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LETTER

The NMR study of reactions of dihydrogen with the monohydrides $RhHCl_2L_2$ ($L=P(CH(CH_3)_2)_3$ and $P(c\text{-}C_6H_{11})_3$)

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Interest in hydride transition metal complexes arises from their catalytic activity [1–4], remarkable structural features [1, 2, 5, 6], unique reactivity and diversity of acid–base equilibria [1, 2, 6, 7]. Of particular interest, among various chemical transformations, are the interactions with molecular hydrogen affording either classical or non-classical hydrides [8, 9], the structure and dynamic behaviour of which are best studied by NMR.

In this work we report on the ^1H, ^2H and ^{31}P study of the coordinately unsaturated monohydrides $RhHCl_2L_2$, where $L=PPr^i_3$ (**1**) and $P(c\text{-}C_6H_{11})_3$ (**2**), as well as on their reactions with molecular hydrogen.

Experimental

Complexes **1** and **2** were prepared as described elsewhere [10]. NMR spectra were recorded on WP-200 and CXP-200 instruments; chemical shifts are reported relative to TMS and H_3PO_4. The ^1H NMR data were obtained in deuterated solvents; the ^2H NMR data were obtained in the corresponding protium analogues. T_1 measurements were made by the inversion-recovery method using the standard programs for calculation of T_1. The number of variable time intervals for evaluation of T_1 was 11–18. The 90° pulse was recalibrated at each temperature.

Solvents were deaerated by a procedure freezing–vacuumation (0.1 torr)–defreezing performed three times. Then, they were recondensed into a 5 mm NMR tube containing a solid complex. A space above the liquid phase was filled with either purified H_2 and D_2 and the tube unsoldered, or purified argon. In the latter case the tube was capped with septum in order to provide the bubbling of gases through the sample using a stainless steel needle.

Results and discussion

Complexes **1** and **2** were characterized by ^1H NMR in $CDCl_3$, C_6D_6 and $C_6D_5CD_3$ solutions. The spectral data showed good agreement with those reported in the literature [10–12].

In the case of complex **1**, however, in $CDCl_3$ we observed a broad line at $\delta=9.6$ ppm with $T_1<0.005$ s together with signals of complex **1**. According to the neutron diffraction data and magnetic measurements, the synthesis of **1**, if started from aqueous $RhCl_3$, leads to a mixture of **1** and the square-planar paramagnetic complex $RhCl_2(PPr^i_3)_2$ (**1a**) the fraction of which is 0.25 [10]. The ^1H NMR measurements in solid complexes **1** and **2** indicated a two term relaxation dependence in each case with $T_1=0.1\pm0.04$ and 1.6 ± 0.4 ms for complex **1** and $T_1=0.2\pm0.1$ and 3.6 ± 0.2 ms for complex **2**. These values are indicative of the paramagnetic mechanism of relaxation of protons of **1** and **2** in the solid state and allow assignment of the rapidly relaxating signal with $\delta=9.6$ ppm in the ^1H NMR spectrum of **1** in $CHCl_3$ to the CH_3 groups of complex **1a** as the most remote from the paramagnetic center. Indeed, the integral intensity of this signal suggests that the fraction of **1a** in solution is equal to 0.25. It is in accord with the literature data [10] on the one hand and independently confirms our assignment, on the other.

The ^1H NMR spectra of solutions of **2** give no direct evidence for the presence of paramagnetic species such as **1a**. Lower values of T_1 for the protons of **2** (C_6D_6 290 K, T_1 for CH, CH_2 and Rh–H are equal to 0.35, 0.2–0.34 and 0.46 s, respectively) in comparison with complex **1** ($CDCl_3$, 290 K, T_1 for CH, CH_3 and Rh–H are equal to 0.83, 0.57 and 0.96 s, respectively) show, however, that solutions of **2** contain the square-planar species of type **1a**. Thus, the NMR data both in the solid phase and in solution demonstrate that on preparation of complexes **1** and **2** a mixture of diamagnetic and paramagnetic species is formed which are difficult to separate. This makes it difficult to study the interaction of dihydrogen with monohydrides **1** and **2** in solution by relaxation measurements. It is known that monohydride **2** under the action of light transforms into a square-planar complex of type **1a** [11b]. We proposed that the reverse reaction is possible, i.e. a transition of **1a**

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into diamagnetic complex **1** under the action of dihydrogen. We have demonstrated that after bubbling of D_2 through a mixture of **1** and **1a** in $CDCl_3$ the intensities of ^1H NMR signals with $\delta = 9.6$ ppm and from the Rh–H proton of **1** decrease significantly. The secondary treatment makes the changes more pronounced.

$$2RhCl_2L_2 + H_2 \longrightarrow 2RhHCl_2L_2 \qquad (1)$$

In the ^2H NMR spectrum, the same experiment generates signals with $\delta = -30.8$ ppm (Rh–D of monohydride) and $\delta = 4.4$ ppm (dissolved D_2) which disappears on bubbling argon. After the action of H_2 on a mixture of **1** and **1a** in benzene or toluene, the intensity of the ^1H NMR signal with $\delta = 9.6$ ppm also decreases and a new signal with $\delta = 4.56$ ppm and $T_1 = 1.5$ s develops which could be assigned [13, 14] to dissolved H_2. Correspondingly, the ^1H and ^2H NMR data obtained confirm reaction (1), i.e. the rearrangement of paramagnetic complex **1a** into diamagnetic **1** in the presence of molecular hydrogen.

In addition to the above described spectral changes which are observed after a short-term (*c*. 1 min) contact of solution of **1** with H_2 and D_2 in the ^1H and ^2H NMR spectra we have noticed a signal at -22 to -23 ppm of low intensity. To assign this signal and to identify the product of interaction of monohydride **1** with dihydrogen, we have studied ^1H, ^2H and ^{31}P NMR spectra of solutions of **1** and **2** in toluene, in sealed NMR tubes under an atmosphere of H_2 and D_2. Note that under these conditions the broad line at $\delta = 9.6$ ppm (CH_3 protons of **1a**) is not observed in the ^1H NMR spectrum due to reaction (1). After a prolonged contact (more than 24 h) of **1** with H_2, in the ^1H NMR spectrum we have observed a signal from the starting monohydride together with a new one, the position (-22.73 ppm) and fine structure (J(P–Rh–H) = 12.5 Hz, J(Rh–H) = 25.5 Hz) of which correspond to the dihydride $RhH_2Cl(PPr^i{}_3)_2$ according to ref. 15. The ^{31}P NMR spectrum recorded without ^1H decoupling also confirms this conclusion. The ^1H and ^{31}P spectra provide the ratio monohydride:dihydride = 5:1 ($\delta^{31}P$ of mono- and dihydride are equal to 47.3 and 65.7 ppm with J(Rh–P) equal to 97 and 114 Hz, respectively). The ^2H NMR spectrum of **1** under D_2 has signals with $\delta = -22.6$ and -30.0 ppm corresponding to the deuterio analogues of the di- and monohydrides. Besides, the ^1H NMR spectrum of solution toluene:**1**:H_2 contains a resonance from dissolved dihydrogen (4.53 ppm), while the ^1H NMR spectrum of solution toluene:**1**:D_2 contains resonances from H_2 and HD ($\delta = 4.49$ ppm, J(H–D) = 43 Hz). Using all the data we suggest the following mechanism of interaction of hydride **1** with molecular hydrogen (eqn. (2)).

$$\underset{\mathbf{1}}{HRhCl_2L_2} + H_2 \rightleftharpoons \underset{\mathbf{3}}{[HRh(H_2)Cl_2L_2]} \rightleftharpoons$$
$$\underset{\mathbf{4}}{[H_3RhCl_2L_2]} \rightleftharpoons \underset{\mathbf{5}}{H_2RhClL_2} + HCl \qquad (2)$$

In principle, the deuterium exchange data can be explained by the redox addition-elimination of H_2, because η^2-complex **3** was not detected by NMR. Nevertheless, we propose eqn. (2) following related studies, namely of transformations of $IrHCl_2(PR_3)_2$ under dihydrogen [16]. We believe that the alternative mechanism with initial loss of HCl and addition of H_2 to $RhCl(PPr^i{}_3)_2$ is less probable because of instability and high reactivity of all compounds of the type $ClRh(PR_3)_2$ [17].

A refinement of the structure of dihydride **5** is possible on the basis of NMR and relaxation measurements carried out for protium and deuterium atoms of **1** in toluene solutions kept under H_2 and D_2. As seen from the data collected in Table 1, there are no T_1 minima in the temperature range 290–197 K which are necessary for evaluation of the time of correlation (τ_c) of motion of molecules **1** and **5**. Therefore, we used the values of T_1 of deuterium Rh–D in **1** and **5**, which relaxate via the quadrupole mechanism, in order to estimate τ_c from eqn. (3) [18]. This is possible as the quadrupole

$$1/T_1 = (3\pi^2/2)((e^2qQ)^2/h^2)\tau_c \qquad (3)$$

coupling constants, e^2qQ/h of ^2H bound to the metal are known and equal to 50–70 kHz [19]. At 260 K the estimate of τ_c for **1** and **5** leads to 2.6×10^{-10} s. Applying the additivity principle to the rates of relaxation, from the value of T_1 for (Rh–H) of **1**

TABLE 1. The time of spin–lattice relaxation $T_1(^1H)$ of monohydride **1** and dihydride **5** in solution D-toluene–dihydrogen

T (K)	T_1 (s)			
	RhH (1)	RhH (5)	CH	CH_3
290	0.82		1.30	0.90
260	0.74[a]	0.33[b]	0.69	0.45
243	0.59	0.24	0.30	0.20
225	0.40	0.15	0.21	0.14
207	0.26	0.091	0.19	0.11
188	0.27	0.083		

[a] For **1** T_1(Rh–D) = 0.081 s. [b] For **5** T_1(Rh–D) = 0.06 s.

and **5** one can calculate the T_1 of the hydridic proton of **5** arising from the dipole–dipole interaction with only an adjacent proton ($1/T_1 = 1/T_1$(dihydride) $- 1/T_1$(monohydride)) on the assumption that the distances between the protons Rh–H and the ^1H or ^{31}P nuclei of the ligands that contribute to the relaxation are not altered on going from **1** to **5**. Thus found the values of T_1 provide an estimation of the distance between the dihydrides in complex **5** of 2.2 Å according to eqn. (4) [20].

$$r^6(\mathrm{cm}) = 8.548 \times 10^{-37} \times \tau^c \times T_1 \tag{4}$$

We have shown that the Rh–H protons and ^{31}P nuclei of dihydride **5** are magnetically equivalent in the NMR spectra even on cooling to 179 K. This, together with J(P–Rh–H) = 12.5 Hz, suggests that **5** is a trigonal bipyramid with the bond angle H–Rh–H of 100° in the basal fragment. (The estimate was done taking into account the value of r found and the bond length Rh–H in monohydride **1** (1.43 Å) determined by neutron diffraction [10].) According to the X-ray data, the complex $H_2RhCl(PBu^t_3)_2$ is a trigonal bipyramid with hydrido and chloro ligands in the equatorial plane [21]. Our findings are in good accord with this structural study.

The data obtained in the present work have been discussed in detail using the example of complex **1**. It should be, therefore, stressed that the interaction of complex **2** with molecular hydrogen proceeds similarly, i.e. affording a mixture of the monohydride and dihydride according to the ^1H and ^2H NMR spectra. As in ref. 11b, the chemical shift from Rh–H of dihydride **5** in toluene is equal to −22.5 ppm (J(Rh–H) = 27 Hz, J(P–H) = 14 Hz).

It should be pointed out in conclusion that the study carried out clarifies the mechanism of interphase-catalyzed reaction of complex **1** with H_2 (benzene–40% NaOH–EtN^+CHPCl^-)leading to dihydride **5** at 20 °C in a matter of 1–2 min in a quantitative yield [22]. Evidently, at least one of the ways of this transformation is associated with shifting equilibrium (2) toward complex **5** as a result of binding HCl with a base.

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