Inorganica Chimica Acta, *179* (1991) 195–201

Is $RuH_4(PPh_3)_3$ in solution indeed a non-classical hydride?

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(Received July 10, 1990)

Abstract

A novel systematic investigation of temperature dependences of ^1H, ^2H, ^{31}P NMR spectra and ^1H T_1, T_2 and ^2H T_1 relaxation times has been carried out for solutions of $RuH_4(PPh_3)_3$ (**5**) and its isotopomers in toluene. The linewidth of the H-ligands of **5** in the 180–310 K temperature range is governed by T_2 and J(H–P), the chemical shift does not depend on the temperature and the character of the T_1 change is the same for all protons of the complex. It has been shown that the ^1H $T_1(T)$ dependences are not consistent with the theoretical data, but the $T_{1\min}$ value can be used to calculate the distances between H-ligands. The calculated distances under the assumption of the classical and non-classical models of **5**, the found quadrupole coupling constant of D-ligands (68±3 kHz) and J(H–D) (*c.* 2.7 Hz) have revealed an inadequacy of those models by a whole set of experimental data. A dynamic structure involving fast pairwise approachment–detachment of the H-ligands is suggested and discussed.

Introduction

Since the first example of a stable dihydrogen complex, $W(CO)_3(Pi\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ (**1**), was reported by Kubas *et al.* in 1984 [1], an increasing number of similar compounds have been synthesized [2–4]. According to crystallographic investigations carried out by the neutron diffraction method, the H_2 molecule in compounds **1** and $[Fe(\eta^2\text{-}H_2)(H)(dppe)_2]BF_4$ (**2**) (dppe = $PPh_2CH_2CH_2PPh_2$) is symmetrically coordinated in an η^2-fashion, the H–H distance being 0.82 Å [1, 5, 6]. Spectral data unambiguously supporting the non-classical structure of the above-cited compounds in solution were obtained: the H–D spin–spin coupling constants (for η^2-HD) are large (30–34 Hz), the ^1H spin–lattice relaxation times (T_1) are small and equal to several milliseconds and for complex **1** the vibrational stretching frequency ν_{H-H} is 2695 cm^{-1} [6, 7].

It is known that the H–H bond of H_2 is weakened at η^2-coordination. Therefore non-classical hydrides are often equilibrated in solution with the classical tautomers [8]. Only in rare cases, for instance, for complexes **1** and $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]BF_4$ (**3**), the equilibrium $M(\eta^2\text{-}H_2) \rightleftarrows MH_2$ is slow on the NMR time-scale and leads to the appearance of more than one signal in the spectra [6, 9].

The number of difficulties for defining the hydride structures by crystallographic methods is well-known, so the conclusion about the nature of the M–H bonding is inferred mainly by spectroscopic measurements. The observation in ^1H NMR spectra of upfield signals with short spin–lattice relaxation times is accepted by many authors as the decisive argument in favour of the non-classical structure (T_1 criterion of Hamilton and Crabtree [10]). It should be noted that recently Luo and Crabtree have improved upon the formulation of the criterion [11]. However, a simplified interpretation of the relaxation data is still used in practice.

It is known that T_1 data are rarely used to determine the internuclear distances in connection with the problem of precise separation of different relaxation contributions. For this reason one should be very careful with quantitative interpretation of T_1 values of H-ligands [12–15]. In our opinion, the H–H distance calculations (even carried out with the correction of Morris and co-workers [7]) often lead to overestimated results. For instance, it is appreciable in respect of the complex identified by the authors in ref. 7 as $[Os(\eta^2\text{-}H_2)H(depe)_2]^+$ (depe = $PEt_2CH_2CH_2PEt_2$) [7], where the calculated r_{H-H} is 1.12 Å. In the absence of any kind of independent arguments, such an interpretation of the relaxation data do not appear convincing.

The present work was dictated by the wish to comprehensively investigate the temperature depen-

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dences of the ^1H T_1, T_2 relaxation times in solutions of hydride complexes (to confirm the fact that the minimum T_1 often observed in the experiment is indeed governed by the rotational correlation time) and, if possible, to isolate correctly the T_1 value characterizing the proton relaxation through the neighbouring proton, the distance to which should be determined.

The object chosen for investigation is the well-known tetrahydride $RuH_4(PPh_3)_3$ (**5**) obtained more than twenty years ago [16, 17] and reformulated in 1986 according to T_1 data as $RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$ [18].

Besides performing ^1H NMR experiments for complex **5** ^2H NMR investigations on its isotopomers were carried out. The temperature dependence of the ^{31}P spectra was also investigated.

Experimental

The tetrahydride $RuH_4(PPh_3)_3$ was prepared according to the procedure previously reported [19].

Absolute toluene-d_8 degassed by means of three freeze–pump–thaw cycles was condensed into an NMR tube containing a weighed amount of complex **5**. The space over the liquid phase was filled with purified H_2 (or D_2) after which the tube was sealed.

^1H, ^2H and ^{31}P NMR spectra were recorded on a Bruker WP 200 spectrometer at 200.13, 81.02 and 30.72 MHz, respectively, with chemical shifts relative to internal toluene and external 85% H_3PO_4. Variable-temperature experiments were performed with a BVT-1000 controller calibrated by a methanol sample (4% CH_3OH in methanol-d_4). Spin–lattice and spin–spin relaxation times were determined by using an inversion–recovery and Carr–Parcel–Meiboom–Gill techniques with a recycle time of at least $5T_1$. Typically, 11–18 points were obtained for each experiment and were analyzed with a non-linear fit routine, using the DISNMRP program. On measuring of T_2, the repetition of the 180° pulse was applied with a delay time of 0.5 ms. The 90° pulse was determined at each temperature.

Results

Temperature dependences of ^1H NMR spectra, spin–lattice (T_1) and spin–spin (T_2) relaxation times for $RuH_4(PPh_3)_3$ in toluene-d_8 solution

The ^1H NMR spectrum of **5** in toluene-d_8 solution under H_2 exhibits the signals of *ortho* (7.39 ppm), *para* and *meta* protons (6.9 ppm) of PPh_3, the signal of dissolved dihydrogen (4.53 ppm), and that of H-ligands whose chemical shift (−7.11 ppm) is practically independent of temperature. The ratio of integral intensities of the ^1H NMR signals is in good agreement with the compound **5** formula, whereas the ratio of the dissolved H_2:the complex is *c.* 1:6. The spin–spin coupling of the hydride protons with ^{31}P of phosphine ligands is resolved at *T* 305 K by applying the Gaussian multiplication procedure. As a result, the −7.11 broad signal is transformed into a quartet with $J(^1H\text{–}^{31}P) = 6$ Hz, due to the spin–spin coupling of the four H-ligands with three ^{31}P nuclei.

The temperature dependences of ln T_1 for protons of **5** given in Fig. 1 are characterized by broad minima in the temperature range 225–255 K. The magnitudes of T_1 at the minima are 20 ± 0.5 ms (H-ligands), 420 ± 20 ms (*ortho* phenyl protons) and 600 ± 40 ms (*para* and *meta* phenyl protons). The slope of the high-temperature section of the $\ln(1/T_1)$ versus $1/T$ dependences is the same for all protons of $RuH_4(PPh)_3$ and corresponds to the activation energy of the molecular motion $E_A = 2.8 \pm 0.3$ kcal/mol.

The spin–spin relaxation times (T_2) and NMR signal widths (Δ) measured for H-ligands in the temperature range of 179–290 K are given in Table 1. The comparison of T_1 and T_2 values indicates their proximity at high temperatures (35 and 31 ms at 290 K, 29 and 26 ms at 280 K, 26 and 22 ms at 271 K) and, consequently, the practically isotropic character of molecular motion for complex **5** in solution. It should be noted that there is a good agreement between the real width of the signal at −7.11 and the theoretical value which can be found from T_2 and $J(^1H\text{–}^{31}P)$.

At 290 K, the saturation of the Ru–H resonance leads to the disappearance of the dihydrogen peak indicating an exchange process between the hydride

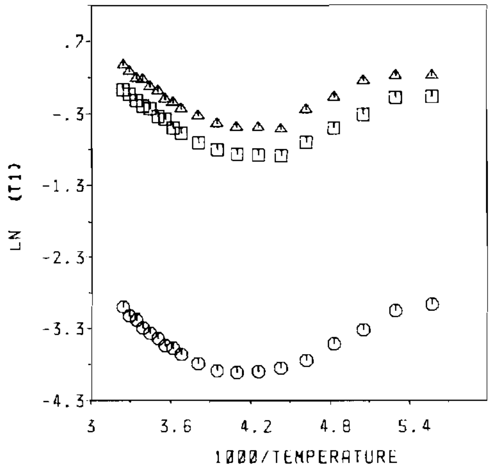


Fig. 1. Proton relaxation time of complex **5** vs. temperature (in Arrhenius coordinates). ○, hydride ligands; △, *para* and *meta* protons of PPh_3; □, *ortho* protons of PPh_3.

TABLE 1. The values of spin–spin relaxation time (T_2) and linewidth (Δ) of Ru–H signal for the solution of 5 in toluene-d_8

	Temperature (°C)										
	290	280	271	262	253	243	234	225	216	198	179
T_2 (ms)[a]	31	26	22	17.9	15.2	12.3	10.2	8.7	7	3	
Δ (Hz)	19	20	22	25	27	31	37	43	53	103	390

[a] ±10%.

protons of 5 and dissolved hydrogen. The H_2 linewidth increases upon heating of the solution of 5 and at 330 K it reaches 85 Hz. Theoretically, observed exchange can increase T_1 of the H-ligands of $RuH_4(PPh_3)_3$. However, this effect can be neglected in view of the slow rate of the exchange below 290 K and the small amount of H_2 ($[H_2]/[\text{complex } 5] = 1{:}6$).

Isotopomers of $RuH_4(PPh_3)_3$. ^1H, ^2H NMR spectra. Temperature dependences of ^2H spin–lattice relaxation times

After shaking the $RuH_4(PPh_3)_3$ solution in toluene-d_8 under D_2, an D_2/H_2 exchange is detected in the ^1H NMR spectra. H_2 and HD signals appear in the 4.5 ppm region and the integral intensity of the H-ligands signal decreases to 0.8–1.3 H.

The residual signal is characterized by a chemical shift of −7.16 ppm and width of 30 Hz at 290 K. These parameters differ significantly from those of the undeuteriated $RuH_4(PPh_3)_3$. However, the spectra recorded at T_1 measurements have shown that the difference is explained by the superposition of isotopomers signals (Fig. 2). One of them with a chemical shift of −7.21 ppm and less relaxation rate is designated as $RuHD_3(PPh_3)_3$ (5-d_3). The other signal (−7.11 ppm) with higher relaxation rate should be assigned to $RuH_2D_2(PPh_3)_3$ (5-d_2).

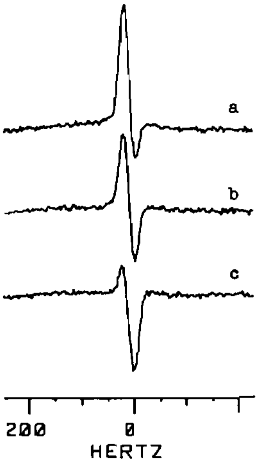


Fig. 2. ^1H NMR signals of H-ligands of incomplete deuterated complex 5 obtained by inversion–recovery method at 280 K.

The T_1 value can be estimated from the time, τ_0, between 180° and 90° pulses at which NMR signal intensity is minimum ($T_1 = \tau_0/\ln 2$). So the T_1 of the H-ligand of 5-d_3 is equal to 0.12 s at 240 K (an error <20%). This value is close to $T_{1\min}$ (0.2 and 0.18 s) of inequivalent hydride ligands of $RuH_2(CO)(PPh_3)_3$ [20]. In accordance with the observations of Hamilton and Crabtree [10] and Morris and co-workers [7] we assume that the $1/T_{10}$ value, caused by dipole–dipole interactions between phosphine and H-ligands, is *c.* 5 s^{-1} at the minimum of spin–lattice relaxation.

Besides the isotopic substitution of H-ligands, *ortho* deuteration of the phenyl rings of phosphine ligands is also observed in the ^1H NMR spectra [21].

At 278 K, the ^2H NMR spectrum of deuterated complex 5 in toluene solution under D_2 (50% D; the most probable isotopomer is 5-d_2) exhibits one resonance in the hydride region at −7.11 ppm. The linewidth is 10 Hz. However, in the $^2H\{^1H\}$ NMR spectrum it decreases to 5 Hz. This value (5 Hz) is in good agreement with the theoretical width which can be found from T_1 (Table 2) and $J(^2H–^{31}P)$ data (usually, $J(^1H–^{31}P)/J(^2H–^{31}P)$ is *c.* 6.5).

The obtained result is unambiguous evidence for the presence of J(H–D) whose value can be estimated by simulation of the observed ^2H NMR signal. The simulations have shown that a satisfactory agreement with the experimental spectrum is achieved if the J(H–D) value does not exceed 2.7 Hz. The same conclusion can be made from the spectral data given in Fig. 2, since the width of the ^1H NMR signal at −7.21 is 20 Hz (280 K).

The results of measurements of the ^2H spin–lattice relaxation times for D-complex 5 are given in Table 2. The analysis of these data in the Arrhenius coordinates provides evidence for the linear character of the dependence $\ln(1/T_1)$ versus $1/T_1$, and the

TABLE 2. The values of ^2H spin–lattice relaxation time (T_1, ms) for D-complex 5 in toluene

	Temperature (°C)										
	308	299	290	280	271	262	253	243	234	216	198
T_1(Ru–D)[a]	250		128	107	89		54		29	19	11
T_1(C–D)[b]	30	25	21	16	12.8	10.1	7.4	5.8			

[a] ±10%. [b] ±5%.

activation energy of molecular motion of the complex is 3.9±0.3 kcal/mol. The D-ligands T_1 is appreciable higher than that for the deuterons in the *ortho* position of the phenyl rings. In this case

$$1/T_1 = 1.5\pi^2(e^2qQ/h)^2\tau_c$$

where e^2qQ/h is the quadrupole coupling constant and τ_c is the rotational correlation time [22]. When τ_c values are coincident for all deuterons of D-complex 5 (the isotropic motion), the observed difference in ^2H T_1 values is determined by the difference in e^2qQ/h values. Since the quadrupole coupling constant for aromatic deuterons is known and equals 182 kHz [23], it is possible to calculate this constant for D-ligands which in our case equals 68.7±3.0 KHz.

Variable-temperature ^{31}P NMR spectra of $RuH_4(PPh_3)$ in solution

The $^{31}P\{^1H\}$ NMR spectrum of complex 5 in toluene-d_8 (290 K) exhibits one signal at 58 ppm. The linewidth is *c.* 7 Hz and relaxation time T_1 is 2.3 s. On cooling down to 200 K the signal broadens (Fig. 3). At 180 K, the exchange of phosphine ligands is slowed down and two resonances (in a ratio 2:1) are observed at 61.7 and 50.7 ppm with both linewidths of *c.* 50 Hz in $^{31}P\{^1H\}$ (or ^{31}P) NMR spectra. The full line-shape analysis of the spectra allowed the rate constants and activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) of the exchange to be estimated. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are 7.3±0.7 kcal/mol and 6.5±0.6 e.u., respectively.

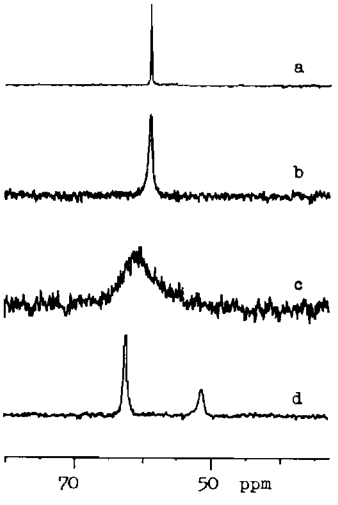


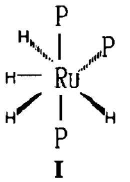
Fig. 3. $^{31}P\{^1H\}$ NMR spectra of complex 5 in toluene-d_3: a, 260 K; b, 230 K; c, 210 K; d, 190 K.

A retardation of the intramolecular exchange of phosphine ligands in $RuH_4(PPh_3)_3$ has not been observed earlier. However, for the related complex $RuH_2(N_2)(PPh_3)_3$, two $^{31}P\{^1H\}$ NMR signals were recorded already at ambient temperature [21].

Discussion

Model choice

The possibility of any equilibrium between non-classical and classical tautomers of $RuH_4(PPh_3)_3$ in toluene can be neglected since T_2 and $J(^1H–^{31}P)$ govern the width of the signal of the H-ligands over the whole investigated temperature range, the chemical shift does not depend on the temperature and the T_1 behavior is the same for all protons of the complex. Hence, two hypotheses concerning the structure of 5 in solution may be made. The first one is the classical tetrahydride $RuH_4(PPh_3)_3$, whose supposed structure (I) corresponds to the structure of classical $OsH_4(PMe_2Ph)_3$ [24]. The second hypothesis is the non-classical $RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$ (structure II [18]) under the condition of degenerated and independent of temperature intramolecular exchange $RuH_2^{*}(\eta^2\text{-}H_2)(PPh_3)_3 \rightleftarrows Ru(\eta^2\text{-}H_2^{*})H_2(PPh_3)_3$. The available data is now summarized and an attempt is made to draw some conclusions.



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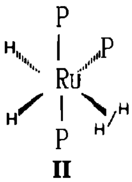

II

^1H T_1 *data and internuclear distances calculations*

As is known, the rate of the spin–lattice relaxation of a pair of interacting protons in diamagnetic solutions is mainly dependent on their dipole–dipole interaction and correlation time of molecular motion [22]

$$1/T_1 = 0.3\gamma_H{}^4\hbar^2 r_{H\cdots H}{}^{-6}\{\tau_c/(1+\omega_0{}^2\tau_c{}^2) + 4\tau_c/(1+4\omega_0{}^2\tau_c{}^2)\} \quad (1)$$

In turn, $\tau_c = \tau_0 \exp(E_A/RT)$.

The relaxation occurs with the maximum rate when $\tau_c = 0.62/\omega_0$ ($\omega_0 = 2\pi\nu$, in our case $\nu = 200$ MHz). After simplifying eqn. (1), we solve it for $r_{H\cdots H}$. This leads to eqn. (2):

$$r_{H\cdots H}\ (\text{Å}) = 2.405(200T_{1min}/\nu)^{1/6} \quad (2)$$

An additional intramolecular rotation of a proton pair relative to the axis perpendicular to the H···H vector with correlation time $\tau \ll \tau_0$ decreases the relaxation rate predicted by eqn. (1) by a factor of 4 [25]. Consequently, the right-hand side of eqn. (2) can have an additional multiplier equal to 0.794 in such cases as proton relaxation of the methyl group [25] or η^2-H_2, for example [7].

Before using eqn. (2) to determine the interproton distances in structures **I** and **II**, the validity of such an approach should be confirmed, i.e. the question whether the observed temperature dependences of T_1 and values of T_{1min} are consistent with the theory should be answered.

As seen from Fig. 1, the observed dependencies can be characterized as follows: (i) the $1/T_1$ values at low temperature are appreciably higher than theoretical ones, (ii) the minima of the dependences are broad (*c.* 30°), (iii) the value of the slope of the high-temperature section corresponds to the E_A energy which is one kilocalorie lower than that given by ^{2}H NMR. All the observed deviations are significant and exceed the possible experimental errors. Furthermore, the reliability of the activation energy, calculated from ^{2}H T_1 data, is supported by low ^{2}H NMR frequency and the quadrupole mechanism of deuterium relaxation.

As for the second part of the above stated question, we can answer affirmatively. In fact, the known H···H distance (2.48 Å) between *meta* and *para* phenyl protons allows us to calculate the theoretical T_{1min} value of 0.6 s (taking into account the interaction of each proton only with two neighboring ones). The found value is in good agreement with the experimental data. Consequently, $r_{H\cdots H}$ can be calculated through the T_{1min} value for the H-ligands as well, if the T_{10} contribution due to the interactions between Ru–H and PPh_3 protons is taken into account.

For the classical structure **I**, fast position exchange leads to a equiprobable interaction of each of the H-ligands with one or two neighboring protons. The additivity of the relaxation rates implies that in this case the experimental $1/T_{1min}$ value is 1.5 times higher than that in the case of the interaction of only two protons ($1/T_{1min}$(H···H)). Thus:

$$1/T_{1min}(\text{H}\cdots\text{H}) = 2(1/T_{1min} - 1/T_{10})/3 \quad (3)$$

Substitution of $T_{1min} = 20 \pm 0.5$ ms and $T_{10} = 200$ ms in eqn. (3) leads to $T_{1min} = 33 \pm 1$ ms which in turn gives $r_{H\cdots H} = 1.37 \pm 0.01$ Å according to eqn. (2).

Earlier, Hamilton and Crabtree [10] obtained a T_{1min} value of 30 ± 3 ms for the H-ligands of complex **5** at 250 MHz. With this number (taking into account the difference of ^{1}H NMR frequences), eqns. (2) and (3) give an $r_{H\cdots H}$ distance of 1.41 ± 0.02 Å for classical structure **I**.

When calculating an $r_{H\text{–}H}$ distance for the η^2-coordinated dihydrogen molecule of the non-classical structure **II**, the dipole–dipole interaction of the non-bonded H-ligands can be neglected. In fact, if $r_{H\cdots H} > 2$ Å, then $1/T_{1min}$ is *c.* 1 s^{-1}. Then:

$$1/T_{1min}(H_2) = 2(1/T_{1min} - 1/T_{10})$$

According to our data, an $r_{H\text{–}H}$ distance of 0.90 ± 0.01 Å is calculated. Using the T_{1min} value reported by Hamilton and Crabtree increases $r_{H\text{–}H}$ up to 0.93 Å.

One should note that the r^{-6} term in eqn. (1) is really $(\bar{r}^{-3})^2$, where the average is over vibrational motions. In some cases this average increases r^{-6} by 5%–10% over the equilibrium distance value [26]. Thus, the above calculated $r_{H\text{–}H}$ and $r_{H\cdots H}$ are at the lower limit of real interproton distances in complex **5**.

At first glance, the $r_{H\text{–}H}$ of 0.90–0.93 Å calculated for the non-classical structure **II** is rather small and supports its formulation by Crabtree and co-workers [3, 10, 18]. However, the structural data evidence for the shorter $r_{H\text{–}H}$ values (0.82 Å) in complexes **1** and **2**. Moreover, apparently no increase in $r_{H\text{–}H}$ occurs on transition from solid state to solution. T_{1min} for the above-mentioned compounds equals some several ms and the $r_{H\text{–}H}$ calculations lead to a satisfactory agreement with the crystallographic data [6, 7].

Analysis of the literature data reveals a surprising coincidence: the lowest T_1 (4 ms (200 MHz), 4 ms (250 MHz) and 5 ms (500 MHz) values for compounds **1**, **3** and $[CpRe(CO)(NO)(\eta^2\text{-}H_2)]BF_4$, respectively, were obtained in those cases when the exchange between classical and non-classical tautomers appeared to be slow on the NMR time-scale [6, 9, 27].

It is quite probable that the exchange process leads to increased values of $T_{1\text{min}}$ and $r_{\text{H-H}}$ for other known η^2-H_2 complexes (especially polyhydrides), which were accounted for by elongation of the H–H bond.

With the above data in hand, we consider that there is no reliable enough experimental evidence for the existence of complexes in which the coordinated H_2 molecule has a bond length of 0.9 Å and more. But in turn, the $r_{\text{H}\cdots\text{H}}$ distance calculated during the analysis of the classical model **I** (of the order of 1.4 Å) is unprecedently small (according to the neutron diffraction data, the least $r_{\text{H}\cdots\text{H}}$ values are equal to 1.65–1.67 Å in $OsH_6(P(iPr)_2Ph)_2$ and $[IrH_3(C_5H_5)PMe_3]^+$ [28, 29], whereas in complex $OsH_4(PMe_2Ph)_3$ it equals 1.84 Å [24]).

^2H T_1 data and quadrupole coupling constants

At the present time quadrupole coupling constants (*QCC*) are known for three classical deuterides of transition metals: $(C_5H_5)_2ZrD_2$, $(C_5H_5)_2MoD_2$ and $(C_5H_5)_2WD_2$. These *QCC* values are equal to 47 ± 5, 52 ± 3 and 54 ± 4 KHz, respectively [30–32]. A correlation is reported to exist between the *QCC* values and M–H vibrational stretching force constants [32]. Indeed, for the above mentioned compounds, the $\nu_{\text{M-H}}$ value increases from 1520 to 1869 cm^{-1} and this is the order of increasing quadrupole coupling constants. The infrared spectrum of $RuH_4(PPh_3)_3$ measured in solution shows a broad band at 1910 cm^{-1} attributable to the stretching vibration of the Ru–H bond [16]. Thus, the *QCC* value of 68 ± 3 KHz determined by us does not in our opinion contradict the classical structure **I** of complex **5**.

Unfortunately, at present, it is impossible to analyze ^2H NMR data in terms of the non-classical model **II**. The *QCC* value is too indefinite for the coordinated dihydrogen (ranging from 120 to 180 KHz [6, 32]). It is also difficult to take into account the influence of the intramolecular rotation of η^2-$^2H_2$ on ^2H T_1 since the angle between the rotation axis and the electric field gradient eq_{zz} for the $M(\eta^2\text{-}^2H_2)$ fragment is unknown.

Spin–spin coupling constants J(H–D) and $J(^1H\text{–}^{31}P)$

As was shown above, averaged H–D coupling in $RuH_2D_2(PPh_3)_3$ does not exceed 2.7 Hz. If the probabilities of different isotope combinations are taken into account, then the expected *J*(H–D) value in the η^2-HD ligand of non-classical structure **II** is not higher than 8.5 Hz. For rigorously proved dihydrogen complexes the observed *J*(H–D) are more than 20 Hz and appreciable exceed this expectation [2–4]. In turn, in classical hydrides *J*(H–D) is approximately 1 Hz. Under this reasoning, from observed *J*(H–D) it is impossible to make any reliable conclusions with regard to the structure of **5**.

The $J(^1H\text{–}^{31}P)$ value for the H-ligands of complex **5** is equal to 6 Hz. Similar values of 6.9–14 Hz were observed in spectra of complexes $RuH_4(P\text{-}i\text{-}Pr_3)_3$ and OsH_4L_3 (L = tertiary phosphine) [33, 34]. The classical structure of one of which, $OsH_4(PMe_2Ph)_3$, in the solid state was confirmed by neutron diffraction [24].

However, classical dihydrides $RuH_2(N_2)(PPh_3)_3$ and $RuH_2(CO)(PPh_3)_3$ (their structures and the non-classical structure **II** are closely related) exhibit large $J(^1H\text{–}^{31}P)$ of 75 Hz when the phosphine and hydride ligands are transoid and $J(^1H\text{–}^{31}P)$ of 15–30 Hz when the phosphine and hydride ligands are cisoid [21, 35]. It should be noted, that the averaged signal of the H-ligands of $FeH_2(\eta^2\text{-}H_2)(PPh_3)_3$ also shows a large $J(^1H\text{–}^{31}P)$ constant of 27 Hz [10]. Consequently, the *J*(H–P) data for complex **5** are most consistent with the classical structure **I**.

Conclusions

Thus, there arises a complicated situation which mirrors the inadequacy between the above considered models and the whole set of experimental data. It allows us to suggest a hypothesis on delocalization of the H-ligands in complex **5** [20]. In terms of semi-classical representation this implies that in complex **5** there occurs a fast pairwise detachment–approachment motion (with the appearance of bonding interaction) of the H-ligands ranging from 2.2–2.5 to 0.8–0.9 Å. In addition, the probabilities of the occurring states are comparable. In other words, the motion of the hydride ligands takes place relative to the equilibrium position with an amplitude of 0.7–0.8 Å, which is somewhat higher than the amplitude of the motion (0.35–0.40 Å) in solid state [28]. In this case the spin–lattice relaxation rate will be determined by the sum $p_i r_i^{-6}$, where r_i is one of the possible $r_{\text{H-H}}$ and p_i its probability. One should take into account, that upon such summation, $r_{\text{H-H}}$ calculated from T_1, may not be an equilibrium distance.

It is known that large amplitude motions of the hydride ligands lead to quantum mechanical exchange [28, 36]. Consequently, in addition to the thermally activated exchange process in complex **5**, quantum mechanical tunneling of H-ligands can take place and explain their averaging in the NMR time-scale.

It cannot be excluded that $RuH_4(PPh_3)_3$ in solid state contains η^2-coordinated dihydrogen. It has been noted that the IR spectra of $RuH_4(PPh_3)_3$ display a $\nu_{\text{Ru-H}}$ band at 1910 cm^{-1} [16], but "considerable shift of the band to 2027 cm^{-1} was observed when the spectrum was taken in solid state" [37].

We would like to note in conclusion, that the supposed dynamic behavior of ruthenium tetrahydride should be intrinsic to several other hydride complexes. This study is now in progress.

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