Inelastic Neutron Scattering Studies of $IrIH_2(H_2)(PPr^i_3)_2$ and Neutron Diffraction Structure Determination of $IrIH_2(H_2)(PPr^i_3)_2{\cdot}C_{10}H_8$: Implications on the Mechanism of the Interconversion of Dihydrogen and Hydride Ligands

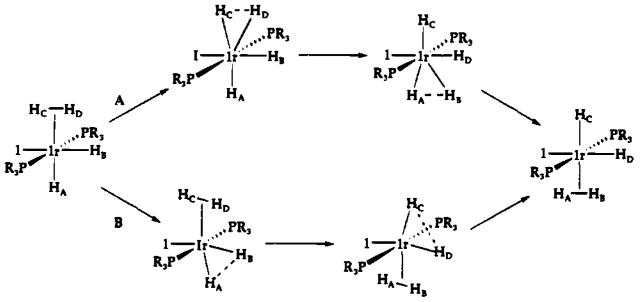
Juergen Eckert,[*,‡] Craig M. Jensen,[*,†] Thomas F. Koetzle,[*,§]
Trang Le Husebo,[†] Jacqueline Nicol,[‖] and Ping Wu[§]

LANCE, MS H805, Los Alamos National Laboratory
Los Alamos, New Mexico 87545
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822
Brookhaven National Laboratory
Upton, Long Island, New York 11973
National Institute of Standards and Technology
Bldg 235, Gaithersburg, Maryland 20899

Received February 27, 1995

There has been considerable speculation about the possible mechanisms of interconversion of dihydrogen and hydride ligands in transition-metal polyhydride complexes.[1,4,5,20] We have found that this process is remarkably facile in the complexes $IrXH_2(H_2)(PPr^i_3)_2$ (X = Cl, Br, I).[2,3] Solution NMR spectroscopy is not an effective probe of this process as the dihydrogen and hydride ligands rapidly interconvert on the NMR time scale to the limit of the freezing temperatures of the solvents.[2,3] A solid state ^1H NMR spectroscopic study of single crystals of $IrClH_2(H_2)(PPr^i_3)_2$ (**1**) has shown that the barrier to the interconversion is "substantially under 3 kcal/mol".[4] It was also determined in this study that the metal-bound hyrogens remain as distinct pairs which do not cross the Cl–Ir–P plane. Thus mechanisms such as direct proton transfer from dihydrogen to hydride can be ruled out. However, this result does not allow differentiation between the two mechanistic possibilities seen Scheme 1. The central feature of pathway A is an initial weakening of the dihydrogen H–H bond while pathway B is initiated by H–H bonding interaction between the hydride ligands. Complex **1** has also been studied through inelastic neutron scattering (INS) techniques.[5] An extremely low, 0.51(2) kcal/mol barrier to rotation of the dihydrogen ligand was determined in these studies. The comparable magnitudes of the barriers of the dihydrogen rotation and dihydrogen/hydride interconversion raise the possibility that the two processes are coupled. We have now determined the molecular structure of $IrIH_2(H_2)(PPr^i_3)_2{\cdot}C_{10}H_8$ ($\mathbf{2}{\cdot}C_{10}H_8$) through a single-crystal neutron diffraction study and carried out INS studies on this complex. We report the result of these studies and their implications on the mechanism of dihydrogen/hydride interchange in the $IrXH_2(H_2)(PPr^i_3)_2$ complexes.

Scheme 1



The INS data for **2** were collected on the TOF spectrometer at the Cold Neutron Research Facility of the National Institute of Standards and Technology at 1.4 K using incident energy 4.51 meV. Approximately 1.5 g of sample were loaded under 1 atm of H_2 into a quartz holder.[6] The spectrum (Figure 1) contains a pair of broad inelastic peaks at ± 5.9(3) cm^{-1} which we attribute to the rotational tunnel splitting of the dihydrogen ligand. The rotational constant, B, of 43.9 cm^{-1} can be derived[7,8] from the 0.86 Å dihydrogen H–H bonding distance that was determined by the single-crystal neutron diffraction study (see below). A 2-fold barrier of 0.98(5) kcal/mol can be calculated[7,8] for the dihydrogen ligand from this value of B and the observed frequency of the inelastic peaks. This is significantly higher than the 0.51(2) kcal/mol barrier previously determined for **1**.[5] However, the magnitude also appears to be within the realm of the barrier to dihydrogen/hydride interconversion.

The dihydrogen complex **2** cocrystallizes with naphthalene[9] in the triclinic space group $P\bar{1}$, $Z = 2$, with $a = 7.999(2)$ Å, $b = 13.981(4)$ Å, $c = 14.461(4)$ Å, $\alpha = 82.49(3)°$, $\beta = 84.39(4)°$, $\gamma = 71.70(2)°$, at $T = 15$ K. A single-crystal X-ray analysis of **2** at 298 K was first carried out to determine the position of the non-hydrogen atoms ($R = 4.03$, $R_w = 5.32$).[10] Neutron diffraction data were subsequently collected at the Brookhaven High Flux Beam reactor on a crystal of dimensions 2.5 × 1.4 × 1.6 mm at 80 K. All the hydrogen atoms were located from successive Fourier difference maps. Refinement was carried out using anisotropic thermal parameters and the full matrix least-squares program UPALS.[11] The metal-bound hydrogens of **2** were located and behaved well during refinement. This result contrasts with the observation of disorder among the metal-bound hydrogens in a single-crystal neutron diffraction study of **1**.[12] Apparently, dynamic disordering of the hydrogens occurs in **1** but not **2** at 15 K. This interpretation is consistent with the higher dihydrogen rotational barrier which was revealed by the INS studies (assuming coupling of the dihydrogen rotation and exchange processes). The refinement converged at a conventional R value of 0.048 for all 3880 measured reflections. A diagram of the molecular structure determined for **2** is seen in Figure 2. Selected bond distances and angles are given in Table 1.

[†] University of Hawaii.

[‡] Los Alamos National Laboratory.

[§] Brookhaven National Laboratory.

[‖] National Institute of Standards and Technology.

(1) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054. (c) Maseras, F.; Duran, M.; Lledos, A.; Bertran, J. *J. Am. Chem. Soc.* **1992**, *114*, 2922. (d) Hall, M. B.; Lin, Z. *J. Am. Chem. Soc.* **1992**, *114*, 2928. (e) Hall, M. B.; Lin, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6102.

(2) (a) Mediati, M.; Tachinaba, G. N.; Jensen, C. M. *Inorg. Chem.* **1990**, *29*, 3. (b) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 1827.

(3) Le-Husebo, T.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 3797.

(4) Wisiniewski, L. L.; Mediati, M.; Jensen, C. M.; Zilm, K. W. *J. Am. Chem. Soc.* **1993**, *115*, 7533.

(5) Eckert, J.; Jensen, C. M.; Jones, G.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 11056.

(6) **2** is stable to loss of H_2 only under an atmosphere of H_2. In order to circumvent the difficulties of sealing the quartz holder under H_2, the holder was connected to a Teflon J. Youngs valve through graded glass seals.

(7) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378.

(8) Eckert, J.; Blank, H.; Bautista, M. T.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 747.

(9) The isopropyl groups of one phosphine ligand were found to be highly disordered in structure obtained from crystals of pure **2**. It was previously found that similar disorder in the structure of the chloro analog, **1**, was absent when the complex was cocrystallized with naphthalene.[2] Cocrystallization of **2** with naphthalene produced crystals from which we were able to obtain a structure without disorder.

(10) The unit cell parameters determined in an X-ray diffraction study at 25 °C are $a = 8.110(5)$ Å, $b = 14.284(6)$ Å, $c = 14.633(7)$ Å, $\alpha = 83.33(4)°$, $\beta = 83.39(4)°$, $\gamma = 73.64(4)°$. The X-ray data was collected on a Nicolet P3 diffractometer with Mo Kα radiation (0.71071 Å) to a 2θ value of 35. The structure was solved by the standard heavy atom method.

(11) Lundgren, J.-O. UPALS: A Full-matrix Least-Squares Refinement Program. Report UUICB 13-4-05; Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982; pp 688–691.

(12) Schultz, A.; Mediati, M.; Jensen, C. M. Unpublished results.

0002-7863/95/1517-7271$09.00/0 © 1995 American Chemical Society

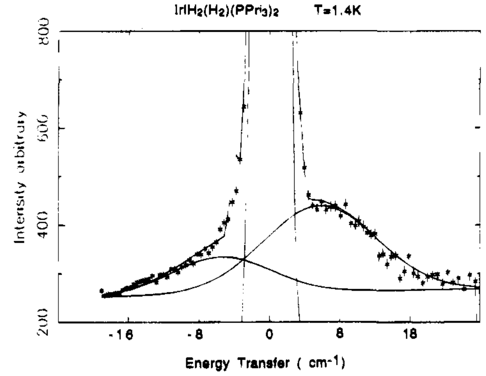


Figure 1. INS spectrum of $IrIH_2(H_2)(PPri_3)_2$ (**2**) collected with incident neutron energy of 4.51 meV. The data were fitted by convolution of a measured resolution function with a δ function for the elastic peak and two Gaussians. Lines shown are for the three components and the convoluted spectrum.

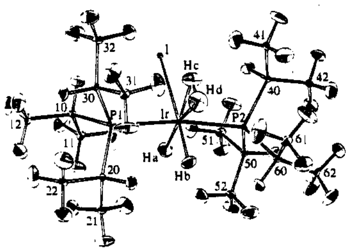


Figure 2. Projection of structure determined for $IrIH_2(H_2)(PPri_3)_2$ (**2**) by neutron diffraction analysis. Labels for hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at 50% probability.

Table 1. Selected Distances and Angles in $IrI(H_2)H_2(PPr^i_3)_2$ (**2**)

	bond distances, Å		
Ir−H(a)	1.579(6)	Ir−P(1)	2.334(4)
Ir−H(b)	1.589(6)	Ir−P(2)	2.338(4)
Ir−H(c)	1.764(7)	Ir−I	2.770(4)
H(c)−H(d)	0.856(9)		
	bond angles, deg		
H(a)−Ir−P(1)	86.3(3)	H(a)−Ir−H(d)	162.8(4)
H(a)−Ir−P(2)	87.8(3)	H(b)−Ir−H(c)	106.9(4)
H(b)−Ir−P(1)	87.3(3)	H(b)−Ir−H(d)	78.7(4)
H(b)−Ir−P(2)	86.5(3)	H(a)−Ir−I	89.6(3)
H(c)−Ir−P(1)	93.6(3)	H(b)−Ir−I	173.7(3)
H(c)−Ir−P(2)	93.3(3)	H(c)−Ir−I	79.4(3)
H(d)−Ir−P(1)	92.7(3)	H(d)−Ir−I	107.6(3)
H(d)−Ir−P(2)	91.3(3)	P(1)−Ir−P(2)	171.8(1)
H(c)−Ir−H(d)	28.2(3)	P(1)−Ir−I	92.5(1)
H(a)−Ir−H(b)	84.1(4)	P(2)−Ir−I	93.1(1)
H(a)−Ir−H(c)	169.0(4)		

INS[5] and variable temperature NMR studies[2,3] have indicated that the dihydrogen ligands of the $IrXH_2(H_2)(PPr^i_3)_2$ complexes are weakly coordinated. Comparison of the Ir−hydride distances of 1.579(6) and 1.589(6) Å to the dihydrogen Ir−H distances of 1.764(7) and 1.748(7) Å verifies the weak Ir−dihydrogen interaction of **2**. The H(c)−H(d) separation of 0.856(9) Å[13] is only slightly expanded from the distance in free dihydrogen, thus confirming that the Ir−dihydrogen bonding in **2** involves only weak π back-bonding from the iridium to the dihydrogen σ^* orbital. Similar bond distances have been determined previously through neutron diffraction studies for the weakly bound dihydrogen ligands of $W(H_2)(CO)_3(PPr^i_3)_2$,[14] $[FeH(H_2)(dppe)_2]BF_4$,[15] *cis,mer*-$FeH_2(H_2)(PEtPh_2)_3$,[16] and $Mo(H_2)(CO)(dppe)_2{\cdot}4.5C_6D_6$.[17] The dihydrogen ligand of **2** provides an interesting structural contrast to *cis*-$IrCl_2H(H_2)(PPr^i_3)_2$, **3**, which has also been characterized through a neutron diffraction study.[18] The latter has a much longer H−H distance of 1.11(3) Å and much shorter Ir−H distances of 1.537(19) and 1.550(17) Å. These differences reflect a significant difference in the degree of back-bonding to the dihydrogen σ^* orbital in the two complexes. The strong back-bonding and "stretching" of the dihydrogen ligand in **3** has been partially attributed to a stabilizing *cis* hydride interaction.[16,18] Although the dihydrogen ligand of **2** is also situated *cis* to a hydride ligand, similar stabilization is not observed. Apparently, the *trans* rather than the *cis* hydride in **2** exerts the more dominant structural influence.

Most notably, the dihydrogen lies essentially in the H(a)−Ir−I−H(b) plane with a dihedral angle between the P−Ir−P and dihydrogen H(c)−Ir−H(d) planes of 88.8(5)°. Thus the dihydrogen is in position to maximize d−σ^* metal−dihydrogen, π back-bonding.[19] Breaking of the dihydrogen H−H bond would require an enhancement of the d−σ^* π bonding interaction. Rotation of the dihydrogen ligand can only result in a weakening of this interaction. Thus pathway A in Scheme 1 is inconsistent with the coupling of dihydrogen rotation and dihydrogen/hydride interconversion.

Our results suggest that the interconversion of dihydrogen and hydride ligands in the $IrXH_2(H_2)(PPr^i_3)_2$ complexes is coupled to rotation of the dihydrogen ligand. Limbach *et al.* have proposed[20] that the mechanism of hydride interchange in transition-metal trihydrides involves the rotation of an intermediate dihydrogen ligand. While it is not clear at this point if dihydrogen/hydride interconversion in the $IrXH_2(H_2)(PPr^i_3)_2$ complexes involves a bis(dihydrogen) intermediate, our results suggest that this process does not involve initial weakening of the dihydrogen H−H bond.

Acknowledgment. We wish to thank Terry Udovic for assistance with the data collection at the CNRF at NIST. The support of this research by the U.S. Department of Energy's Hydrogen Program is gratefully acknowledged. Work at Los Alamos National Laboratory was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supporting Information Available: Tables of crystal data, bond distances and angles, and atom coordinates and anisotropic thermal parameters for $IrIH_2(H_2)(PPr^i_3)_2{\cdot}C_{10}H_8$ ($\mathbf{2}{\cdot}C_{10}H_8$) (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950671A

---

(13) A relationship between ^1H NMR T_1(min) values and the H−H distances of coordinated dihydrogen has been reported (Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173 and references therein). Unfortunately, the determination of T_1(min) for the dihydrogen ligand of **2** is not possible due to the rapid dihydrogen/hydride exchange process. The signal for the exchanging hydrogens of **2** was found[3] to have a T_1(min) of 43 ms (500 MHz) at −60 °C. A T_1(min) of 23 ms (500 MHz) can be estimated (Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813) for the dihydrogen ligand of **2** from this result. However, a H−H distance of 1.10 Å is predicted by Halpern's equation from this value of T_1(min).

(14) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. J.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Vergamini, P. J.; Wasserman, H. J.; Koetzle, T. F.; Kubas, G. J. Unpublished results.

(15) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823.

(16) Van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.

(17) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, R. K.; Jackson, S. S.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569.

(18) Alberto, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pelissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300.

(19) A reviewer suggested that the dihydrogen ligands adopts this position to avoid steric interactions with the phosphine ligands. However, this seems unlikely as the dihydrogen ligand is aligned along the P−W−P axis in the bis(triisopropylphosphine) complex $W(H_2)(CO)_3(PPr^i_3)_2$.[14]

(20) Limbach, H.-H.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1369.