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Article

Coordination Chemistry of H_2 and N_2 in Aqueous Solution. Reactivity and Mechanistic Studies Using *trans*-$Fe^{II}(P_2)_2X_2$-Type Complexes (P_2 = a Chelating, Water-Solubilizing Phosphine)

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The reactions of the *trans*-$Fe(DMeOPrPE)_2Cl_2$ complex (**I**; DMeOPrPE = 1,2-bis(bis(methoxypropyl)phosphino)ethane) and its derivatives were studied in aqueous and nonaqueous solvents with a particular emphasis on the binding and activation of H_2 and N_2. The results show there are distinct differences in the reaction pathways between aqueous and nonaqueous solvents. In water, **I** immediately reacts to form *trans*-$Fe(DMeOPrPE)_2(H_2O)Cl^+$. Subsequent reaction with H_2 or N_2 yields *trans*-$Fe(DMeOPrPE)_2(X_2)Cl^+$ (X_2=H_2 or N_2). In the case of H_2, further reactivity occurs to ultimately give the *trans*-$Fe(DMeOPrPE)_2(H_2)H^+$ product (**III**). The pathway for the reaction **I** → **III** was spectroscopically examined: following the initial loss of chloride and replacement with H_2, heterolysis of the H_2 ligand occurs to form $Fe(DMeOPrPE)_2(H)Cl$; substitution of the remaining chloride ligand by another H_2 molecule then occurs to produce *trans*-$Fe(DMeOPrPE)_2(H_2)H^+$. In the absence of H_2 or N_2, *trans*-$Fe(DMeOPrPE)_2(H_2O)Cl^+$ slowly reacts in water to form $Fe(DMeOPrPE)_3^{2+}$, **II**. Experiments showed that this species forms by reaction of free DMeOPrPE ligand with *trans*-$Fe(DMeOPrPE)_2(H_2O)Cl^+$, where the free DMeOPrPE ligand comes from dissociation from the *trans*-$Fe(DMeOPrPE)_2(H_2O)Cl^+$ complex. In nonaqueous solvents, the chloride ligand in **I** is not labile, and a reaction with H_2 only occurs if a chloride abstracting reagent is present. Complex **III** is a useful synthon for the formation of other water-soluble metal hydrides. For example, the *trans*-$[Fe(DMeOPrPE)_2H(N_2)]^+$ complex was generated in H_2O by substitution of N_2 for the H_2 ligand in **III**. The *trans*-$Fe(DHBuPE)_2HCl$ complex (DHBuPE = 1,2-bis(bis(hydroxybutyl)phosphino)ethane, another water-solubilizing phosphine) was shown to be a viable absorbent for the separation of N_2 from CH_4 in a pressure swing scheme. X-ray crystallographic analysis of **II** is the first crystal structure report of a homoleptic tris chelate of Fe^{II} containing bidentate phosphine ligands. The structure reveals severe steric crowding at the Fe center.

Introduction

The coordination chemistry of H_2 and N_2 with transition metal complexes has been comprehensively investigated,[1−9] beginning with the seminal papers by Kubas[10] and Allen and Senoff.[11] Very few studies, however, have dealt with the binding and subsequent activation of these small molecules

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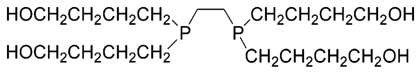
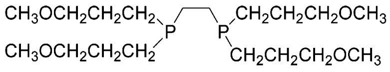
in H_2O.[12−17] Given the fundamental importance of such binding in the realm of metalloenzymes (e.g., hydrogenase and nitrogenase[18−22]), it is surprising that so few reports to date have examined the coordination chemistry of these molecules in water. Outside of biomimicry, the coordination chemistry of these small molecules in water is important for a number of reasons. For example, one relevant industrial application for transition metal complexes that are capable of binding H_2 and N_2 in aqueous solution is as gas “scrubbers.” In particular, the behavior of hydrogen in aqueous systems has drawn considerable attention to the detrimental process of hydrogen embrittlement.[23,24] This industrial problem results from the interaction of a metal surface with absorbed hydrogen (formed in situ by galvanic splitting of H_2O), causing a reduction of tensile strength and ductility of the metals. Embrittlement eventually leads to cracking and therefore severely reduces the lifetime of these metals. Relatively small amounts of hydrogen are needed to cause embrittlement, and high strength steel, titanium and aluminum alloys are particularly susceptible. To prevent embrittlement, the development of an aqueous phase H_2 scrubber is desirable.

There is also considerable interest in aqueous phase dinitrogen scrubbers. Natural gas currently accounts for approximately 25% of the total energy consumed in the U.S. annually.[25] However, 15−20% of current feedstocks are deemed unusable due to contamination by N_2 (>4% N_2).[26] The current techniques (cryogenic, membrane, or absorption/adsorption) for N_2 separation from CH_4 gas streams are costly and inefficient. It has been noted that pressure swing adsorption (PSA) techniques (binding at high pressure, releasing at low pressure) utilizing a cheap medium such as water in which N_2 and CH_4 are poorly soluble could potentially be deployed in a successful N_2 removal process.[27,28] A water-soluble transition metal complex that is able to bind N_2 in aqueous solution is extremely attractive for this purpose.

We recently reported the synthesis of the water-solubilizing phosphines DMeOPrPE (1,2-bis(bis(methoxypropyl)phosphino)ethane) and DHBuPE (1,2-bis(bis(hydroxybutyl)phosphino)ethane) and their water-soluble complexes of Fe^{II}.[29] As we reported, these complexes bind and heterolytically cleave H_2 in aqueous solution,[30] and they are active in a Leigh-type reduction cycle of N_2 to ammonia and hydrazine.[31] We report here the full details of the aqueous coordination chemistry of these Fe^{II} phosphine complexes, including their ability to bind N_2 and H_2.



DHBuPE



DMeOPrPE

Experimental

Unless otherwise noted, all manipulations were carried out in either a Vacuum Atmospheres Co. glove box (argon or N_2-filled) or on a Schlenk line using argon or nitrogen. *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (**I**) was prepared as reported previously.[29] HPLC-grade THF and diethyl ether (Burdick and Jackson) were dried and deoxygenated by passing it through commercial columns of CuO followed by alumina under an argon atmosphere. Toluene (Aldrich) was distilled under N_2 from CaH_2 and degassed via three freeze−pump−thaw cycles. Water was purified to a resistivity of 17−18 MΩ cm with a Barnstead Ultrapure system and deoxygenated with an argon purge before use. $Ba(ClO_4)_2$ and $Ba(NO_3)_2$ (Aldrich) were used as received. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on either a Varian Unity/Inova 300 spectrometer at an operating frequency of 299.94 (^1H) and 121.42 (^{31}P) MHz or a Varian Unity/Inova 500 spectrometer at an operating frequency of 500.62 (^1H) and 202.45 (^{31}P) MHz. The ^1H and ^{31}P chemical shifts were referenced to the solvent peak and to an external standard of 1% H_3PO_4 in D_2O, respectively. When required, the samples were sealed under argon in 7 mm tubes fitted with Teflon valves. Samples that were run under pressure were sealed in high-pressure tubes and sealed with a Teflon valve. Note that the ^1H NMR data for complexes containing the DMeOPrPE ligand were generally broad and uninformative. Infrared spectra were recorded on a Nicolet Magna 550 FT-IR with OMNIC software. Samples were prepared as either neat oils using NaCl windows or in solution using a CaF_2 cell. Mass spectra were obtained using a Thermo Finnigan LCQ DECA XPplus Spectrometer. The samples were dissolved in methanol or 50:50 methanol:water and introduced into the ionization head (ESI) using the infusion method. The experimental isotope patterns of the parent peaks are shown in the Supporting Information.

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Magnetic Measurements. Measurements were carried out using a Johnson-Matthey Evans Balance. Samples were loaded under argon and sealed with clay. Data were recorded at room temperature. The magnetic susceptibility was corrected for diamagnetic contributions using the appropriate Pascal's constants.[32] The molar magnetic susceptibility, χ_m, was calculated by multiplying χ (calculated magnetic susceptibility) by the molecular weight of the sample. The effective magnetic moment was calculated using the formula, $\mu_{eff} = 2.828(\chi_m T)^{1/2}$. Solution magnetic moments were measured using the Evans method in toluene, THF, or methanol solution.[33,34]

X-ray Crystallography. Single crystals suitable for diffraction were grown as stated in the experimental procedure for each complex. The crystals were mounted on a glass fiber under Paratone N oil, and diffraction data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using $Mo_{k\alpha}$ radiation ($\lambda = 0.71073$ Å) at 152 K. Data were corrected for Lorentz and polarization effects, and for absorption using the SADABS v2.02 area-detector absorption correction program (Siemens Industrial Automation, Inc., 1996). The structures were solved by direct methods; refinement was based on $|F|^2$, and hydrogen atoms were placed in calculated positions and given isotropic U values 1.2 times that of the atom to which they are bonded. All crystallographic calculations were conducted with the Oxford *Crystals for Windows* program package.[35,36]

N_2 Binding Experiments. The apparatus used to measure N_2 binding by the Fe−phosphine compounds consisted of Fischer−Porter tubes fitted with a pressure transducer, which was interfaced to a personal computer running OPTO 22 data-collection software (OPTO 22, Temecula, CA). For pressures exceeding 150 psia, the experiments were conducted in a stainless-steel Parr reactor (Parr Co., Moline, IL). The temperature of the apparatus was maintained at 40.0 ± 0.1 °C by immersing the apparatus in a temperature-controlled water bath.

In the experiment, a known pressure and volume of N_2 (typically 45 − 90 mL of gas at pressures between 1 and 10 atm) was contacted with a known volume (5−10 mL) and concentration (0.1 − 0.5 M) of a solution of an N_2 absorbent in the sealed vessel. When stirring is commenced, the N_2 pressure decreased and was recorded as a function of time until no further pressure decrease was noted. The amount of N_2 that physically dissolved in the solvent (measured independently) was subtracted from the total amount of N_2 absorbed to give N_2 complexed by the transition-metal compound. The amount of N_2 absorbed was then confirmed during the desorption experiment, which was conducted under a known pressure of argon (the N_2 partial pressure is negligible at the beginning of the desorption). Thus, during the desorption experiment, N_2 release was measured by the pressure increase in the apparatus and by the N_2 content in the headgas at the end of the experiment, as determined by gas chromatography.

Synthesis of $[Fe(DMeOPrPE)_3][ClO_4]_2$ (II−ClO_4). *cis*-Fe(DMeOPrPE)$_2$SO$_4$ (0.10 g, 0.112 mmol) was dissolved in 5.0 mL of water and stirred for 24 h at ambient temperature, initially giving a purple solution but which turned orange over the 24 h period. The $^{31}P\{^1H\}$ NMR spectrum at 23 °C of the reaction mixture showed one resonance at δ 49.5 (s). $Ba(ClO_4)_2$ (0.037 g, 0.112 mmol) was then added to the solution, producing a white precipitate ($BaSO_4$) that was removed by filtration. The H_2O was removed by vacuum, leaving an orange oil. X-ray quality crystals were obtained by layering Et_2O on top of a concentrated solution of the oil in EtOH and allowing the solution to stand sealed in the freezer at −10 °C. $^{31}P\{^1H\}$ NMR of the crystals (CD_3OD): δ 49.5 (s). ^1H NMR (D_2O): δ 3.4 (br, m), 1.9 (br, m), 1.5 (br, m), 1.3 (br). Yield: 23 mg, 30%. Anal. Found: C, 45.83; H, 8.11. Calcd for $C_{54}H_{120}Cl_2FeO_{20}P_6$: C, 46.26; H 8.63.

Generation of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]Cl$ (III−Cl). *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (0.100 g, 0.112 mmol) was dissolved in 5 mL of deionized water in a sealed Fischer−Porter tube, producing a deep purple solution. The resultant solution was immediately charged with 1−2 atm H_2 and stirred at ambient temperature. The solution changed color from deep purple to transparent yellow over a period of 20 min but was stirred overnight to ensure completion of the reaction. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a major resonance at δ 88.9 (s). The ^1H NMR spectrum (ethanol-d_6) of the hydride region at − 40 °C showed resonances at δ −10.9 (s, br) and δ −15.1 (quintet,^2J_P−H = 45 Hz), respectively. This complex could not be isolated pure (see Discussion section) because it formed an oil when the solvent was removed. Furthermore, the oil decomposed when the H_2 atmosphere was removed. Mass spectrometric analysis showed that the complex reacted with the N_2 purge gas to form $[Fe(DMeOPrPE)_2H(N_2)^+]$ in the mass spectrometer: m/z calcd for $[Fe(DMeOPrPE)_2H(N_2)^+]$ 849.43. Found: [M$^+$], 849.33. The complete mass spectrum and isotope pattern, which matches the calculated pattern, are found in the Supporting Information.

Generation of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]PF_6$ (III−PF_6). *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (0.100 g, 0.112 mmol), $TlPF_6$ (0.076 g, 0.224 mmol), and Proton Sponge (0.024 g, 0.112 mmol) were combined as solids in a 120 mL Fischer−Porter tube. Diethyl ether (5 mL) was added, and the resulting solution was immediately charged with 1 atm H_2. The solution turned from green to orange to a faint yellow with the production of a white precipitate (TlCl and protonated Proton Sponge) over a period of 1 h but was allowed to stir overnight to ensure completion of the reaction. The solution was then filtered through celite under an argon atmosphere. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a resonance at δ 88.9 (s), as well as at δ −143.0 (septet, J_P−F = 709 Hz). ^1H NMR spectrum (ethanol-d_6, −40 °C): δ 3.4 (br, m), 2.0 (br, m), 1.7 (br, m), 1.6 (m), −10.9 (s, br), and −15.1 (quintet,^2J_P−H = 45 Hz). As was the case for the complex with the chloride counterion above, this complex with the PF_6^- counterion could not be isolated (see Discussion section).

Alternative Generation of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]PF_6$ (III−PF_6). *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (0.4167 g, 0.4673 mmol), $TlPF_6$ (0.2579 g, 0.7382 mmol), and $NaBH_4$ (0.0713 g, 1.886 mmol) were combined in a Schlenk flask and cooled to −40 °C. The addition of 150 mL of pre-cooled ethanol (150 mL) resulted in a yellow-green turbid solution. After 6 h, the solution was transparent bright yellow and contained a metallic solid. The solution was filtered, and the solvent was removed using H_2 as a sweeping gas, yielding a yellow oil. Repeated attempts to obtain a solid from the oil were unsuccessful. $^{31}P\{^1H\}$ spectra of the reaction mixture showed major resonances at δ 88.9 (s) as well as δ −143.0 (septet, J_{P-F} = 709 Hz). ^1H NMR (CD_3OD) of the hydride region at − 40 °C showed resonances at δ −10.9 (s, br) and δ −15.1 (quint.,$^2J_{HP}$= 45 Hz).

Generation of *trans*-$[Fe(DMeOPrPE)_2H(N_2)]^+$. A solution containing *trans*-$[Fe(DMeOPrPE)_2H(H_2)]^+$ was prepared by either method described above. That solution was charged with 2 atm of

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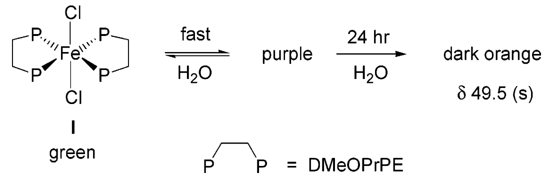
Scheme 1. Reaction of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (**I**) with H_2O over 24 h



N_2 and then stirred for 24 h. When the reaction is carried out in diethyl ether, the solution turns light yellow. When the reaction is carried out in H_2O, the solution turns from light yellow to light brown. The solvent in each case was removed using N_2 as the sweeping gas, yielding an oil. Repeated attempts to obtain a solid from the oil were unsuccessful. IR(neat): (ν_{NN}) 2093 cm^{-1}, (toluene) 2089 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_3$OD): δ 77.5 (s). ^{31}P NMR (CD$_3$OD): δ 77.5 (d,$^2J_{P-H} = 49$ Hz). ^{1}H NMR (CD$_3$OD): δ 3.6 (br, m), 3.3 (br, s), 2.0 (br, m), 1.6 (br, m), 1.2 (s), and −18.5 (quintet,^2J_P−H = 49 Hz).

Results and Discussion

Reactivity of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ (I) in H_2O. When green crystals of **I** were added to water, the crystals instantly dissolved to form a purple solution. No resonances were observed in the ^{31}P{^{1}H} NMR spectrum of the purple solution at room temperature. (The absence of resonances at room temperature is not unusual for Fe(P$_2$)$_2$X$_2$-type complexes, where P$_2$ is a bidentate phosphine. As shown in prior papers, this result can be attributed to either a diamagnetic/paramagnetic spin crossover or a rapid coordination/decoordination of the phosphine ligands.[37]) If the reaction of **I** in H_2O was allowed to proceed for 24 h at room temperature, the solution changed from purple to dark orange (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of the orange solution at room temperature showed only a single sharp resonance at δ 49.5 (s).[38] Repeated attempts to isolate the orange product by precipitation or by solvent removal were unsuccessful. Attempts to isolate the purple product were also unsuccessful because removing the water solvent merely regenerated **I**.

The orange product was successfully isolated by reacting *cis*-Fe(DMeOPrPE)$_2$SO$_4$ (instead of **I**) with H_2O. Dissolution of the purple *cis*-Fe(DMeOPrPE)$_2$SO$_4$ complex in H_2O gave a purple solution that turned dark orange over a period of 24 h. The ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed a single resonance at δ 49.5 (s), identical to the resonance that formed when **I** was dissolved and reacted in H_2O. On addition of BaX$_2$ (where X=ClO$_4^-$ or NO$_3^-$), a white precipitate of BaSO$_4$ formed. On removing the H_2O solvent from the filtered reaction mixture, an orange oil resulted, which still showed a ^{31}P{^{1}H} NMR resonance at δ 49.5 (s; ethanol-d_6).

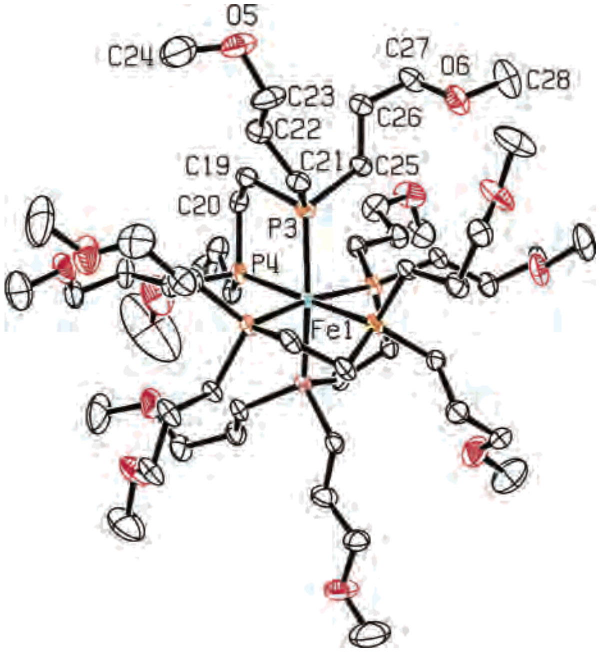


Figure 1. ORTEP plot (ellipsoids at 50% probability) of [Fe(DMeOPrPE)$_3$]-[ClO$_4$]$_2$ (**II−ClO$_4$**). The hydrogen atoms and counterions have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Fe(DMeOPrPE)$_3$][2ClO$_4$]

Fe(1)−P(4)	2.3484(13)	Fe(1)−P(5)	2.3482(14)
Fe(1)−P(1)	2.3668(14)	Fe(1)−P(2)	2.3296(13)
Fe(1)−P(6)	2.3554(13)	Fe(1)−P(3)	2.3548(14)
Fe−P (mean)	2.3505(5)	Fe^{II}−P(bidentate) (mean)[a]	2.282(2)
P(4)−Fe(1)−P(1)	94.73(5)	P(6)−Fe(1)−P(2)	95.07(5)
P(4)−Fe(1)−P(6)	88.21(5)	P(5)−Fe(1)−P(2)	89.46(5)
P(1)−Fe(1)−P(6)	93.86(5)	P(4)−Fe(1)−P(3)	83.16(5)
P(4)−Fe(1)−P(5)	94.21(5)	P(1)−Fe(1)−P(3)	90.77(5)
P(1)−Fe(1)−P(5)	170.29(5)	P(6)−Fe(1)−P(3)	170.53(5)
P(6)−Fe(1)−P(5)	82.60(5)	P(5)−Fe(1)−P(3)	94.09(5)
P(4)−Fe(1)−P(2)	175.38(5)	P(2)−Fe(1)−P(3)	93.77(5)
P(1)−Fe(1)−P(2)	81.82(5)		

[a] The average Fe−P distance from the complexes **I**, *trans*-Fe(DHBuPE)$_2$Cl$_2$, *trans*-[Fe(DHBuPE)$_2$(CO)(OSO$_3$), *trans*-Fe(DMeOPrPE)$_2$Br$_2$, *trans*-[Fe(DHBuPE)$_2$ (CO)Cl]$^+$, and *trans*-Fe(DHPrPE)$_2$(CO)(OSO$_3$) (DHPrPE = 1,2-bis(bis(hydroxypropyl)phosphine)ethane).

X-ray analysis of orange crystals grown from the orange oil revealed that the product was the octahedral, homoleptic tris−chelate complex, [Fe(DMeOPrPE)$_3$][ClO$_4$]$_2$ (**II**−ClO$_4$; Figure 1; Tables 1 and 2). To our knowledge, this is the first X-ray structural report of a homoleptic Fe^{II} complex containing three bidentate phosphine ligands. (Although homoleptic Fe^{II} complexes with the bidentate DMPE and DEPE phosphine ligands were recently synthesized,[39] no structural data were reported.) The average Fe−P distance in **II−ClO$_4$** is 2.35 Å, which is relatively long and indicative of severe steric crowding at the Fe^{II} center. (For comparison, the average of the Fe−P distances in **I**, *trans*-Fe(DHBuPE)$_2$Cl$_2$, *trans*-[Fe(DHBuPE)$_2$(CO)(OSO$_3$), *trans*-Fe(DMeOPrPE)$_2$Br$_2$, *trans*-[Fe(DHBuPE)$_2$ (CO)Cl]$^+$, and *trans*-Fe(DHPrPE)$_2$-

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(38) The ^{1}H NMR spectra of the molecules reported herein are relatively broad and generally similar to the spectra of the uncoordinated phosphine ligand. Consequently, they were nondiagnostic in terms of checking for either purity of the sample or the identity of the molecule. In contrast, the ^{31}P{1H} NMR spectra, when observable, were simple, had no overlapping resonances, and were spread over a wide range of chemical shifts. Thus, they provided an excellent means for characterizing and identifying the products and for checking their purity. For free ligand ^{1}H NMR spectra, see Herbowski, A.; Deutsch, E. A. *J. Organomet. Chem.* **1993**, *460*, 19 and reference 29.

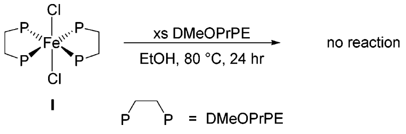
(39) La Pensee, A. A.; Bickley, J.; Higgins, S. J. *J. Chem. Soc. Dalton Trans.* **2002**, 3241−3244.

Table 2. Crystal Data and Structure Refinement for [Fe(DMeOPrPE)$_3$][2ClO$_4$]

identification code	jdg16sx	
empirical formula	$C_{54}H_{120}Cl_2FeO_{20}P_6$	
fw	1401.62	
temp	153(2) K	
wavelength	0.71073 Å	
cryst syst	monoclinic	
space group	$C2/c$	
unit cell dimens	$a = 25.5544(19)$ Å	
	$b = 14.0778(10)$ Å	$\beta = 106.718(2)°$
	$c = 41.888(3)$ Å	
vol	14432.2(18) Å^3	
Z	8	
density (calcd)	1.290 Mg/m^3	
absorption coefficient	0.480 mm^{-1}	
F(000)	6027.966	
cryst size	0.11 × 0.23 × 0.27 mm^3	
θ range for data collection	1.660−28.304°	
index ranges	$-10 \le h \le 32$ $-18 \le k \le 18$ $-49 \le l \le 43$	
reflns collected	26 802	
independent reflns	14 383, 8436 ($I > 2.0\sigma(I)$)	
R_{int}	0.026	
absorption correction	none	
refinement method	full-matrix least-squares on F^2	
data/restraints/params	8436/0/757	
GOF on F^2	0.94	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0585, wR2 = 0.1280	
R indices (all data)	R1 = 0.1094, wR2 = 0.1516	
largest diff. peak and hole	0.86 and −0.44 e.Å^{-3}	

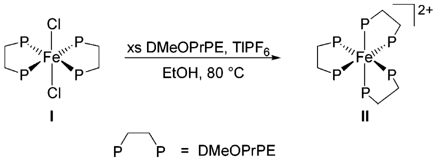
(CO)(OSO$_3$) (DHPrPE = 1,2-bis(bis(hydroxypropyl)phosphine)ethane) is 2.28 Å).[29]

In order to investigate the mechanism by which **II** is formed, **I** was reacted in EtOH with excess DMeOPrPE ligand. However, a solution of **I** with 10 equiv of DMeOPrPE in EtOH heated to 80 °C for 24 h gave no **II** (eq 1), as indicated by the absence of a peak at δ 49.5 in the ^{31}P{^{1}H} NMR spectrum.



(1)

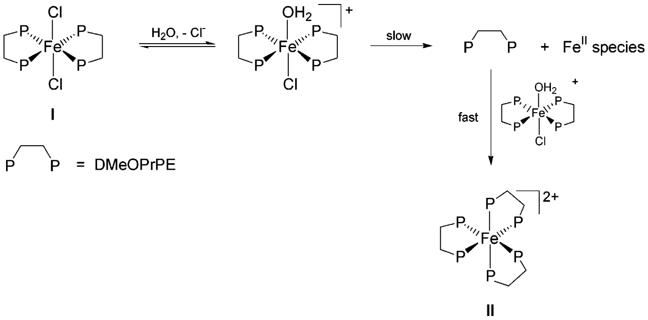
Only on addition of 2 equiv of TlPF$_6$, a Cl$^-$ abstractor, did **II** form (eq 2):

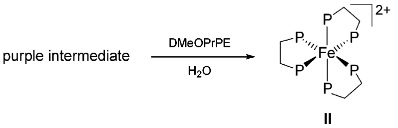


(2)

The mechanistic implication of these results is that a chloride ligand must be removed from **I** in order for **II** to form. It is suggested that, because water is an excellent medium for solvating chloride ions, a chloride ligand will dissociate from complex **I** in H$_2$O but will not dissociate from **I** in EtOH. In support of this suggestion, it was found that added chloride inhibited the formation of the purple intermediate (and consequently also **II**, see Scheme 1) when crystals of **I** were added to an aqueous solution of NaCl (1M).[40] Following chloride loss in water, it is proposed that some dissociation of DMeOPrPE ligand occurs from the purple intermediate, which can then react with the purple intermediate to form **II**.[41] A straightforward experiment confirmed this last suggestion: addition of free DMeOPrPE ligand to an aqueous solution of the purple intermediate resulted in the immediate formation of a dark orange solution. The ^{31}P NMR spectrum of this solution showed the formation of [Fe(DMeOPrPE)$_3$]$^{2+}$ (δ 49.5), eq 3. To reiterate, the slow formation of **II** over 24 h in Scheme 1 is likely due to slow dissociation of DMeOPrPE ligand from the purple complex.

Scheme 2. Reactivity of the *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ Complex in Aqueous Solution





(3)

The stoichiometry of the reaction that forms **II** from **I** in Scheme 1 was established by integrating the resonance at δ 49.5 in an inverse-gated ^{31}P{^{1}H} NMR spectrum of a solution of **I** reacted in H$_2$O for 24 h. The integration, referenced to an internal [P^{n}Bu$_4$]Br standard, revealed[42] that 9.74 × 10^{-2} mmols of **II** formed from 1.85 × 10^{-1} mmol of **I**. (The integration did not change after the addition of 10 equiv of DMeOPrPE and 2 equiv of TlPF$_6$ to the reaction solution.) The 2:1 stoichiometry in eq 4 is thus suggested:[43]

$$2\,\mathrm{Fe(P_2)_2X} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{II}}{[\mathrm{Fe(P_2)_3}][\mathrm{X}]} + \mathrm{P_2} + \mathrm{Fe^{II}X} \qquad (4)$$

P_2 = DMeOPrPE
X = SO_4^{2-} or 2 Cl^-

Identification of the Purple Intermediate. Although the purple intermediate formed on addition of **I** to water could not be isolated, several experiments suggest that this species is the *trans*-Fe(DMeOPrPE)$_2$(H$_2$O)Cl$^+$ complex: (1) Addition of excess NaCl to an aqueous solution of the purple complex (generated by the addition of **I** to water) results in

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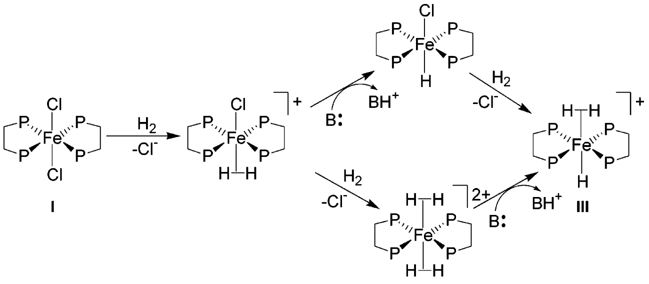
(40) The inhibition was complete because crystals of **I** did not dissolve when they were added to the aqueous solution of NaCl.

(41) In a similar set of experiments, no reactivity was observed when *cis*-Fe(DMeOPrPE)$_2$SO$_4$ was heated to 80 °C in EtOH in the presence of 10 equivalents of DMeOPrPE. In this case, conversion to **II** was achieved only on addition of Ba(ClO$_4$)$_2$, as monitored by ^{31}P{1H} NMR spectroscopy. The interpretation of these results is analogous to the interpretation above for the reactivity of **I**: addition of Ba^{2+} removes the sulfate ligand as BaSO$_4$ (s), which leads to DMeOPrPE ligand dissociation from the complex. The uncoordinated ligand in turn reacts with an aquated Fe(II) species to form **II**.

(42) See Supporting Information for details.

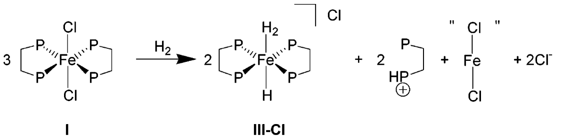
(43) No free phosphine is observed. It is likely bound to FeX^{n+}; see refs. 44−46.

Scheme 3. Possible Pathways for the Heterolysis of H_2 in Nonaqueous Solvents

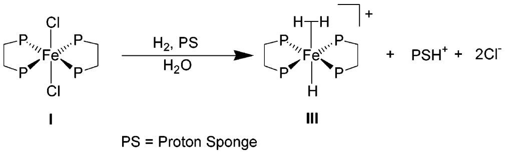


the rapid re-formation (and precipitation) of **I**. (2) Formation of the purple complex is inhibited when **I** is added to a 1M NaCl aqueous solution. (3) Complex **I** is regenerated when the water is removed from an aqueous solution of the purple intermediate generated from **I**. (4) The analogous *trans*-Fe(DHBuPE)$_2$(H$_2$O)(OSO$_3$) complex forms when *cis*-Fe(DHBuPE)$_2$SO$_4$ is dissolved in water.[29] In summary of these results, it is proposed that **I** reacts in water according to Scheme 2.

Reactivity of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ with H$_2$. *Heterolytic Activation of H$_2$.* Previously, we reported that **I** reacted with H_2 in aqueous solvents to give products resulting from H_2 heterolysis (eq 5).[30] Specifically, it was shown that **I** reacted with 2 equiv of H_2 in H_2O to produce *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]Cl (**III**−Cl) and H^+. The protons released in the formation of **III**−Cl were shown to react with complex **I** to degrade it and form [DMeOPrPEH$^+$],[30] and the reaction stoichiometry in eq 5 was established. The present study found that **I** could be quantitatively converted to **III**−Cl by addition of Proton Sponge (1,8 bis-(dimethylamino)napthalene)[47] to the reaction solution (eq 6). Alternatively, **III**−Cl was quantitatively formed if the reaction of **I** with H_2 was run in a pH 7 aqueous solution buffered with MOPS (3-(N-morpholino)propanesulfonic acid).



(5)

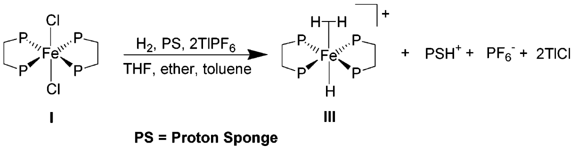


(6)

Complex **III**−Cl is fluxional, as shown by the variable temperature ^{1}H NMR spectra of the hydride region (Figure S3 in the Supporting Information). At temperatures above 253 K, the hydride region in the ^{1}H NMR spectra can be explained by an intramolecular exchange process $[M(\eta^2\text{-}H_2)(H^*)P_4]^+ \rightleftharpoons [M(\eta^2\text{-}HH^*)(H)P_4]^+$, as has been reported for other $[Fe(\eta^2\text{-}H_2)(H)P_4]^+$ complexes.[48,49] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the exchange of the hydrogen atoms in *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$ are 12.0 ± 1.3 kcal/mol and 4.0 ± 3.2 cal/mol K, respectively, as measured by the line broadening method over the temperature range −20 to 25 °C.[2] (See Supporting Information for the Eyring plot.) These values are similar to values reported for analogous complexes. (See Table 10, page 197 in reference 2.)

Although complex **III**−Cl is stable in H_2O for weeks, attempts to isolate the complex were unsuccessful because it degraded when the solvent was removed under vacuum. Likewise, removing the solvent with H_2 as a sweeping gas yielded a yellow oil of **III**−Cl that decomposed when the H_2 atmosphere was removed.[50] Finally, it is noted that attempts to isolate **III**−Cl by adding a nonpolar solvent and precipitating the complex were also unsuccessful. The reason is that the DMeOPrPE ligand imparts solubility to many complexes in solvents spanning a wide range of polarities (generally from H_2O to hexanes).[51] Thus, addition of a nonpolar solvent had no effect on the solubility and the complex could not be precipitated from solution.[52]

The H_2-heterolysis reactions in eqs 5 and 6 were also investigated in nonpolar solvents. When solutions of **I** in diethyl ether, THF, or toluene were charged with 2 atm of H_2, no reaction occurred. Addition of Proton Sponge to the reaction mixture also yielded no reaction. However, on addition of a chloride abstractor (such as TlPF$_6$) an immediate reaction was observed, as indicated by a color change (from green to orange to yellow) and by the appearance in the ^{31}P-{^{1}H} NMR spectrum of a resonance at δ 88.9 (s), assigned to complex **III**−**PF$_6$** (eq 7). Additional NMR experiments using an internal standard indicated quantitative conversion of **I** to **III**−**PF$_6$** in these reactions:[30]



(7)

The H$_2$-Heterolysis Pathway. As discussed in a prior section, chloride ligand dissociation from complex **I** does not occur spontaneously in nonaqueous solvents, and therefore addition of a chloride abstractor is required to produce an open coordination site for bonding the H_2 ligand. Following the addition of H_2 there are two possible pathways for the formation of **III**−Cl (Scheme 3). The H_2 can either be heterolytically cleaved by reaction with a base (top path,

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(44) Levason, W.; McAuliffe, C. A.; Khan, M. M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1975**, 1778−83.

(45) Baker, W. A. Jr.; Lutz, P. M. *Inorg. Chim. Acta* **1976**, *16*, 5−8.

(46) Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763−8.

(47) Decomposition of **I** was observed when conventional bases, such as hydroxide or an amine, were used.

(48) 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*, 4876−87.

(49) An example of intramolecular exchange by a pendant amine base was recently reported by Dubois and Dubois. See Henry, R. M.; Shoemaker, R. K.; Newell, R. H.; Jacobsen, G. M.; Dubois, D. L.; Dubois, M. R. *Organometallics* **2005**, *24*, 2481.

(50) Hydrogen bonding (DHHB) with the solvent is proposed to be responsible for the observed stability of **III-Cl** in H_2O. Szymczak, N. K.; Zakharov, L. N.; Tyler, D. R. *J. Am. Chem. Soc.* **2006**, *128*, 15830−15835.

(51) All of the complexes mentioned in this paper are soluble in H_2O except *trans*-[Fe(DMeOPrPE)$_2$(CH$_3$CN)$_2$][PF$_6$]$_2$, which is described in the Supporting Information.

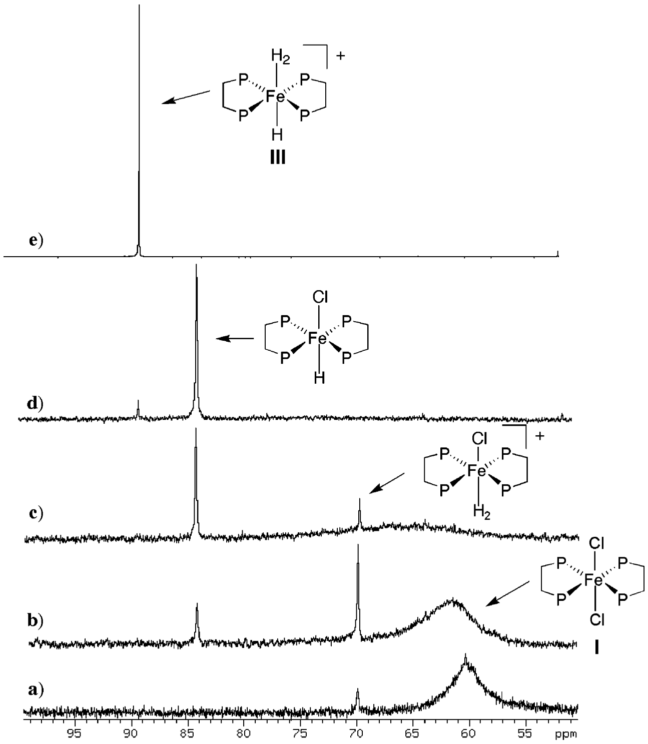

Figure 2. $^{31}P\{^1H\}$ NMR spectra (toluene-d_8) of **I**, 2 equiv of $TlPF_6$, 1 equiv of Proton Sponge, and H_2 (1 atm) after (a) 3 min at −15 °C, (b) 16 min at 0 °C, (c) 19 min at 0 °C, (d) 22 min at 15 °C, and (e) 12 h at room temperature. Species are as follows: δ 60, (**I**); δ 69.8, *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$; δ 83.5, *trans*-$Fe(DMeOPrPE)_2HCl$; δ 88.9, (**III**).

Scheme 3), or a second H_2-substitution may occur to give a *bis*-η^2-H_2 species (bottom path, Scheme 3). Note that *bis*-η^2-H_2 complexes are uncommon and typically are only stabilized by second- and third-row transition metals such as ruthenium or osmium.[53,54]

NMR spectroscopy provided evidence for the upper pathway in Scheme 3. Immediately after the addition of two equivalents of $TlPF_6$ and one equivalent of Proton Sponge to a toluene-d_8 solution of **I** in an NMR tube, the solution was frozen in liquid nitrogen. While frozen, the headspace of the NMR tube was evacuated and backfilled with an atmosphere of H_2. As shown in Figure 2, the $^{31}P\{^1H\}$ spectrum shows that after approximately 3 min at −15 °C a new species was formed. (The ^1H NMR spectrum of the reaction solution shows the same result. See Figure S4 in the Supporting Information). This new species is assigned as the *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$ complex. This assignment is based on observation of a singlet resonance at δ 69.8 (s) in the $^{31}P\{^1H\}$ NMR spectrum, indicative of a trans geometry, and a broad resonance at δ −24.2 (s, br) in the ^1H NMR spectrum, which is typical of an η^2-H_2 ligand.[1,2] By analogy to other *trans*-$[Fe(P_2)_2(H_2)Cl]^+$ complexes (where P_2 = a bidentate phosphine), the H_2 ligand in *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$ is likely acidic[2] and is subsequently deprotonated to yield *trans*-$Fe(DMeOPrPE)_2(H)Cl$. This argument is supported by the observation that after ≈10 min at −15 °C the resonance characteristic of *trans*-$Fe(DMeOPrPE)_2(H)Cl$ at δ 83.5 began to appear with a concomitant decrease in the resonances assigned to *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$ (Figure 2). Similar observations were observed in the ^1H NMR spectrum; Figure S4. Note that *trans*-$Fe(DMeOPrPE)_2(H)Cl$ was generated independently[42] and has a characteristic resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 83.5, identical to that observed in Figure 2. That this species is a hydride is indicated by the doublet in the ^{31}P (uncoupled) NMR spectrum at δ 83.5 and the quintet observed in the ^1H NMR spectrum at δ −31.8. Both resonances have $J = 45$ Hz, indicative of *cis* P−H coupling.[55] The subsequent substitution of the second Cl^- by H_2 to yield **III**−Cl is slow in the NMR tube, likely because of poor mixing. As shown in Figures 2 and S4, after 12 h at room temperature all of the orange *trans*-$Fe(DMeOPrPE)_2(H)Cl$ was converted to **III**−Cl. In summary, these data strongly suggest that the pathway for the heterolysis in nonaqueous solvents occurs through the top pathway in Scheme 3.[48,56]

In H_2O, the mechanism of the reaction with H_2 to give *trans*-$[Fe(DMeOPrPE)_2H_2H]^+$ is proposed to be the same as in nonaqueous solvents. Recall that, in water, chloride dissociates from complex **I** without assistance from a chloride abstractor. A vacant coordination site is thus available for the entering H_2 ligand, if it is introduced immediately to the system. (Control experiments showed that **II** is inert to the reaction with H_2.) The reaction of **I** with H_2 is evident by the immediate color change from purple to light yellow upon charging the system with H_2. As shown in Figure S5 in the Supporting Information, both the intermediate species *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$ and *trans*-$Fe(DMeOPrPE)_2HCl$ are observed after 6 min at −15 °C in an NMR experiment similar to the one described above in toluene (with ethanol-d_6/D_2O, 60/40 wt %, substituted for toluene-d_8). After 9 min at −15 °C, **III**−Cl is present in significant quantity, suggesting that the deprotonation and subsequent substitution (Scheme 3, top) are very fast.

While intermolecular heterolysis cannot be ruled out, the fact that the heterolysis of coordinated H_2 is achieved without the addition of an external base (and that a protonated phosphine forms) suggests that the deprotonation step occurs in an intramolecular step. Restated, it is suggested that an uncoordinated arm of the phosphine ligand may act as the base. Alternatively, because most dihydrogen complexes are known to be acidic ($pK_a < 15.7$),[57] it is possible that H_2O is basic enough to deprotonate the *trans*-$[Fe(DMeOPrPE)_2(H_2)Cl]^+$ intermediate. This latter suggestion is consistent with the observation that no free phosphine was observed and that

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(52) The ligand DMeOPrPE is somewhat of a “universal solubilizer.” Neutral complexes, such as **I**, and even cationic species, such as of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]PF_6$ (**III-PF$_6$**) (discussed below), are soluble in solvents ranging from H_2O to hexane. This selectivity obstacle is another corollary (the first being H_2O as a ligand or reactant) that needs to be considered when bridging traditional nonaqueous chemistry with aqueous chemistry.

(53) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473−80.

(54) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *178−180*, 381−407.

(55) See the references in Table 1 of ref 30.

(56) A similar mechanism has been proposed in the *trans*-$Fe(depe)_2Cl_2$ system.

(57) Fong, T. P.; Lough, A. J.; Morris, R. H.; Mezzetti, A.; Rocchini, E.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2111−2114.

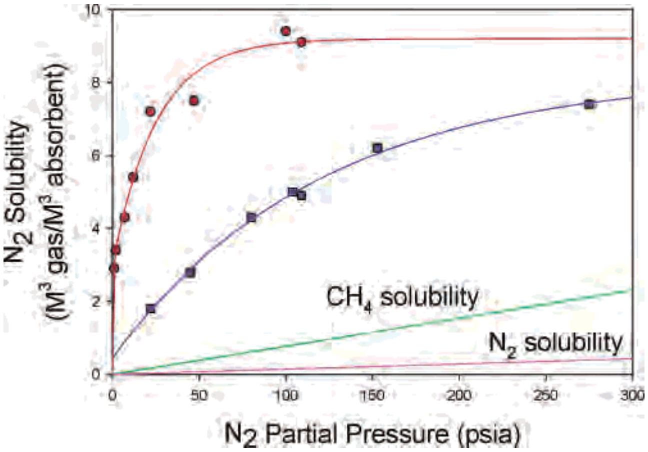
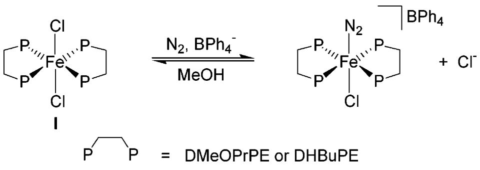


Figure 3. N_2 binding isotherms for **I** in dyglme (blue) and *trans*-Fe-(DHBuPE)$_2$HCl in H_2O (red). The chloride abstractor, $NaBPh_4$ (1 equiv) was used in the experiments involving **I**. The physical solubilities of N_2 and CH_4 are also shown. The metal complex concentrations were 0.2 M.

the conversion of **I** to **III**−Cl was quantitative in aqueous solution buffered at pH 7 with MOPS.

In summary, **I** is inert to H_2 in nonaqueous solvents in the absence of a chloride abstractor and extraneous base. In H_2O, however, the reaction with H_2 is facile. In this latter reaction, H_2O provides the medium necessary for the dissociation of the chloride ligand(s), which allows for the coordination and subsequent cleavage of H_2.

Reactivity of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ and *trans*-Fe-(DHBuPE)$_2$(H)Cl with N$_2$. In order to utilize a reversibly binding N_2−metal complex in a natural gas purification scheme, the absorbent complex must be soluble in a solvent in which methane is not (e.g., H_2O) and the absorbent must be able to reversibly bind N_2 under relatively gentle conditions (i.e., at low temperature and pressures). In an earlier paper,[29] we reported that *trans*-Fe(DHBuPE)$_2$Cl$_2$ and *trans*-Fe(DMeOPrE)$_2$Cl$_2$ reacted in methanol with N_2 in the presence of $NaBPh_4$ to yield the products *trans*-[Fe(DHBuPE)$_2$-(N$_2$)Cl]BPh$_4$ and *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)Cl]BPh$_4$, respectively (eq 8). IR spectroscopy showed this reaction was reversible, as indicated by the appearance of an N≡N stretch at 2094 cm^{-1} when the solution was exposed to N_2 and the disappearance of the peak when N_2 was removed.



(8)

The present study extended this result to aqueous solution, in which it was found that the *trans*-Fe(DHBuPE)$_2$HCl complex reacted with N_2 in a reaction analogous to that in eq 8. (The *trans*-Fe(DHBuPE)$_2$HCl complex was used in this study because it can be isolated and purified.[42] Recall that the *trans*-Fe(DMeOPrE)$_2$HCl species could not be isolated pure.) The isotherm for the uptake of N_2 by *trans*-Fe-(DHBuPE)$_2$HCl in H_2O is shown in Figure 3.

Table 3. Effective Magnetic Moments (μ_B) at 23 °C of a Series of *trans*-Fe(P$_2$)$_2$Cl$_2$ Complexes in Various Solvents

complex	toluene-d_8	THF-d_8	MeOH-d_4
trans-Fe(DEPE)$_2$Cl$_2$[a]	0.59	0.73	
trans-Fe(DMeOPrPE)$_2$Cl$_2$	0.63	1.03	1.18
trans-Fe(DPrPE)$_2$Cl$_2$[a]	0.69	1.23	

[a] Values taken from ref 37.

The effect of the *trans* ligand on the N_2 binding was studied by comparing *trans*-Fe(DHBuPE)$_2$HCl to *trans*-Fe-(DMeOPrE)$_2$Cl$_2$. Although water is the solvent of choice for N_2-scrubbing reactions, it was not possible to use *trans*-Fe-(DMeOPrE)$_2$Cl$_2$ in aqueous solution because the complex reacts with water (Scheme 2). Diglyme was therefore used in its place. The isotherm for the uptake of N_2 by *trans*-Fe-(DHBuPE)$_2$HCl in diglyme is also shown in Figure 3. Note that the *trans*-Fe(DMeOPrE)$_2$Cl$_2$ complex is not as efficient at binding N_2 as *trans*-Fe(DHBuPE)$_2$HCl. (Also note that the solubility of N_2 in H_2O and diglyme is essentially the same,[58] indicating that the increase in N_2 absorption with the Fe complexes present is attributed only to an Fe−N_2 bonding interaction.)

A likely explanation for the difference in N_2-binding ability comes from the work of Tuczek,[59,60] who reported that the lability of the Fe−N_2 bond in the [FeCl(N$_2$)(DEPE)$_2$]$^+$ complex compared to [FeH(N$_2$)(DEPE)$_2$]$^+$ (where DEPE is 1,2-bis(diethylphosphino)ethane) is due to thermal population (at room temperature) of a dissociative triplet state along the Fe−N coordinate in [FeCl(N$_2$)(DEPE)$_2$]$^+$. In contrast, the Fe−N reaction coordinate for the [FeH(N$_2$)(DEPE)$_2$]$^+$ complex does not have such a spin crossover, and hence this molecule is more thermally stable.

The substantially stronger N_2-binding isotherm for the *trans*-Fe(DHBuPE)$_2$HCl complex compared to *trans*-Fe-(DMeOPrE)$_2$Cl$_2$ is also apparent from the reversibility of the reaction of these complexes with N_2. As previously reported, the reaction of *trans*-Fe(DMeOPrE)$_2$Cl$_2$ with N_2 was completely reversible at room temperature.[29] That is, a reversible disappearance/reappearance of the IR stretch and resonance in the $^{31}P\{^1H\}$ NMR spectrum was observed after venting the reaction vessel and subsequently re-exposing it to N_2. The *trans*-Fe(DHBuPE)$_2$HCl complex, on the other hand, requires heating to 85 °C under reduced pressure to achieve desorption of the N_2.

In summary of this section, it is noted that these complexes fulfill the three requirements of a viable dinitrogen scrubber. First, the complexes are soluble in solvents in which dinitrogen and methane are not appreciably soluble (H_2O and, for the purpose of this study, diglyme). Second, they have a propensity to bind and release the dinitrogen under non-severe conditions. And finally, the complexes are stable for weeks under absorption/desorption conditions.

Solution Magnetic Behavior of I and II. In prior studies,[37] it was shown that water-insoluble Fe(P$_2$)$_2$X$_2$-type complexes are paramagnetic in solution (although not in the

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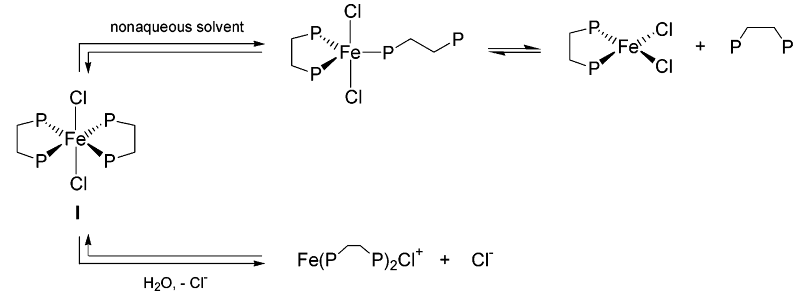
(58) Diglyme was utilized in these studies due to the reactivity of **I** with H_2O.

(59) Franke, O.; Wiesler, B. E.; Lehnert, N.; Naether, C.; Ksenofontov, V.; Neuhausen, J.; Tuczek, F. *Inorg. Chem.* **2002**, *41*, 3491−3499.

(60) Franke, O.; Wiesler, B. E.; Lehnert, N.; Tuczek, F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2395−2402.

Scheme 4. Coordination Equilibria of the Ligands in the *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ Complex in Solution



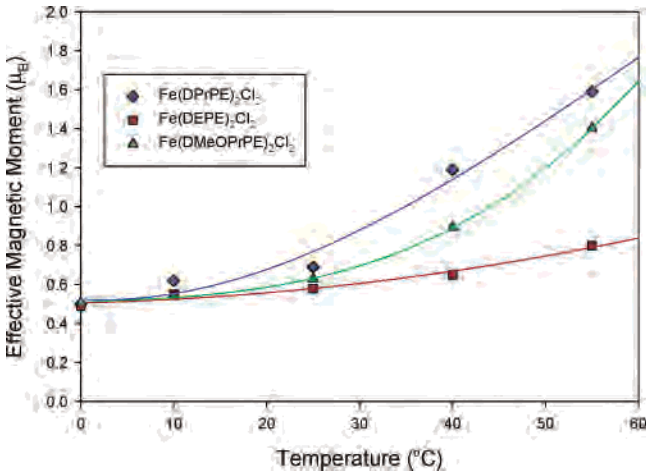


Figure 4. Plots of magnetic moments in solution for a series of *trans*-Fe(P$_2$)$_2$Cl$_2$ complexes (P$_2$ = a bidentate phosphine) as a function of temperature (°C) in toluene. *trans*-Fe(DPrPE)$_2$Cl$_2$ and *trans*-Fe(DEPE)$_2$Cl$_2$ data from ref 37.

solid state), and the magnetic moment in solution typically increases with increasing temperature. (Their paramagnetism in solution explains why there are no observable resonances in the $^{31}P\{^1H\}$ NMR spectrum at room temperature.) The solution paramagnetism and the increase in the magnetic moment with increasing temperature were attributed to equilibria involving decoordination/recoordination of a bidentate phosphine ligand (top reaction in Scheme 4). To probe the magnetic behavior of **I** in nonaqueous solvents, the solution paramagnetism was measured by the Evans method in toluene at various temperatures. A plot of magnetic moment versus temperature is shown in Figure 4. Note that, as in the case of the water-insoluble analogues, the magnetic moment increases with increasing temperature.

Additional measurements showed that complex **I** is diamagnetic in the solid state. To probe if the solution paramagnetism is caused by rapid decoordination/recoordination of a phosphine ligand, the room temperature $^{31}P\{^1H\}$ NMR spectra of **I** and *cis*-Fe(DMeOPrPE)$_2$SO$_4$ were obtained in EtOH both with and without 10 added equivalents of DMeOPrPE. Consistent with the decoordination/ recoordination hypothesis, resonances were observed only in the solutions containing the added DMeOPrPE.[42] It is suggested that addition of the ligand drives the equilibria toward a diamagnetic six-coordinate species. (In a related experiment, addition of 10 equiv of LiCl to an ethanol solution of **I** had no effect on the room temperature ^{31}P NMR spectrum, a result which suggests that Fe−Cl bond dissociation is likely not involved in the solution paramagnetism.)

Additional experiments showed that the solution paramagnetism of **I** (and the other *trans*-Fe(P$_2$)$_2$Cl$_2$ complexes) increases with increasing solvent polarity (Table 3). Presumably, the species in which one arm of the bidentate phosphine is uncoordinated, and the species in which total loss of the bidentate ligand occurs[44−46] (top reaction in Scheme 4) are polar and are stabilized in a more polar solvent.

One final observation about the magnetic properties of these species needs comment, namely, the observation that the $^{31}P\{^1H\}$ NMR resonance of **II** is observable at room temperature, while that of **I** is only observable at lower temperatures (e.g., −40 °C). Apparently, ligand decoordination/recoordination in **II** is slow on the NMR time scale. This result is attributed to the higher molecular charge in **II** compared to **I**. Consistent with this observation, experiments to measure the magnetic moment by the Evans method showed that solutions of pure **II** are diamagnetic at room temperature. Note, however, that the product-containing solution from the reaction of **I** with H_2O (which contains **II**) has a magnetic moment that increases with increasing temperature. This observation can be explained by the fact that when **II** is formed (eq 1), unligated (or low-coordinate) Fe^{II} is also formed. Aqueous Fe(II) is high spin (as is low-coordinate Fe^{II})[44−46] and this accounts for the observation of the high solution moments. Finally, recall that a chloride abstractor such as TlPF$_6$ is required in the reaction of **I** with H_2 in nonaqueous solvents. This result suggests that H_2 will not react at a vacant coordination site created by dissociation of a phosphorus atom of a coordinated phosphine in **I**. In other words, the mechanism for the reaction of **I** with H_2 does not involve the sequence: dissociation of a Fe−P bond, addition of H_2, followed by displacement of chloride by a recoordinating P atom.

Key Insights and Conclusions

Water-soluble complexes with H_2 and N_2 ligands are uncommon, and this study reports a number of new such complexes based on an Fe−bis(bidentate phosphine) scaffold. Because of their ability to bind N_2 or H_2 in aqueous solution, a potential application for these complexes is as gas scrubbers to separate N_2 or H_2 from gas streams. This study demonstrated that complexes **I**, **III** and *trans*-Fe(DHBuPE)$_2$HCl all bind N_2. Because of its high N_2 binding, the latter complex in particular may be potentially useful for the separation of N_2 from CH_4 in a pressure swing scheme. The ease of N_2

release in these complexes is affected by the trans ligand; the N_2 ligand is bound more strongly trans to hydride than trans to chloride, a result likely explained by the presence or absence of spin crossover in these complexes. With regard to H_2 binding, it is noted that the H_2 ligand is acidic, which often leads to the formation of a hydride complex, as was observed in the reaction of *trans*-Fe(DMeOPrPe)$_2$Cl$_2$ with H_2 to form *trans*-Fe(DMeOPrPe)$_2$(H$_2$)H$^+$.

A fundamental concern when doing aqueous transition metal chemistry is that water is a potential reactant.[61] For example, the ability of water to substitute for ligands or to hydrolyze complexes is well-known. This study highlighted another characteristic of water that must be considered when doing aqueous chemistry, namely the ability of water to induce ligand dissociation from a complex because of its increased polarity and solvating ability compared to organic solvents. In particular, it was found that chloride ligand readily dissociates from **I** in aqueous solution. This reactivity is not found in nonaqueous solvents, where instead an equilibrium involving coordinated and uncoordinated phosphine ligands occurs (Scheme 4).

Finally, it is noted that the ability to carry out the H_2 heterolysis reaction in eq 7 in a range of solvents, as was demonstrated herein, has potential applications in a number of areas. For example, the heterolytic cleavage of H_2 is proposed to be an important step in ionic hydrogenation reactions of polar double bonds.[62,63] If an appropriate catalyst could be developed that was soluble in a range of solvents then a wider array of molecules with varying functional groups would be accessible for such hydrogenations.

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Supporting Information Available: Syntheses of *trans*-[Fe(DMeOPrPE)$_2$(MeCN)$_2$][PF$_6$]$_2$, *trans*-Fe(DHBuPE)$_2$HCl, and *trans*-Fe(DMeOPrPE)$_2$HCl. Crystallographic information for *trans*-[Fe(DMeOPrPE)$_2$(MeCN)$_2$][PF$_6$]$_2$ and *cis*-Fe(DHBuPE)$_2$(SO$_4$), including the .cif files and tables of bond lengths and angles. Mass spectra, including isotope patterns, of *trans*-[Fe(DMeOPrPE)$_2$H(CO)]$^+$, *trans*-[Fe(DMeOPrPE)$_2$H(CH$_3$CN)]$^+$, *trans*-[Fe(DMeOPrPE)$_2$H(N$_2$)]$^+$, and **II**. Variable-temperature ^{1}H NMR spectra of **III.** ^{1}H NMR spectra of the formation of **I**. ^{31}P{^{1}H} NMR spectra (−15 °C) of the reaction mixture of **I** with H$_2$. ^{31}P{^{1}H} NMR spectra of **I** and *cis*-Fe(MeOPrPE)$_2$(SO$_4$) with excess DMeOPrPE. This material is available free of charge via the Internet at http://pubs.acs.org.

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