plexes is predicted to be 8.4 × 10^{-3} kJ/mol on the basis of molecular orbital calculations;[23] this is about 3 orders of magnitude smaller than the observed activation energy. Second, a comparison of the experimental values of the activation energies with the predicted values based on the nonbonded atom–atom interaction indicates that the potential energy surface for Cp ring reorientation is dominated by the intermolecular interactions of the types Cp–Cp and Cp–CO.[7a] Moreover, intermolecular forces also seem to play an important role in the activation energy for the Cp ring rotation in ferrocene; the activation energy for Cp ring rotation in ferrocene in 4 kJ/mol in the gas phase as measured from electron diffraction studies[24] whereas, in the solid state, the barrier is 8.3 kJ/mol as measured from proton NMR spin–lattice relaxation times.[7c] Since the activation energy found for $(\mu\text{-CO})_2[\text{FeCp(CO)}]_2$ is 12.5 (3) kJ/mol, it is likely that the rotation barrier originates with the contacts between nonbonding atoms rather than from electronic factors. The fact that both $(\mu\text{-CO})_2[\text{FeCp(CO)}]_2$ and $[\text{Mo(CO)}_3\text{Cp}]_2$ have higher Cp ring rotation barriers than those of $\text{Cp(CO)}_3\text{Mn}$ and $\text{Cp(CO)}_3\text{Re}$ may be due to the effect of intramolecular contacts present in the dimers (i.e., half of the molecule interacting with the other half) but not in the monomers.

Conclusions

We have determined the characteristics of the cyclopentadienyl ring rotation in $(\mu\text{-CO})_2[\text{FeCp(CO)}]_2$ in the solid state by analysis of the anisotropy of the deuterium spin–lattice relaxation times in the temperature range 100–300 K. Our results show that the reorientation of the Cp ligands in the solid state proceeds with nearest-neighbor jump rates in the range 1.20 (24) × 10^7 to 2.4 (5) × 10^{11} s^{-1}. The activation energy for the ring rotation has been estimated to be 12.5 (3) kJ/mol. On the basis of T_2 anisotropy experiments, C_5 rotations rather than C_5^2 rotations are dominant at 100 K, and since the Arrhenius plot is linear in the range 100–300 K, C_5 rotations seem to prevail for all temperatures studied.

One conclusion of this work is that there is a good agreement between our results and the results obtained from Raman spectroscopy, from quasi-elastic neutron scattering, and especially from proton NMR spin–lattice relaxation times for Cp ring rotation in other complexes. This shows that solid-state deuterium NMR spectroscopy is an excellent alternative for the study of solid-state motions in organometallic compounds. More importantly, deuterium NMR methods have the special advantage of selective labeling, thus overcoming the frequent problem of assignment of the spectral lines in the Raman or quasi-elastic neutron scattering experiments. Another advantage of using solid-state deuterium NMR spectroscopy for motional studies is that both the model of motion and the rate of motion can be evaluated simultaneously; in all the other techniques, except for quasi-elastic neutron scattering, the data directly available from the experiment are the kinetic parameters, but little is learned directly about the type of motion associated with those parameters, as assumptions must be made about the mode of motion.

Acknowledgment. The support of the National Science Foundation (Grant CHE8715517), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the LSU Center for Energy Studies is gratefully acknowledged (L.G.B.). The purchase of the solid-state 200-MHz NMR spectrometer (LSU) was made possible by NSF Grant CHE8711788.

---

(23) (a) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–57. (b) Albright, T. A.; Hoffmann, R.; Tse, Y.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812–21.

(24) Haaland, A.; Nilsson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653–70.

(25) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper and Row: New York, 1967.

Contribution from the Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France,
and Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Dynamics of Molecular Hydrogen in the Complex *trans*-$[\text{Fe}(\eta^2\text{-H}_2)(\text{H})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{BF}_4$ in the Solid State As Revealed by Neutron-Scattering Experiments

Juergen Eckert,*[†,‡] Herma Blank,[†] Maria T. Bautista,[§] and Robert H. Morris[§]

Received July 5, 1989

The vibrational spectrum of the $\text{Fe}(\eta^2\text{-H}_2)\text{H}$ fragment in *trans*-$[\text{FeH}(\text{H}_2)(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{BF}_4$ has been obtained by inelastic neutron scattering in the range 200–1000 cm^{-1}. High-resolution neutron spectroscopy was also utilized to observe the rotational tunnel splitting of the librational ground state of the dihydrogen ligand at 2.1 cm^{-1}. This and the torsional transitions assigned at 225 and 255 cm^{-1} are consistent with a modulated double-minimum potential for rotation with one angular degree of freedom. The resulting barrier to rotation of about 2.3 kcal/mol is discussed in terms of its origin in electronic and steric factors and compared with similar results on other molecular hydrogen complexes.

Most of the dynamical information on the $\eta^2\text{-H}_2$ ligand in the recently discovered[1] molecular hydrogen complexes has been obtained from NMR measurements.[2–5] In fact, in a vast majority of these compounds NMR evidence is the primary indicator for the presence of the dihydrogen ligand. These measurements typically show values for δ of −3 to −12 in the ^1H NMR spectrum and in the isotopically substituted complexes show large values of $J(\text{H,D})$ that are well above those for hydride–deuteride coupling but below that for HD in the gas phase. In addition, the minimum value of T_1 can also be taken as a diagnostic for the presence of the $\eta^2\text{-H}_2$ ligand, and such data can in fact be analyzed to yield H–H separations under the assumption that dipolar relaxation dominates T_1.[3,4] NMR measurements have also been successful at monitoring the exchange between dihydrogen and hydride ligands in cases where the latter is present.[6–15] Vibrational data

---

[†] Institute Laue-Langevin.

[‡] Permanent address: LANSCE, Mail Stop H805, Los Alamos National Laboratory, Los Alamos, NM 87545.

[§] University of Toronto.

(1) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(2) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(3) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031.

(4) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(5) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837.

(6) Crabtree, R. H.; Lavin, M.; Bonnevoit, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(7) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056.

(8) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

on the metal–dihdyrogen fragment, on the other hand, appear to be much more difficult to obtain. Only one complete determination of the six normal modes of vibration of a $M(H_2)$ complex has been accomplished, namely that of $W(CO)_3(H_2)(P\text{-}i\text{-}Pr_3)_2$ with the use of Raman, IR and inelastic neutron-scattering measurements.[1] Some IR data, notably the H–H stretch, are also available on many of the complexes that have been prepared in liquid or solid rare-gas solution,[16,17] but for many other systems, particularly those that exist in ionic form, no spectroscopic data at all are available.

One of us has recently demonstrated that inelastic neutron-scattering techniques can be successful in determining the low-lying vibrational excitations of the η^2-H_2 ligand in these complexes and has also been able to observe the rotational tunnel splitting of the librational ground state.[18] The latter, particularly when combined with a determination of the transition(s) to the excited librational state, i.e. the (η^2-H_2) torsion, can be used to derive a value for the height of the barrier hindering the rotation of the dihydrogen ligand. Thus, for example, the barrier to rotation in $W(CO)_3(H_2)(PCy_3)_2$ was determined to be 2.2 kcal mol^{-1} by an analysis of the neutron-scattering data in terms of a simple double-minimum potential with one angular degree of freedom, i.e. $V = (V_2/2)(1 - \cos 2\phi)$, where ϕ is the angle about the H_2–W–C–O axis and V_2 is the barrier height of the 2-fold potential. More recently, an attempt was made to determine the relative contribution to this barrier from the direct electronic interaction that forms the metal–dihydrogen bond on the one hand and from steric effects of the bulky phosphine ligands on the other.[19] It should be noted in this context that the rotational tunnel splitting is extremely sensitive to small variations in the rotational barrier, since it depends (for low to medium barrier heights) approximately exponentially on the barrier height. Thus, for example, replacement of W by Mo in the PCy_3 complex changed the tunnel splitting by a factor of 3.

In view of the success of neutron-scattering techniques in providing much needed information on the rotational and vibrational dynamics of the η-H_2 ligands, we have undertaken such a study on one of the more stable complexes of this type, namely *trans*-$[FeH(H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$, which is also one of the few molecular hydrogen complexes for which a full single-crystal neutron diffraction study (of the corresponding BPh_4^- salt) has been performed.[20] It should therefore be possible to relate information about the rotational barrier to structural details. In this work, Ricci et al. find that the H–H axis of the dihydrogen ligand is essentially aligned parallel to one of the P–Fe–P axes (at an angle of 0.3°). Furthermore, the H_2–Fe–H axis is a 2-fold axis, and the Fe–H distances are 1.62 Å for the dihydrogen and 1.54 Å for the terminal hydride. The H–H bond length was found to be 0.82 (2) Å (vs 0.74 Å for the free H_2 molecule), which is virtually identical with all such determinations by neutron diffraction.[1,21]

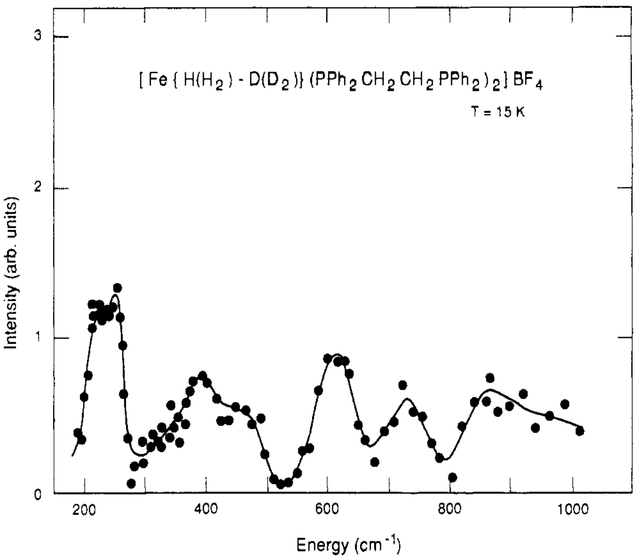

Figure 1. Difference vibrational spectra of the $FeH(\eta^2\text{-}H_2)$ fragment in $[FeH(\eta^2\text{-}H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$ obtained by subtraction of the spectrum partially deuteriated analogue from that of the fully protonated compound (see text). The solid line is intended to guide the eye.

Experimental Section

The complexes *trans*-$[FeH(H_2)(L)_2]BF_4$, L = $PPh_2CH_2CH_2PPh_2$ and $(C_6D_5)_2PCH_2CH_2P(C_6D_5)_2$, were prepared as described elsewhere.[3,10]

The compound *trans*-$[Fe(\eta^2\text{-}D_2)(D)(PPh_2CH_2CH_2PPh_2)_2]BF_4$ was prepared by stirring a solution of 2 g of *trans*-$[Fe(\eta^2\text{-}HD)(D)(PPh_2CH_2CH_2PPh_2)_2]BF_4$[8] in 50 mL of tetrahydrofuran under 1-atm D_2 for 1 h, then removing the D_2/H_2 under vacuum, and then reexposing the sample to 1-atm D_2 for a further 1 h. The sample was then recovered by evaporating the THF under vacuum to 2 mL and then filtering off the resulting precipitate. A ^1H NMR sample spectrum of the sample in acetone-d_6 verified the absence of hydride and dihydrogen resonances. A broad singlet at 92.5 ppm (versus 85% H_3PO_4) in the $^{31}P\{^1H\}$ NMR spectrum was the only resonance present as expected.

The neutron-scattering vibrational spectra were taken on the filter difference spectrometer at the Los Alamos Neutron Scattering Center by using two samples that both had fully protonated diphos ligands, except that in one case the dihydrogen and hydride ligands were deuteriated. The inelastic neutron-scattering spectrum of the latter was then subtracted from the former, a procedure that leaves essentially those vibrational modes involving the dihydrogen and hydride ligands,[22] since the scattering cross section for D is more than 1 order of magnitude less than that of H. Vibrational modes involving only D therefore cannot be "seen" in the presence of many more modes that include H motions, i.e. those of the diphos ligands.

The low-frequency rotational tunneling spectra were obtained on the cold-neutron time-of-flight spectrometer IN5 at the Institut Laue-Langevin (Grenoble, France) with an incident neutron wavelength of 5 Å. The sample (about 1.5 g) used in this experiment had fully deuteriated phenyl rings in the phosphine ligands in order to reduce the incoherent background from the strongly scattering H atoms. It was not necessary in this case to take data on a "blank" sample with η-D_2 and terminal D ligands, since neither the deuteriated phenyl rings nor the bridging $-CH_2$ groups would be expected to have observable excitations in the frequency range of interest (≤ 5 cm^{-1}) of this measurement.

Results and Discussion

The difference vibrational spectrum for the $FeH(H_2)$ fragment is shown in Figure 1. If we can assume that any mixing of dihydrogen or hydride modes with those of the other ligands is small on the scale of the instrumental resolution (about 20–50-cm^{-1} fwhm depending on frequency, in this range), the subtraction would leave only vibrations of the former ligands. Apart from a likely observation of ν(Fe–H) for the hydride at 1919 cm^{-1},[10] no other vibrational data are available on this compound. We

---

(9) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124.

(10) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

(11) Hampton, C.; Cullen, W. R.; James, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 6918.

(12) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *353*, C19.

(13) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072.

(14) Chaudret, B.; Commenges, G.; Jalon, F.; Otero, A. *J. Chem. Soc., Chem. Commun.* **1989**, 210.

(15) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 757.

(16) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645.

(17) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

(18) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466.

(19) Kubas, G. J.; Eckert, J.; Van Der Sluys, L. S.; Vergamini, P. J.; Ryan, R. R.; Khalsa, G. R. K. Presented at the Third Chemical Congress of North America, Toronto, Canada, 1988; paper INORG 290. Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.*, in press.

(20) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.*, in press.

(21) 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.*, in press.

(22) Howard, J.; Waddington, T. C. *Advances in Infrared and Raman Spectroscopy*; Vol. 7; Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1980; Vol. 7, Chapter 3.

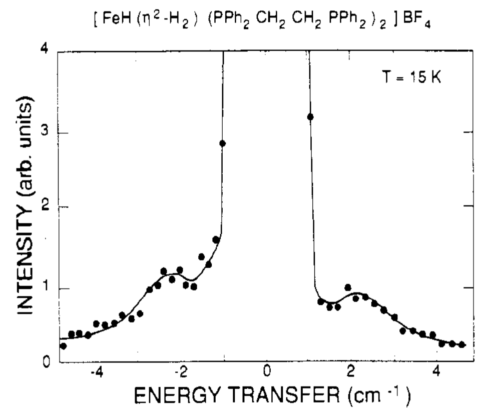

Figure 2. Rotational tunneling spectrum of the dihydrogen ligand in $[FeH(\eta^2\text{-}H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$. The solid line is intended to guide the eye.

can therefore only propose plausible assignments based on INS intensity consideration[22] and comparison with similar data obtained for $W(CO)_3(H_2)(PCy_3)_2$. The most intense feature, a doublet at 225 and 255 cm^{-1}, should thus be associated with the η^2-H_2 torsion. The other two deformation modes δ(Fe–H_2) would also be expected to have relatively strong INS intensities and are therefore likely to be contained in the broad bands at 400 and 610 cm^{-1}. These values may be compared with those of the W–PCy_3 complex, namely 325 and 370 cm^{-1} for the torsion and 450 and approximately 650 cm^{-1} for the other deformation modes. The peak at 725 cm^{-1} should be assigned to the Fe–H bend for the hydride in accordance with typical values for this mode.[22] This leaves, in the range of the present data, ν_s(Fe–H_2), which may well be contained in the broad band at ca. 870 cm^{-1}. Again, the value obtained for the W–PCy_3 complex of 953 cm^{-1} is noticeably higher, as for the other modes that we have tentatively assigned. The vibrational data on the FeH(H_2) fragment thus clearly suggest metal–dihydrogen binding weaker than that in the W–PCy_3 complex. Comparison with vibrational data obtained on the matrix-isolated molecule $FeCO(NO)_2(H_2)$[17] substantiates this conclusion. A tentative assignment of ν_s(Fe–H_2) at 870 cm^{-1} agrees well with the present results, and the value of ν(H–H) of 2973 cm^{-1} is also significantly higher than what is observed for similar W compounds.

The low-frequency spectrum shown in Figure 2 shows two weak peaks at ±2.1 cm^{-1}, which correspond to transitions within the librational ground state of the η^2-H_2 ligand, the rotational tunnel splitting. This transition involves a change in the nuclear spin wave function of the H_2 molecule (ortho to para hydrogen transition) and can therefore not be observed by optical techniques. Since the neutron's nuclear spin however can couple to that of the scatterer, such transitions can be observed by neutron scattering if $\Delta I = \pm 1$.[23]

This value is more than twice that observed for $W(CO)_3(H_2)(PCy_3)_2$, for example, and indicates a lower barrier to rotation than the 2.2 kcal/mol in the latter complex, provided that the shape of the potential is the same. The three rotational transitions hereby observed, namely 2.1, 225, and 255 cm^{-1}, can be utilized in an attempt to derive a rotational potential for the η^2-H_2 ligand. If we assume as before[18] that the rotation of the η^2-H_2 ligand is constrained to lie in a plane perpendicular to the H-Fe-(H_2) axis, then

$$V(\phi) = \sum_n (V_n/n)[1 - \cos(n\phi)] \qquad (1)$$

Since the crystal structure determination showed a well-defined equilibrium orientation for η^2-H_2, it can be assumed a 2-fold barrier term V_2 dominates the above expansion. The presence of the four P ligands in an approximately square arrangement about the Fe center suggests, however, that unlike the case of the W–PCy_3 complex a potential term with 4-fold symmetry may contribute significantly to the barrier. A model that allows the dihdyrogen ligand two rotational degrees of freedom cannot be fitted to the observed rotational transition data in any satisfactory manner. Moreover, this possibility seems unphysical on account of the high energy of the vibrations that involve motion of the dihydrogen ligand out of the plane of rotation.

Table I. Vibrational and Rotational Transitions of the FeH(H_2) Fragment in $[FeH(H_2)(PPh_2CH_2CH_2PPh_2)_2]BF_4$ at Low Temperatures with Likely Assignments and Comparisons to Related Systems (in cm^{-1}) and Rotational Transitions and Barrier Heights

(A) Transitions and Assignments

	1[a]	2[b]	3[c]
τ(FeH_2)	225 (7)/255 (8)	325/370	
δ(Fe–H_2)	400 (10)	462	
δ(Fe–H_2)	610 (15)	~650	
δ(Fe–H)	725 (15)		
ν_s(Fe–(H_2))	870 (20)	951	870
ν_a(Fe–H_2)		1568	
ν(H–H)		2690	2973

(B) Rotational Transitions and Barrier Heights

exptl	$V_2 = 12.7B$	$V_2 = [15.4\ (15)]B$, $V_4 = [-5.8\ (1)]B$
2.1	(2.1)	(2.1)
225	280	228
255	315	246

[a] Title compound. [b] $W(CO)_3(H_2)(PCy_3)_2$.[1] [c] $Fe(CO)(NO)_2(H_2)$.[17]

We have therefore fitted the rotational transitions to the model for planar rotation (eq 1) with either one or two terms. Given the ground-state splitting of 2.1 cm^{-1} and a value of B (=50 cm^{-1}) calculated with the H–H bond length (0.82 Å) determined by the neutron diffraction experiment, the barrier height V_2 is found to be 12.7B. Transitions to the excited states would then be expected to occur at 280 and 315 cm^{-1}, whereas the observed transitions are at 225 and 255 cm^{-1}. This indicates that the potential well is somewhat broadened by the addition of the V_4 term. We have therefore computed the rotational energy levels for combinations of V_2 and V_4 (eq 1) by diagonalization of the Hamiltonian matrix using one-dimensional free rotor states.[24] The best agreement with the observed rotational transitions was achieved for a potential with $V_2 = 15.4B$ and $V_4 = -5.8B$, for which the computed torsions are at 228 and 246 cm^{-1}. These results are summarized in Table I along with the vibrational data discussed above. This potential has a broad double minimum, each of which is in itself a very shallow double minimum. The latter are at about ±22.5° to $\phi = 0$ and $\phi = 180$, and the barrier in between is approximately 0.4B. If this is in fact realistic, it would suggest that at low temperatures the H–H axis may be oriented in either of two possible ways, 22.5° on either side of the P–Fe–P axis identified in the crystal structure determination.[10] At higher temperature, however, the mean orientation of the H–H axis would simply by along P–Fe–P with η^2-H_2 showing the expected large librational amplitude.

It is tempting to conclude that while the direct electronic interaction between the η^2-H_2 ligand and the metal strongly favors the simple double-minimum potential on account of the symmetry of the electron wave functions involved in the back-bonding to the σ^* orbital, the steric interactions, possibly with the large phenyl rings, which lie more along the P–Fe–P axes, could then have the effect of moving the H–H axis slightly off to the side.

This conclusion would appear to be qualitatively supported by recent preliminary molecular mechanics calculations,[19,25] which do not, of course, take any account of the direct electronic in-

---

(23) See, for example: Press, W. *Single Particle Rotations in Solids*; Springer Tracts in Modern Physics, Vol. 92; Springer: Berlin, 1981.

(24) Kearley, G. J. Private communication.

(25) Farrar, D. H.; Morris, R. H. Submitted results, 1989. Hall, J. H. Private communication. These (MM2) calculations were carried out by using Chem-X software (Chemical Design Ltd., Oxford, England) with coordinate positions for the atoms taken from the crystal structure determination.[20]

teraction between the dihydrogen and the metal. They indeed find the potential minimum when rotating the η^2-H_2 ligand about the H_2–Fe–H axis about 20° off to one side of the equilibrium orientation determined by the crystal structure analysis. If one were to add an electronic component to this with a strong preference for an H–H orientation parallel to the P–Fe–P axis, it is not difficult to see how the potential derived in our analysis could arise. It should be added, however, that the parametrization for the rotational potential that we used in terms of sinusoidal function may not be an accurate representation of the "true" potential curve and that therefore our result has to be regarded as tentative in this sense. It is, however, consistent with all available experimental data as described.

As far as the value for the barrier height is concerned, the molecular mechanics calculation yields a value of about 1.7 kcal/mol, while our results are either 1.8 kcal/mol for the pure V_2 potential or effectively about 2.3 kcal/mol for the modulated form. If one were to add an electronic component of approximately 1–2 kcal/mol[21] to the "steric" part given by the molecular mechanics calculation, the total comes out somewhat higher than these experimental values. Nonetheless, the agreement must be viewed as remarkable, since these values for barrier heights are below what is normally considered a reliable range for these type of calculations.

In conclusion, we have obtained the first vibrational and rotational data for the dihydrogen ligand in one of the most studied molecular hydrogen complexes, *trans*-[FeH(H_2)($PPh_2CH_2CH_2PPh_2$)$_2$]BF_4. We have analyzed the rotational transitions including the tunneling transition within the ground state in terms of planar rotation with one angular degree of freedom and derived a potential that appears to reflect some competition between the nonbonded interactions of the dihydrogen and the other ligands on the one hand and the direct dihydrogen–metal binding on the other. Further neutron-scattering studies on these systems are in progress with the aim of trying to separate the contributions to the rotational barrier from each other and to study the high-temperature rotational dynamics of the dihydrogen ligand.

Acknowledgment. This research was supported by grants to R.H.M. from the Natural Sciences and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank J. H. Hall for communicating the results of his molecular mechanics calculations. The work has benefited from the use of facilities at the Los Alamos Neutron Scattering Center, a national user facility funded as such by the DOE/Office of Basic Energy Sciences.

Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada 89557-0020,
and Varian Instrument Division, Palo Alto, California 94303

Solid-State Structures of $(R_3P)_2PtX_2$ Complexes As Determined by a Combination of $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Spectroscopy

Jeffrey A. Rahn,[1a] Laima Baltusis,[1b] and John H. Nelson*[,1a]

Received June 19, 1989

Cross-polarization, combined with magic-angle spinning, has been employed to obtain high-resolution solid-state ^{13}C and ^{31}P NMR spectra of a series of 31 $(R_3P)_2PtX_2$ complexes. These data together with spectra obtained in solution were used to compare the solid-state structures with those in solution. It was found that most of these complexes, which have regular square-planar structures in solution, are distorted in the solid state. The extent of the solid-state distortion is a function of the bulk of the coordinated ligands and increases as the ligand size increases. The solid-state distortions appear to result from intramolecular steric effects for *cis*-$(R_3P)_2PtX_2$ and probably from intermolecular crystal packing forces for *trans*-$(R_3P)_2PtX_2$.

Introduction

The technique of cross-polarization combined with magic-angle spinning (CP/MAS) has tremendous potential for structure determination by NMR in the solid state.[2] In a recent study,[3] we showed that CP/MAS ^{13}C and ^{31}P spectroscopy were useful for elucidation of the solid-state structures of palladium(II) and platinum(II) complexes of $MePh_2P$ and Me_2PhP. Though they possess regular square-planar structures in solution, most of these complexes were distorted in the solid state. Their CP/MAS ^{31}P NMR spectra were straightforward and easy to interpret. In contrast, only the methyl region of their CP/MAS ^{13}C NMR spectra provided meaningful information. The aromatic regions of these spectra were broad unresolved envelopes. The isomeric structures of the platinum complexes (cis or trans) were easily determined from the magnitude of ^1J(PtP). In order to gain greater understanding of the driving force for these solid-state distortions and to further explore the utility of CP/MAS spectroscopy for solid-state structural determination, we have prepared a series of 31 $(R_3P)_2PtX_2$ complexes containing ligands of significantly different size and obtained their CP/MAS ^{13}C and ^{31}P NMR spectra. These data are compared with $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra obtained in $CDCl_3$ solutions at 300 K.

Experimental Section

A. Reagents and Physical Measurements. All chemicals used were reagent grade and were used as received or synthesized as described below. All solvents when necessary were dried by standard procedures and stored over Linde 4-Å molecular sieves. All reactions involving phosphines were conducted under an N_2 atmosphere. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN 37921.

The solution $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 25- and 40.26-MHz respectively on a JEOL FX-100 spectrometer. Carbon chemical shifts were obtained relative to internal Me_4Si, while phosphorus chemical shifts were referenced to Ph_3P in $CDCl_3$ ($\delta = -6$ ppm) and converted to a 85% H_3PO_4 reference with positive values being downfield of the respective references. Cross-polarization magic-angle spinning (CP/MAS) $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian VXR-300 spectrometer operating at 75 and 121.4 MHz, respectively. The proton-decoupling field was 65 KHz. Carbon chemical shifts were referenced to an external sample of poly(dimethylsilane) ($\delta = 0$ ppm), while phosphorus chemical shifts were referenced to an external sample of Ph_3P ($\delta = -6$ ppm). The uncertainties in chemical shifts and coupling constants are estimated to be ±0.5 and ±20 Hz, respectively, for the CP/MAS measurements.

B. Synthesis. Most of the phosphines were obtained from either Strem Chemical or Organometallics, Inc., and were used as received. Tribenzylphosphine,[4] dibenzylphenylphosphine,[5] 1-phenyldibenzophosphole[6] (DBP), 1-phenyl-3,4-dimethylphosphole[7] (DMPP), and

---

(1) (a) University of Nevada. (b) Varian Instrument Division.

(2) Fyfe, C. A. *Solid State NMR for Chemists.* CFC: Guelph, Canada, 1984.

(3) Rahn, J. A.; O'Donnell, J.; Palmer, A. R.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 2631.

(4) Hilton, R. C.; Mann, F. G. *J. Chem. Soc.* **1952**, *15*, 2835.

(5) Mann, F. G.; Millar, I. T.; Stewart, F. H. C. *J. Chem. Soc.* **1954**, 2832.

(6) Affandi, S.; Green, R. L.; Hsieh, B. T.; Holt, M. S.; Nelson, J. H.; Alyea, E. C. *Synth. React. Inorg. Met-Org. Chem.* **1987**, *17*, 307.