Inorg. Chem. **1994,** *33,* 4413–4414

H_2 Binding to [(*i*-$Pr_3P)_2Ir(H)Br_2$] in Solution. Evidence for the Formation of *cis*- and *trans*-[(*i*-$Pr_3P)_2Ir(H)(H_2)Br_2$]

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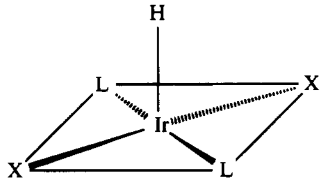
Received March 23, 1994

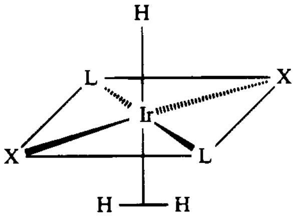
Stereoelectronic control of the stability of transition metal dihydrogen complexes[1] was recently reported[2] for the interaction between H_2 and [(*i*-$Pr_3P)_2Ir(H)Cl_2$] (**1**) in solution. This reaction leads to a pair of the isomeric dihydrogen complexes, [(*i*-$Pr_3P)_2$-$Ir(H)(H_2)Cl_2$], with *trans* and *cis* arrangements of the H and H_2 ligands,[2,3] respectively.



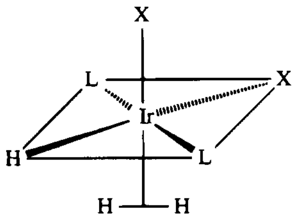
1, L = *i*-Pr_3P; X = Cl

2, L = *i*-Pr_3P; X = Br

Complex **1** reacts rapidly with H_2 at 25 °C to give the relatively labile *trans* adduct **A** with a short H—H distance, whereas another, slower reaction in the same system results in the quite stable *cis* complex **B** with a remarkably elongated H—H bond (1.11 Å). Although the *trans* complex **A** (X = Cl) is too labile for isolation, it was reliably characterized in solution. Being much more stable, the *cis* isomer **B** (X = Cl) was successfully isolated in excellent yield and characterized in solution and in the solid state by a single-crystal neutron diffraction study.[2,3] The influence of the *cis* interaction between H and H_2 ligands on the stability and structure of nonclassical polyhydrides of iron was recently studied by *ab initio* methods.[4]



A



B

L = *i*-Pr_3P; X = Cl, Br

It seemed conceivable that the rare phenomenon of coexistence of a pair of η^2-H_2 complexes isomeric by virtue of stereochemistry at the metal center could be observed in the reaction of the isostructural monohydride [(*i*-$Pr_3P)_2Ir(H)Br_2$] (**2**) with hydrogen. In the present note, we report that the interaction between **2** and H_2 in solution indeed leads to the two isomeric bromo hydrido complexes of **A**- and **B**-type structures.

Complex **2** was prepared by treatment of its chloro analog **1** with anhydrous $AlBr_3$ in dibromomethane and characterized by elemental analysis and IR and NMR spectroscopy. The 300 K ^1H NMR spectrum of **2** in toluene-d_8 exhibits a well-resolved triplet at −48.5 ppm with ^2J(P—H) = 12.2 Hz (IrH) and two multiplets at 3.4 ppm (CH) and 1.4 ppm (dd, CH_3, ^3J(P—H) = J(H—H) = 7 Hz), due to the phosphine ligands. A singlet at 26.1 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum of **1**. The collected data are consistent with the square pyramidal geometry of **2**, similar to that found earlier[5–7] for the dichloro monohydrido complex **1**.

For the NMR studies of the reaction between **2** and H_2, 3 mg of **2** and 0.5 mL of degassed toluene-d_8 were placed in a standard 5-mm NMR tube which was subsequently sealed under hydrogen, in order to provide an excess of H_2 for the reaction system. The 188 K ^1H NMR spectrum of the thus prepared sample showed a singlet for free H_2 at 4.6 ppm, broadened resonances at 2.7 and 1.2 ppm for the *i*-Pr_3P ligand, and two new signals at −11.8 and −10.6 ppm (3.7:1 integral intensity) due to hydrido species **3** and **4**, respectively. These broadened hydrido resonances corresponded to the signals at 17.4 and 34.0 ppm (4.9:1) found in the $^{31}P\{^1H\}$ NMR spectrum of the sample.

Heating the solution up to 240 K resulted in a reversible (on the NMR time scale) exchange between the resonances at 4.6 and −10.6 ppm. The spin saturation transfers observed for these lines at 210 K provided unambiguous support for the exchange. At 240 K, the IrH signal at −11.8 ppm transformed to a well-resolved triplet with J(H—P) = 7.7 Hz. Unsealing the NMR tube, followed by removal of hydrogen (standard freeze—pump—thaw technique) and purging with argon, led to the disappearance of both **3** and **4** and formation of a new complex, **5**. The spectra of this species contained a triplet resonance at −32.8 ppm (J(H—P) = 12.1 Hz) in the hydride region of the ^1H NMR and a singlet at 54.7 ppm in the ^{31}P NMR. The phosphine ligands gave multiplets at 3.55 and 1.45 ppm for the CH and CH_3 protons, respectively. These NMR parameters, along with the integral intensities of the proton resonances, led to the formulation of compound **5** as [(*i*-$Pr_3P)_2Ir(H)_2Br$].[8] The $T_{1\min}$ value of 82 ms (200 MHz) found for the IrH signal of **5** at 190 K is consistent with this formulation.[9]

Taking into account the spectroscopic behavior of complex **1** in the presence of H_2 under similar conditions,[2,3] we conclude that the reaction between **2** and H_2 at ambient temperature rapidly gives rise to a ca. 5:1 mixture of *cis*-[(*i*-$Pr_3P)_2Ir(H)$-$(H_2)Br_2$] (**3**) and [(*i*-$Pr_3P)_2Ir(H_2)(H)_2Br$] (**4**),[8] according to eqs

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(9) Similar $T_{1\min}$ values were very recently obtained for **5**[8] and a series of highly related complexes [$L_2Ir(H)_2X$] (L = *t*-$Bu_2(Ph)P$, *t*-$Bu_2(Me)P$; X = Cl, Br, I).[10]

(10) (a) Hauger, B. E.; Gusev, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208. (b) Gusev, D. G. Personal communication.

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1–3. Clearly, placing the reaction mixture under vacuum results

$$\underset{\mathbf{2}}{[(i\text{-}Pr_3P)_2Ir(H)Br_2]} + H_2 \xrightarrow[\text{temp}]{\text{room}} \underset{\mathbf{3} = \mathbf{B}\ (X = Br)}{cis\text{-}[(i\text{-}Pr_3P)_2Ir(H)(H_2)Br_2]} \quad (1)$$

$$\underset{\mathbf{3} = \mathbf{B}\ (X = Br)}{cis\text{-}[(i\text{-}Pr_3P)_2Ir(H)(H_2)Br_2]} \rightarrow \underset{\mathbf{5}}{[(i\text{-}Pr_3P)_2Ir(H)_2Br]} + HBr \quad (2)$$

$$\underset{\mathbf{5}}{[(i\text{-}Pr_3P)_2Ir(H)_2Br]} + H_2 \rightarrow \underset{\mathbf{4}}{[(i\text{-}Pr_3P)_2Ir(H)_2(H_2)Br]} \quad (3)$$

in the formation of **5** via dehydrogenation of **4** and dehydrobromination of **3**. That **5** forms upon interaction between **2** and H_2 in solution was confirmed by simultaneously observing of the IrH resonances of **3**–**5** in the 200 K ^1H NMR spectrum of the sample prepared from **2** and a 1:4 (by volume) mixture of H_2 and argon.

The structural formulation of **3** and **4** as nonclassical hydrides is consistent with the relaxation data obtained (200 MHz). The $T_{1\text{min}}$ (206 K) values of 39 and 16 ms found for the hydrido resonances of **3** and **4**, respectively, are in full accord with those previously reported[2,3] for the corresponding chloro hydrides. For **3**, r_{H-H} of 1.08 and 1.36 Å can be calculated for the lower and upper limits of the (H_2) ligand rotation, respectively.[1a,2] As mentioned above, the ^1H NMR spectra revealed a positional exchange for the free H_2 resonance and the signal of the $Ir(H)_2(H_2)$ ligands in **4** between 190 and 240 K. This observation clearly demonstrates that the metal-bound hydrogens of **4** are in rapid exchange with free H_2 in solution, thus providing additional evidence for the nonclassical nature of **4**. Very recently, Le-Husebo and Jensen[8] came to similar conclusions concerning complex **4**.[11]

It was shown earlier[2,3] that complex **1** reacts rapidly with H_2 to yield complex **A** (X = Cl) with *trans* arrangement of the H and H_2 ligands. The more stable *cis* isomer, **B** (X = Cl), was observed as the product of the second, slower reaction. In this connection, we studied the reaction of **2** with H_2 at low temperature. A frozen, degassed solution of **2** in toluene-d_8 was sealed under H_2 in a 5-mm NMR tube, and the sample was immediately thermostated in the NMR probe at 190 K. Melting the solution led to the observation of a broadened resonance at −16.9 ppm which could be assigned to the H ligand of *trans*-$[(i\text{-}Pr_3P)_2Ir(H)(H_2)Br_2]$ (**6** = **A** (X = Br)). As in the case of the chloro hydride **A** (X = Cl), the H_2 ligand of the bromo analog, **6**, or **A** (X = Br), was not detectable in the spectrum. In order to support the assignment of the signal at −16.9 ppm to **6**, the experiment at 190 K was repeated with HD. As anticipated, an additional triplet resonance at −0.9 ppm with $J(H-D)$ = 32 Hz was observed, indicating the presence of the H_2 structural unit in **6**. It was also found that, in the temperature range 176–207 K, the Ir(HD) T_1 value passes through a minimum of 64 ms (200 MHz, 189 K). From the ratio, $T_{1\text{min}}(H\cdots D)/T_{1\text{min}}(H\cdots H)$ = 17[12a] or 16[12b] for dipole–dipole relaxation, the $T_{1\text{min}}$ value for the (H_2) ligand of **6** was estimated to be 4 ms, which corresponds to a very short H··H distance of 0.76 Å for the lower limit and 0.96 Å for the upper limit of the (H_2) ligand rotation.[1a] Heating the sample to 250 K and cooling it back to 190 K led to a mixture of **3**, **4**, and **6** in a 1.5:1:2.3 molar ratio, due to the partial isomerization of **6**. After the sample was warmed to ambient temperature, only the resonances due to **3** and **4** were observed in the ^1H NMR spectrum (190 K), indicating complete conversion of **6**. Interestingly, H_2 binding to bromo complex **2** seems to be more facile than the analogous reactions of chloro complex **1** under the same conditions.[2,3] In addition, the isomerization of **A** to **B** is faster when X = Br than when X = Cl. For instance, **3** is formed within minutes when H_2 is introduced to a solution of **2** at 20 °C, whereas the conversion of **1** to **B** (X = Cl) in the presence of hydrogen requires days at ambient temperature or hours at 50 °C.[2,3] We believe that these effects might be due to the difference in electronegativity between Cl and Br[8] and to the increase of the multiple-bond character between the metal center and the halide ligands ($X \rightarrow Ir$ π-donation) upon going from Br to Cl.[10a,13,14]

In conclusion, this work provides evidence for the coexistence of a pair of isomeric molecular dihydrogen complexes which form when **2** reacts with H_2 in solution. Depending on the conditions, the reaction of **2** can lead to **6** (**A**, X = Br) and/or **3** (**B**, X = Br) as the kinetic and thermodynamic products of H_2 binding, respectively. In addition to the similar transformations of **1**,[2,3] these data provide good support for the suggested[2] concept of stereoelectronic control of the stability of η^2-H_2 transition metal complexes.

Experimental Section

All NMR data were collected with a Bruker WP-200 spectrometer and a standard temperature unit. The temperature was calibrated by ^1H NMR with a standard methanol sample. The inversion–recovery method (180-TAU-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.

Synthesis of 2. $[(i\text{-}Pr_3P)_2Ir(H)Cl_2]$[7] (0.45 g) was added to a solution of anhydrous $AlBr_3$ (1.1 g) in dry dibromomethane (6 mL), and the mixture was stirred for 20 min. The reaction was quenched with water, and the organic layer was separated from the mixture and evaporated. A benzene solution of the residue was filtered through a silica plug, and the filtrate was evaporated to dryness. The dark crystals were washed with EtOH and dried under vacuum. The yield of analytically and spectroscopically pure **2** was 0.20 g. Anal. Calcd for $C_{18}H_{43}Br_2IrP_2$: C, 32.05; H, 6.58; Br, 23.69. Found: C, 32.17; H, 6.67; Br, 23.82. IR, cm^{-1} (Nujol): 2002 (ν_{Ir-H}).

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[11] Le-Husebo and Jensen[8] reported $T_{1\text{min}}$ = 54 ms for **4** at 500 MHz, which would correspond to 22 ms at 200 MHz. This value obtained at 213 K[8] is slightly higher than ours (16 ms; 206 K), probably due to the exchange between **4** and H_2 on the T_1 NMR time scale, established in the present work (see above).

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