Kinetics of H_2 Dissociation from Some Iridium−Dihydrogen Complexes with Structurally Different (H_2) Ligands

Vladimir I. Bakhmutov,* Evgenii V. Vorontsov, and Alexey B. Vymenits

Institute of Organo-Element Compounds, Russian Academy of Sciences, 117813 GSP-1,
28 Vavilova, Moscow, Russia.

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The variable-temperature ^1H NMR spectra permit the determination of $\Delta H°$ (−7.1 kcal/mol) and $\Delta S°$ (−16.0 eu) for formation of *trans*-$IrH(H_2)Cl_2(PPr^i_3)_2$ from $IrHCl_2(PPr^i_3)_2$ and H_2 in toluene-d_8. The (H_2) ligand of the related complex *trans*-$IrH(H_2)Cl_2(PCy_3)_2$ was characterized by a T_{1min} value of 3.4 ms at 200 MHz using T_1 measurements for dissolved H_2 in the presence of $IrHCl_2(PCy_3)_2$. Analysis of the variable-temperature ^1H NMR spectra and T_1 measurements resulted in estimation of the rate, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for H_2 dissociation from both *trans*- and *cis*-$IrH(H_2)Cl_2(PPr^i_3)_2$ and $IrH_2(H_2)X(PPr^i_3)_2$ (X = Cl, Br) in toluene-d_8. The rate of H_2 loss decreases dramatically from 10^5 to $<7\ s^{-1}$ (234 K), with elongation of the H−H bond in the (H_2) ligand from 0.74 to 1.1 Å. The height of the $\Delta H^{\ddagger}$ barrier is a direct consequence of the Ir−H_2 bond strength.

Introduction

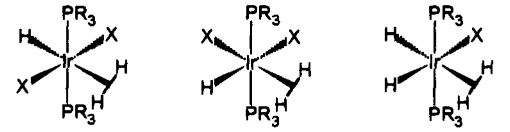
Stereoelectronic control of the stability of transition metal dihydrogen complexes[1a] has been recently reported for the solution interaction between H_2 and monohydrides, $IrHX_2(PR_3)_2$ where X = Cl, R = Pr^i (**1a**),[1a,b] X = Br, R = Pr^i (**1b**),[1c] and X = Cl, R = Cy (**1c**).[1b]

The H_2 binding leads to a pair of the isomeric dihydrogen complexes with *trans* and *cis* arrangement of the H and (H_2) ligands.[1] The stability of these compounds is strongly different in solution: the *trans*-$IrH(H_2)X_2(PR_3)_2$ (**2**) (see Chart 1) lose H_2 on the NMR time scale even at low temperatures. The *cis*-$IrH(H_2)X_2(PR_3)_2$ (**3**) complexes are quite stable at 80 °C and lose H_2 very slowly. Instead, they are prone to elimination of HX to yield the classical dihydrides $IrH_2X(PR_3)_2$ (**4**).[1] H_2 Binding of **4** occurs again rapidly, resulting in the dihydrogen complexes $IrH_2(H_2)X(PR_3)_2$ (**5**).[1,2]

Thus, the reaction between H_2 and **1** in solution is a sequence of complex transformations which lead to related dihydrogen compounds with structurally different (H_2) ligands. Therefore it is clear that such Ir complexes could provide a unique opportunity for a correct comparison between kinetic parameters of H_2 loss and structural characteristics of the (H_2) ligands. In fact, the H−H distance in the stable complex **3a** is elongated up to 1.11 Å[1a] versus 0.84 Å reported for the (H_2) ligands of the less stable complexes **5b,c**.[1b,c]

H_2 Dissociation is known to be the initial step in some hydrogenation reactions catalyzed by transition metal dihydrogen complexes.[3] For this reason a detailed study of the H_2 loss would also be interesting for catalysis.

Chart 1



X=Cl, R=Pr^i (**2a**)
X=Br, R=Pr^i (**2b**)
X=Cl, R=Cy (**2c**)
A

X=Cl, R=Pr^i (**3a**)
X=Br, R=Pr^i (**3b**)
X=Cl, R=Cy (**3c**)
B

X=Cl, R=Pr^i (**5a**)
X=Br, R=Pr^i (**5b**)
X=Cl, R=Cy (**5c**)
C

Results

It has been previously reported that equilibrium 1 is rapidly established in solution on the ^1H NMR time scale, and can be shifted completely to the right site only at low temperatures[1]

$$\underset{\mathbf{1}}{IrHX_2(PR_3)_2} + H_2 \rightleftharpoons \underset{\mathbf{2}}{trans\text{-}IrH(H_2)X_2(PR_3)_2} \qquad (1)$$

reflecting the low stability of the *trans* dihydrogen complexes. In the present work the variable-temperature ^1H NMR spectra have been collected for toluene-d_8 solution of **1a** under H_2 between 170 and 290 K, and $\Delta H°$ and $\Delta S°$ values of −7.1 ± 0.2 kcal/mol and −16.0 ± 1.0 eu were calculated for formation of **2a**. It should be noted that similar negative $\Delta H°$ and $\Delta S°$ values have been recently reported for H_2 binding to the formally unsaturated $RuHCl(CO)(PPr^i_3)_2$.[4a] Enthalpies of −10.0, −6.5, and −7.0 kcal/mol characterize H_2 binding to the metal centers of $M(CO)_3(PCy_3)_2$ where M = W, Mo, and Cr, respectively.[4b]

In spite of the above low-temperature shift of equilibrium (1) the Ir(H_2) signals of complexes **2** have never been observed in the 170 K ^1H NMR spectra[1] due to very strong broadening effects of the relaxation nature. For this reason the dihydrogen complexes **2a** and **2b** were characterized only by the *J*(H−D) constants of 34[1a] and 32[1c] Hz, respectively. It seems reasonable that these large magnitudes correspond to very short H−H bonds. Nevertheless, it was very interesting to estimate the H−H distance in such ligands.

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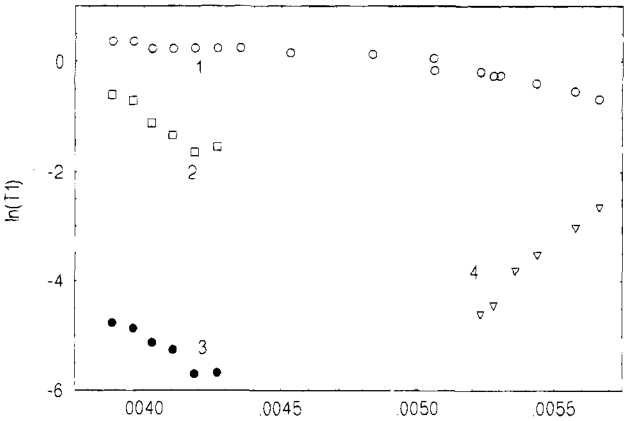

Figure 1. Variable-temperature T_1 data for the signal of H_2 in toluene-d_8 solution in the absence (1) and in the presence of **1c** (2), for the signal of hydrogen in the toluene-d_8 solution of **1a** and **2a** (4) and for the "unobserved" (H_2) ligand of **2c** in toluene-d_8 (3).

To determine the $T_{1\min}$ parameter for the "unobserved" (H_2) ligand we have measured T_1 times for hydrogen in toluene-d_8 in the absence (Figure 1, curve 1) and in the presence (Figure 1, curve 2) of monohydride **1c**.[5a] Between 234 and 257 K in the presence of **1c**, when the H_2 resonance was averaged between the two positions of free H_2 (4.55 ppm) and the η^2-(H_2) ligand (−0.3 ppm[1]), the averaging and shortening of the $T_1(H_2)$ time were observed.

The data collected in Figure 1 permit the calculation of the $T_1(\eta^2(H_2))$ time in eq 2[6] where T_1(obs) is the relaxation time of

$$1/T_1(\text{obs}) = P(H_2)/T_1(H_2) + P(\eta^2(H_2))/T_1(\eta^2(H_2)) \quad (2)$$

H_2 in the presence of **1c**, $T_1(H_2)$ and $T_1(\eta^2(H_2))$ are relaxation times of free H_2 and the (H_2) ligand, and P are corresponding mole fractions determined from positions of the averaged H_2 signal and the signals of free and coordinated H_2. It is important that eq 2 can be used when the life time of the (H_2) ligand $\tau(\eta^2(H_2)) \ll T_1(\eta^2(H_2))$.[6] This should be valid above 230 K because, for example, the $\tau(\eta^2(H_2))$ value calculated for **2a** from the line shapes of the IrH signals (see below) is equal to 0.000 048 s at 234 K.

Plot 3 in Figure 1 displays the fact that for the *trans* complex **2c** the $T_1(\eta^2(H_2))$ time reaches a minimum of about 3.4 ms in the region of 235 K at 200 MHz. The same temperature region was earlier reported for the isomeric complex **3c**,[1b] supporting well the validity of our approach. According to the common $T_{1\min}$ method,[7a] the value of 3.4 ms corresponds to the H−H distance of 0.74[5b] and 0.93 Å in the lower and upper limit of (H_2) rotation, respectively. It is noteworthy that the reported relaxation time has one of the smallest values known for dihydrogen complexes with short H−H distances.[7b]

Equilibrium 1 has been shown to operate on the NMR time scale for all *trans*-dihydrogen complexes **2**, demonstrating their similar stability in solution.[1] It is important that the IrH resonances of **1** and **2** have been found to reflect a full temperature evolution from the separated lines at low temperatures (slow positional exchange) to the averaged lines at high temperatures (fast positional exchange).[1a,b] Using the standard lineshapes analysis[8] of the IrH signals, we have determined the rates of H_2 dissociation from **2a** in toluene-d_8 between 289 and 198 K. In order to expand the temperature region of the kinetic study the relaxation approach[6] was used and the times T_1(obs) (eq 3) were measured for the H_2 signal from 186 to 176 K when the exchange (eq 1) was slow on the NMR time scale. Curve 4 in Figure 1 demonstrates a significant elongation of the relaxation time while decreasing the temperature. The corresponding life times τ ($\eta^2(H_2)$ of the (H_2)) ligand of **2a** were

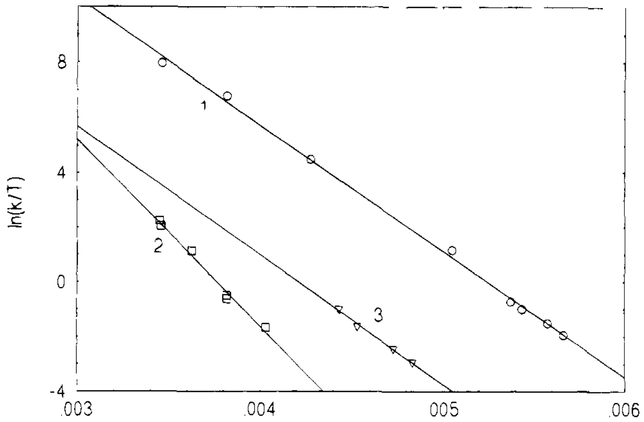

Figure 2. Eyring plots of rate data for H_2 loss from *trans*-$IrH(H_2)Cl_2(PPr^i_3)_2$ (**1**) and $IrH_2(H_2)Br(PPr^i_3)_2$ (**3**) and for HCl loss from *cis*-$IrH(H_2)Cl_2(PPr^i_3)_2$ (**2**).

$$1/T_1(\text{obs}) = 1/T_1(H_2) + P/\{T_1(\eta^2(H_2)) + \tau(\eta^2(H_2))\} \quad (3)$$

calculated in accordance with eq 3 using the relaxation times of free H_2 in Figure 1 (curve 1). From the above described line shapes analysis data, the $\tau(\eta^2(H_2)$ value of 0.012 s can be calculated for 186 K. Thus, one might anticipate the ratio $\tau(\eta^2(H_2) > T_1(\eta^2(H_2))$ to be valid below 186 K, and therefore the rates of H_2 loss ($1/\tau(\eta^2(H_2))$) were obtained on this approximation.

Figure 2 displays an Eyring plot for the rates of H_2 loss determined for **2a** by two independent methods (plot 1) which corresponds to the activation parameters $\Delta H^\ddagger$ of 9.1 ± 0.1 kcal/mol and $\Delta S^\ddagger$ of 0.7 ± 1.0 eu. Comparable values were recently reported for related Ir complexes $Ir(H_2)H_2X(PBu_2Me)_2$ with X = Cl, Br, and I.[9]

The experimental data[1] and *ab initio* calculations[1a] have clearly revealed that the *cis* dihydrogen complexes **3** with elongated H−H bonds are stable thermodynamic products of the reactions between H_2 and **1**. It was clearly established that **1a** and **3a** coexist in equilibrium (eq 4) in toluene-d_8 under H_2

$$\underset{\mathbf{3}}{cis\text{-}IrH(H_2)X_2(PR_3)_2} \rightleftharpoons \underset{\mathbf{1}}{IrHX_2(PR_3)_2} + H_2 \quad (4)$$

with very slow rates of H_2 binding and elimination even at 80 °C. At the same time, complexes **3** can eliminate HX molecules more rapidly[1,10] to give dihydrides **4** (eq 5). For example a brief

$$\underset{\mathbf{3}}{cis\text{-}IrH(H_2)X_2(PR_3)_2} \xrightarrow{\text{KOH or } H_2O} \underset{\mathbf{4}}{IrH_2X(PR_3)_2} + HX \quad (5)$$

contact of **3a,c** with solid KOH in toluene leads immediately to a mixture of **3a,c** and **4a,c**.[1a,b] The conversion of **3** to **4** was

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(5) (a) The complex $IrHCl_2(PCy_3)_2$ was taken for the T_1 study because the PCy_3 ligands provide the observation of the $T_{1\min}$ at moderate temperature at 200 MHz. (b) It is obvious that the problem of calculations of H−H distances in (H_∞) ligands from $T_{1\min}$ data still takes place. In fact, the value of 0.74 Å corresponds to the H−H distance of free H_2.

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Table 1. Comparison of Some "Structural" Parameters of the (H_2) Ligands with Kinetic Parameters for the H_2 Dissociation for Iridium Dihydrogen Complexes **2a**, **3a**, and **5a** in Toluene-d_8

parameter	*trans*-$IrH(H_2)Cl_2(PPr^i_3)_2$	$IrH_2(H_2)Cl(PPr^i_3)_2$	*cis*-$IrH(H_2)Cl_2(PPr^i_3)_2$
k^{234K} (s^{-1})	2.1×10^5	6.8×10^2, 0.85×10^2 [a]	<7.3[e]
$\Delta H^{\ddagger}$ (kcal/mol)	9.1	10.1[a]	>13.7
T_{1min} (ms, 200 MHz)	3.4	7.1[b]	25.2[b]
J(H−D) (Hz)[c]	34		≤12
r(H−H) (Å)[d]	0.74	0.84	1.07, 1.11[f]

[a] The value was found for complex **5b**. [b] The values were taken from ref 1a,b. [c] The J(H−D) constants were found for the (HD) ligand in ref. 1a. [d] The r(H−H) values were calculated by assuming very fast (H_2)-spinning. [e] The value of 7.3 s^{-1} was found as the effective rate of HCl elimination from **3a** (eq 5) and was used as an upper limit for the rate of H_2 dissociation from this molecule. [f] From ND data.[1a]

also detected by NMR after addition of **3** to water−toluene.[1a] Placing a mixture of the *cis*-dihydrogen complex **3b** and complex **5b** under vacuum gave dihydride **4b**[1c] as a result of HBr and H_2 elimination.[1c]

In this connection, it is obvious that for **3**, some limits of the rates and the $\Delta H^{\ddagger}$ values for H_2 loss could be determined by studying kinetics of reaction 5. In the present work, variable-temperature ^{1}H NMR spectra were collected for a mixture of **3a** and **4a** in toluene-d_8 under Ar, in the temperature region 248−290 K. The reaction mixture was prepared in the NMR tube as result of contact **3a** with solid KOH.[1a] Therefore, the ^{1}H NMR study was made in the presence of the solid base. Within the temperature region 248−290 K, we observed a typical pattern of NMR exchange for the IrH signals of **3a** and **4a**, due to reaction 5 as was reported earlier.[1a]

The effective rates of HCl elimination ($1/\tau$ in eq 6) were calculated using the known approximation of slow exchange[8] on the NMR time scale in eq 6 where $\Delta\nu_{obs}$ is the linewidth of

$$\Delta\nu_{obs} = \Delta\nu_0 = 1/\pi\tau \qquad (6)$$

the IrH signal of **3a**, $\Delta\nu_0$ is the line width observed for the IrH signal of **3a** in the absence of NMR exchange and, τ is the life time of **3a** in reaction 5. The Eyring plot in Figure 2 (plot 2) reflects $\Delta H^{\ddagger}$ of 13.7 ± 0.3 kcal/mol and $\Delta S^{\ddagger}$ of +4.2 ± 1.5 eu. The HX elimination seems to be a bimolecular process which can be affected by the presence of H_2O in the reaction mixture.[1a] Since the concentration of water remains unknown, the $\Delta S^{\ddagger}$ value cannot be seriously discussed. Nevertheless, it is obvious now that for the H_2 dissociation from **3a**, $\Delta H^{\ddagger} > 13.7$ kcal/mol and the energy difference $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}$ (**3a**) $- \Delta H^{\ddagger}$ (**1a**) > 5 kcal/mol. It is noteworthy that the calculated H_2 bond dissociation energy was 13.4 kcal/mol for *trans*-$IrH(H_2)(Cl)_2(PH_3)_2$ and 23.7 kcal/mol for *cis*-$IrH(H_2)(Cl)_2(PH_3)_2$.[1a]

Nonclassical complexes **5** of the formula $IrH_2(H_2)(PR_3)_2X$ have been well characterized by IR, NMR[1b,c,2] and X-ray data.[2a] Their (H_2) ligands have been found to be quite labile in toluene solutions and equilibrium (7) has been shown to operate on the NMR time scale at room temperature and below.[1,2] It should

$$\underset{\textbf{5}}{IrH_2(H_2)X(PR_3)_2} \rightleftharpoons \underset{\textbf{4}}{IrH_2X(PR_3)_2} + H_2 \qquad (7)$$

be emphasized that among complexes **5** with various R and X, the $T_{1min}(IrH_2(H_2))$ value changes weakly from 14.7 to 21.6 ms[1,2] at 200 MHz. Hence, insignificant deviations in the H−H distances and similar H−H bonding in the (H_2) ligands can be expected for these compounds.

In order to determine the rates of H_2 loss in eq 7, the variable-temperature ^{1}H NMR spectra were collected for mixtures of **5a** and **4a** or **5b** and **4b** in toluene-d_8. These solutions were prepared by interaction between H_2 and the corresponding complex **1**.[1] For **5b**, it was possible to obtain the activation parameters using the above mentioned relaxation approach between 206 and 225 K, i.e. when the exchange (eq 7) was slow on the NMR time scale. The following values were obtained: $\Delta H^{\ddagger} = 10.1 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -4.7 \pm 1.5$ e.u. (see plot 3 in Figure 2). It should be noted that $\Delta H^{\ddagger}$ of 10.2 kcal/mol and $\Delta S^{\ddagger}$ of 2.4 eu. were recently reported for the related complex, $Ir(H_2)H_2Br(PBu^t_2Me)_2$, in toluene.[9] It is important that in both cases the $\Delta S^{\ddagger}$ function is very close to zero, which is in full accord with the monomolecular character of H_2 loss.

Discussion

According to the literature data,[7] the rate of H_2 dissociation covers the very large region from 10^3 to 10^{-7} s^{-1} (298 K) for dihydrogen and hydrido transition metal complexes with various metal centers and ligands. Nevertheless, the data available in the literature is insufficient for correct comparison of kinetic parameters for H_2 dissociation from dihydrogen complexes versus structural characteristics of the H_2 ligands. The present work provides a such possibility within the series of related Ir complexes. These data are summarized in Table 1.

It is well known that the M−H_2 bond strength depends on two bonding interactions, namely $H_2(\sigma) \rightarrow M(\sigma)$ donation and $M(\pi) \rightarrow H_2(\sigma^*)$ back-donation.[7] The latter is very sensitive to electron density on the metal center. Thus, the stability and behavior of dihydrogen complexes strongly depend on the nature of the metal atom and on the ligand environment. The compounds discussed in the present work (Chart 1) are all complexes of the same metal with very similar ligand environment and structure. The structure of **B** was established by X-ray and ND methods.[1a,b] The structure of **A** corresponds well to the NMR behavior of **2** in solution including the fact that the deuterated species $IrH(D_2)Cl_2(PR_3)_2$ does not exhibit any (D_2)/IrH exchange during 5 h.[1a,b] Finally, the structure of **C** was assigned on the basis of X-ray[2a] and NMR data,[1,2] and *ab initio* calculations.[1a]

Chart 1 shows the main feature of **A** connected with the *trans* location of the dihydrogen and hydride ligands. The strong *trans* effect of the H ligand diminishes the strength of the Ir−H_2 bond,[1a] and therefore monohydrides **1** bind H_2 quite weakly ($\Delta H^{\circ} = -7.1$ kcal/mol). Besides the presence of the same trans (H_2)IrH fragment, there is also a *cis* contact between the (H_2) and (H) ligands in **C**. This location leads to a very fast (H_2)/H exchange in solution,[1,2] probably due to the *cis* (H_2)••(H) interactions suggested in refs.[1a,11] Similar *cis* interactions and a weaker trans effect of Cl[1a] characterize the structure of **B**-type. We believe that at least among iridium dihydrogen compounds

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2, **3**, and **5**, the combination of the above listed factors determines the behavior of the ($\eta^2(H_2)$) ligands.

The data in Table 1 clearly show that the rate of H_2 loss decreases dramatically with the elongation of the H–H bond in the (H_2) ligand. Thus, the height of the $\Delta H^{\ddagger}$ barrier strongly correlates with the Ir–H_2 bond strength. Such a situation might take place if the Ir–H bond is cleaved only partially in the transition state of the dissociation process. This idea is well supported by nearly zero $\Delta S^{\ddagger}$ values for H_2 loss from different iridium dihydrogen complexes obtained earlier[9] and in this work.

Experimental Section

All manipulations were performed under H_2 or Ar atmosphere by standard techniques. Toluene-d_8 was dried and freshly distilled before use.

^{1}H NMR data were obtained on a Bruker WP-200 SY spectrometer at 200 MHz. The ΔH° and ΔS° values of eq 1 were found for complex **1a** from the corresponding equilibrium constants determined with the help of the averaged chemical shifts of the Ir–H lines.

The inversion-recovery method (180–τ–90) was used to determine T_1 relaxation times. The calculations of the relaxation times were performed using the nonlinear three-parameter fitting routine of the spectrometer. The durations of the pulses were controlled at every standard temperature. The temperature was calibrated by ^{1}H NMR with a standard methanol sample.

The following compounds were prepared as described in the literature: $IrHCl_2(PPr^i_3)_2$,[12] $IrHCl_2(PCy_3)_2$,[1b] and $IrHBr_2(PPr^i_3)_2$.[1c] The interactions between H_2 and $IrHX_2(PR_3)_2$ **1** resulting in corresponding dihydrogen complexes **2**, **3**, and **5** were carried out and investigated in the sealed NMR tubes as described elsewhere.[1] All NMR parameters of the Ir complexes were consistent with those reported earlier.[1,2]

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