Supporting Information

H_2 Activation in Aqueous Solution: Formation of *trans*-$[Fe(DMeOPrPE)_2H(H_2)]^+$ via the Heterolysis of H_2 in Water

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Materials and Reagents. Unless otherwise noted, all manipulations were carried out in an argon-filled Vacuum Atmospheres Co. glove box or on a Schlenk line using argon or nitrogen. The 1,2-(bis(methoxypropyl)phosphino)ethane and *trans*-$Fe(DMeOPrPE)_2Cl_2$[10] were prepared as reported previously. Reagent grade ethanol, nitromethane, and sodium tetrahydroborate were obtained from Aldrich. The nitromethane was distilled from $CaCl_2$ and ethanol was distilled from Mg turnings. These solvents were deoxygenated with either three freeze-pump thaw cycles or an argon purge before being brought into the glove box. Water was purified to a resistivity of 17-18 MΩ-cm with a Barnstead Ultrapure system and deoxygenated with an argon purge before use. Solutions of 0.2M $HClO_4$ in nitromethane (made by dilution of 8.4 ml reagent grade 70% $HClO_4$ (Baker) with 500 ml nitromethane) were degassed with an argon purge before being brought into the glovebox.

Instrumentation and Procedures. $^{31}P\{^1H\}$ NMR and ^1H NMR were run 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 NMR and $^{31}P\{^1H\}$ NMR 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 7mm tubes fitted with Teflon valves. Samples that were run under pressure were sealed in high-pressure tubes and sealed with a Teflon valve. pH and mV measurements were performed with an Orion model 230 A pH meter equipped with a glass electrode and a Ag/AgCl reference electrode.

Generation of *trans*-[Fe(DMeOPrPE)$_2$H(H$_2$)]Cl. *trans*-$Fe(DMeOPrPE)_2Cl_2$ (0.100g, 0.112mmol) was dissolved in 5 mL 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 stirred and at ambient temperature. The solution changed color from deep purple to transparent yellow over a period of twenty minutes, but was allowed to stir overnight to ensure completion of the reaction. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a major resonance at δ 88.9(s). ^1H NMR (ethanol-d_6/D_2O; 60:40 wt%) of the hydride region at – 40°C showed resonances at δ –10.9 (s, br) and δ –15.1 (quintet, $^2J_{P\text{-}H}$= 45 Hz).

Generation of *trans*-[Fe(DMeOPrPE)$_2$H(HD)]Cl. To an NMR tube containing *ca*. 10 mg (0.001 mmol) *trans*-$Fe(DMeOPrPE)_2Cl_2$ with an excess of $NaBH_4$ was added 0.5 mL CD_3CD_2OD. The addition was accompanied by gas evolution (HD) and a color change from green/brown to yellow. After two hours a ^1H NMR spectrum (-40°C) was obtained revealing a 1:1:1 triplet at δ –10.9 ($^1J_{HD}$ = 29.8 HZ).

Determination of p*K*a's of DMeOPrPE. In a typical experiment, the method of Allman and Goel[38] was employed. A millimole of material was dissolved in 25 mL of nitromethane and titrated with 0.2 M perchloric acid solution. Three separate titrations were performed on both a reference material (PPh_3), and DMeOPrPE. The endpoints were determined from derivative plots and the half neutralization potentials (HNPs) were recorded. Aqueous p*K*a values were determined algebraically within ± 0.2 pK_a units using the formula of Streuli[39] and the value of HNP for PPh_3 as a reference.

Generation of DMeOPrPEH$^+$. DMeOPrPE (0.050g, 0.131 mmol) was dissolved in 10 mL of CH_2Cl_2. The resultant solution was treated with 1 equivalent (1.31mL of a 0.1M solution) of triflic acid in CH_2Cl_2. $^{31}P\{^1H\}$NMR spectra of the resultant solution showed resonances at δ 19.5 (d, $^3J_{P\text{-}P}$ 35Hz) and –23.5 (d, $^3J_{P\text{-}P}$ 35Hz), as well as a minor resonance for the free ligand, DMeOPrPE, at δ –26.7 (s). ^1H coupled ^{31}P NMR of the resultant solution revealed that the resonance at δ 19.5 split further into a doublet of 448 Hz ($^1J_{P\text{-}H}$) while the other two resonances were unaffected (Figure S1).

Generation of DMeOPrPEH$_2^{2+}$. DMeOPrPE (0.050g, 0.131 mmol) was dissolved in 10 mL of CH_2Cl_2. The resultant solution was treated with an excess (4mL of a 0.1M solution) of triflic acid in CH_2Cl_2. $^{31}P\{^1H\}$NMR spectra of the resultant solution showed one resonance at δ 20.5 (s). ^1H coupled ^{31}P NMR of the resultant solution revealed that the resonance at δ 20.5 split into a doublet of 513 Hz ($^1J_{P\text{-}H}$) (Figure S2). This complex has been generated before by Herbkowski[40] and essentially identical spectra were obtained in our work.

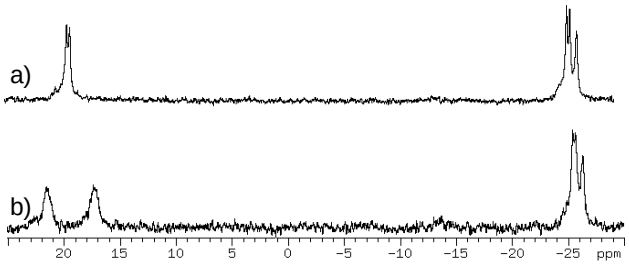

Figure S1. $^{31}P\{^{1}H\}$ NMR spectra (RT): (a) reaction mixture of DMeOPrPE treated with approximately one equivalent triflic acid in CH_2Cl_2; (b) same sample with ^{1}H decoupler off.

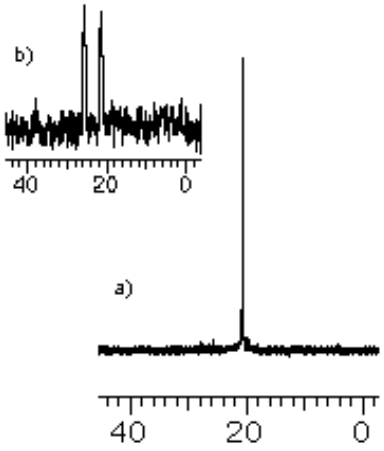

Figure S2. $^{31}P\{^{1}H\}$ NMR spectra (RT): (a) reaction mixture of DMeOPrPE treated with an excess of triflic acid in CH_2Cl_2; (b) same sample with ^{1}H decoupler turned off.

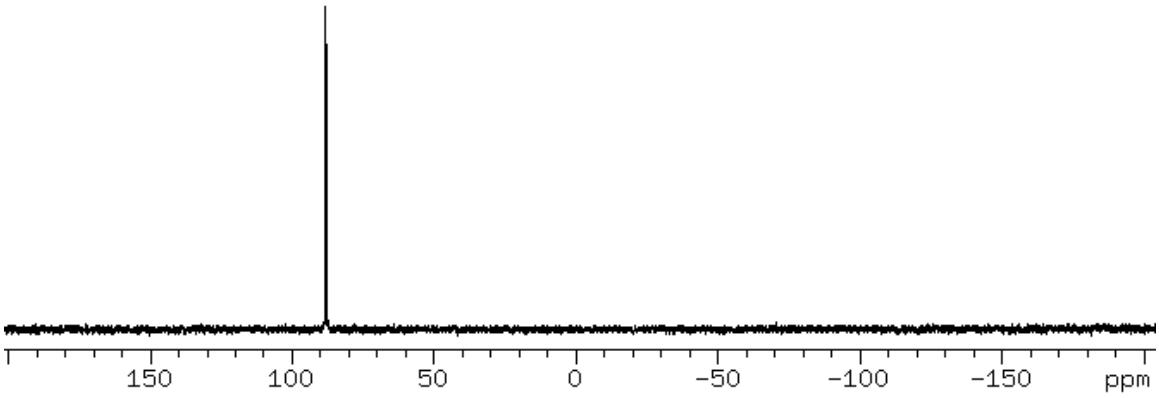

Figure S3. $^{31}P\{^{1}H\}$ NMR spectra (233K): reaction mixture of **I** with H_2 (1-2 atm) in ethanol-d_6/D_2O (60/40 wt%) in the presence of one equivalent Proton Sponge

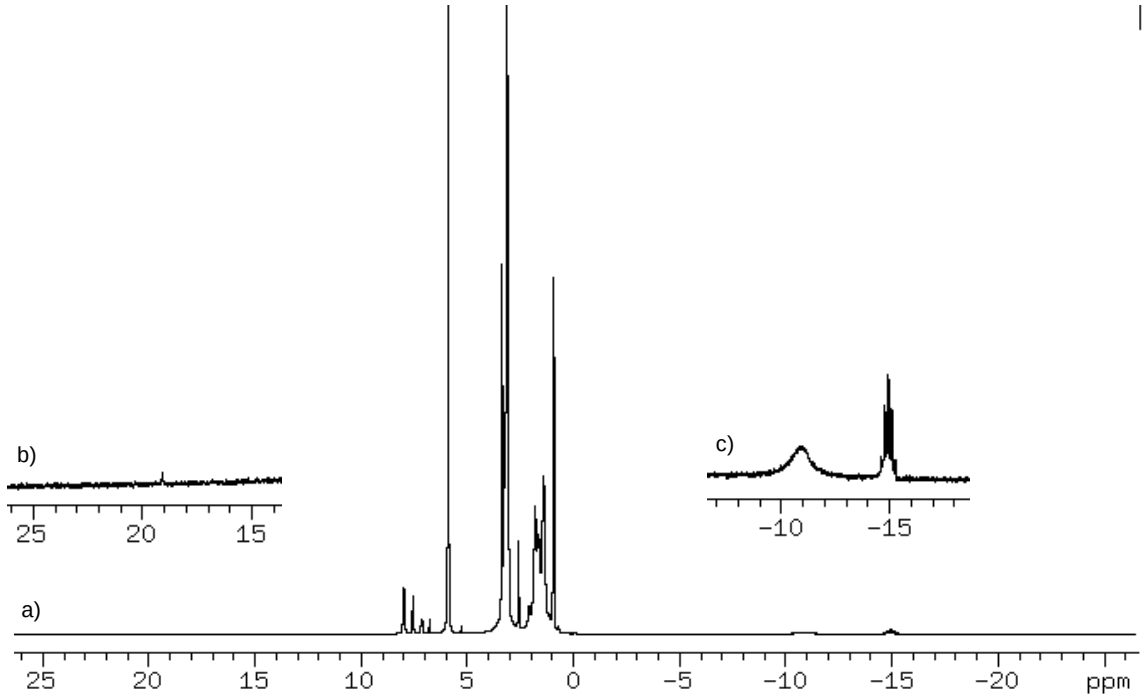

Figure S4. 500MHz ^{1}H NMR spectra (233K): (a) reaction mixture of **I** with H_2 (1-2 atm) in ethanol-d_6/D_2O (60/40 wt%) in the presence of one equivalent Proton Sponge; (b) expanded NHN^+ region of same sample; (c) expanded hydride region of same sample.

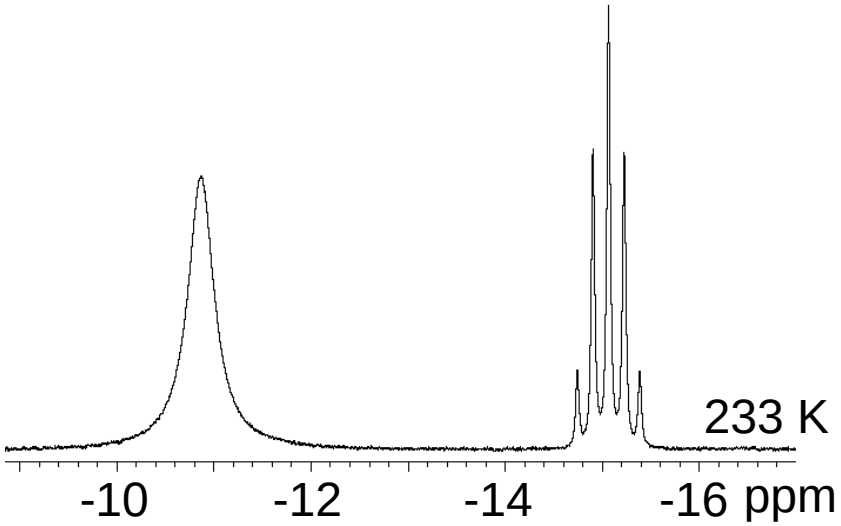

Figure S5. 500MHz ^{1}H NMR spectra (233K) of the hydride region of reaction mixture of **I** with H_2 (1-2 atm) in ethanol-d_6/D_2O (60/40 wt%)

Additional References

(38) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**. *60*, 716.
(39) Streuli, C.A. *Anal. Chem.* **1959**. *31***,** 1652.
(40) Herbowski, A.; Deutsch, E.A. *J. Organomet. Chem.* **1993**, *460*, 19.