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π-Bonding of the Dihydrogen Ligand Probed by Mössbauer Spectroscopy

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Introduction

There is much evidence for the importance of dπ–σ^* back-bonding in the stabilization of transition metal-dihydrogen bonding. The H_2 ligand in the Kubas complex $W(H_2)(CO)_3(P^iPr_3)_2$ is oriented along the P–W–P axis in the solid state to maximize π-bonding.[1] This leads to a barrier to H_2 rotation which can be detected in the inelastic neutron scattering (INS) spectra for $M(H_2)(CO)_3(PCy_3)_2$ (M = Cr, Mo, W), $Mo(H_2)(CO)(dppe)_2$, $[Fe(H_2)H(dppe)_2]^+$, $Fe(H_2)(H)_2(PEtPh_2)_3$, $[M(H_2)H(PP_3)]^+$ (M = Fe, Ru), and $Ru(H_2)_2(H)_2(PCy_3)_2$.[2,3] The energy of the dπ electrons as probed by electrochemistry correlates qualitatively with the stability of dihydrogen complexes with respect to loss of H_2 (d energy too low) and to splitting of the H_2 (d energy too high).[4] However there was not a correlation between electrochemical parameters and the barrier derived from INS.[2] Infrared studies of metal carbonyl complexes containing a dinitrogen or a dihydrogen ligand suggest that H_2 and N_2 have similar bonding properties.[5–7] The separation of σ- and π-bonding contributions on the basis of reported CO stretching frequencies is a difficult problem; Andrea et al.[8] on the basis of an analysis of the spectra of $W(H_2)(CO)_5$ concluded that the dihydrogen ligand is a relatively strong π-acceptor. NMR studies have provided evidence for a barrier to rotation in $[Ru(C_5Me_5)(H_2)(dppm)]^+$ [9] and recent work confirms that this is due to a preferred orientation of the H_2 ligand determined by π-bonding.[10] Theoretical studies suggest that both σ-bonding ($\sigma(H_2) \rightarrow d(M)$) and π-back-bonding ($d\pi(M) \rightarrow \sigma^*(H_2)$) are important in stable complexes.[11–15] There is some indication that the σ-interaction dominates. For example cationic dihydrogen complexes appear qualitatively to be more stable than neutral ones of the same metal.[16] However this might have to do with destabilization of the coordinatively unsaturated decomposition product rather than stabilization of the dihydrogen complex. Some recent attempts at preparing H_2 complexes with strong Lewis acids that do not have dπ electrons have failed, even in a low-temperature matrix.[17] However the adduct of H_2 with CH_3^+, $(H_2)CH_3^+$, is stable in the gas phase and in strong acid solution at low temperature;[18] here the C–H_2 bonding is described as 3-center, 2-electron with no barrier to rotation of the H_2.[19]

Mössbauer spectroscopy has been used by Bancroft et al.[20 21] to estimate the relative importance of σ- and π-effects in complexes of the type *trans*-$[Fe(L)H(depe)_2]BPh_4$.[3] A plot of isomer shift versus quadrupole splitting showed a linear correlation for the ligands L = CH_3CN, PhCN, $P(OMe)_3$, and $(CH_3)_3CNC$ where σ-bonding was thought to dominate. By contrast, strong π-acid ligands N_2 and CO deviate significantly from the line, signaling an important π-effect. The use of additive partial isomer shifts and partial quadrupole splittings (pqs) allowed the definition of a slightly different line on the basis of a wider range of purely σ-bonding ligands; this work revealed that $P(OMe)_3$ and ArNC ligands also have a π-bonding component.[21] Bancroft's studies suggested that N_2 is a very poor σ-donor and a moderate π-acceptor, whereas CO is a good π-acceptor and moderately good σ-donor.[22] This work was extended to a wider range of ligands L[23] and to a parallel series of complexes *trans*-$[Fe(L)H(dppe)_2]^+$ [24] and *trans*-$FeH(X)(dppe)_2$.[23,24] In the dppe series, the ligands L = $P(OMe)_3$, PhCN, CH_3CN, and NH_3 defined a line for mainly σ-bonding ligands while π-acid ligands deviated from the line to a greater extent following the trend $CNCH_2Ph < N_2 < CO$.[24] Use of the anionic ligands X = CN, NO_2, NCS, Cl, N_3, Br, and I provided a line parallel to and close to the line for the σ-donor ligands just mentioned.[24] Our dihydrogen complexes $[Fe(H_2)H(dppe)_2]BF_4$ and $[Fe(H_2)H(depe)_2]BPh_4$[25] are the subject of the present study.

Experimental Section

The complexes were prepared as described previously.[25] Samples (150 mg) were sealed with epoxy resin into poly(methyl methacrylate) cells in a argon-filled glovebag. The Mössbauer spectra were collected at room temperature for 2 days. Isomer shifts were referenced to stainless steel; some literature data[24] were converted from the sodium nitroprusside scale by subtracting 0.16 from the isomer shift.

Results and Discussion

The isomer shifts and quadrupole splittings for the dihydrogen complexes are listed in Table 1 along with those reported for related complexes. Also included are ^1H NMR chemical shifts of the terminal hydride of the complexes in solution. The chemical shifts for the dihydrogen complexes have to be measured at low temperature where intramolecular exchange of H atoms is frozen out.[25]

Plots of isomer shift versus quadrupole splitting (Figures 1 and 2) reveal that dihydrogen has the largest deviation from the lines defined by Bancroft [21] (Figure 1) and Mori and Takashima[24] (Figure 2) for σ-donor ligands. The position of H_2 on the plots suggests that it is a very weak σ-donor ligand and a strong π-acid ligand. The magnitude of the deviation indicates that π-bonding is relatively more important for H_2 than for CO or N_2. A combination of σ-withdrawal from the $\sigma(H_2)$ orbital and π-back-

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(1) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324–2332.

(2) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378–2384.

(3) dppe = $PPh_2CH_2CH_2PPh_2$, PP_3 = $P(CH_2CH_2PPh_2)_3$, and depe = $PEt_2CH_2CH_2PEt_2$.

(4) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471–1478.

(5) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674–83.

(6) Zheng, Y. F.; Wang, W. H.; Lin, J. G.; She, Y. B.; Fu, K. J. *J. Phys. Chem.* **1992**, *96*, 9821–9827.

(7) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804–4813.

(8) Andrea, R. R.; Vuurman, M. A.; Stufkens, D. J.; Oskam, A. D. *Recl. Trav. Chim. Pays Bas* **1986**, *105*, 372–374.

(9) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161–171.

(10) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Morris, R. H.; Fong, T. P.; Albinati, A. Submitted for publication.

(11) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705–710.

(12) Jean, Y.; Lledos, A.; Maouche, B.; Aiad, R. *J. Chim. Phys., Phys. Chim. Biol.* **1987**, *84*, 805–8.

(13) Maseras, F.; Duran, M.; Lledos, A.; Bertran, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879–2884.

(14) 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*, 4831–4841.

(15) Albinati, 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, R. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300–7312.

(16) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913–926.

(17) Moroz, A.; Sweany, R. L. *Inorg. Chem.* **1992**, *31*, 5236–5242.

(18) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119 and references therein.

(19) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649–5657.

(20) Bancroft, G. M.; Mays, M. J.; Prater, B. E.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2146–2149.

(21) Bancroft, G. M. *Coord. Chem. Rev.* **1973**, *11*, 247–262.

(22) Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Chem., Radiochem.* **1972**, *15*, 59–245.

(23) Silver, J. *Inorg. Chim. Acta* **1991**, *184*, 235–242.

(24) Mori, G.; Takashima, Y. *Chem. Lett.* **1979**, 425–428.

(25) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876–4887.

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Table 1. Mössbauer and ^1H NMR Data for the Complexes *trans*-$[Fe(L\ or\ X^-)H(diphos)_2]^+$

trans complex	Mössbauer IS, mm s^{-1}	Mössbauer QS, mm s^{-1}	NMR $\delta(^1H)$, ppm
$[Fe(H_2)H(depe)_2]BPh_4$	–0.03	0.00	–14.6
$[Fe(CO)H(depe)_2]BPh_4$[a]	–0.04	–1.00	–10.9
$[Fe(CNCMe_3)H(depe)_2]BPh_4$[a]	0.05	–1.13	–13.9
$[Fe(P(OMe)_3)H(depe)_2]BPh_4$[a]	0.09	–0.90	–14.4
$[Fe(N_2)H(depe)_2]BPh_4$[a]	0.16	–0.33	–18.2
$[Fe(NCMe)H(depe)_2]BPh_4$[a]	0.19	–0.46	–23.8
$Fe(Cl)H(depe)_2$	0.23[a]	0.0[a]	–31.9
$[Fe(H_2)H(dppe)_2]BF_4$	0.00	–0.56	–12.9
$[Fe(CO)H(dppe)_2]BF_4$	0.12[b]	–1.32[b]	–7.8[c]
$[Fe(P(OMe)_3)H(dppe)_2]BF_4$	0.25[b]	–1.51[b]	
$[Fe(N_2)H(dppe)_2]BF_4$	0.31[b]	–0.63[b]	–15.3[c]
$[Fe(NCPh)H(dppe)_2]BF_4$	0.33[b]	–1.01[b]	
$[Fe(NCMe)H(dppe)_2]BF_4$	0.34[b]	–0.85[b]	–20.5[c]
$[Fe(NH_3)H(dppe)_2]BF_4$	0.38[b]	–0.78[b]	
$Fe(CN)H(dppe)_2$	0.25[b]	–1.77[b]	–13.1[d]
$Fe(Cl)H(dppe)_2$	0.38[b]	–0.75[b]	–29.2

[a] Data from ref 20. [b] Reference 24. [c] Reference 29. [d] Reference 30.

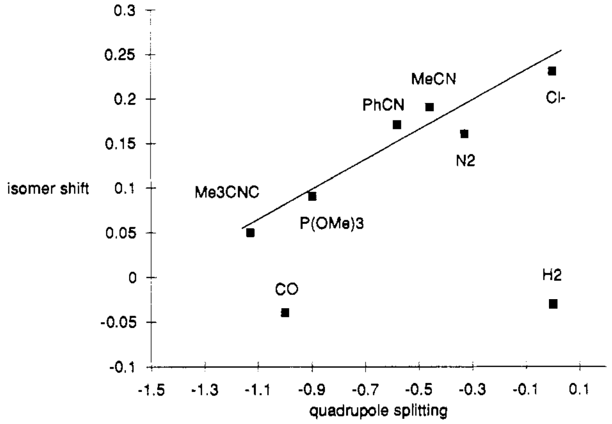

Figure 1. Plot of isomer shift (mm s^{-1}) versus quadrupole splitting (mm s^{-1}) for some complexes *trans*-$[Fe(L\ or\ X^-)H(depe)_2]BPh_4$. Isomer shifts are referenced to stainless steel. The line for σ-donating groups is similar to the one found in ref 22.

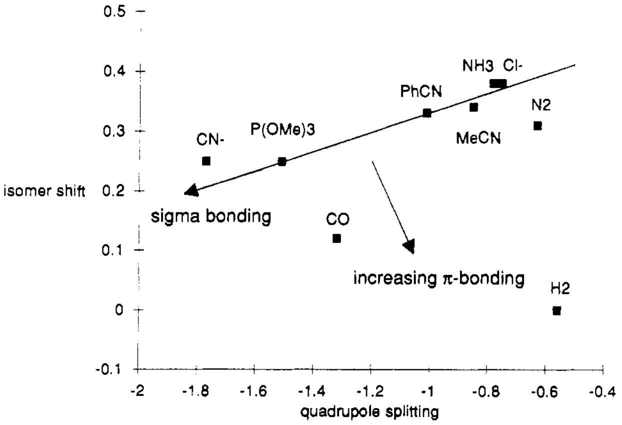

Figure 2. Plot of isomer shift (mm s^{-1}) versus quadrupole splitting (mm s^{-1}) for some complexes *trans*-$[Fe(L\ or\ X^-)H(dppe)_2]BPh_4$. Isomer shifts are referenced to stainless steel. The line for σ-donating groups was drawn as in ref 24.

bonding to the $\sigma^*(H_2)$ orbital by the iron results in a lengthening of the H–H bond from 0.74 Å in free H_2 gas to about 0.86 Å in these Fe complexes.[25] Despite the dominance of the π-bonding contribution indicated by this Mössbauer study, the H–H bond does not completely split to give the hypothetical trihydride tautomer of these complexes. This has been explained in terms of the stability of the octahedral geometry of low-spin Fe(II) (d^6) and the destabilization of seven-coordinate Fe(IV) (d^4) by interligand repulsions around the small Fe center which is not compensated for by the formation of iron-hydride bonds.[26] Several other dihydrogen complexes have an observable dihydride tautomer.[26]

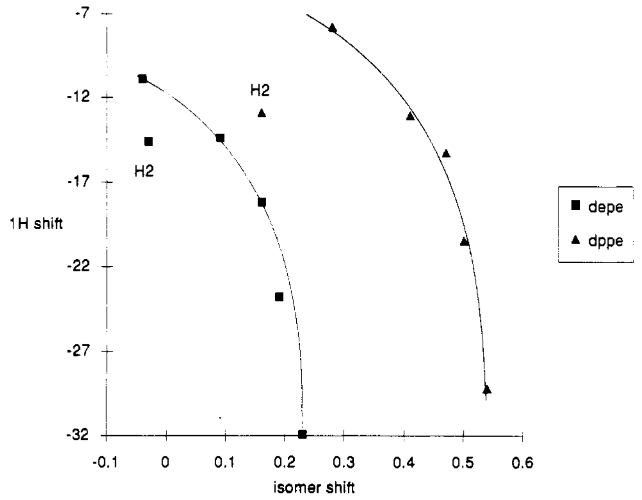

Figure 3. Plot of hydride NMR chemical shift (ppm) versus isomer shift (mm s^{-1}) for the complexes. Refer to Table 1 for the identity of the points.

A plot (Figure 3) of the ^1H NMR shift of the terminal hydride versus the isomer shift of the Fe for the complexes $[Fe(L\ or\ X^-)H(diphos)_2]^+$ displays parallel curves for diphos ligands depe and dppe. A correlation between these parameters might be expected because both depend to a certain extent on the s electron density at the Fe center. The isomer shifts and/or the ^1H chemical shifts for the dihydrogen complexes are more negative than would be expected from such a trend (Figure 3). Although the interpretation of ^1H NMR chemical shifts of hydrides is very complex,[27] one possible explanation is that the strong π-acid ligand, dihydrogen, has removed 3d electron density from the iron to an unusually large extent (compared to CO and N_2) which reduces the shielding of the Fe nucleus from the 4s electrons by the 3d electrons. An increase in s electron density at the Fe nucleus is known to decrease the isomer shift. This would have the indirect effect of diamagnetically shielding the hydride as well.

A partial quadruple coupling constant, pqs(H_2), of –0.22 for the dihydrogen ligand is calculated from the data for the dppe and depe complexes. For this calculation values of pqs(depe) = –0.62,[21] pqs(dppe) = –0.50,[28] and pqs(H) = –1.04[21] were used. Such pqs values might be useful in predicting quadrupole complexes in related, unknown complexes and to distinguish between cis and trans stereochemistries.[21, 23]

Conclusions

Mössbauer spectroscopy has been used to show that π-bonding in transition metal dihydrogen complexes is very significant, more so than for N_2 or CO complexes. It will be interesting to see if the Mössbauer parameters for a range of iron complexes can be correlated with barriers to rotation derived from inelastic neutron scattering work.

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(26) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284.
(27) McCue, J. P. *Coord. Chem. Rev.* **1973**, *10*, 265.
(28) The pqs(dppe) value was derived from all the literature data.[20-24] The calculation of a value of 0.60 by Silver[23] was done without including all of the data of ref 24.
(29) Stanley, D. D. Phil. Thesis, University of Sussex, 1980.
(30) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432–3437.