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^1H, ^2H and ^{31}P NMR Study of the Structure and Behaviour of $IrH_2Cl(HCl)(PPr^i_3)_2$ in Solution

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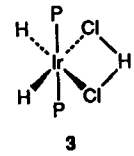
HCl coordination in $IrH_2Cl(HCl)(PPr^i_3)_2$ and the reversible transformation of the complex into monohydride $IrHCl_2(PPr^i_3)_2$ and dihydride $IrH_2Cl(PPr^i_3)_2$ in solution have been confirmed by ^1H, ^2H and ^{31}P NMR spectroscopy.

We have recently reported[1] evidence for the existence of a dynamic equilibrium (1) between $IrHCl_2(PPr^i_3)_2$ **1** and the η^2-dihydrogen complex, $IrH(\eta^2\text{-}H_2)Cl_2(PPr^i_3)_2$ (**2**) which has previously been assumed by Mura and co-workers[2–4] to arise in solutions of **1** and H_2.

$$\underset{\mathbf{1}}{IrHCl_2(PPr^i_3)_2} + H_2 \rightleftharpoons \underset{\mathbf{2}}{IrH(\eta^2\text{-}H_2)Cl_2(PPr^i_3)_2} \qquad (1)$$

Together with equilibrium (1), we have observed a slow transformation of **1** into the new hydride complexes $IrH_2Cl(HCl)(PPr^i_3)_2$ (**3**) and $IrH_2(\eta^2\text{-}H_2)Cl(PPr^i_3)_2$ (**4**). The latter can be prepared by the action of H_2 on $IrH_2Cl(PPr^i_3)_2$ (**5**) and the reverse transformation takes place when argon is bubbled through a solution of **4**.[1,5]

Complex **3** has previously been prepared by photolysis of a solution of **1** and H_2 and identified by IR and NMR spectroscopy as the classical trihydride, $IrH_3Cl_2(PPr^i_3)_2$.[4] However, our X-ray (without locating the hydride ligands) and NMR studies have revealed that the structure of **3** may be described as that of a dihydride, with the HCl ligand being stabilized by an intramolecular bridge.[1] Recently, the coordination of HCl has been reported by Sellmann and co-workers for two neutral ruthenium complexes.[6]



3

In this communication we report evidence for the existence of a rapid equilibrium (2) and the reversibility of the transformation of monohydride **1** into complex **3**.

$$\underset{\mathbf{5}}{IrH_2Cl(PPr^i_3)_2} + HCl \rightleftharpoons \underset{\mathbf{3}}{IrH_2Cl(HCl)(PPr^i_3)_2} \qquad (2)$$

The solutions investigated were prepared as follows. A red

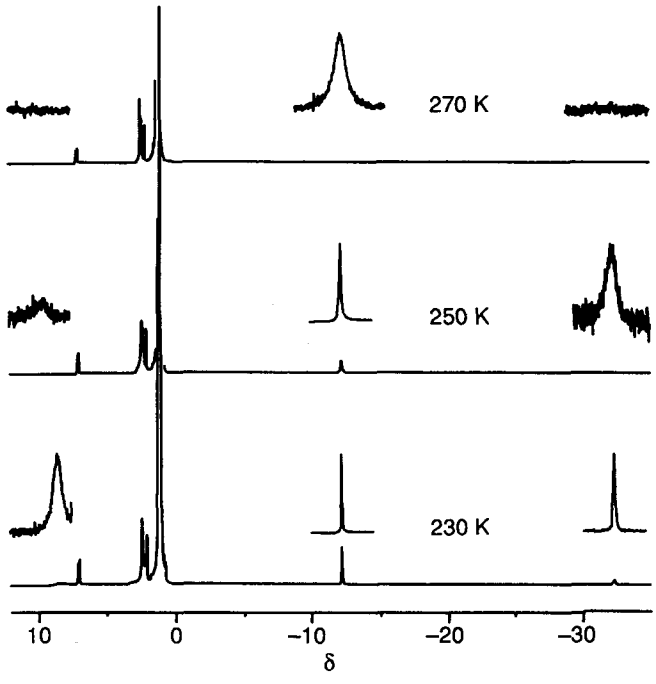


Fig. 1 Variable-temperature ^{1}H NMR spectra of $IrH_2Cl(HCl)(PPr^i_3)_2$ and $IrH_2Cl(PPr^i_3)_2$ (7:2) in [$^2H_8$]toluene solution

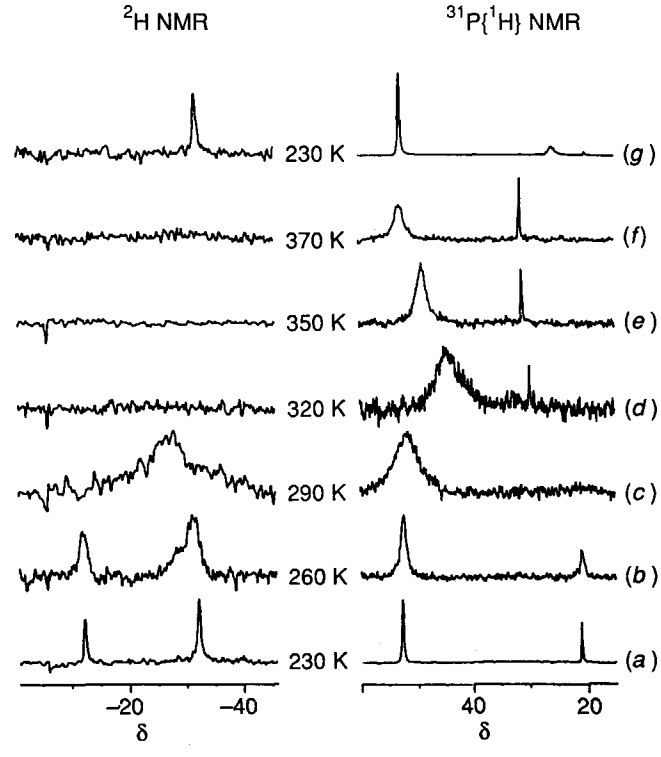


Fig. 2 Variable-temperature ^{2}H and ^{31}P{^{1}H} NMR spectra of $IrD_2Cl(HCl)(PPr^i_3)_2$ and $IrD_2Cl(PPr^i_3)_2$ (1:2) in toluene solution. The spectra (*g*) were obtained after fast cooling of the solution heated up to 370 K.

solution of **1** in toluene was carefully degassed and sealed under H_2 in 5 mm NMR tubes. After 1.5 months the tubes were unsealed and argon was bubbled through the yellow solution formed of **3** and **4**. The resulting samples with different [**3**]/[**4**]/[**5**] ratios (depending on the duration of the bubbling) were sealed once more and used in the NMR experiments.

Variable-temperature ^{1}H NMR spectra of $IrH_2Cl(HCl)(PPr^i_3)_2$ and $IrH_2Cl(PPr^i_3)_2$ (7:2) at 200 MHz in [$^2H_8$]toluene solution are shown in Fig. 1. The low-temperature (230 K) spectrum exhibits signals of phosphine protons, two resonances of hydride ligands [δ − 12.2 (IrH_2, **3**) and − 32.3 (IrH_2, **5**)] and a broad signal at δ 8.5 (relative intensity *ca.* 0.9 H) which can be attributed to the HCl. When aqueous HCl is introduced, the solution becomes colourless. In the ^{1}H NMR spectrum of the resulting mixture (230 K) the signals of **5** disappear but the signals of the CH, CH_3 and IrH_2 protons of **3** are observed in the ratio 6:36:2. The resonance at δ 8.5 is replaced by a new one at δ 9.4 which belongs to the exchanging protons of HCl and H_2O. On addition of a mixture of DCl + D_2O the signal at δ 8.5 disappeared, however, contrary to our expectations no H–D exchange between DCl and the hydride ligands of **3** was detected. These observations rule out the trihydride structure suggested by Mura and co-workers[4] and confirm our assignment of the resonance at δ − 12.2 to the two hydride ligands of **3**. Previously, we have observed the fast transformation of **3** into **5** upon addition of a small amount of KOH to a solution of these complexes.[1] The [**5**]/[**3**] ratio also increases markedly when argon is bubbled through the solution for a long period.

At 190(± 5) K, the IrH_2 resonances of **3** and **5** show T_1 minima of 38 and 108 ms, respectively, and these values do not depend on the [**3**]/[**5**] ratio. However, the relaxation times begin to average on heating and equilibration of **3** and **5** is detected by spin saturation transfer. At 240 K, irradiating the IrH_2 resonance of **5** saturates the IrH_2 resonance of **3** (and *vice versa*) and at this temperature the two T_1s are completely averaged.

Between 230 and 270 K, the hydride resonances of **3** and **5** are in slow exchange on the NMR time scale and appear as separate broadened signals (Fig. 1). Surprisingly, however, in the temperature range between 290 and 370 K the averaged hydride resonance is not observed.

Fig. 2 displays the variable-temperature ^{2}H and ^{31}P NMR spectra of $IrD_2Cl(HCl)(PPr^i_3)_2$ ([$^2H_2$] **3**) and $IrD_2Cl(PPr^i_3)_2$ ([$^2H_2$] **5**) (1:2) in toluene (these complexes were prepared by bubbling D_2 gas through a toluene solution of **3** and **5**). At temperatures above 290 K, no D-ligand resonances are observed in the ^{2}H NMR spectra, but an averaged phosphine ligand signal of [$^2H_2$] **3** and [$^2H_2$] **5** is clearly detected by ^{31}P NMR. On heating the sample up to 370 K, this broad signal undergoes a strong lowfield shift and a new sharp peak appears at δ 32. This peak is assigned to $IrHCl_2(PPr^i_3)_2$ (the broad-band decoupled ^{31}P{^{1}H} spectrum of $IrHCl_2(PPr^i_3)_2$ shows a singlet at δ 31.66)[7] and such an interpretation is confirmed by the appearance of a resonance due to the hydride of **1** in the ^{1}H NMR spectrum of **3** and **5** in [$^2H_8$]toluene at 350 K. These observations can be explained as a manifestation of equilibrium (3), which moves in favour of the monohydride **1** at high temperatures. However, this equilibrium should be rather slow on the NMR time scale, because the ^{31}P resonances are well separated and the signal of **1** is not broad.

$$\underset{\mathbf{3}}{IrH_2Cl(HCl)(PPr^i_3)_2} \rightleftharpoons \underset{\mathbf{1}}{IrHCl_2(PPr^i_3)_2} + H_2 \qquad (3)$$

In the spectrum which was recorded after fast cooling of the sample [Fig. 2(*g*)], the ^{31}P resonance of **1** is strongly broadened and shifted upfield in agreement with the existence of a fast equilibrium (1). It should be noted that the ratios [**5**]/[**3**] and [**5**]/[**3** + **1**] at the beginning and at the end of the ^{31}P NMR experiment are the same. A similar experiment was carried out with a solution of complexes **3**, **4** and **5** and we observed that the ratio [**3** + **1**]/[**4**]/[**5**] at the end of the experiment (200 K) was equivalent to the initial ratio [**3**]/[**4**]/[**5**] (7:1:2).

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The disappearance of the Ir—H(D) signals and the marked broadening of the ^{31}P averaged signal in the NMR spectra of a heated solution of **3** and **5** can be explained by the presence of an unknown paramagnetic compound. This explanation is supported by the detection of a very weak ESR signal for the above solution.

The ^{1}H NMR spectra of **1** and **5** are known to be well resolved at 290 K.[1,7] Consequently, one can propose that some reversible transformation of **3** leads to the paramagnetic compound. On the other hand, the anion $[IrH_2Cl_2(PPr^i_3)_2]^-$, which **3** can form as an acid, and the paramagnetic dihydride $IrH_2Cl_2(PPr^i_3)_2$ are isostructural (the formation of the dihydride in a solution of **1** has been suggested by Mura and co-workers[2,3]). In this case, the above mentioned broadening and disappearance of the NMR signals at high temperatures may result from fast electron transfer between $IrH_2Cl_2(PPr^i_3)_2$ and $[IrH_2Cl_2(PPr^i_3)_2]^-$ in the solvent cell.

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