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H_2 Activation in Aqueous Solution: Formation of *trans*-[Fe(DMeOPrPE)$_2$H(H_2)]$^+$ via the Heterolysis of H_2 in Water

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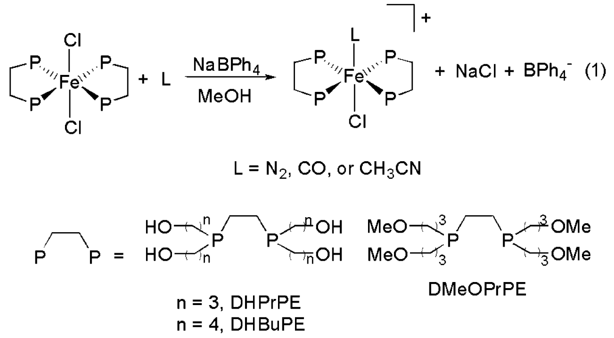
The water-soluble iron phosphine complex *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (DMeOPrPE = 1,2-bis(bis(methoxypropyl)phosphino)ethane) reacts with H_2 in water to produce *trans*-[Fe(DMeOPrPE)$_2$H(H_2)]$^+$ and H^+. The product is a water-soluble η^2-H_2 metal hydride complex, formed via the heterolysis of coordinated H_2 in water.

The inorganic chemistry of dihydrogen metal complexes has been comprehensively investigated[1−3] during the two decades since Kubas's seminal paper in 1984,[4] although only one investigation has studied such complexes in aqueous solution. The Ru−aquo complex [Ru(H_2O)$_5$(H_2)]$^{2+}$ was reported[5] to form in situ; however, high pressures of hydrogen were required to generate the complex. This result, as well as work by Kubas[6] and Crabtree,[7] was instrumental in revealing the ability of H_2 to bind in preference to other σ-donors and seemingly better ligands. If a stable metal−ligand framework could be found that was both water-soluble and capable of binding H_2 at relatively low pressures (1−2 atm), there would be a number of important applications. For example, such materials could be used as hydrogen "scrubbers" in aqueous environments to prevent hydrogen embrittlement of metals and alloys[8,9] and perhaps as catalysts in homogeneous hydrogenations and related chemical transformations.[1]

In a recent paper,[10] we reported that complexes of the type *trans*-Fe(P_2)$_2$Cl$_2$ (P_2 = a water-soluble chelating bidentate phosphine ligand) reacted with N_2, CO, and CH_3CN in methanol to give *trans*-[Fe(P_2)$_2$(L)Cl]$^+$ (L = N_2, CO, CH_3CN) (eq 1). In related work,[11] we found that analogous reactivity occurred in *aqueous* solution and that the binding of N_2 was reversible. This intriguing result inspired us to investigate the reactivity of *trans*-Fe(P_2)$_2$Cl$_2$ with H_2. In this paper we report the results of our study of the reaction of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (**I**) with H_2 and the subsequent heterolysis of H_2 in aqueous solution.



Reaction of the green complex **I** with H_2 (1−2 atm) in water (pH 6.5) for 20 h resulted in the formation of the yellow *trans*-[Fe(DMeOPrPE)$_2$H(H_2)]$^+$ complex (eq 2). When the reaction vessel was vented, the yellow product disappeared over the course of an hour and an orange color appeared.[12] For that reason, the yellow product was characterized in situ under an H_2 atmosphere.

The room temperature $^{31}P\{^1H\}$ NMR spectrum of the solution exhibited one major resonance at 88.9 ppm and two broad, minor resonances[13] of equal intensity at −23.5 and 19.5 ppm (Figure 1).[14] Insight into the identity of the major resonance was gained by ^1H coupled ^{31}P NMR experiments, which revealed a doublet with a *J* coupling value of 45 Hz. This value suggests cis $^2J_{P-H}$ coupling, a spectroscopic motif consistent with a terminal hydride ligand bound to an iron

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(1) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*; Kluwer Academic/Plenum: New York, 2001.
(2) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev*. **1992**, *121*, 155.
(3) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev*. **1993**, *93*, 913.
(4) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc*. **1984**, *106*, 451.
(5) Aebischer, N.; Frey, U.; Merbach, A. E. *Chem. Commun*. **1998**, 2303.
(6) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Slus, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390.
(7) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc*. **1986**, *108*, 4032.
(8) Oriani, R. A. *Proc. Electrochem. Soc*. **2002**, *2002-13*, 385.
(9) Carter, T. J.; Cornish, L. A. *Eng. Failure Anal*. **2001**, *8*, 113.
(10) Miller, W. K.; Gilbertson, J. D.; Leiva-Paredes, C.; Bernatis, P. R.; Weakley, T. J. R.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem*. **2002**, *41*, 5453.
(11) Miller, W. K.; Lyon, D. K.; Tyler, D. R. Unpublished observations.
(12) The orange color observed is attributed to *trans*-[Fe(DMeOPrPE)$_2$(H_2O)$_2$]$^{2+}$. See ref 10.
(13) These resonances are actually exchanged broadened doublets with J_{P-P} = 35 Hz. See Figure S1 in Supporting Information.
(14) The very weak resonance at 70 ppm in Figure 1 is assigned to a [Fe(DMeOPrPE)$_2$(H_2)Cl]$^+$ species and will be discussed in a subsequent paper.

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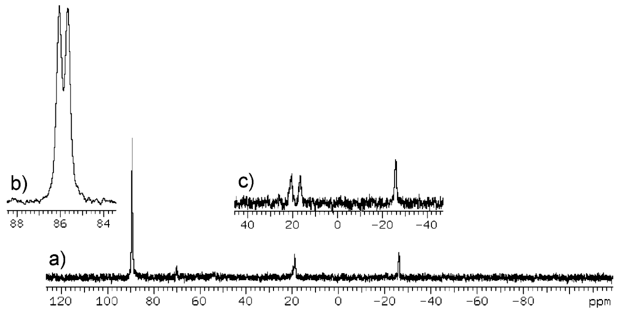
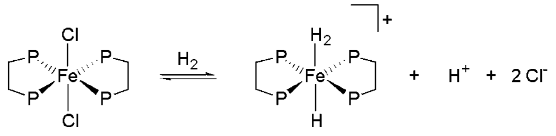


Figure 1. $^{31}P\{^1H\}$ NMR spectra (233 K): (a) reaction mixture of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ dissolved in ethanol/H$_2$O mixture (60/40 wt %), with H$_2$ (1−2 atm); (b,c) same sample (expanded) with ^1H decoupler off.

atom.[15] Further clues to the structure of the yellow product were provided by the ^1H NMR spectrum of the yellow solution at 233 K,[21] which showed resonances at −15.1 (quintet, $^2J_{P-H} = 45$ Hz) and −10.9 ppm (s, br). Essentially identical ^1H and $^{31}P\{^1H\}$ NMR spectra were observed for *trans*-[Fe(P$_2$)$_2$H(η^2-H$_2$)]$^+$-type complexes (Table 1), and it is logical therefore to suggest that the yellow product is *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$ (eq 2).



(2)

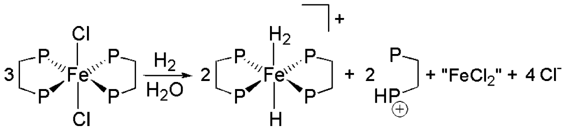
Further evidence for an η^2-H$_2$ ligand comes from an examination of T_1(min) by the inversion recovery method.[22] These measurements yielded a T_1(min) of 19.5 ms at 500 MHz, which corresponds to an H−H bond distance of 0.85 Å, assuming fast rotation, and 1.07 Å for slow rotation of the H$_2$ ligand. These distances are clearly indicative of a nonclassical H$_2$ ligand. (H−H distances <1.2 Å are considered nonclassical and H−H distances >1.5 Å are considered classical.[1]) The H−H bond distance was further confirmed by the J(H,D) method,[23] which gave a J coupling value of 29.8 Hz corresponding to an H−H distance of 0.92 Å.

As indicated in eq 2, protons are produced in the reaction of H$_2$ with *trans*-Fe(DMeOPrPE)$_2$Cl$_2$. Accordingly, the pH decreased from 6.5 to 4.4 during the course of the reaction. This result, along with the formation of the metal hydride complex, suggests that H$_2$ is heterolytically cleaved during the course of the reaction (eq 2).

In order to verify the reaction stoichiometry in eq 2, inverse-gated $^{31}P\{^1H\}$ NMR spectroscopy (25 °C) was used to quantify the amount of *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$ produced in the reaction. The experimental data revealed, on average, a 65% conversion[24] of **I** to *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$, which should correspond to a pH of 2.6. Repeated reaction trials, however, yielded a pH ≥4.4. As described next, the H$^+$ not accounted for in these experiments was found to be bonded to uncoordinated DMeOPrPE.

Control experiments[25] showed that the resonances at 19.5 and −23.5 ppm in Figure 1 are due to DMeOPrPEH$^+$, the monoprotonated form of the uncoordinated ligand. The ^1H coupled ^{31}P NMR spectrum revealed a doublet with a J coupling constant of 448 Hz (indicative of $^1J_{P-H}$ coupling), consistent with protonation of one of the phosphorus atoms.[26] To account for these observations, it is proposed that some of the H$^+$ generated in the reaction of H$_2$ with **I** reacts with the complex to degrade it and form monoprotonated ligand. Further credence to this suggestion was given by evaluation of the aqueous pK_a values for each phosphorus on the DMeOPrPE. The values of 8.2 and 5.4, for p$K_{a(1)}$ and p$K_{a(2)}$, respectively, reveal the buffering capacity of the ligand.

Integration of the inverse-gated $\{^1H\}^{31}P$ NMR spectra of the product resonances shows an average [*trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$]:[DMeOPrPEH$^+$] ratio of 1.2, corresponding to the production of essentially one proton for every Fe−hydride species in solution.[27] This ratio, coupled with the observation of a ≈67% conversion of **I** to *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$, suggests the stoichiometry in eq 3.[28]



(3)

In an attempt to demonstrate that a clean conversion to the *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$ product in eq 2 is possible, the reaction was run in the presence of a proton trap (Proton Sponge).[29] The *only* product observed in the $^{31}P\{^1H\}$ NMR spectrum[30] at both room temperature and 233 K was *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$ (88.9 ppm). Consistent with this result, the ^1H NMR spectrum[30] (233 K; ethanol-d_6/D$_2$O (60/40 wt %)) only showed resonances for *trans*-

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(15) See references in Table 1.

(16) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546.

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

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

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

(20) 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.

(21) An ethanol/H$_2$O mixture (60/40 wt %) was used as the reaction solvent to maintain fluidity at low temperatures. It should be noted that there was no change in the $^{31}P\{^1H\}$ NMR spectra of the products at both room and low temperatures when these solvents were substituted.

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

(23) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(24) In a typical experiment, 0.023 mmol of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ reacted with H$_2$ in water to afford 0.014 mmol of *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]$^+$, a value that corresponds to approximately 65% conversion.

(25) See Figures S1 and S2 and experimental procedures in the Supporting Information.

(26) The resonance at 19.5 ppm is assigned to the protonated phosphorus atom (P1) of the DMeOPrPEH$^+$ due to the fact that the protonated P resonance should shift downfield when the shielding effect of the lone pair is removed by the formation of the quaternary phosphonium salt.

(27) Over 95% of the phosphorus in solution is accounted for, well within experimental error.

(28) The FeCl$_2$ most likely exists as the hexaaquo species, [Fe(H$_2$O)$_6$]$^{2+}$.

(29) Conventional bases such as hydroxide or triethylamine were not suitable because they reacted with the *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ complex and degraded it. To avoid the problems associated with nucleophilic bases, the nonnucleophilic base 1,8-bis(dimethylamino)-naphthalene (Proton Sponge) was used.

(30) See Figures S3−S5 in the Supporting Information.

Table 1. NMR Data for Selected $[Fe(P_2)_2H(\eta^2\text{-}H_2)]^+$-Type Complexes[a]

complex	^1H NMR	$^{31}P\{^1H\}$	J_{H-D}, Hz	T_1(min), ms[b]	ref
trans-$[Fe(DMPE)_2H(H_2)]^+$	-17.1 (q, $^2J_{P-H} = 50.3$ Hz), -11.8 (s, br)	68.9[d]	31		16
trans-$[Fe(DEPE)_2H(H_2)]^+$	-14.5 (q, $^2J_{P-H} = 47.3$ Hz), -10.5 (s, br)	95.2[d]	28	12 (200)	16, 17
trans- $[Fe(DEDPPE)_2H(H_2)]^+$	-13.6 (q, $^2J_{P-H} = 47.3$ Hz), -9.2 (s, br)		32	7 (200)	18
trans- $[Fe(DPrPE)_2H(H_2)]^+$	-14.6 (q, $^2J_{P-H} = 48.5$ Hz), -10.7 (s, br)	89.9[d]			16
trans- $[Fe(DPPE)_2H(H_2)]^+$	-12.9 (q, $^2J_{P-H} = 47$ Hz), -8.0 (s, br)	92.5[e]	32	8.5 (200)	19, 20
trans- $[Fe(DMeOPrPE)_2H(H_2)]^+$	-15.1 (q, $^2J_{P-H} = 45$ Hz), -10.9 (s, br)	88.9[e]	30	19.5 (500)	*c*

[a] DMPE = 1,2-bis(dimethylphosphino)ethane, DEPE = 1,2-bis(diethylphosphino)ethane, DEDPPE = 1-(diethylphosphino)-2-(diphenylphosphino)ethane, DPrPE = 1,2-bis(dipropylphosphino)ethane, DPPE = 1,2-bis(diphenylphosphino)ethane. [b] Spectrometer frequency (in MHz) listed in parentheses. [c] This work. [d] Anhydrous ethanol. [e] Ethanol-d_6.

$[Fe(DMeOPrPE)_2H(H_2)]^+$ (Table 1) and for protonated Proton Sponge at 19.1 ppm (s).

The mechanism for the formation of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]^+$ is currently under investigation. It is suggested to proceed via formation of an $[Fe(DMeOPrPE)_2(H_2)Cl]^+$ intermediate followed by heterolysis of the H−H bond to yield a neutral $[Fe(DMeOPrPE)_2(H)Cl]$ species that may undergo subsequent ligand substitution by H_2. In support of this pathway, it is noted that Morris has proposed a similar mechanism[31,32] for the heterolysis of H_2 in nonaqueous systems (although the addition of a chloride sequestering agent and external base were required). Heinekey[33] has shown that H_2 can displace the normally strongly bound Cl^- unaided, and Eisenberg has proposed heterolytic activation of H_2 in systems containing a cationic metal center with labile ligands.[34]

In summary, this work showed that heterolysis of H_2 is possible in aqueous solutions by reacting *trans*-$Fe(DMeOPrPE)_2Cl_2$ with H_2 in water to produce *trans*-$[Fe(DMeOPrPE)_2H(H_2)]^+$ and H^+.[35] To our knowledge, H_2 heterolysis in aqueous solution by a transition metal phosphine complex is unprecedented. The protons produced in the heterolysis are noninnocent in the sense that they lead to decomposition of the starting material. As shown, addition of a proton trap inhibits the decomposition of the starting material caused by the protons produced during heterolysis.

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Supporting Information Available: Text describing experimental data, control experiments involving DMeOPrPE with H^+, and selected NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437.

(32) 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.

(33) Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792.

(34) Albietz, P. J.; Houlis, J. F.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 2001.

(35) Early work by Halpern[36] and James[37] on homogeneous catalytic hydrogenations by ruthenium complexes involved heterolysis of H_2 in aqueous solution. However, no η^2-H_2 complexes were observed.

(36) Halpern, J. *J. Phys. Chem.* **1959**, *63*, 398.

(37) Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc.* **1966**, *88*, 5150.