# NMR spectra and the products of interaction of iridium monohydrides $IrHCl_2L_2$ ($L = P(CH(CH_3)_2)_3$ and $P(c\text{-}C_6H_{11})_3$) with molecular hydrogen

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**Abstract**

Rapid and reversible $\eta^2$-coordination of molecular hydrogen to the monohydrides $IrHCl_2L_2$, with $L = PPr^i_3$ (**I**) and $P(c\text{-}C_6H_{11})_3$ (**II**), has been established by $^1H$ and $^2H$ NMR. The complexes formed eliminate HCl to afford the dihydrides $IrH_2ClL_2$. The spectral data are reported and discussed in connection with the structure of the proposed intermediates.

## Introduction

The catalytic activity and unique structural features are the factors that permanently stimulate studies of transition metal hydrides. Of particular interest is their interaction with molecular hydrogen leading to both classical and non-classical hydrides.

Kubas *et al.* have reported that the five-coordinated molybdenum and tungsten complexes $M(CO)_3(PR_3)_2$ bind dihydrogen in a $\eta^2$-fashion in solution to form six-coordinated species [1]. More recently similar interactions have been found for other transition metal complexes [2–4].

We have shown [5] that the complexes $RhHCl_2L_2$ ($L = PPr^i_3$ and $P(c\text{-}C_6H_{11})_3$) lose HCl on reacting with $H_2$. It has been postulated, that the reaction involves the $\eta^2$-bonded dihydrogen species as short-living intermediates.

In the present work we have studied the reactions of the iridium monohydrides $IrHCl_2L_2$, where $L = P(CH(CH_3)_2)_3$ (**I**) and $P(c\text{-}C_6H_{11})_3$ (**II**), with molecular hydrogen with the hope of observing the $\eta^2$-species and to follow their further conversion in solution by NMR. Aside from the commonly used $^1H$ NMR technique, we employed $^2H$ NMR which provides additional spectral information.

## Experimental

*General data*

Deuterated solvents (benzene-$d_6$ and toluene-$d_8$) were kept under $LiAlH_4$ and a degassing freezing–pumping (0.1 torr) procedure was carried out three times prior to preparation of a sample. Then the solvent was recondensed into a 5 mm NMR tube containing a weighted amount of the complex. The space above the liquid phase was filled with either purified $H_2$ or argon and the tube was sealed (or capped for the bubbling of gases through the solution). Samples for $^2H$ NMR studies were prepared in 10 mm tubes in toluene under an atmosphere of argon and $D_2$ was bubbled through the solutions just before NMR measurements.

$^1H$, $^{31}P$ and $^2H$ NMR spectra were recorded on Bruker CXP 200 and WP 200 instruments operating at 200.13, 81.02 and 30.72 MHz, respectively. $T_1$ measurements were made using the inversion–recovery method. The number of variable delays in the $T_1$ measurements was 11–18. The 90° pulse was controlled at each temperature.

*Synthesis of the complexes*

Unless otherwise noted, all manipulations were carried out in argon atmosphere. The complex $IrHCl_2(PPr^i_3)_2$ (**I**) was prepared according to the procedure previously reported [6].

*$IrHCl_2(PCy_3)_2$ (II)*

A solution of $H_2IrCl_6$ (1g, 36.8% Ir) in 10 ml of degassed isopropanol was heated. When metallic iridium began to precipitate, tricyclohexylphosphine (2 g, 7.1 mmol) was immediately added and the mixture was refluxed for 6 h. The formed precipitate was separated, dissolved in warm benzene (50 °C), passed through a silica-gel (40/100) layer and dried.

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Then the complex was washed with pentane (3×5 ml) and dried in vacuum. Yield: 0.55 g (35%). *Anal.* Found: C, 52.7; H, 8.6; Cl, 8.7. Calc. for $C_{36}H_{67}Cl_2IrP_2$: C, 52.4; H, 8.2; Cl, 8.6%.

*$IrH_2Cl(HCl)(PPr^i_3)_2$ (Y)*

A solution of complex **I** (0.11 g, 0.19 mmol) in 2 ml of degassed benzene was heated in an atmosphere of purified $H_2$ at 50 °C for 4 h. Then the reaction mixture was kept at 20 °C for 2.5 days. The solution became bright-orange, and pale-yellow crystals formed. Eight ml of degassed pentane was added to the mother liquor. The resulting mixture was kept at −15 °C for 5 h, and an additional amount of the complex was precipitated. The crystals were collected, washed with pentane (2×2 ml) and dried. Total yield: 0.06 g (54%). *Anal.* Found: C, 37.3; H, 7.7; Cl, 12.3. Calc. for $C_{18}H_{45}IrP_2Cl_2$: C, 36.9; H, 7.7; Cl, 12.1%.

$^1H$ NMR ($\delta$ ppm, toluene-$d_8$, 230 K); 2.43 (6H, m); 1.04 (36H, m); −12.18 (2H, t $^2J(^1H-^{31}P) = 8$ Hz).

## Results and discussion

*$^1H$ NMR spectra of iridium monohydrides I and II*

The $^1H$ chemical shifts of the iridium-bound hydrogen are equal to −48.5 and −47.2 ppm for **I** and **II**, respectively, in d-toluene at 290 K. The phosphine protons resonate in the region 1–3 ppm. The multiplets of the CH (2.97 ppm) and $CH_3$ (1.22 ppm) groups are well resolved in the case of isopropyl complex **I**. The cyclohexyl groups of **II** provide a more complicated but also resolved spectrum. The integral intensities of the $^1H$ NMR signals of complexes **I** and **II** are in a good agreement with their structural formulation. Surprisingly, the Ir–H chemical shift in **II** differs significantly from that reported in ref. 7 ($\delta = -32.3$ ppm) where the compound was first characterized.

For compound **II** no change of $\delta$(Ir–H) was observed on decreasing the temperature of toluene solution to 200 K. In contrast, the $^1H$ NMR spectra of **I** were strongly dependent on temperature. In particular, the Ir–H peak migrates, on cooling, downfield, strongly broadens, and even disappears (similar spectral changes were reported in ref. 8 and accounted for by formation of the paramagnetic dihydride). At 170 K the peak becomes again apparent in the region −49.55 ppm. Also a new signal at −33 ppm arises. The nature of this peak is presently being investigated. It is already clear that observed spectral behavior of complex **I** in solution results from dynamic processes rather than paramagnetic relaxation.

Thus, the spectral behavior of complexes **I** and **II** in d-toluene is markedly different. It turns out, however, that the differences disappear in the presence of an excess of dihydrogen.

*$^1H$ and $^2H$ NMR spectra of iridium monohydrides I and II in toluene in the presence of an excess of dihydrogen*

The interaction between complexes **I**, **II** and dihydrogen was studied in standard NMR tubes sealed so as to ensure the presence of pure dihydrogen above the solution. Considering the low solubility of dihydrogen (2–4 $\mu$mol/cm$^3$ in most organic solvents), low concentrations of complexes **I** and **II** were used to achieve an excess of dihydrogen.

The chemical shift of dihydrogen dissolved in toluene, benzene, $CDCl_3$ and $CD_2Cl_2$ is equal to 4.53–4.58 ppm in the temperature range 170–320 K. In other words, this shift is practically independent of temperature.

Figure 1 shows the $^1H$ NMR signals of Ir–H and dissolved dihydrogen from a d-toluene solution of tricyclohexylphosphine complex **II** and dihydrogen at a molar ratio dihydrogen/complex = 2/1 (determined from the integral intensities of $^1H$ NMR signals). It is seen that in the temperature range 170–310 K the changes in the positions and lineshapes of the $H_2$ and hydride signals are strongly correlated. These observations can be rationalized in terms of an exchange process in which complex **IIa** containing $\eta^2$-bound dihydrogen involves

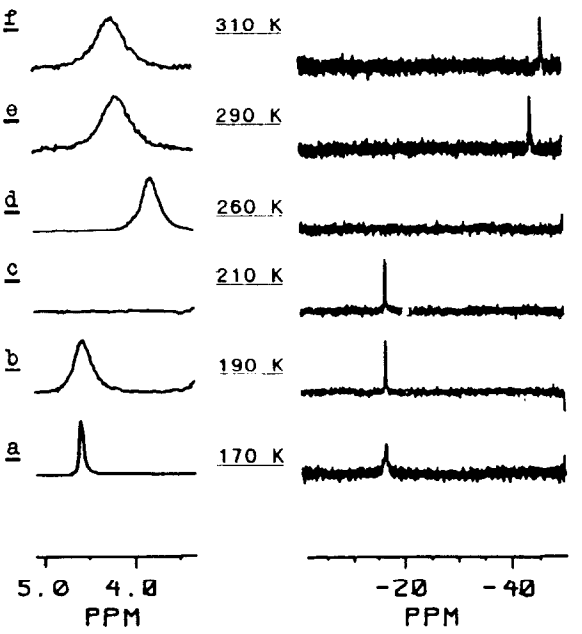



Fig. 1. The temperature dependences of positions and lineshapes of $^1H$ NMR signals of $H_2$ (left) and Ir–H (right) for the system complex **II**–$H_2$–toluene-$d_8$. The spectra were scaled to the equal intensities.

$$IrHCl_2(PCy_3)_2 + H_2 \rightleftharpoons IrH(H_2)Cl_2(PCy_3)_2 \quad (1)$$
**II** **IIa**

Actually, the spectra show that the cooling of the solution is accompanied by two phenomena. These are, first, a shift of equilibrium (1) toward the formation of the complex with molecular hydrogen (**IIa**) and, second, decrease in the exchange rate (i.e. an increase in the lifetimes of the exchanging states). At 170–190 K, the exchange (1) becomes slow on the NMR time scale, and the equilibrium is almost completely shifted to the right. The signal at $\delta = -16.69$ ppm corresponds to the Ir–H of **IIa** (note that this spectral region is typical of the six-coordinated iridium compounds [9]). The presence of an excess of dihydrogen is responsible for a sharp singlet at 4.5 ppm. An indirect argument in favor of eqn. (1) is a change in color of the solution from pink (290 K) to colorless (170–190 K), which is typical of the formation of coordination-saturated octahedral complexes.

Unfortunately, in the region of $-1$ to $-50$ ppm the signal from $\eta^2$-$H_2$ of **IIa** is not observed (probably due to strong line broadening at 170–190 K). The evolution of the dihydrogen NMR signal in Fig. 1 shows that the temperature, below which the rate of positional exchange becomes slow on the NMR time scale, is lower by 20–30° than the corresponding temperature for the Ir–H signal. Considering principles of dynamic NMR [10] and the Ir–H chemical shift difference between complexes **II** and **IIa** ($\Delta\delta = -17-48 = 31$ ppm) and assuming that 10° temperature change should lead to a two to three-fold change in the exchange rate, one can estimate the position of the signal from $\eta^2$-bound dihydrogen to be 0 to $-2$ ppm. As will be shown below, this signal is detected by $^2H$ NMR just in this spectral region.

Spectral changes indicative of equilibrium (1) have also been observed for complex **I**. In this case the value of $\delta$(Ir–H) of the complex with molecular hydrogen (**Ia**) is equal to $-17.03$ ppm. It should be also pointed out that the position of the $-CH-$ signal of the isopropyl group is 2.97 and 3.10 ppm in **I** and **Ia**, respectively.

The $^1H$ NMR spectra of complexes **I** and **II** under an atmosphere of $H_2$ show that for complex **I** the retardation temperature of exchange (1) is 10–20° lower. This is, probably, due to a higher ability of **II** to bind dihydrogen.

To locate signals of $\eta^2$-bound dihydrogen in complexes **Ia** and **IIa** the $^2H$ NMR technique has been used. The spectra of complex **I** recorded in toluene under $D_2$ are shown in Fig. 2. In this Figure the arrows denote the signals from toluene. The

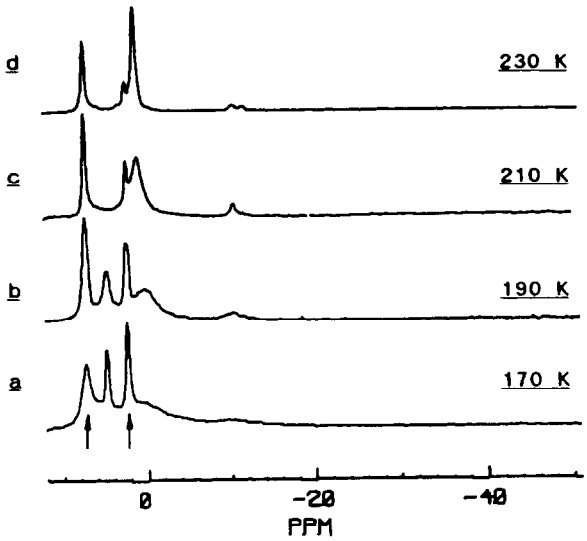



Fig. 2. The $^2H$ NMR spectra of $IrHCl_2(PPr^i_3)_2$ in toluene under $D_2$.

other lines arise from the presence of $D_2$ in the system, the signal at 4.5 ppm being attributed to free dihydrogen (cf. Figs. 1a, b and 2a, b). At 190 K in the region predicted above one can see a broad signal at $\delta = -0.3$ ppm (Fig. 2b) which becomes even broader at 170 K. This effect is undoubtedly due to a decrease in molecular mobility of **Ia**. Actually, the signal of free $H_2$ sharpens on going from 190 to 170 K indicating a retardation of the exchange process (1). In the fast exchange limit the averaged signal sharpens and migrates upfield (1.9 ppm at 260 K). Thus, the obtained data confirm that equilibrium (1) is valid and that the $^2H$ NMR signal at $\delta -0.3$ ppm arises from the $\eta^2$-bound dihydrogen in complex **Ia**. Similar $^2H$ NMR studies of complex **II** led to identical results.

The $^2H$ NMR spectra discussed above have no signals at $-16$ to $-50$ ppm. Therefore, there is no intramolecular isotope exchange in complexes **Ia** and **IIa** during the experiments. Thus, the H–H bond remains quite strong in the coordinated dihydrogen and complexes **Ia** and **IIa** yield no classical trihydrides.

The data show a decreasing of the rate of process (1) at the same temperature in $^1H$ and $^2H$ NMR spectra despite an almost seven-fold decrease (on the frequency scale), in the chemical shift difference of the exchanging states on going from $^1H$ to $^2H$. This indicates that equilibrium (1) is much slower in the case of $D_2$ (by a factor of 6–7) than in the case of $H_2$. In other words, one deals here with a primary kinetic isotope effect.

If the NMR chemical shifts of free and bound dihydrogen are known, one can estimate the ratio of the equilibrium constants (1) $K_{eq}(D)/K_{eq}(H)$ from

the chemical shift of averaged signals in the fast exchange limit. Such a ratio obtained by $^1H$ and $^2H$ NMR for complex **II** at 260 K under the $H_2$ and $D_2$ atmosphere in toluene is indicative of the presence of the thermodynamic isotope effect as well, $K_{eq}(D)/K_{eq}(H) = 2$.

To conclude the discussion of the spectral data, it should be pointed out that during the $^2H$ NMR studies, which are more time consuming compared to the $^1H$ NMR ones, we have noticed new spectral changes which are completed by an irreversible transformation of complexes **I** and **II**. Spectra in Fig. 2 contain weak peaks in the region $-10$ to $-12$ ppm which suggest that dihydrogen is involved in additional interactions. This result has stimulated a $^1H$ NMR study of solutions of complexes **I** and **II** in sealed NMR tubes after a prolonged exposure to $H_2$. Note that the exposure of such solutions to $H_2$ is accompanied by a color change from red (or pink, depending on the concentration of **I** and **II**) to gold–yellow. It turns out that both the lowering of concentration and heating (up to 60°) accelerate the process and it takes several hours to perform the reaction.

Unexpectedly, the $^1H$ NMR spectra of the yellow solutions do not display hydride resonances at 290 K. On cooling, however, one can observe (Fig. 3) temperature evolution of two signals at $\delta = -10.67$ and $-11.81$ ppm or $-10.89$ and $-12.14$ ppm for complexes **II** or **I**, respectively. The $^{31}P$ NMR spectra also contain two lines which are seen at 35.9 and 21.3 ppm in the case of **I**, for example. Unsealing of the tube containing the products of conversion of **I** in order to substitute argon for $H_2$ leads to disappearance of the signal at $\delta$ $-10.89$ ppm and appearance of a new signal at $\delta = -32.5$ ppm whose integral intensity is a half of the former. The position and fine structure of this signal unequivocally indicate

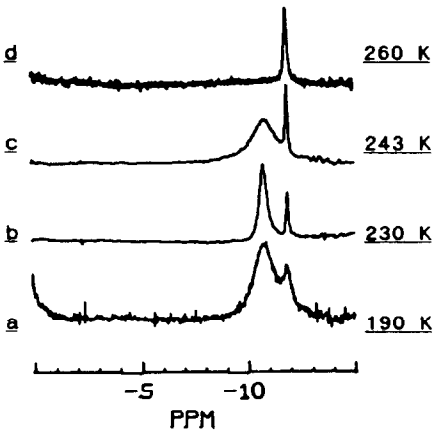



Fig. 3. The hydride region of $^1H$ NMR spectra of $IrHCl_2[P(c\text{-}C_6H_{11})_3]_2$ in toluene-$d_8$ after prolonged keeping under $H_2$.

the formation of the dihydride $IrH_2Cl(PPr^i_3)_2$ (**III**) [11]. Similar changes are seen in the $^{31}P$ NMR spectra where the signal at $\delta = 35.9$ ppm transforms into a line at $\delta = 53.1$ ppm arising from dihydride **III**. Thus, prior to removal of dihydrogen the yellow solutions contain $IrH_4ClL_2$ (**IY**) which is formed from $IrH_2ClL_2$ and $H_2$ and shows one signal for all hydride ligands ($\delta = -10.89$ ppm for $L = PPr^i_3$ and $-10.67$ ppm for $L = P(c\text{-}C_6H_{11})_3$).

Measurements of the spin-lattice relaxation times $T_1(^1H)$ (Table 1) carried out for the conversion products of monohydride **II** (Fig. 3) have demonstrated that the minimum value of $T_1$ ($\approx -30$ °C) for the signal at $\delta = -10.67$ ppm is equal to 20 ms. Therefore, according to the criterion of Hamilton and Crabtree [12] one can argue that compound **IY** contains a $\eta^2$-coordinated $H_2$ molecule on condition of the fast exchange (2) on the NMR time scale.

$$IrH_2(H_2^*)ClL_2 \rightleftharpoons Ir(H_2)H_2^*ClL_2 \quad (2)$$

An analysis of the temperature dependence of the $^1H$ NMR spectra of the system studied reveals a signal of free dihydrogen ($\delta = 4.53$ ppm) appearing below 230 K. The value of $T_1$ of this signal is not lowered, as is typical of small molecules in the liquid phase, and grows from 27 to 324 ms on cooling to 190 K. Therefore, besides exchange (2), there must be equilibrium (3)

$$IrH_2ClL_2 \overset{H_2}{\rightleftharpoons} IrH_2(H_2)ClL_2 \quad (3)$$

which, considering the values of $T_1$ of dissolved dihydrogen [12], leads to overestimation of the observed $T_{1min}$ value of the H ligands according to

$$1/T_{1min} = m/T_1(H_2) + n/T_{1min}(Ir\text{–}H)$$

where $m = 0.33$, $n = 0.67$ from the $^1H$ NMR integral intensities.

TABLE 1. The time of spin-lattice relaxation $T_1$ (ms) of the hydride protons formed on interaction of complex **II** with dihydrogen in toluene-$d_8$

| Chemical shift (ppm) | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | 290 | 260 | 243 | 230 | 210 | 190 |
| 4.56 (dihydrogen) | | | | 27 | 87 | 324 |
| 1.31 ($-P(c\text{-}C_6H_{11})_3$; $-CH_2-$) | 250 | 140 | 118 | 127 | 235 | 592 |
| −11.18 (Ir–H) | | 49 | 34 | 36 | 46 | 82 |
| −10.67 (Ir–H) | | | 20 | 24 | 31 | 73 |

Using this equation together with the method of Hamilton and Crabtree [12] and correction coefficient of Morris and coworkers [13] we have calculated $T_{1min}(\eta^2\text{-}H_2)$ for complex **IY** to be 7.1 ms and the H–H distance to be 0.84 Å.

To conclude this part of our discussion it should be noted that unsealing the tubes with the yellow conversion products of monohydrides **I** and **II** in order to replace $D_2$ for $H_2$ results in complete disappearance of $^1H$ NMR signals in the hydride region even at low temperatures. In our opinion, this isotope exchange provide an additional argument in favor of equilibria (2) and (3).

The elimination of $H_2$ from the tubes with the conversion products of **I** and **II**, and subsequent addition of a small amount of NaOH, lead to appearance of the sole $^1H$ NMR signal of dihydrides **III**. Therefore, the signals at $\delta = -12.14$ and $-11.81$ ppm (see above) are due to hydrides which are intermediates on the loss of HCl by complexes **I** and **II** under the action of dihydrogen.

The conversion product of monohydride **I** resonating at $-12.14$ ppm (complex **Y**) was isolated in the crystalline state and characterized. The following information was obtained.

(i) The only upfield $^1H$ NMR signal (at $-12.14$ ppm) appears at 260 K and sharpens at 230 K to give a poorly resolved triplet with $^2J(^1H-^{31}P) = 8$ Hz indicating the presence of two phosphines in the molecule.

(ii) The integral intensity of the hydride resonance (referenced to the isopropyl signals) is equal to 2H.

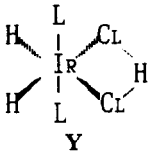
(iii) The minimum of $T_1$ for this signal is rather low and equal to 38 ms at 190 K ($T_1$ value for the conversion product of monohydride **II**, see Table 1).

(iv) The analytical data indicate the presence of two chlorine atoms in the molecule.

(v) Yanovsky and Struchkov are presently carrying out an X-ray study of this complex. According to preliminary results (only heavy atoms have been located), iridium is coordinated by two Cl and two triisopropylphosphine ligands. The coordination polyhedron is octahedron with two unidentified neighboring apexes, the chloro and phospine ligands being *cis* and *trans*, respectively.

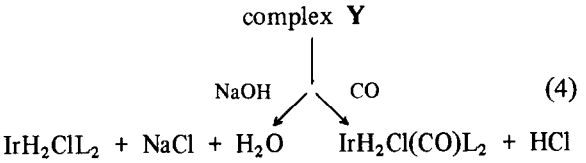
(vi) It has been shown by $^1H$ NMR that the complex under study reacts readily with hydroxide ions and CO in solution affording dihydrides $IrH_2Cl(PPr^i_3)_2$ (**III**) and $IrH_2Cl(CO)(PPr^i_3)_2$ (**YI**) whose $^1H$ NMR hydride signals (290 K, toluene-$d_8$) are seen at $-32.5$ ppm ($^2J(^1H-^{31}P) = 13$ Hz) for **III** [11] and at $-20.2$ ppm ($^2J(^1H-^{31}P) = 12.7$ Hz, $^2J(^1H-^1H) = 5.2$ Hz) and $-8.8$ ppm ($^2J(^1H-^{31}P) = 17.2$ Hz) for **YI** (complex **YI** was alternatively prepared from $IrCl(CO)(PPr^i_3)_2$ and $H_2$ in benzene).

By summarizing all the data obtained we assume that hydride complex **Y**, an intermediate in the production of HCl, has an unusual structure



**Y**

To explain the low $T_{1min}$ value the existence of H–H bonding interactions in **Y** can be assumed. Probably the exchange $IrH_2Cl\text{-}L_2 + HCl \rightleftarrows IrH_2(HCl)ClL_2$ in the time scale of NMR is responsible for broadening (even disappearance) of the hydride ligands signal at 290–330 K. Such a structure allows one to rationalize both the spectral data and the interactions of complex **Y** with NaOH and CO (eqn. (4)).




(4)

In conclusion, the results described in this work throw a fresh light on the mechanism of interphase-catalyzed reactions of complexes $IrHCl_2(PPr^i_3)_2$ and $IrH_2Cl(PPr^i_3)_2$ with $H_2$ to afford the pentahydride $IrH_5(PPr^i_3)_2$ in a quantitative yield [6]. It is likely that the starting complexes, when reacting with $H_2$ and $OH^-$, first transform to the dihydride $IrH_2Cl(PPr^i_3)_2$ which reacts in a similar way with $H_2$, but subsequent elimination of HCl gives the pentahydride species.

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