Inorganic Chemistry

Article

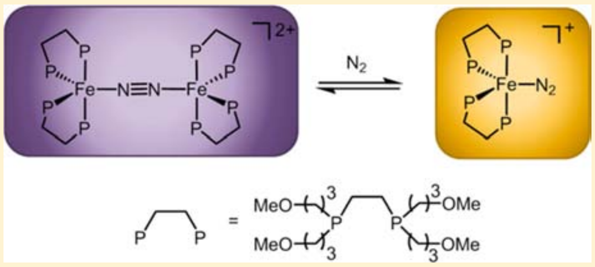
pubs.acs.org/IC

Characterization of an Intermediate in the Ammonia-Forming Reaction of $Fe(DMeOPrPE)_2N_2$ with Acid (DMeOPrPE = 1,2-[bis(dimethoxypropyl)phosphino]ethane)

Chantal G. Balesdent, Justin L. Crossland, Daniel T. Regan, Coralys T. López, and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403, United States

Supporting Information

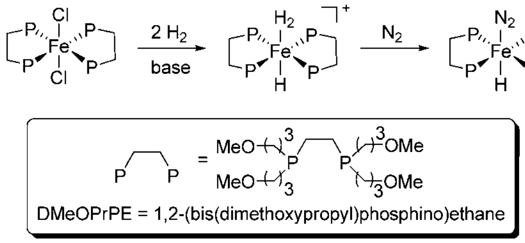


ABSTRACT: The reactivity of $Fe(DMeOPrPE)_2N_2$ with water and acid was explored. (DMeOPrPE is the bidentate phosphine 1,2-[bis(dimethoxypropyl)phosphino]ethane.) The complex reacts with acid to form *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ and small amounts of ammonia and hydrazine. When reacted with H_2O, *cis*-$Fe(DMeOPrPE)_2(H)_2$ is formed. To increase the yields of ammonia and hydrazine, we investigated the effect of anion, solvent, and acid addition rate on the yields of ammonia. Of these parameters, only the properties of the anion (i.e., of the acid) had a significant impact on the yields of ammonia. The highest yields of NH_3 occurred with the largest/least-coordinating anion (triflate). A short-lived purple intermediate ($\tau_{1/2} < 5$ s at 23 °C) was observed in the reaction of $Fe(DMeOPrPE)_2N_2$ with triflic acid. Because the structure of this purple species could potentially provide valuable insights into the mechanism of ammonia formation, a method was developed for independently synthesizing and stabilizing the complex. Spectroscopic characterization of the purple species identified it as the paramagnetic $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ complex (**1**). This purple dimer (**1**) exists in equilibrium with yellow, monomeric, paramagnetic $[Fe(DMeOPrPE)_2N_2]^+$ (**2**). The role of **1** in the formation of hydrazine and ammonia was probed by reacting **1** with acid.

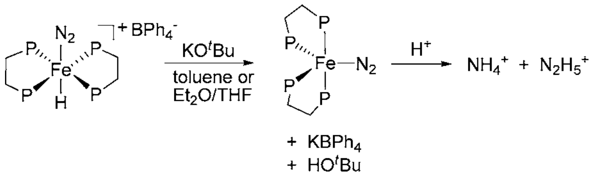
■ INTRODUCTION

Low-energy alternatives to the industrial production of ammonia are sought because the Haber-Bosch process consumes 1–2% of the energy used globally each year and it produces a corresponding amount of greenhouse gases.[1,2] In pursuit of a homogeneous catalyst for the formation of ammonia from N_2, numerous metal–N_2 complexes have been studied with the goal of identifying low-energy pathways for the activation and reduction of N_2.[3−17] In recent work, we showed that the *trans*-$Fe(DMeOPrPE)_2Cl_2$ complex (where DMeOPrPE is 1,2-[bis(dimethoxypropyl)phosphino]ethane) reacted with H_2 to form *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$, which could then react with N_2 to form *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ (Scheme 1). Based on the work of Leigh, we showed that the *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ complex could be deprotonated to make $Fe(DMeOPrPE)_2N_2$ (Scheme 2) and that reprotonation of $Fe(DMeOPrPE)_2N_2$ produced a small quantity of ammonia.[15] The object of our recent research has been to study the mechanism of the ammonia-forming reaction with the goal of learning how to improve the yield of ammonia.[18,19]

Scheme 1. Formation of *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ from *trans*-$Fe(DMeOPrPE)_2Cl_2$



Scheme 2. Deprotonation of *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ Forms $Fe(DMeOPrPE)_2N_2$, Which Is Protonated to Yield Ammonia



Our initial report[15] on the protonation of $Fe(DMeOPrPE)_2N_2$ described how the yellow THF/diethyl ether solution of $Fe(DMeOPrPE)_2N_2$ became colorless when triflic acid was added to the solution. (A white precipitate of ammonium salts also formed.) It has since been observed that when the acid is added slowly, the solution briefly becomes deep purple before becoming colorless. This short-lived purple

Received: August 13, 2013
Published: November 20, 2013

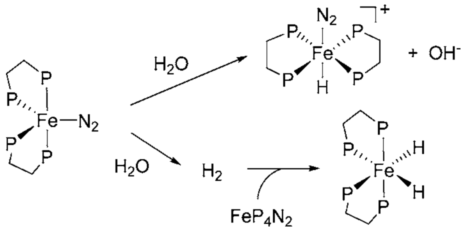
dx.doi.org/10.1021/ic402081q | *Inorg. Chem.* 2013, 52, 14178−14187

intermediate caught our attention because of its brief lifetime, its intense color, and the correlation between its appearance and the successful formation of ammonia. Although very little information could be gathered about this purple intermediate in situ (because it was unable to be isolated from the reaction mixture due to its short lifetime), we were able to synthesize the purple complex by an alternative route. In this paper, we describe the characterization of the intermediate purple complex and its relevance to the ammonia-forming reaction. The effects of the solvent, the acid addition rate, and the type of acid on the yields of ammonia in the protonation of Fe(DMeOPrPE)$_2$N$_2$ are also reported.

■ RESULTS AND DISCUSSION

Stability of Fe(DMeOPrPE)$_2$N$_2$. An early goal was to generate ammonia from Fe(DMeOPrPE)$_2$N$_2$ in aqueous solution by the route in Scheme 2. However, Fe(DMeOPrPE)$_2$N$_2$ could not be generated in water by deprotonation of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H]$^+$; the strong base needed to remove the hydride ligand (^{t}BuO$^-$) must be used in a nonaqueous solvent to avoid the leveling effect of the base in water.[20] Furthermore, the Fe(DMeOPrPE)$_2$N$_2$ complex is highly reactive with water. The ^{31}P{^{1}H} NMR spectrum of Fe(DMeOPrPE)$_2$N$_2$ in THF-*d*$_8$ with added water showed the complete disappearance of the starting material, the appearance of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H]$^+$ (76.8 ppm),[21] free DMeOPrPE ligand (−26.5 ppm),[22] and the appearance of a product with two broad resonances at 98 and 84 ppm (see the Supporting Information, Figure S1). The formation of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H]$^+$ is explained by the protonation of the iron center by water (Scheme 3, top).

Scheme 3. Degradation of Fe(DMeOPrPE)$_2$N$_2$ in Water Occurs by Two Routes: (i) Protonation by Water (top pathway) and (ii) Proton Reduction to Produce H$_2$, Followed by the Reaction of H$_2$ with Fe(DMeOPrPE)$_2$N$_2$ to Form *cis*-Fe(DMeOPrPE)$_2$(H)$_2$ (bottom pathway)



NMR analysis of the species with broad resonances at 98 and 84 ppm suggests this product is *cis*-Fe(DMeOPrPE)$_2$(H)$_2$. The low-temperature (−20 °C) ^{31}P{^{1}H} NMR spectrum in DMSO-*d*$_6$ showed that the broad resonances are triplets (δ 98, t, $^2J_{\mathrm{PP}}$ = 17 Hz; δ 84 ppm, (t, $^2J_{\mathrm{PP}}$ = 17 Hz)), consistent with a *cis* arrangement of the two hydride ligands (Figure 1). Upon warming, the peaks at 98 and 84 ppm broaden and then coalesce into a single peak at about 91.5 ppm. This behavior is consistent with a fluxional process in which the two types of P atoms in *cis*-Fe(DMeOPrPE)$_2$(H)$_2$ become equivalent (eq 1).The identification of the product as *cis*-Fe(DMeOPrPE)$_2$(H)$_2$ was further supported by two alternative syntheses of the molecule. Specifically, the oxidative addition of H$_2$ to Fe(DMeOPrPE)$_2$N$_2$ and the deprotonation[23] of *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$ (Scheme 4) both resulted in a product that showed two peaks at 98 and 84 ppm in the ^{31}P{^{1}H} NMR spectrum. (See the Experimental section and the Supporting Information for details of these two alternative syntheses and the corresponding spectra.)

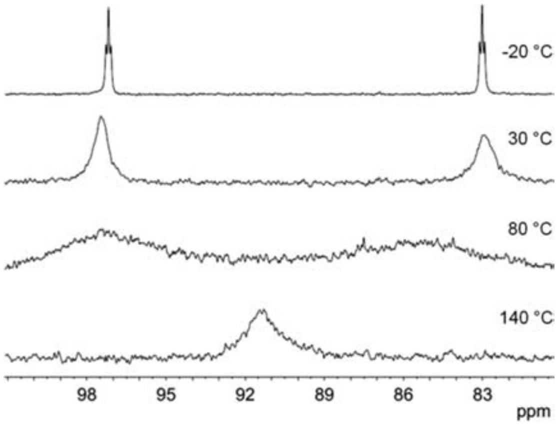
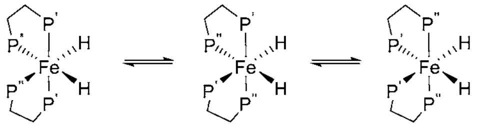
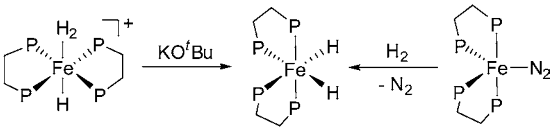


Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra of Fe(DMeOPrPE)$_2$(H)$_2$ in DMSO-*d*$_6$.



(1)

Scheme 4. Alternative Syntheses for *cis*-Fe(DMeOPrPE)$_2$(H)$_2$



At −60 °C in toluene, the ^{1}H NMR spectrum in the hydride region of the product formed by deprotonation of *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$ showed a broad peak at −14.8 ppm that, upon warming, sharpened into a quintet, as would be expected for a system with four equivalent P atoms in a fluxional molecule (eq 1; see Figures S3 and S4 in the Supporting Information).

The oxidative addition of H$_2$ to Fe(DMeOPrPE)$_2$N$_2$ is likely the pathway that results in the formation of *cis*-Fe(DMeOPrPE)$_2$(H)$_2$ from the reaction of Fe(DMeOPrPE)$_2$N$_2$ with water. It is suggested that Fe(DMeOPrPE)$_2$N$_2$ reduces water to H$_2$, which then further reacts with a second molecule of Fe(DMeOPrPE)$_2$N$_2$ to form *cis*-Fe(DMeOPrPE)$_2$(H)$_2$ (Scheme 3, bottom).

Optimization of Fe(DMeOPrPE)$_2$N$_2$ Protonation. Once the Fe(DMeOPrPE)$_2$N$_2$ complex is generated, it can be protonated with a strong acid to yield a mixture of ammonia and hydrazine.[15] Because very little was known about what reaction conditions favor ammonia formation, several variables were tested in order to optimize the yields of ammonia and hydrazine.

Effect of Anion. A series of strong acids was selected to test whether the anion of the acid affected the yields of ammonia. The hypothesis was that, as the coordinating and/or ion-pairing ability of the anion increased, the yields of ammonia would decrease because the dinitrogen ligand would be blocked by the anion from protonation. Triflic acid (TfOH), tetrafluoroboric acid (HBF$_4$), and hydrochloric acid (HCl), all as 1 M diethyl ether solutions, were used to protonate $Fe(DMeOPrPE)_2N_2$. TfOH gave the highest yields of ammonia (17% with respect to Fe), followed by HBF_4 (7%), and finally HCl (4%). This trend agrees with the hypothesis that the coordinating/ion-pairing ability of the anion decreases the yield of ammonia.[24] Interestingly, these acids each produced a uniquely colored solution that disappeared within seconds after acid addition. Thus, addition of TfOH resulted in a dark purple solution (see below); HBF_4 gave a dark blue solution; and HCl resulted in a pale pink solution.

Solvent. The reaction solvent appeared to have little or no effect on the yields of ammonia: toluene (17%) and a THF/Et_2O solvent system (13%) gave comparable yields.

Acid Addition Rate. The effect of the acid addition rate to the solution of $Fe(DMeOPrPE)_2N_2$ was studied using a syringe pump. The addition rate of 1 M triflic acid (2 mL) to a 5 mL solution of 0.01 M $Fe(DMeOPrPE)_2N_2$ was varied from 0.15 to 3 mL/min (1.5×10^{-4} to 3×10^{-3} mol/min), but no difference was observed in the yields of ammonia.

Effect of Iron. In the course of these optimization studies, it was discovered that the presence of iron significantly altered the yields of ammonia measured by the analytical method used in our prior studies.[25] Specifically, iron has a positive interference on the yields of ammonia, increasing the measured yields by as much as 50%. To prevent interference, a new method was developed in which the ammonia and hydrazine are isolated using a base distillation technique. The new procedure for quantitating ammonia is the one reported in the Experimental section.

Determining the Oxidation State of Iron After the Protonation of $Fe(DMeOPrPE)_2N_2$. Because no external reducing agents are added in the protonation/N_2-reduction reaction (Scheme 2), the $Fe(DMeOPrPE)_2N_2$ complex must be the source of all the electron equivalents required for the reduction of N_2 to ammonia. An important step in determining the mechanism of ammonia formation therefore is to determine how many electrons each iron center donates to the overall reduction of N_2. The reduction of N_2 to 2 equiv. of ammonia is a six-electron process. All six electrons cannot come from a single iron center so, to determine how many electrons each iron center donates, a spectrophotometric determination of the iron(II) concentration was carried out.[26]

The concentration of iron(II) was determined at various stages of the protonation reaction: a solution containing only *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$, which is used in the preparation of $Fe(DMeOPrPE)_2N_2$ (Scheme 2); a solution containing the $Fe(DMeOPrPE)_2N_2$ complex prior to protonation; and last, the reaction mixture after protonation of $Fe(DMeOPrPE)_2N_2$ (Table 1). The determination was done under strictly anhydrous conditions because, as discussed above, $Fe(DMeOPrPE)_2N_2$ degrades in water. A standard calibration curve using phenanthroline in THF was prepared, and from this standard curve the concentration of iron(II) was determined. The results are shown in Table 1.

Table 1. Summary of the Iron(II) Spectrophotometric Analysis (L = DMeOPrPE)

solution of...	concentration of iron(II) (M)
trans-$[FeL_2(N_2)H]^+$	1.65×10^{-5}
FeL_2N_2	$<2 \times 10^{-7}$
$FeL_2N_2 + H^+$	1.75×10^{-5}

The key point from the results in Table 1 is that after the protonation reaction was complete, the concentration of iron(II) returned to the level present in the solution of the original *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ starting material. Thus, each iron center only donates two electrons to the reduction of N_2.

Observation of a Purple Intermediate During the Protonation of $Fe(DMeOPrPE)_2N_2$. Because TfOH gave the best yields of ammonia, it was used for all further investigations. Experiments showed that when less than a 1:1 stoichiometric amount of acid was used in the protonation reaction of $Fe(DMeOPrPE)_2N_2$, a short-lived ($\tau_{1/2} < 5$ s at 23 °C) purple intermediate formed. To identify this intermediate, a sample was frozen in an NMR tube in liquid nitrogen for transfer to the NMR instrument. Low-temperature (−40 °C) $^{31}P\{^1H\}$ NMR studies showed that the major species present was *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ at 76.6 ppm (Figure 2), the expected thermodynamic product from the protonation of $Fe(DMeOPrPE)_2N_2$.[27] Some unreacted $Fe(DMeOPrPE)_2N_2$ was also observed at 79 ppm. A small amount of *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$ (88.4 ppm) was also present, as well as a significant amount of *cis*-$Fe(DMeOPrPE)(H)_2$ (84.2 and 98.1 ppm). These latter two products indicate that H_2 is being formed, probably by the reduction of protons. Note that hydrogen production is a common side reaction in dinitrogen reduction;[6] the nitrogenase enzyme itself makes at least 1 equiv. of H_2 for every 2 equiv. of NH_3.[28]

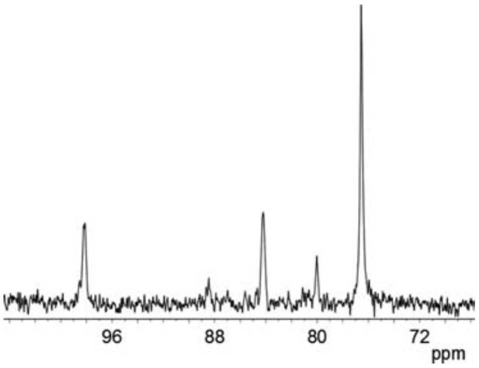


Figure 2. $^{31}P\{^1H\}$ spectrum at −40 °C of the protonation of $Fe(DMeOPrPE)_2N_2$ with TfOH.

Because the only species observed during the protonation of yellow-orange $Fe(DMeOPrPE)_2N_2$ are tan *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$, tan *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$, and yellow *cis*-$Fe(DMeOPrPE)_2(H)_2$, it was hypothesized that the purple intermediate is perhaps a product of the reaction of these complexes with each other. However, reactions of all combinations of these four complexes did not give a purple solution (Table 2).

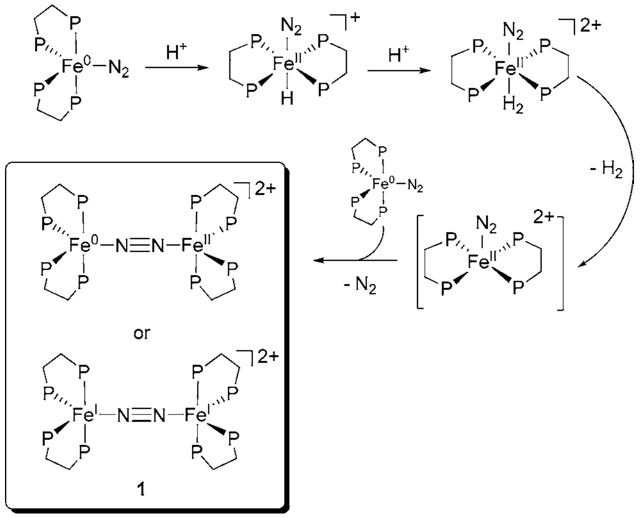
Independent Generation of the Purple Intermediate. It was then hypothesized that the purple color was the result of a mixed valence N_2-bridged dimer (**1**), formed as shown in Scheme 5. (Note that only one example of a mixed-valence N_2-bridged iron dimer has been reported.[29]) In this scheme, the open-coordinate Fe(II) species likely comes from a double protonation of the $Fe(DMeOPrPE)_2N_2$ starting material (Scheme 5). This is supported by the observation that H_2 is always observed as a product of the protonation reaction of $Fe(DMeOPrPE)_2N_2$ (see discussion above).

Table 2. Combinations of the Observed Products of the Protonation Reaction of FeL_2N_2 (L = DMeOPrPE)

	cis-$FeL_2(H)_2$	*trans*-$[FeL_2(H_2)H]^+$	*trans*-$[FeL_2(N_2)H]^+$
FeL_2N_2	no reaction	FeL_2N_2, *cis*-$FeL_2(H)_2$[a]	FeL_2N_2[b]
trans-$[FeL_2(N_2)H]^+$	no reaction	no reaction	
trans-$[FeL_2(H_2)H]^+$	*cis*-$FeL_2(H)_2$[c]		no reaction

[a] FeL_2N_2 is always formed in the presence of excess base, so *trans*-$[FeL_2(H_2)H]^+$ is deprotonated to make *cis*-$FeL_2(H)_2$. [b] Again, FeL_2N_2 contains excess base, so any *trans*-$[FeL_2(N_2)H]^+$ is deprotonated to make more Fe L_2N_2. [c] Similarly, *cis*-$FeL_2(H)_2$ contains excess base and so converts *trans*-$[FeL_2(H_2)H]^+$ to *cis*-$FeL_2(H)_2$.

Scheme 5. Proposed Formation of an N_2-Bridged Dimer (1) during the Protonation of $Fe(DMeOPrPE)_2N_2$



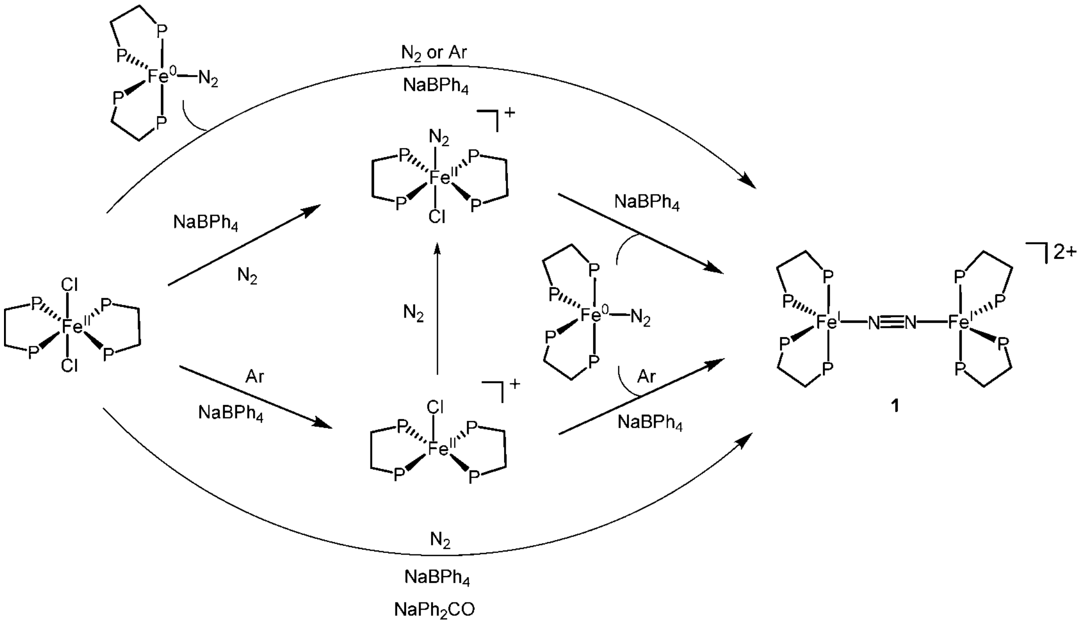
To independently generate the purple intermediate, we used iron chloride complexes in conjunction with a chloride abstractor as a source of open-coordinate Fe(II) complexes containing the DMeOPrPE ligand. Thus, excess $NaBPh_4$ was added to a solution of $Fe(DMeOPrPE)_2N_2$ in 2:1 Et_2O/THF, followed by dropwise addition of *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl][BPh_4]$ in THF until the solution became dark purple (Scheme 6).[30] (A minimum of 2 equiv. of *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl]^+$ was needed to form the purple color.[31]) Control experiments showed that no reactions occurred between $Fe(DMeOPrPE)_2N_2$ and $NaBPh_4$ or between *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl]^+$ and $Fe(DMeOPrPE)_2N_2$, and that no color change was observed in the reaction of brown *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl]^+$ with $NaBPh_4$. The purple intermediate can also be formed by adding an excess of $NaBPh_4$ to *trans*-$Fe(DMeOPrPE)_2Cl_2$ and $Fe(DMeOPrPE)_2N_2$ under an N_2 atmosphere. This route eliminates the step needed to make the *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl]^+$ complex from *trans*-$Fe(DMeOPrPE)_2Cl_2$ (Scheme 6). Note that the purple intermediate, generated by the routes above, is stable for at least 24 h in Et_2O/THF or THF solutions under argon.

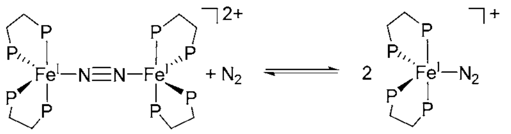
NMR Characterization of the Purple Intermediate. No peaks other than uncoordinated DMeOPrPE were observed in the ^{31}P NMR spectrum of the purple intermediate generated by one of the routes above (even down to −40 °C). This result suggests that **1** is paramagnetic, a result confirmed by measuring the magnetic susceptibility using the Evans method (see Figure S5 in the Supporting Information).[32,33] (These results are discussed in the following section.)

Intriguingly, when samples of the purple species were cooled for NMR experiments, the color of the solution changed from purple to yellow (see the detailed experimental results below). To explain this result, it is proposed that the purple intermediate (**1**) is in equilibrium with a yellow monomeric complex, suggested to be $[Fe(DMeOPrPE)_2N_2]^+$ (**2**) (eq 2). The remainder of this paper discusses evidence consistent with this hypothesis.

Magnetic Susceptibility. The magnetic susceptibility of the yellow species (**2**) at 25 °C was measured by the Evans

Scheme 6. Summary of the Routes Used to Generate the Purple Intermediate (1)





1 **2** (2)

method, which yielded a magnetic moment of 1.6 μ_B. (See the Supporting Information for the magnetic moment calculations. The method used to obtain the yellow intermediate at room temperature is discussed below.) This result is consistent with the proposed $S = 1/2$ Fe(I) $[Fe(DMeOPrPE)_2N_2]^+$ complex.[34,35] The purple species, **1**, has a magnetic moment of 1.1 μ_B, which is lower than expected for a molecule with two unpaired electrons. Note that because of the proposed equilibrium between **1** and **2** there is likely some contamination from **2** affecting the observed magnetic moment of **1** (see the Supporting Information).

EPR Spectroscopy of 1 and 2. Complexes **1** and **2** both displayed axial splitting patterns (Figure 3) in their EPR spectra. The *g*-values for **2** are 2.00 ($g_{\parallel}$) and 2.14 ($g_{\perp}$). The spectrum of dimer **1** is a composite of some residual monomer **2** and a new EPR signal, with more fine splitting, attributed to the dimer (see Figure S6 in the Supporting Information). This splitting is likely due to coupling to the phosphorus ligands. Complex **1** has *g*-values of 2.01 ($g_{\parallel}$) and 2.10 ($g_{\perp}$) with a small rhombic impurity at 2.38. The spectra of **1** and **2** can be simulated (see Figure S7 in the Supporting Information), and are similar to the EPR spectra of other Fe(I) complexes (see Figure S8 in the Supporting Information).[34,36]

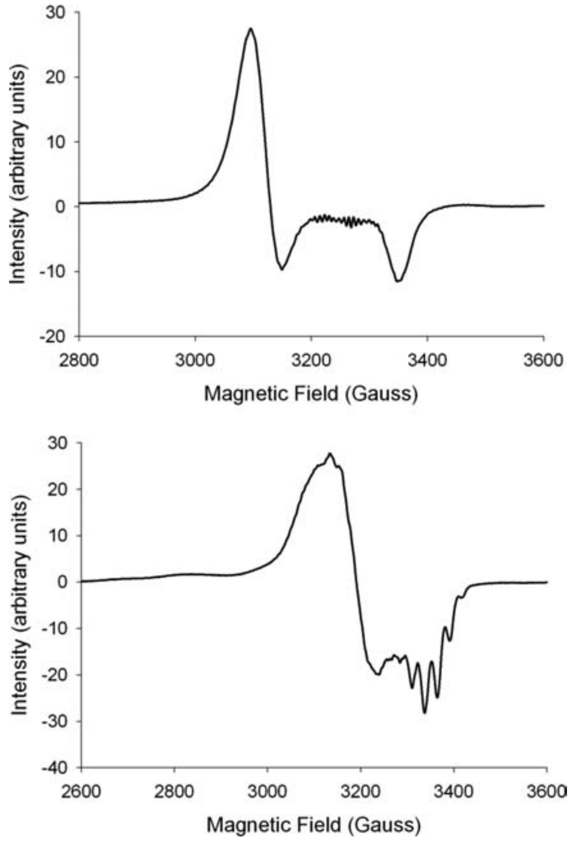


Figure 3. EPR spectra of $[Fe(DMeOPrPE)_2N_2]^+$ (**2**) (top) and $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) (bottom).

IR Spectroscopy of 1 and 2. The IR spectrum of yellow $[Fe(DMeOPrPE)_2N_2]^+$, (**2**; as a neat oil on salt plates) showed a sharp band at 2054 cm^{-1} (Figure 4), attributed to ν(NN) of a coordinated N$_2$ ligand. This stretch appears in frequency between the known ν(NN) bands for the Fe(0) Fe(DMeOPrPE)$_2$N$_2$ complex (1966 cm^{-1}) and the Fe(II) *trans*-$[Fe(DMeOPrPE)_2(N_2)H][BPh_4]$ complex (2088 cm^{-1}),[37] consistent with the formulation of **2** as an Fe(I)N$_2$ complex. For comparison, ν(NN) of the recently synthesized five-coordinate Fe(I) complex $[Fe(N_2)P(CH_2CH_2PCy_2)_3][BPh_4]$ was reported at 2059 cm^{-1};[36] another five-coordinate Fe(I) complex, $(SiP^{Ph}{}_3)FeN_2$, has ν(NN) at 2041 cm^{-1}.[35]

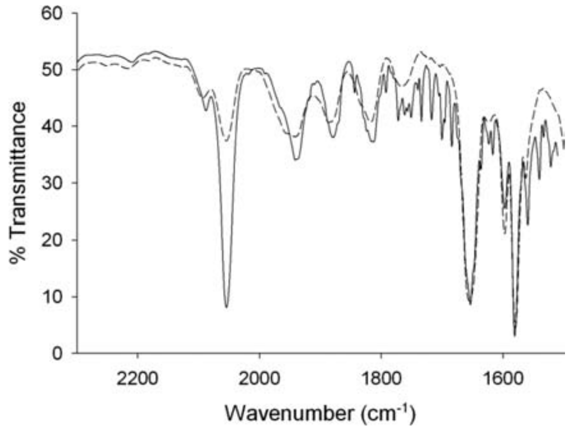


Figure 4. IR spectra of $[Fe(DMeOPrPE)_2N_2]^+$ (**2**) (solid line) and $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) (dashed line).

A normalized IR spectrum of purple **1** is shown in Figure 4 for comparison to **2**. Note that in **1**, the ν(NN) band has almost completely disappeared, as would be expected for a symmetric Fe-NN-Fe-containing complex. Although this band should be observable by Raman spectroscopy, attempts at obtaining a Raman spectrum of **1** were unsuccessful because the complex decomposed in the beam of the instrument. It is noted that decomposition during the Raman experiment was also observed with *trans*-$[\{FeCl(DEPE)_2\}_2N_2][BPh_4]_2$, which has a similar Fe-NN-Fe unit.[38] The decomposition of **1** was visible as clear spots in the film where the Raman laser had irradiated the complex, even at low laser intensities.

Monomer/Dimer Equilibrium. Complexes **1** and **2** are in a temperature-dependent equilibrium, with complex **1** favored at high temperature. As shown in Figure 5, bands at 580 and 480 nm increase in intensity as the temperature is raised, and accordingly these are assigned to complex **1**. (Qualitatively, it is noted that the purple color becomes more intense as the solution is heated.) As the solution temperature is lowered below 10 °C, the bands at 480 and 580 nm decrease in intensity and the yellow color of **2** appears. In addition, an intense band at 1010 nm appears, assigned to **2**. This heat/cool cycle with its associated color change can be repeated many times without decomposing the complexes and can be explained by the thermally induced loss of an N$_2$ ligand at higher temperatures, which leads to formation of **1** (eq 2). To verify that the color dependence was indeed the binding/dissociation of N$_2$, a sample of the purple dimer (**1**) was placed under vacuum to remove any uncoordinated N$_2$, then cooled. As was expected with no N$_2$ present, the solution remained purple, even at −80 °C.

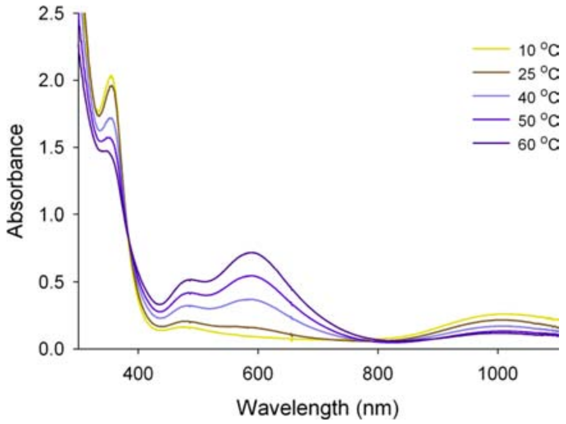
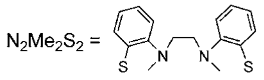


Figure 5. UV−vis spectra of $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) at various temperatures.

Under high concentrations of N_2 (e.g., bubbling N_2 through the purple solution), the purple solution of $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ turns yellow. In the UV−vis spectrum, this result manifests itself as a decrease in the intensities for the bands at 480 and 580 nm. However, exposing this yellow solution to vacuum or by bubbling argon gas through it caused the intense purple color of **1** to return. The color change can be repeated several times by alternating N_2 pressure and vacuum, consistent with the process in eq 2. Similar conversions between monomeric and dimeric complexes of N_2 have previously been observed in ruthenium[39] (eq 3) and iron[7] (eq 4) complexes.

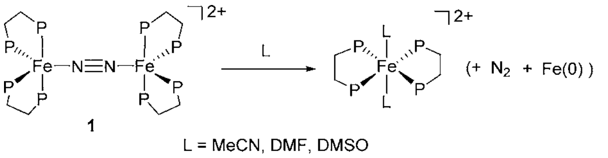
$$[Ru(N_2)(P^iPr_3)(N_2Me_2S_2)] \underset{}{\overset{-\,N_2}{\rightleftharpoons}} [\mu\text{-}N_2\{Ru(P^iPr_3)(N_2Me_2S_2)\}_2] \qquad (3)$$



$$[FeH(N_2)(PP_3)]^+ \rightleftharpoons [FeH(PP_3)(\mu\text{-}N_2)FeH(PP_3)]^{2+}$$

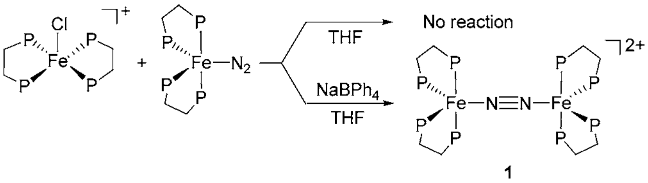
$$PP_3 = P(CH_2CH_2PMe_2)_2 \qquad (4)$$

When **1** is redissolved in toluene after isolation as an oil (see the Experimental section), the purple color is again observed. However, redissolving it in acetonitrile, DMF, or DMSO produced a yellow solution instead. These results suggest that **1** is fragmented by coordinating solvents,[40] creating various monomeric yellow species (eq 5). For example, in acetonitrile, *trans*-$[Fe(DMeOPrPE)_2(CH_3CN)_2]^{2+}$ was observed as a product, as indicated by the resonance in the $^{31}P\{^1H\}$ NMR spectrum at 62.0 ppm.[22] Additionally, when these solvato-complexes were heated, they remained yellow, verifying that they were not $[Fe(DMeOPrPE)_2N_2]^+$ (**2**), which dimerizes to purple **1** when warmed. (Note that the Fe(0) complexes that must be formed in these reactions were not observed.[41])To verify that dimer **1** does not contain any chloride, we reacted the open-coordinate $[Fe(DMeOPrPE)_2Cl][BPh_4]$ complex with $Fe(DMeOPrPE)_2N_2$ (Scheme 7). No reaction was evident until $NaBPh_4$ was added, at which point the purple **1** immediately formed.



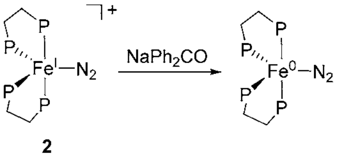
(5)

Scheme 7. Chloride Abstractor ($NaBPh_4$) is Needed to Produce 1 from $[Fe(DMeOPrPE)_2Cl][BPh_4]$ and $Fe(DMeOPrPE)_2N_2$



Reducing Equivalents. As further evidence for the proposed structure of **1**, it was found that $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) can be formed from *trans*-$Fe(DMeOPrPE)_2Cl_2$ and a reducing agent. Thus, reaction of *trans*-$Fe(DMeOPrPE)_2Cl_2$ with sodium benzophenone ketyl ($NaPh_2CO$) and $NaBPh_4$ formed **1**. The product was only formed when the experiment was carried out under an N_2 atmosphere; an argon atmosphere yielded no product (Scheme 6). *trans*-$Fe(PR_3)_4Cl_2$-type complexes are known to react with reducing agents to form Fe(0) complexes,[42] so the reaction of *trans*-$Fe(DMeOPrPE)_2Cl_2$ with $NaPh_2CO$ likely involves the initial formation of $Fe(DMeOPrPE)_2N_2$. The $Fe(DMeOPrPE)_2N_2$ could then react with the remaining $Fe(DMeOPrPE)_2Cl_2$ and a chloride abstractor ($NaBPh_4$) to form **1**.

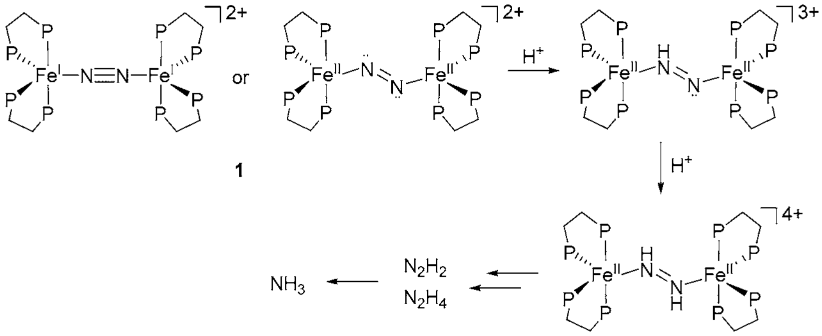
By varying the equivalents of $NaPh_2CO$ used to make dimer **1**, it was determined that fewer than 2 equiv. (electrons) were needed to produce the complex (as indicated by UV−vis spectroscopy, Figure S9 in the Supporting Information). When more than 2 equiv of reducing agent were used, purple **1** degraded, as monitored by the decrease in intensity of the peaks at 480 and 580 nm in the UV−vis spectrum. With excess $NaPh_2CO$, the observed product in the ^{31}P NMR spectrum is $Fe(DMeOPrPE)_2N_2$ (79 ppm), which is the result of further reduction of yellow $[Fe(DMeOPrPE)_2N_2]^+$ (eq 6). No ^{31}P NMR signal attributable to $Fe(DMeOPrPE)_2N_2$ was observed when fewer than 2 equiv. of reducing agent were used, that is, when the reaction is stopped after purple **1** is formed. It should be possible to oxidize $Fe(DMeOPrPE)_2N_2$ to reform yellow **2**. However, chemical oxidation attempts using ferrocenium, *tert*-butyl hydroperoxide, and various Ag(I), Cu(II), and Fe(III) salts proved unsuccessful.



(6)

Protonation of $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$. No NH_4^+ or $N_2H_5^+$ was observed by ^1H NMR spectroscopy when a solution of purple $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) was treated with 1 M TfOH under N_2 or Ar (see Figure S10 in the Supporting Information). It is possible that dimer **1** is protonated at the reduced dinitrogen to make a diazene (N_2H_2) complex (Scheme 8). DFT calculations support the formation of $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2H_2)]^{4+}$ and favor the dissociation

Scheme 8. Suggested Protonation Pathway for $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (1)^a



^{a}Two possible structures for complex **1** are shown, one structure having two Fe(I) centers with an N≡N bridging ligand, the other structure having two Fe(II) centers with a bridging N_2^{2-} ligand.

of the N_2H_2 ligand from this complex.[43] In the presence of a metal center, diazene is known to decompose into N_2H_4 (hydrazine), which can then form NH_3.[44−47] However, without any remaining electron equivalents for the iron centers to donate, it is likely that the reduction stops at diazene.

To test for diazene formation, we carried out the protonation of purple $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ (**1**) in the presence of the known diazene traps phenylacetylene, norbornene, and azobenzene.[48] However, all three traps were ineffectual. Thus, phenylacetylene reacted with dimer **1**, acting as a coordinating ligand and turning the solution yellow. In the case of norbornene, the overlap of many peaks in the ^{1}H NMR spectrum (**1**, the acid, and the trap) made it a impractical to detect the formation of norbornane. Purple $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$ was unreactive toward azobenzene, but control reactions showed that the trapped product, diphenylhydrazine, was unstable in the presence of acid, thus rendering this trap ineffective. Finally, it is noted that regardless of whether these traps are effective, diazene can be protonated by triflic acid, so it is possible that even if N_2H_2 is forming in the protonation of dimer **1**, it is protonated before it can react with the trap.

■ CONCLUSIONS

Reaction of $Fe(DMeOPrPE)_2N_2$ with a strong acid results in the formation of NH_3 and N_2H_4 with relatively low yields (Scheme 2). To improve the yields of ammonia, we investigated the effects of anion, solvent, and acid addition rate on the yields. Of these three factors, only the identity of the anion (i.e., the acid) had a significant effect on the observed yields. Specifically, TfOH gave the highest yields of ammonia, followed by HBF_4, and then HCl, from which it is concluded that higher yields are obtained with less coordinating (or less ion-pairing) anions. It is suggested that coordinating or strongly ion-pairing anions may sterically prevent protonation of the N_2 ligand.

Experiments showed that a single $Fe(DMeOPrPE)_2N_2$ complex donates only two electrons to the overall six-electron reduction of N_2 to NH_3. There are two possible implications of this result. First, if either ammonia or hydrazine is the primary reduced product then multiple $Fe(DMeOPrPE)_2N_2$ complexes are required for the N_2-reduction. Alternatively, if the reaction pathway involves only a single two-electron reduction then diazene is the primary product; any hydrazine and ammonia that form would have to come from the disproportionation of diazene. Either possibilty explains why the yield of ammonia is low: a pathway involving multiple electron transfers from multiple $Fe(DMeOPrPE)_2N_2$ molecules would be inherently inefficient, and likewise, the disproportionation of diazene to hydrazine and then to ammonia is inefficient and would result in low overall yields.

Careful addition of acid to $Fe(DMeOPrPE)_2N_2$ resulted in the formation of a short-lived purple intermediate (**1**). Spectroscopic and reactivity studies suggest that **1** is $[((DMeOPrPE)_2Fe)_2(\mu\text{-}N_2)]^{2+}$. Experiments were inconclusive as to whether **1** is a productive intermediate in the formation of NH_3 from $Fe(DMeOPrPE)_2N_2$. Neither ammonia nor hydrazine was formed in the protonation of **1**, but this result may simply indicate that these products are formed indirectly by the disproportionation of diazene. Unfortunately, experimental limitations of diazene traps prevented a definitive conclusion as to whether diazene forms when acid is added to **1**. If diazene does not form then a conclusion is that **1** is not involved in the formation of ammonia and hydrazine. If diazene does form, the conclusion of significance is that it will be difficult to increase the yields of ammonia because the disproportionation of diazene to hydrazine and then to ammonia is inherently so inefficient.

■ EXPERIMENTAL SECTION

Materials and Reagents. All manipulations were carried out either in a Vacuum Atmospheres Co. glovebox (Ar- or N_2-filled) or on a Schlenk line using Ar or N_2. HPLC grade THF, hexanes, and diethyl ether (Burdick and Jackson) were dried and deoxygenated by passing them 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. Commercially available reagents were used as received. *trans*-$[Fe(DMeOPrPE)_2(N_2)H][BPh_4]$ was synthesized as previously reported.[21] Deuterated solvents were purchased from Cambridge Isotope Laboratories and degassed via three freeze−pump−thaw cycles.

Instrumentation. $^{31}P\{^1H\}$ and ^{1}H NMR spectra were recorded on either a Varian Unity/Inova 300 spectrometer at an operating frequency of 299.94 (^{1}H) and 121.42 (^{31}P) MHz or on a Varian Unity/Inova 500 spectrometer at an operating frequency of 500.62 (^{1}H) and 202.45 (^{31}P) MHz. The ^{1}H and ^{31}P chemical shifts were referenced to the solvent peak or to an external standard of 1% H_3PO_4 in D_2O, respectively. NMR samples were sealed under argon or dinitrogen in 7 mm J. Young tubes. Note that the ^{1}H NMR data for the methyl and methylene regions in complexes containing the DMeOPrPE ligand were generally broad and uninformative and therefore are not reported in the synthetic descriptions below.

EPR spectra were recorded at 4 K on an Elexsys E500 X-band spectrometer at 9.4 GHz. Samples were prepared under argon (**1**) or

N_2 (**2**) by dissolving the complex in a mixture of THF and isopentane, then sealed in EPR tubes. UV−vis/NIR spectra were recorded on a PerkinElmer Lambda 1050 UV/vis/NIR spectrophotometer. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Raman spectra were collected on a WITec alpha300 S instrument at 532.3 nm. UV−vis spectra were collected on either an Agilent 8453 spectrophotometer or an Agilent Cary 100 spectrophotometer (for temperature-controlled studies).

METHODS

Generation of Fe(DMeOPrPE)$_2$N$_2$. Solid ^{t}BuOK (2 equiv) was added to a stirring solution of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H][BPh$_4$] in toluene or Et$_2$O/THF (2:1) in a dinitrogen-filled glovebox. The reaction was stirred for 14−16 h, after which time the solution was bright yellow in color with a white precipitate. The solution was filtered through Celite and immediately used in the protonation reaction. ^{31}P{^{1}H} NMR (toluene-*d*$_8$): δ 79.9 (s). ^{31}P NMR (toluene-*d*$_8$): δ 79.9 (s).

Synthesis of *cis*-Fe(DMeOPrPE)$_2$(H)$_2$. A solution of Fe(DMeOPrPE)$_2$N$_2$ in THF was charged with 1 atm of H$_2$ in a 50 mL Fisher-Porter tube and vigorously stirred for 6 h. The yellow oil was isolated by removing the solvent in vacuo. ^{31}P{^{1}H} NMR (DMSO-*d*$_6$) at 253 K: δ 98.9 (t, $^2J_{P-P}$ = 20 Hz), δ 84.8 (t, $^2J_{P-P}$ = 20 Hz). ^{1}H NMR (DMSO-*d*$_6$) of the hydride region: −14.5 (quintet, $^2J_{P-H}$ = 36 Hz), −14.7 (ddt, $^2J_{P-H}$ = 37 Hz, $^2J_{P-H}$ = 14 Hz, $^2J_{P-H}$ = 58 Hz). Both trans and cis isomers are seen at various temperatures by ^{1}H and ^{31}P NMR spectroscopy, a feature previously reported for analogous iron dihydride complexes.[49]

Alternative Synthesis of *cis*-Fe(DMeOPrPE)(H)$_2$. To a stirring solution of *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H][PF$_6$] (50 mg, 0.056 mmol) in THF was added solid ^{t}BuOK (13 mg, 0.112 mmol). The reaction was stirred for 2 h and then filtered through Celite. The yellow oil was isolated by removing the solvent in vacuo. The NMR spectra of the product synthesized by this route were identical to those described above.

Protonation of Fe(DMeOPrPE)$_2$N$_2$ and Determination of NH$_3$ and N$_2$H$_4$ Yields. In an N$_2$-filled glovebox, a solution of Fe(DMeOPrPE)$_2$N$_2$ prepared by the method above was immediately protonated with the appropriate acid (HCl, HBF$_4$, or HOTf) in a septum-sealed 2-neck round-bottom flask, and allowed to stir for 2 h after acid addition was complete. The flask was then removed from the glovebox and the volatiles were vacuum-transferred onto a frozen HCl solution (1 M HCl in Et$_2$O). A THF solution of ^{t}BuOK was then added to the remaining reaction mixture and stirred for 30 min. The volatiles were again vacuum-transferred into the same frozen HCl flask.[11] The flask was allowed to thaw and then the solvents were removed in vacuo. The remaining residue was dissolved in water and analyzed for ammonia and hydrazine using the indophenol[50] and *p*-(dimethylamino)benzaldehyde[51] methods, respectively. Yields of ammonia and hydrazine are reported relative to the amount of the *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H][BPh$_4$] starting material used.

Colorimetric Determination of Iron(II). Iron determinations were performed in a glovebox under a dinitrogen atmosphere sealed in airtight cuvettes before being analyzed on the UV−vis spectrometer. A 1 mM stock solution of iron(II) chloride was prepared, along with a 0.05 M 1,10-phenanthroline stock solution. A standard curve was obtained by mixing 1.0 mL of the 1,10-phenanthroline solution and 0.2−1.0 mL of the iron(II) chloride stock solution, diluting to 10 mL total volume, and allowing to stand for 30 min before the absorption reading was taken. The concentration of iron(II) in the starting complex, *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H][BPh$_4$], was measured by diluting the complex to an appropriate concentration (within the measured standard curve), then adding 1.0 mL of the 1,10-phenanthroline solution, diluting to 10 mL of total volume, and allowing to stand for 30 min. The reductive deprotonation and subsequent protonation reactions were then performed. An aliquot of the resulting reaction mixture was diluted to the appropriate volume, mixed with 1.0 mL of the 1,10-phenanthroline solution, diluted to 10 mL and allowed to stand for 30 min. All of the above procedures were initially performed in H$_2$O. However, the H$_2$O was found to react with Fe(DMeOPrPE)$_2$N$_2$; thus, anhydrous THF was used for these oxidation state determinations.

Protonation of Fe(DMeOPrPE)$_2$N$_2$ and NMR Analysis of Products. Fresh Fe(DMeOPrPE)$_2$N$_2$ was prepared as described above, and protonations were immediately carried out in an N$_2$-filled glovebox in a small scintillation vial with a septum cap. Triflic acid (1 M in Et$_2$O) was injected dropwise through the septum with a syringe. The resulting purple solution was quickly transferred to an NMR tube, removed from the glovebox, and frozen in liquid nitrogen for transfer to the NMR instrument. ^{31}P{^{1}H} NMR (2:1 Et$_2$O/THF) at 233 K: δ 76.6 (*trans*-[Fe(DMeOPrPE)$_2$(N$_2$)H]$^+$), δ 79 (Fe(DMeOPrPE)$_2$N$_2$), δ 88.4 (*trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$), δ 84.2 and δ 98.1 (*cis*-Fe(DMeOPrPE)(H)$_2$).

Combinations of Protonation Products from Table 2. All reactions were run in THF (or Et$_2$O/THF) under N$_2$ or Ar at room temperature. Equimolar amounts of each reactant were stirred in scintillation vials, filtered, and transferred to NMR tubes. Chemical shifts were referenced to known values;[15,21] no new peaks were observed.

Synthesis of [((DMeOPrPE)$_2$Fe)$_2$(μ-N$_2$)]$^{2+}$ (1) from *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)Cl][BPh$_4$]. To a solution of Fe(DMeOPrPE)$_2$N$_2$ in 2:1 Et$_2$O/THF under N$_2$ or Ar was added excess NaBPh$_4$, followed by dropwise addition of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)Cl][BPh$_4$] in THF until the solution became dark purple (a minimum of 2 equiv. of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$)Cl]$^+$ were needed). NaCl was removed by filtering the solution through Celite. The complex was precipitated as an oil by addition of hexanes to the solution. After the solvents had been removed and the complex was allowed to dry, a brown oil was obtained.

Synthesis of [((DMeOPrPE)$_2$Fe)$_2$(μ-N$_2$)]$^{2+}$ (1) from *trans*-Fe(DMeOPrPE)$_2$Cl$_2$. An excess of NaBPh$_4$ was added to a stirring solution of Fe(DMeOPrPE)$_2$N$_2$ under either an argon or N$_2$ atmosphere. *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ was dissolved in THF and added until the purple color formed. By studying the intensities of the UV−vis spectra, it was determined that 2.5−3 equiv of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ was necessary to form the purple complex. The mass spectrum of **1** did not show any of the dimer, but several peaks corresponding to mononuclear complexes were observed: ESI-MS (THF, +ve) *m*/*z* calculated for [Fe(DMeOPrPE)$_2$(N$_2$)]$^+$ (**2**) 848.42; found [M$^+$] 848.93. The five-coordinate [Fe(DMeOPrPE)$_2$H]$^+$ species was also observed: *m*/*z* calculated for [Fe(DMeOPrPE)$_2$H]$^+$ 821.33; found [M$^+$] 821.33. Some remaining Fe(DMeOPrPE)$_2$Cl$_2$ was observed: *m*/*z* calculated for [Fe(DMeOPrPE)$_2$Cl$_2$]$^+$ 890.35; found [M$^+$] 890.02. The complete mass spectrum and isotope patterns, which match the calculated patterns, are found in the Supporting Information (Figure S11).

Synthesis of [((DMeOPrPE)$_2$Fe)$_2$(μ-N$_2$)]$^{2+}$ (1) Using a One-Electron Reductant. NaPh$_2$CO was prepared by dissolving benzophenone in THF and letting it react with Na^0 for 2 h. To a solution of *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ in THF under N$_2$ was added excess NaBPh$_4$, followed by dropwise addition of the NaPh$_2$CO solution. Less than 2 equiv. of reducing agent were needed to produce **1**. Above 2 equiv., the intensity of peaks in the UV−vis spectrum begin to decrease because of the decomposition of the complex when exposed to reducing agents (see Figure S9).

Temperature-Dependent UV−Vis Spectrum of [((DMeOPrPE)$_2$Fe)$_2$(μ-N$_2$)]$^{2+}$ (1). [((DMeOPrPE)$_2$Fe)$_2$(μ-N$_2$)]$^{2+}$ was generated from *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ and Fe(DMeOPrPE)$_2$N$_2$ with NaBPh$_4$ under a N$_2$ atmosphere (see above). The complex was diluted with THF in an airtight quartz UV−vis cuvette. The temperature was varied in the instrument chamber with stirring against a THF background sample, also temperature-controlled, from 10 to 60 °C.

Tracking the Appearance of Fe(DMeOPrPE)$_2$N$_2$ in the Formation of 1. *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ and NaBPh$_4$ were dissolved in THF and NaPh$_2$CO was added under N$_2$ until the solution turned purple. ^{31}P{^{1}H} NMR: δ −27 (broad, free DMeOPrPE). Additional NaPh$_2$CO was added until the purple solution became yellow, and then faintly green because of the excess of

$NaPh_2CO$. $^{31}P\{^1H\}$ NMR: δ −26.9 (s, DMeOPrPE), δ 79.1 (s, $Fe(DMeOPrPE)_2N_2$). ^{31}P NMR: δ −26.9 (s), δ 79.1 (s, $Fe(DMeOPrPE)_2N_2$).

Protonation of the Purple Complex. Triflic acid was added to the purple complex in the same manner as described above for the protonation of $Fe(DMeOPrPE)_2N_2$. Unfortunately, no NH_4^+ was observed in the products of this reaction. $^{31}P\{^1H\}$ NMR: δ 87.8 (s, *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$), δ 76.7 (s, *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$), δ 59.1 (s, *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl]^+$), δ 20.1, and δ 18.8 (s, $DMeOPrPEH^+$, $DMeOPrPEH_2^{2+}$). A weaker acid (2,6-lutidinium tetraphenylborate) produced the same results.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

$^{31}P\{^1H\}$ and ^1H NMR spectra of the reaction of $Fe(DMeOPrPE)_2N_2$ with H_2O; alternative synthesis and ^{31}P and ^1H NMR spectra of *cis*-$Fe(DMeOPrPE)_2(H)_2$; Evans test calculations and results; EPR simulations, parameters used for simulations, and comparisons to other Fe(I) complexes; UV−vis spectra of the synthesis of **1** with varying amounts of reducing agent; ^1H NMR spectrum of the protonation of **1**; and the ESI mass spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dtyler@uoregon.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the NSF (CHE-0809393), the NSF GK-12 (Award #0742540), and the NSF REU (Award #1063144) for funding. We also acknowledge the NSF for funding to purchase the EPR spectrometer at the University of Oregon (CHE-0840478).

■ REFERENCES

(1) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W. *Nat. Geosci.* **2008**, *1*, 636−639.

(2) Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*; The MIT Press: Cambridge, MA, 2001.

(3) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature* **1976**, *259*, 204.

(4) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; pp 1073−1106.

(5) George, T. A.; Kaul, B. B. *Inorg. Chem.* **1990**, *29*, 4969−4974.

(6) Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862.

(7) Field, L. D.; Messerle, B. A.; Smernik, R. J. *Inorg. Chem.* **1997**, *36*, 5984−5990.

(8) Hirano, M.; Akita, M.; Morikita, T.; Kubo, H.; Fukuoka, A.; Komiya, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3453−3458.

(9) Sellmann, D.; Hennige, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 276−278.

(10) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200−202*, 379−409.

(11) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.

(12) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252−6254.

(13) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.

(14) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14574−14582.

(15) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184−10185.

(16) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120−125.

(17) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. *Science* **2011**, *334*, 780−783.

(18) Crossland, J. L.; Balesdent, C. G.; Tyler, D. R. *Dalton Trans.* **2009**, 4420−4422.

(19) Crossland, J. L.; Balesdent, C. G.; Tyler, D. R. *Inorg. Chem.* **2012**, *51*, 439−445.

(20) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295−3299.

(21) Crossland, J. L.; Young, D. M.; Zakharov, L. N.; Tyler, D. R. *Dalton Trans.* **2009**, 9253−9259.

(22) 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*, 5453−5465.

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

(24) A reviewer suggested that the counterion might substitute for the N_2 ligand. Better coordinating counterions would thus lower the yield of ammonia. However, control experiments showed that chloride will not substitute N_2 in $Fe(DMeOPrPE)_2N_2$ in basic solution. Substitution might occur in acidic solution, however.

(25) Russell, J. A. *J. Biol. Chem.* **1944**, *156*, 457−462.

(26) Fortune, W. B.; Mellon, M. G. *Ind. Eng. Chem. Anal. Ed.* **1938**, *10*, 60−64.

(27) Yelle, R. B.; Crossland, J. L.; Szymczak, N. K.; Tyler, D. R. *Inorg. Chem.* **2009**, *48*, 861−871.

(28) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983−3012.

(29) Field, L. D.; Guest, R. W.; Turner, P. *Inorg. Chem.* **2010**, *49*, 9086−9093.

(30) Although triflate gave the highest yields of ammonia in the experiments that investigated the role of the counterion, triflate was not used in these experiments because we were unable to synthesize the purple intermediate when triflate was used. We used $NaBPh_4$ instead of triflate because the synthesis of the purple species was successful with BPh_4^-.

(31) An excess of *trans*-$[Fe(DMeOPrPE)_2(N_2)Cl][BPh_4]$ is needed because much of the low-valent Fe(II) that is generated decomposes rapidly (seen as free DMeOPrPE in the ^{31}P NMR spectrum).

(32) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

(33) Girolami, G. S.; Rauchfuss, T. B.; Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry: A Laboratory Manual*, 3rd ed.; University Science Books: Sausalito, CA, 1999.

(34) Adams, C. J.; Bedford, R. B.; Carter, E.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Huwe, M.; Cartes, M. Á.; Mansell, S. M.; Mendoza, C.; Murphy, D. M.; Neeve, E. C.; Nunn, J. *J. Am. Chem. Soc.* **2012**, *134*, 10333−10336.

(35) Mankad, N. P.; Whited, M. T.; Peters, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 5768−5771.

(36) Gilbert-Wilson, R.; Field, L. D.; Colbran, S. B.; Bhadbhade, M. M. *Inorg. Chem.* **2013**, *52*, 3043−3053.

(37) Crossland, J. L.; Tyler, D. R. *Coord. Chem. Rev.* **2010**, *254*, 1883−1894.

(38) Bellerby, J. M.; Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1232−1236.

(39) Sellmann, D.; Hille, A.; Heinemann, F. W.; Moll, M.; Rösler, A.; Sutter, J.; Brehm, G.; Reiher, M.; Hess, B. A.; Schneider, S. *Inorg. Chim. Acta* **2003**, *348*, 194−198.

(40) Díaz-Torres, R.; Alvarez, S. *Dalton Trans.* **2011**, *40*, 10742−10750.

(41) Addition of a chloride source (tetraethylammonium chloride) to a THF solution of purple **1** generated a green solution reminiscent of the color of the $Fe(DMeOPrPE)_2Cl_2$ complex. However, the UV−vis spectrum of the green solution did not match that of $Fe(DMeOPrPE)_2Cl_2$, and no peaks were observed in the low-temperature (−60 °C) $^{31}P\{^1H\}$ NMR spectrum, thereby eliminating *trans*-$Fe(DMeOPrPE)_2Cl_2$ (61.5 ppm) as well as $[Fe(DMeOPrPE)_2Cl]^+$ (55.9 ppm) as the identity of the green solution.

(42) Komiya, S.; Akita, M.; Yoza, A.; Kasuga, N.; Fukuoka, A.; Kai, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 787−788.
(43) Yelle, R. B. *personal communication*; University of Oregon: Eugene, OR, 2013.
(44) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 758−759.
(45) Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. *Inorg. Chem.* **2005**, *44*, 3768−3770.
(46) Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747.
(47) Crossland, J. L.; Zakharov, L. N.; Tyler, D. R. *Inorg. Chem.* **2007**, *46*, 10476−10478.
(48) Miller, C. E. *J. Chem. Educ.* **1965**, *42*, 254−259.
(49) Baker, M. V.; Field, L. D.; Young, D. J. *Appl. Organomet. Chem.* **1990**, *4*, 551−556.
(50) Chaney, A. L.; Marbach, E. P. *Clin. Chem.* **1962**, *8*, 130−132.
(51) Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006−2008.