands in the series of perdeuterated complexes **1**–**4** were measured using variable-temperature ^2H NMR spectra. The DQCCs for the dideuterium ligands were determined from the $T_{1\,min}$ data using different models of internal D_2 motion. The angle α and the asymmetry parameter η were estimated by MO calculations. Among the motion models considered, it has been shown that the librational one accounts the most realistically for the behaviour of complexes $[pp_3Ru(D_2)D]^+$ ($[D_3]$**3**), $[pp_3Os(D_2)D]^+$ ($[D_3]$**4**), $[OsD(D_2)(CO)Cl\{P(iPr)_3\})_2]$ ($[D_3]$**8**) and $[ReD_2(PMe_3)_4CO]^+$ ($[D_2]$**10**). According to this model, the calculated DQCC values in the non-classical complexes studied are in the range 47–86 kHz (or 56–101 kHz if α is close to the magic angle), demonstrating clearly that DQCC values for the dideuterium ligands may be lower than for the corresponding classical deuteride systems. This result can be interpreted in terms of a strong back-bonding interaction between the transition metal centre and the hydrogen ligand in an $M-H_2$ *triangulo* moiety.[13]

Experimental Section

The NMR studies were carried out in standard 5 mm NMR tubes containing solutions of the complexes in CH_2Cl_2 or in CH_2Cl_2–$[H_8]$toluene mixtures. The solvents were dried by conventional procedures and were freshly distilled under an inert atmosphere before use. The ^2H NMR data were collected with a Bruker AMX 400 spectrometer operating at 61.402 MHz, or for complex $[D_2]$**11** on a Bruker DRX 500 instrument operating at 76.773 MHz. The conventional inversion–recovery method (180-τ-90) was used to determine the variable-temperature longitudinal-relaxation time T_1. The relaxation times were calculated using the appropriate nonlinear three-parameter fitting routine. In each experiment, the waiting period was longer than five times the expected relaxation time and 16–20 variable delays were employed. The duration of the pulses was controlled at each temperature. The errors in T_1 determinations were below 5% (this was checked with various samples).

Theoretical calculations of the electric field gradients and DQCC were carried out with the GAUSSIAN 94 package of programs.[15a] Calculations were performed on the model complexes $[P(CH_2CH_2PH_2)_3Ru(D)(D_2)]^+$, $[P(CH_2CH_2PH_2)_3Os(D)(D_2)]^+$, $[Os(PH_3)_2(CO)(Cl)(D)(D_2)]$, $[W(PH_3)_2(CO)_3(D_2)]$ and $[W(PH_3)_2(CO)_2(D)(NO)]$ at the Becke3LYP computational level.[14b–d] The basis set was LANL2DZ for the metal atoms, and for the P and Cl atoms;[15e,f] 6-31G was used for the other atoms.[15g] Polarisation d functions were added for P and Cl,[15h] as well as for N and O atoms.[15i] Polarisation functions were also added for all carbon atoms directly attached to the metal centres. All geometries were fully optimised with this computational method, with no symmetry restrictions.

Computed H–H distances in $[Ru(P(CH_2CH_2PH_2)_3)(H)(H_2)]^+$ (0.8134 Å), $[Os(P(CH_2CH_2PH_2)_3)(H)(H_2)]^+$ (0.8656 Å) and $[Os(PH_3)_2(CO)(Cl)(H)(H_2)]$ (0.8112 Å) correspond well with the dihydrogen nature of the complexes. The H–H separations for the two pp_3 model complexes match well with the bond distance previously calculated by ab initio methods.[10c] The perdeuterated hydrides $[pp_3RuD_2]$ ($[D_2]$**1**) and $[pp_3OsD_2]$ ($[D_2]$**2**) were prepared according to the published procedure for the protiated analogues[7a,b] by using deuterated solvents and reagents. They were recrystallised from benzene–$[D_1]$ethanol mixtures. The isotopic purity was generally higher than 95% (checked by ^1H NMR integration). Complexes $[D_3]$**3** and $[D_3]$**4** were prepared by protonation of $[D_2]$**1** and $[D_2]$**2** with CF_3COOD. The perdeuterated isotopomer $[Cp^*Ru(D_2)(dppm)]BF_4$ ($[D_2]$**11**) ($Cp^* = C_5Me_5$) was prepared as described in the literature for the protiated analogue by deuteration of $[Cp^*Ru(D)(dppm)]$ with $DBF_4 \cdot OMe_2$ in $[D_8]$THF.[14a] Deuterated solvents and reagents were used throughout the synthetic procedure. The isotopic purity of $[D_2]$**11** was higher than 90%.

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[1] a) G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. Wasserman, *J. Am. Chem. Soc.* **1984**, *106*, 451; b) D. M. Heinekey, W. J. Oldham, *Chem. Rev.* **1993**, *93*, 913; c) P. G. Jessop, R. H. Morris, *Coord. Chem. Rev.* **1992**, *121*, 155.

[2] D. G. Hamilton, R. H. Crabtree, *J. Am. Chem. Soc.* **1989**, *110*, 4126.

[3] a) L. G. Butler, E. A. Keiter, *J. Coord. Chem.* **1994**, *32*, 121, and references therein; b) A. J. Kim, F. R. Fronczek, L. G. Butler, S. Chen, E. A. Keitler, *J. Am. Chem. Soc.* **1991**, *113*, 9090; c) H. Guo, W. L. Jarrett, L. G. Butler, *Inorg. Chem.* **1987**, *26*, 3001.

[4] D. Nietlispach, V. I. Bakhmutov, H. Berke, *J. Am. Chem. Soc.* **1993**, *115*, 9191, and references therein.

[5] a) G. J. Kubas, C. F. Unkefer, B. I. Swanson, E. Fukushima, *J. Am. Chem. Soc.* **1986**, *108*, 7000; b) J. B. Lambert, F. G. Riddel, *The Multinuclear Approach to NMR Spectroscopy*, D. Reidel, Boston, **1982**, pp. 151–167; c) K. W. Zilm, J. M. Millar, *Adv. Magn. Opt. Reson.* **1990**, *15*, 163.

[6] a) A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, New York, **1971**; b) D. G. Gusev, D. Nietlispach, A. B. Vymenits, V. I. Bakhmutov, H. Berke, *Inorg. Chem.* **1993**, *32*, 3270; c) V. I. Bakhmutov, E. V. Vorontsov, *Rev. Inorg. Chem.* **1998**, *18*, 183.

[7] a) C. Bianchini, P. J. Perez, M. Peruzzini, A. Vacca, F. Zanobini, *Inorg. Chem.* **1991**, *30*, 279; b) C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca, F. Zanobini, *Inorg. Chem.* **1993**, *32*, 2366.

[8] a) D. G. Gusev, A. B. Vymenits, V. I. Bakhmutov, *Inorg. Chim. Acta*, **1991**, *179*, 195; b) D. G. Gusev, D. Nietlishpach, I. L. Eremenko, H. Berke, *Inorg. Chem.* **1993**, *32*, 3628.

[9] a) V. I. Bakhmutov, J. Bertran, M. Esteruelas, A. Lledos, F. Maseras, J. Modrego, L. A. Oro, E. Sola, *Chem. Eur. J.* **1996**, *2*, 815; b) H. Berke, personal communication.

[10] 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. Duran, A. Lledos, J. Bertran, *J. Am. Chem. Soc.* 1991, 113,2879; c) C. Bianchini, D. Masi, M. Peruzzini, M. Casarin, C. Maccato, G. A. Rizzi, *Inorg. Chem.* **1997**, *36*, 1061.

[11] The theoretical DQCC values have been obtained from the equation: DQCC $= 672\,q_{zz}$ on the basis of the MO-calculated q_{zz}. The conversion factor of 672 is based on the currently accepted value for the quadrupole moment of D.[3a] We performed very high-level calculations on free D_2 and obtained $q_{zz} = -0.397$, yielding DQCC = 267 kHz, whereas 227 kHz was found experimentally.[3a] Therefore, the discrepancy between theory and experiment is up to 18%.

[12] a) R. H. Morris, R. Witterbort, *J. Magn. Reson. Chem.* **1997**, *35*, 243; b) D. E. Woessner, *J. Chem. Phys.* **1962**, *36*, 1; c) R. Gelabert, M. Moreno, J. M. Lluch, A. Lledos, *J. Am. Chem. Soc.* **1997**, *119*, 9840.

[13] B. R. Bender, G. J. Kubas, L. H. Jones, B. I. Swanson, J. Eckert, J; K. B. Capps,. C. D. Hoff, *J Am. Chem. Soc.* **1997**, *119*, 9179

[14] a) G. Jia, A. J. Lough, R. H. Morris, *Organometallics* **1992**, *11*, 161; b)W. T. Klooster, T. F. Koetzle, G. Jia, T. P. Fong, R. H. Morris, A. Albinati, *J Am. Chem. Soc.* **1994**, *116*, 7677.

[15] a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, GAUSSIAN 94, Gaussian, Inc., Pittsburgh (PA), **1995**; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* B **1988**, *37*, 785; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623; e) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299; f) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; g) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; h) A. Hollwarth, M. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp, G. Frenking *Chem. Phys. Lett.* **1993**, *208*, 237; i) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* 1973, 28, 213.

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