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Coordination of a Complete Series of N_2 Reduction Intermediates (N_2H_2, N_2H_4, and NH_3) to an Iron Phosphine Scaffold

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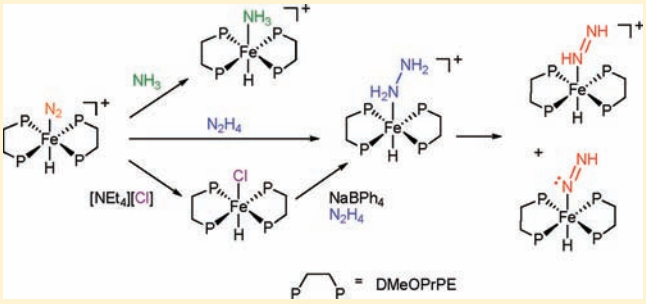
Ⓢ *Supporting Information*

ABSTRACT: The series of dinitrogen reduction intermediates (N_2H_2, N_2H_4, and NH_3) coordinated to the $Fe(DMeOPrPE)_2H^+$ (DMeOPrPE = 1,2-[bis(dimethoxypropyl)phosphino]ethane) scaffold has been synthesized or generated. The synthesis of *trans*-$[Fe(DMeOPrPE)_2(NH_3)H][BPh_4]$ and generation of *trans*-$[Fe(DMeOPrPE)_2(N_2H_4)H][BPh_4]$ were achieved by substitution of the dinitrogen ligand on *trans*-$[Fe(DMeOPrPE)_2(N_2)H][BPh_4]$. The *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$ complex and its deprotonated conjugate base, *trans*-$Fe(DMeOPrPE)_2(N_2H)H$, were observed by ^{31}P and ^1H NMR from decomposition of *trans*-$[Fe(DMeOPrPE)_2(N_2H_4)H]^+$ in the presence of excess hydrazine. Attempts to chemically oxidize *trans*-$[Fe(DMeOPrPE)_2(N_2H_4)H]^+$ to *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H][BPh_4]$ with a variety of oxidizing agents yielded only decomposition products consistent with the intermediate formation of *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$ prior to decomposition.



INTRODUCTION

The coordination chemistry of N_2 reduction products, i.e., N_2H_2, N_2H_4, and NH_3, coordinated with iron is becoming increasingly important as mounting evidence suggests that these species are likely formed during nitrogenase turnover.[1−3] Nonbiological systems that produce ammonia may also involve such intermediates. An iron phosphine dinitrogen complex, $Fe^0(DMeOPrPE)_2N_2$ (**1**, where DMeOPrPE is the water-soluble 1,2-[bis(dimethoxypropyl)phosphino]ethane ligand), was shown to generate ammonia upon the addition of acid.[4] Although the mechanism of this transformation is still unknown, previous work established the syntheses and interconversion of coordinated *cis*-hydrazine and *cis*-hydrazido species that are potential reaction intermediates in the ammonia-forming reaction (Scheme 1, top pathway, species **4**−**6**).[5]

Recent density functional theory calculations showed that the first protonation of the five-coordinate **1** is thermodynamically more likely to occur at the iron center than at the terminal (distal) nitrogen atom.[6] This leads to a proposed alternative mechanism involving *trans*-hydride complexes (Scheme 1, species **7**−**10**). Herein we report characterization of the complete series of these *trans*-hydride intermediates that contain N_2, N_2H_2, N_2H_4, and NH_3 ligands bonded to the $Fe(DMeOPrPE)_2H^+$ scaffold.

RESULTS AND DISCUSSION

Complex *trans*-$[Fe(DMeOPrPE)_2(NH_3)H]^+$ (10). Because the N_2 ligand in the *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ complex (**7**) is labile,[7] it was hypothesized that this complex could provide a convenient entry into coordination complexes of N_2H_2, N_2H_4, and NH_3. The reaction of **7** with a saturated solution of NH_3 in tetrahydrofuran (THF) for 2 days under argon resulted in a color change from pale brown to bright yellow and the appearance of a new resonance at 82.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. This resonance splits into a doublet in the proton-coupled ^{31}P NMR spectrum ($^1J_{PH} = 48$ Hz), suggesting that the hydride ligand is still bonded to the iron center (Figure 1). Experiments aimed at optimizing the yield showed that an argon atmosphere (instead of N_2) must be used in order for the reaction to go to completion and excess ammonia must be bubbled through the solution to remove any residual N_2. The ^1H NMR spectrum of the product showed resonances for coordinated DMeOPrPE[8] as well as additional resonances at −29.6 ppm (assigned to a hydride ligand) and a broad singlet at −0.8 ppm (Figure 1). For comparison, the hydride resonance in the previously reported *trans*-$[Fe(DMPE)_2(NH_3)H]^+$ complex is found at −29.61 ppm and the coordinated NH_3 resonance appears as a broad singlet at −1.61 ppm.[9] Because of these spectroscopic similarities, the product from the reaction of **7** with NH_3 is assigned as **10**. The ^{15}N (−441 ppm, quartet, $^1J_{NH} = 64$ Hz) and $^{15}N\{^1H\}$ (−441 ppm, singlet) NMR spectra for *trans*-$[Fe(DMeOPrPE)_2(^{15}NH_3)H]^+$ (Figure S1 in the Supporting Information) also match that of *trans*-$[Fe(DMPE)_2(^{15}NH_3)H]^+$ (−443.1 ppm),[11] which confirms the coordination of ammonia to iron. In addition, the IR spectrum of the product showed the disappearance of the $\nu(NN)$ stretch at 2088 cm^{-1} of the starting material, **7**, and the appearance of new NH_3 vibrations

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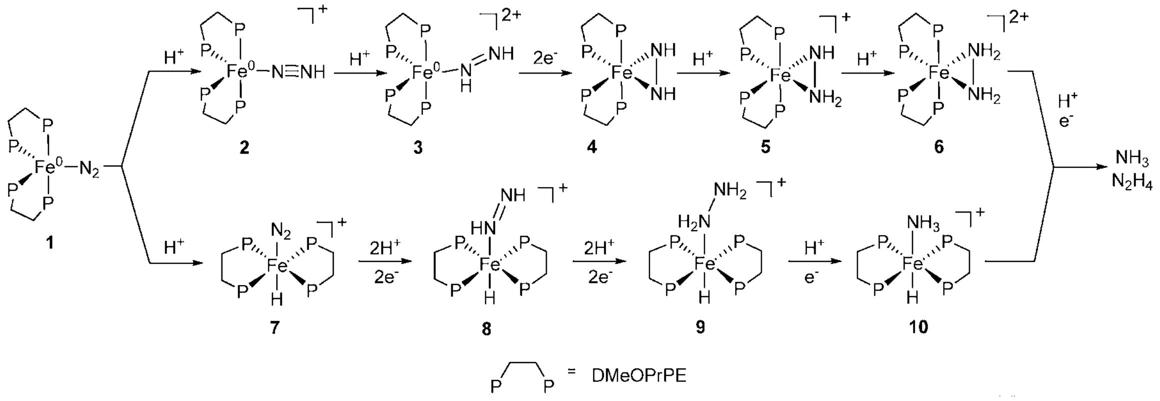
Scheme 1. Two Potential Mechanisms for the Formation of Ammonia Starting with 1[a,4,5]



[a]The top pathway starts with protonation of the terminal nitrogen atom, while the more energetically favored bottom pathway follows protonation of the iron atom.

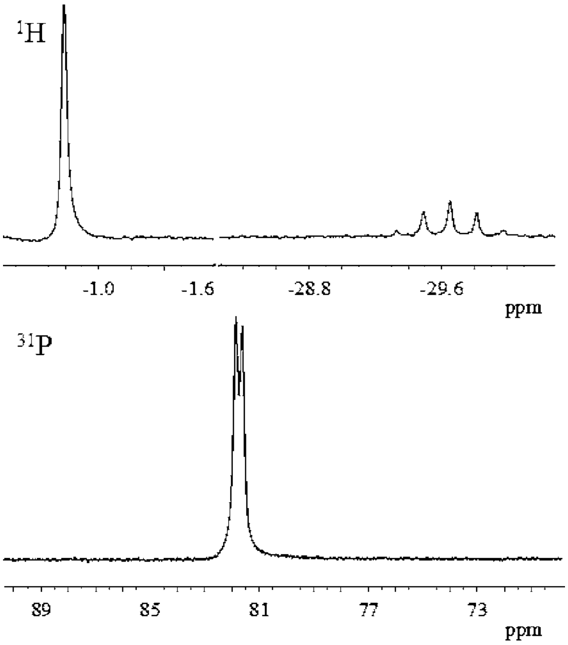
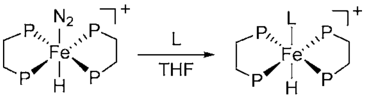


Figure 1. ^1H (top) and ^{31}P (bottom) NMR spectra for **10**.

(see the Experimental Section for details). On the basis of these data, the reaction in Scheme 2 is proposed (L = NH_3).

Scheme 2. Substitution of the N_2 Ligand on 7 with Ammonia or Hydrazine Leading to 10 or 9, Respectively



L = NH_3 (**10**), N_2H_4 (**9**)

Complex *trans*-[Fe(DMeOPrPE)$_2$(N_2H_4)H]$^+$ (9). The hydrazine complex **9** was also generated by substitution of the N_2 ligand in **7** (Scheme 2). Excess hydrazine was stirred with a THF solution of **7** for 12 h under an argon atmosphere. The bright-yellow product of this reaction, assigned below as complex **9**, showed a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at 81.3 ppm, which was split into a doublet when the proton decoupler was turned off (Figure 2). Similar to the reaction with ammonia, the N_2 complex is seemingly more stable than the hydrazine complex and N_2 had to be removed by the addition of excess hydrazine under an argon atmosphere for the reaction to proceed to completion. The ^1H NMR spectrum of the proposed product **9** showed a hydride resonance at −29.3 ppm (Figure 2), similar to that of **10**. The ^{31}P and ^1H NMR data suggest that hydrazine is coordinated to the iron center; however, to confirm the bonding geometry of the hydrazine ligand, the ^{15}N isotopologue was synthesized. The $^{15}N\{^1H\}$ NMR spectrum showed two resonances at −317 and −383 ppm, suggesting inequivalent nitrogen atoms and thus an η^1 geometry. Close inspection of these resonances revealed that they are doublets with $^1J_{NN}$ splitting of 5 Hz. In the proton-coupled ^{15}N NMR spectrum, both of these resonances are observed as triplets ($^1J_{NH}$ = 63 and 69 Hz, respectively; Figure 2). By a comparison of these ^{15}N coupling constants with those of the various resonances in the ^1H NMR spectrum, the proton resonances for hydrazine could be identified (Figure S2 in the Supporting Information). On this basis, the two broad doublets observed at 3.68 ($^1J_{NH}$ = 68 Hz) and 2.87 ($^1J_{NH}$ = 59 Hz) ppm were assigned to the hydrazine protons. This assignment was also confirmed using a 1D $^1H-^{15}N$ HMQC experiment, which displayed ^{15}N correlation only with those two protons. (See the Supporting Information for details and the results of the HMQC experiment.)

Attempts were made to isolate **9**; however, the complex decomposed in a THF solution over the course of several hours. Although Field et al. were able to characterize the related *trans*-[Fe(DMPE)$_2$(N_2H_4)H]$^+$ complex by single-crystal X-ray diffraction,[11] the corresponding DMeOPrPE complexes are oils that do not crystallize easily. (This is a common problem when using the DMeOPrPE ligand because of the $-CH_2CH_2CH_2OCH_3$ groups.) As shown by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S4 in the Supporting Information), **9** decomposed in THF into a mixture of **10**, **7**, and *trans*-[Fe(DMeOPrPE)$_2$(H_2)H]$^+$ (Table 1). These products likely arise from disproportionation and decomposition of the coordinated hydrazine (eqs 1 and 2), which are common reactions for hydrazine in the presence of transition metals.[12−15] Note that disproportionation of N_2H_4 could potentially be the source of, or contribute to, the ammonia

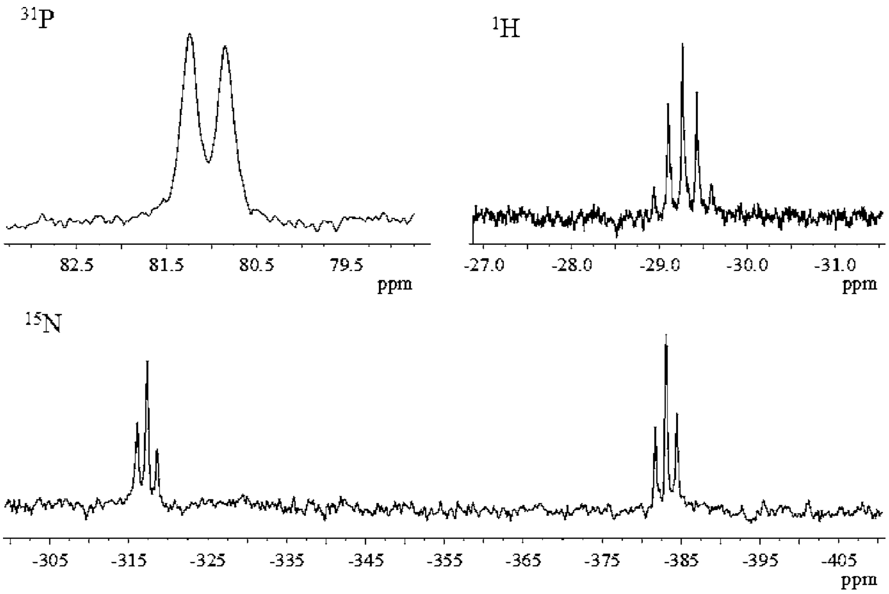


Figure 2. ^{31}P (top left), ^{1}H (top right), and ^{15}N (bottom) NMR spectra for *trans*-[Fe(DMeOPrPE)$_2$($^{15}N_2H_4$)H]$^+$.

Table 1. NMR Data for *trans*-Fe(DMeOPrPE)$_2$(L)H^{n+} Complexes

complex	^{31}P (ppm)	^{1}H of the hydride ligand (ppm)	$^{2}J_{PH}$ (Hz)	solvent
trans-[Fe(DMeOPrPE)$_2$(N$_2$)H]$^+$ (7)[7]	75.8	−18.6, quin	49	toluene-*d*$_8$
trans-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$ [7]	85.0	−15.1, quin	47	toluene-*d*$_8$
trans-[Fe(DMeOPrPE)$_2$(NH$_3$)H]$^+$ (**10**)[a]	82.0	−29.6, quin	48	C$_6$D$_6$
trans-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)H]$^+$ (**9**)[a]	81.3	−29.3, quin	49	THF-*d*$_8$
trans-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$ (**8**)[a]	79.6	−17.8, quin	49	toluene-*d*$_8$
trans-Fe(DMeOPrPE)$_2$(N$_2$H)H (**8b**)[a]	80.8	−19.2, quin	49	toluene-*d*$_8$
trans-Fe(DMeOPrPE)$_2$(Cl)H[a]	83.0	−32.5, quin	49	C$_6$D$_6$

[a] This work.

formed in the reaction of **1** with acid (Scheme 1).

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \quad (1)$$

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad (2)$$

Reactions of *trans*-Fe(DMeOPrPE)$_2$(Cl)H. An alternative starting material for the generation of complexes **9** and **10** was sought because the ligand exchange reaction with **7** was slow and **9** started to decompose on the time scale of the ligand exchange. It was hypothesized that if the *trans*-Fe(DMeOPrPE)$_2$(Cl)H complex could be formed cleanly, then the reaction of this complex with a chloride abstractor and the desired ligand (NH$_3$ or N$_2$H$_4$) should provide clean and relatively fast conversion to these complexes. *trans*-Fe(DMeOPrPE)$_2$(Cl)H was previously synthesized by reacting *trans*-Fe(DMeOPrPE)$_2$Cl$_2$ with a hydride source; however, the complex was never generated cleanly by this route.[16] Because **7** can be synthesized as an analytically pure solid,[7] the reaction of this complex with chloride should provide a clean synthesis of *trans*-Fe(DMeOPrPE)$_2$(Cl)H. Indeed, this reaction proceeded smoothly in THF using tetraethylammonium chloride as the organic-soluble chloride source. The *trans*-Fe(DMeOPrPE)$_2$(Cl)H complex was isolated as a bright-orange oil and characterized in solution by NMR spectroscopy.[17] This route provides a much cleaner synthesis of *trans*-Fe(DMeOPrPE)$_2$(Cl)H, with the only impurities being uncoordinated DMeOPrPE (as assayed by ^{31}P NMR), which was removed using chromatography (Figure S5 in the Supporting Information), and [NEt$_4$][BPh$_4$], which was removed by filtering the reaction mixture through Celite. Unfortunately, *trans*-Fe(DMeOPrPE)$_2$(Cl)H was soluble in all organic solvents, even hexane and pentane, and thus all attempts at recrystallization and, in particular, mixed solvent recrystallization were unsuccessful. As a consequence, the complex could only be isolated as an oil by in vacuo solvent removal.

The reaction of *trans*-Fe(DMeOPrPE)$_2$(Cl)H with excess $^{15}N_2H_4$ in the presence of TlPF$_6$ resulted in the generation of a myriad of species. The ^{31}P{^{1}H} NMR spectrum showed seven different products (Figure 3). Most of the products could be assigned straightforwardly because they had been previously

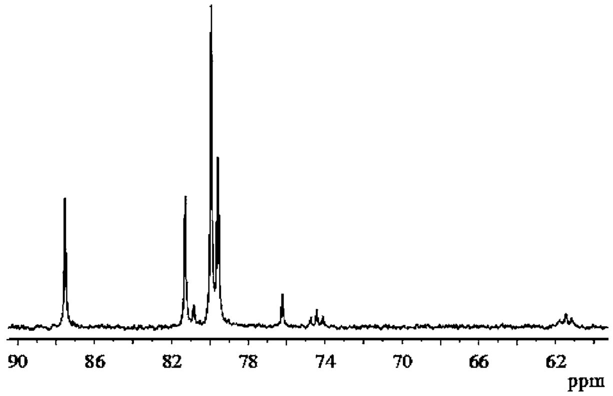


Figure 3. ^{31}P{^{1}H} NMR spectrum of the products from the reaction of *trans*-Fe(DMeOPrPE)$_2$(Cl)H with TlPF$_6$ and excess $^{15}N_2H_4$.

synthesized using alternative routes. Thus, the mixture contained *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$ (87.5 ppm), **10** (81.3 ppm), **9** (79.9 ppm), **7** (76.2 ppm), and *cis*-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)]$^{2+}$ (74.4 and 61.5 ppm).[15] However, there were also two peaks at 79.6 and 80.8 ppm that had not been previously observed. For each of these species, the singlet ^{31}P{^{1}H} resonance splits into a doublet in the ^{31}P NMR spectrum, which suggests a *trans*-pseudooctahedral geometry of the complex with a hydride ligand and four equivalent phosphorus atoms. As explained next, the structures of these *trans*-Fe(DMeOPrPE)$_2$(L)H^{n+} complexes could be definitively identified using ^{1}H NMR data.

Diazene Complexes. The two unidentified species both exhibited a multiplet in the downfield region (13−15 ppm) of the ^{1}H NMR spectrum (Figure 4, bottom). By comparison to the ^{1}H NMR spectra of the previously reported *trans,trans*-[W(^{15}NH=^{15}NH)(CO)$_2$(NO)(PPh$_3$)$_2$][SO$_3$CF$_3$][19] and [Ru(NH=NH){P(OEt)$_3$}$_5$][BPh$_4$]$_2$[20] complexes (Figure S6 in the Supporting Information), which display end-on N$_2$H$_2$ bonding, these multiplets are assigned to *trans*-[Fe(DMeOPrPE)$_2$(^{15}N$_2$H$_2$)H]$^+$ and *trans*-Fe(DMeOPrPE)$_2$(^{15}N$_2$H)H (Figure 5, **8** and **8b**, respectively). Further confirmation of the **8** assignment comes from the *WinDNMR* simulation of the ^{1}H splitting pattern (Figure 4, top; see the Supporting Information for details of the simulation).

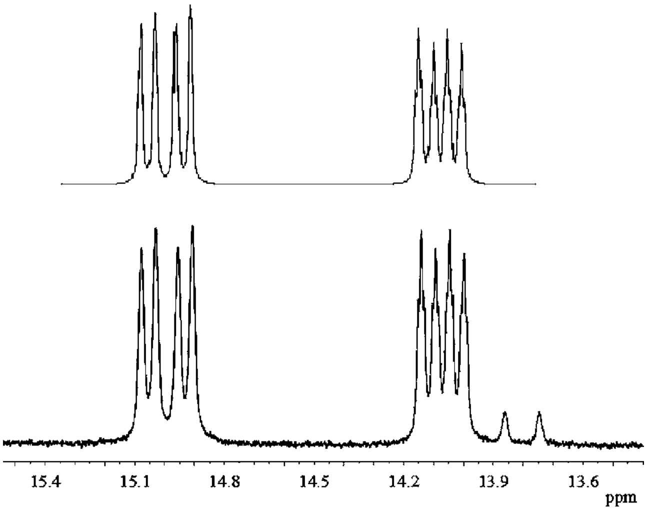
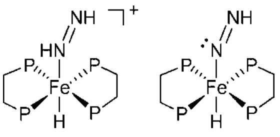


Figure 4. Bottom: downfield ^{1}H NMR spectrum of a product from the reaction of *trans*-Fe(DMeOPrPE)$_2$(Cl)H with excess ^{15}N$_2$H$_4$ in the presence of TlPF$_6$. Top: simulated ^{1}H NMR spectrum (ABM$_2$XY spin system) of the N$_2$H$_2$ resonances in *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$. The spectrum was simulated using *WinDNMR-Pro*.[21]



8 **8b**

Figure 5. Proposed structures of **8** and **8b**.

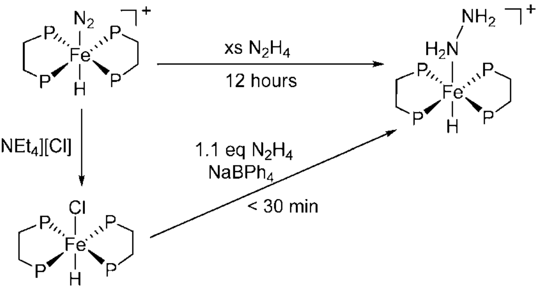
On the basis of the literature assignments for the ^{1}H NMR spectra of [W(^{15}NH=^{15}NH)(CO)$_2$(NO)(PPh$_3$)$_2$][SO$_3$CF$_3$] and [Ru(NH=NH){P(OEt)$_3$}$_5$][BPh$_4$]$_2$, the resonance at 15 ppm is assigned to the proton attached to the terminal (distal) nitrogen atom of the coordinated diazene, with coupling to ^{15}N and the other diazene proton causing the doublet of doublets splitting pattern. A similar coupling at 14.1 ppm is observed for the proximal proton, with added coupling to four equivalent phosphorus atoms resulting in a doublet of doublet of multiplets. The pathway for the formation of **8** is unclear. Hydrazine is known to produce diazene upon oxidation;[22,23] thus, **8** could be formed by oxidation of *trans*-[Fe(DMeOPrPE)$_2$(^{15}N$_2$H$_4$)H]$^+$, presumably by adventitious O$_2$. More likely, however, is a pathway in which the diazene is formed by decomposition of hydrazine (eq 3). Because other complexes with ligands from decomposition or disproportionation of hydrazine are also observed in this reaction, this pathway is suggested to be the most likely.

$$N_2H_4 \rightarrow N_2H_2 + H_2 \tag{3}$$

It is proposed that the remaining resonance at 13.8 ppm in the ^{1}H NMR spectrum represents the lone proton on the terminal nitrogen atom of the coordinated deprotonated diazene in **8b**. This resonance is in close proximity to the N$_2$H$_2$ signals and in the expected region for coordinated diazene and its derivatives.[24] A doublet is observed due to coupling with ^{15}N. It is proposed that **8b** arises from deprotonation of **8** by excess hydrazine present in the solution. It has previously been shown that the proximal proton of a diazene coordinated to a metal is quite acidic[26] and can be easily deprotonated to form the diazenido complex.[29,30]

Synthesis of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$. The decomposition products observed in the reaction of N$_2$H$_4$ with *trans*-Fe(DMeOPrPE)$_2$(Cl)H likely result from the excess N$_2$H$_4$ used in the reaction. When only 1.1 equiv of N$_2$H$_4$ was added to a solution of *trans*-Fe(DMeOPrPE)(Cl)H with NaBPh$_4$, pure **9** was formed within minutes (Scheme 3), making this a much faster route to the hydrazine complex than the substitution of N$_2$ on **7**. Again, however, the complex was unstable in solution at 23 °C, and over several hours at room temperature, it decomposed to the products discussed above. Nevertheless, the faster formation of **9** allowed for the complex to be generated in situ and used immediately in further reactions. In particular, the direct synthesis of the diazene complex *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$ was attempted by chemical oxidation of **9**. Initial attempts to oxidize **9** using O$_2$ introduced from the air resulted only in exchange of the N$_2$H$_4$ ligand for N$_2$, forming **7**, as indicated by a resonance at 76.3 ppm in the ^{31}P{^{1}H} NMR spectrum. The addition of pure O$_2$ to a sample of **9** resulted in the formation of **7** and *trans*-[Fe(DMeOPrPE)$_2$(H$_2$)H]$^+$, as indicated by resonances at 76.4

Scheme 3. Synthesis of 9 by Substitution of the N$_2$ Ligand of 7 (Top) or by Abstraction of the Cl Ligand from *trans*-Fe(DMeOPrPE)$_2$(Cl)H (Bottom)



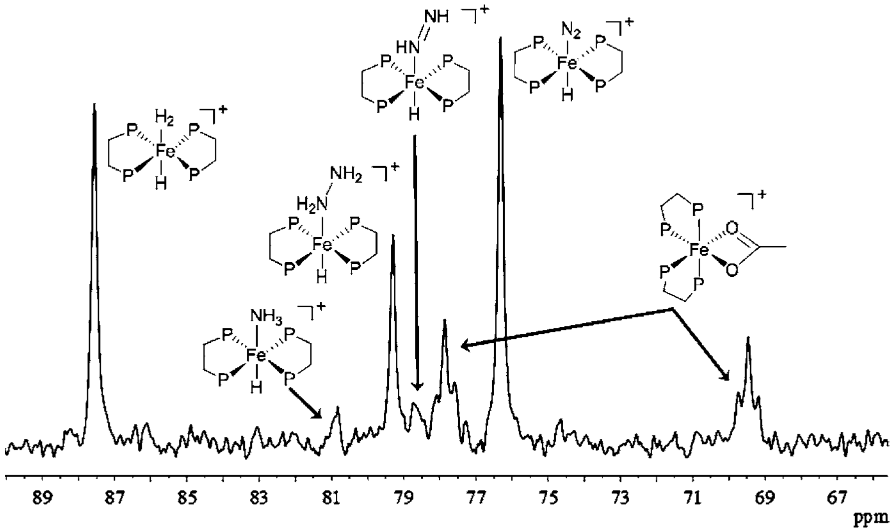
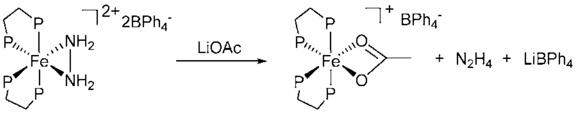


Figure 6. $^{31}P\{^1H\}$ NMR spectrum of the products from the oxidation of **9** with $Pb(OAc)_4$.

and 87.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. A total of 2 equiv of either $[FeCp_2][PF_6]$ or ^tBuOOH added to a THF solution of **9** also produced a mixture of **7** and *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$. The N_2 and H_2 ligands in these products likely came from decomposition of N_2H_4, although N_2 and H_2 are also decomposition products of N_2H_2. None of these reactions showed any ^{31}P NMR evidence for the formation of *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$.

On the basis of literature precedents, the most promising oxidant for coordinated hydrazine is lead(IV) acetate, a two-electron oxidant that has been used at low temperatures and high purity to oxidize hydrazine ligands to diazene in tungsten,[20] ruthenium, osmium,[31] and, recently, iron[32] complexes. However, previous work[33] with *cis*-$[Fe(DMeOPrPE)_2(N_2H_4)]^{2+}$ showed that acetate will displace the hydrazine ligand and chelate to the iron center, forming purple *cis*-$[Fe(DMeOPrPE)_2(O_2CCH_3)]^+$ (eq 4). Not surprisingly, therefore, the reaction of *cis*-$[Fe(DMeOPrPE)_2(N_2H_4)]^{2+}$ with $Pb(OAc)_4$ led only to acetate substitution and no oxidation of the N_2H_4 ligand.



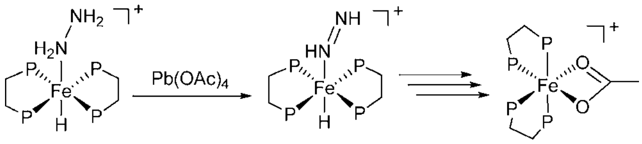
(4)

To test for acetate binding to the iron center in **9**, the complex was exposed to excess sodium acetate or lithium acetate. For both salts, the solution did not change color and the $^{31}P\{^1H\}$ NMR spectra of the products showed only the singlet of **9** at 79.3 ppm undiminished in intensity over a period of 1 day. These results indicated that acetate does not react with **9**. Thus, in an attempt to generate *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$, high-purity $Pb(OAc)_4$ was added to a cold solution (−78 °C) of **9**. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (Figure 6) revealed (by comparison to the resonances in Figure 3) the starting material (79.3 ppm) as well as *cis*-$[Fe(DMeOPrPE)_2(O_2CCH_3)]^+$ (triplets at 69.5 and 77.9 ppm), **7** (76.3 ppm), *trans*-$[Fe(DMeOPrPE)_2(H_2)H]^+$ (87.6 ppm), **10** (80.8 ppm), and a small peak at 78.8 ppm that is assigned to *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$ (78.8 ppm; see the Results and Discussion section).

This reactivity suggests that *trans*-$[Fe(DMeOPrPE)_2(N_2H_2)H]^+$ may be forming, but it is unstable, which leads the diazene ligand to dissociate from the iron center and decompose into N_2 and H_2 (eq 5), which allows the acetate ion to bind (Scheme 4). In any case, the conversion is not quantitative enough to make it useful for isolation of the diazene complex.

$$N_2H_2 \rightarrow N_2 + H_2 \qquad (5)$$

Scheme 4. Suggested Pathway for the Formation of *cis*-$[Fe(DMeOPrPE)_2(O_2CCH_3)]^+$ from the Reaction of 9 with $Pb(OAc)_4$



■ CONCLUSIONS

A long-term goal is to increase the yield of ammonia and hydrazine that form when acid is added to **1**. (The combined yield of hydrazine and ammonia is <20%.) An additional goal is to make the reaction catalytic by using H_2 as the source of electrons. Mechanistic information about the reaction pathway will be helpful in achieving these goals. Unfortunately, the reaction is not amenable to traditional kinetic studies, so we have implemented an approach involving the synthesis and/or generation of proposed reaction intermediates as a way to gain mechanistic insights. The new complexes **8**–**10** were reported in this study, and thus every numbered complex in Scheme 1 has now been either synthesized or generated and spectroscopically characterized with the exception of molecules **2** and **3**. To our knowledge, this is the first time that coordination complexes of N_2, N_2H_2, N_2H_4, and NH_3 ligands on the same iron scaffold have been characterized. All of the complexes react or decompose under acidic conditions to form hydrazine and/or ammonia, and thus superficially all of the species are potential intermediates in the reaction to form hydrazine and ammonia. On this basis, it is not yet possible to differentiate between the top and bottom pathways in Scheme 1. Obviously, the mechanisms for several of the transformations (e.g., **8** → **9**) are considerably more intricate than suggested, and detailed studies are underway to probe these intimate mechanisms now that we have access to the intermediates.

It is interesting to note that both the top and bottom pathways in Scheme 1 involve the "symmetric" protonation of the coordinated N_2 unit. In this regard, these pathways are different from the "asymmetric" protonation pathway proposed for some Mo−N_2 complexes that form ammonia. Recent studies suggest a "symmetric" protonation pathway for nitrogenase[3] (which has iron in its active site), and it may well be a general conclusion that Fe−N_2 species produce ammonia via a symmetric protonation mechanism.

With regard to nitrogenase, the spectroscopic data for the intermediates in Scheme 1 are also useful for a comparison with trapped intermediates in nitrogenase turnover.[1−3] A subsequent paper will report on one such comparison and the implications for the mechanism of nitrogen fixation with nitrogenase.[34]

■ EXPERIMENTAL SECTION

Materials and Reagents. All manipulations were carried out either in a Vacuum Atmospheres Co. glovebox (argon- or N_2-filled) or on a Schlenk line using argon or N_2 gas. HPLC-grade THF, hexane, 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. Commercially available reagents were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and degassed via three freeze−pump−thaw cycles. *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4] was synthesized as previously reported.[7]

Instrumentation. NMR samples were sealed under argon or N_2 in 7 mm J. Young tubes. $^{31}P\{^1H\}$ 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. Note that the ^1H 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. ^{15}N NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at an operating frequency of 50 MHz. The ^{15}N chemical shifts were referenced to an external standard of neat nitromethane (set to 0 ppm). IR spectra were recorded on a Nicolet Magna 550 FT-IR with *OMNIC* software. Samples were prepared either as neat oils using NaCl windows, as KBr pellets, or in solution using a CaF_2 cell. Mass spectra were obtained using an Agilent LC/MS mass spectrometer. The samples were dissolved in THF and introduced into the ionization head (electrospray ionization, ESI) using the infusion method.

Synthesis of *trans*-[Fe(DMeOPrPE)$_2$(NH_3)H][BPh_4] (10). THF saturated with NH_3 (2 mL) was added to a stirring THF solution of *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4] (0.049 g, 0.042 mmol) under argon. The solution was stirred for 2 days, over which time the solution color changed from pale brown to bright yellow. Alternatively, excess ammonia can be bubbled directly through a THF solution of *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4], yielding *trans*-[Fe(DMeOPrPE)$_2$(NH_3)H][BPh_4] after 4 h. The solvent was allowed to evaporate, leaving a bright-orange-yellow oil. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 82.0 (s). ^{31}P NMR (C_6D_6): δ 82.0 (d, $^2J_{PH}$ = 48 Hz). ^1H NMR (C_6D_6) of the hydride region: δ −0.86 (s, br) and δ −29.6 (quintet, $^2J_{HP}$ = 48 Hz). $^{15}N\{^1H\}$ NMR (THF-d_8): δ −441 (s). ^{15}N NMR (THF-d_8): δ −441 (quartet, $^1J_{N-H}$ = 64 Hz). The ^{15}N isotopologue was prepared by degredation of *trans*-[Fe(DMeOPrPE)$_2$($^{15}N_2H_4$)H][BPh_4] prepared by the reaction of $^{15}N_2H_4$ with *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4]. ESI-MS(+) (THF): *m/z* 838.5 ([Fe(DMeOPrPE)$_2$(NH_3)H]$^+$). The complex reacted with the N_2 purge gas to form [Fe(DMeOPrPE)$_2$(N_2)H]$^+$ in the mass spectrometer. Calcd for [Fe(DMeOPrPE)$_2$(N_2)H]$^+$: *m/z* 849.43. Found: *m/z* 849.5 [M$^+$]. The five-coordinate [Fe(DMeOPrPE)$_2$H]$^+$ species from loss of the labile NH_3 ligand was also observed. Calcd for [Fe(DMeOPrPE)$_2$H]$^+$: *m/z* 821.42. Found: *m/z* 821.5 [M$^+$]. The complete MS spectrum and isotope pattern, which matches the calculated pattern, are found in the Supporting Information. IR (neat): ν_{NH_3} 3329 and 3211 cm^{-1}; δ_{NH_3} 1615 and 1258 cm^{-1}. Using a liquid IR cell, ν_{FeH} was observed at 1961 cm^{-1}.

Synthesis of *trans*-[Fe(DMeOPrPE)$_2$(N_2H_4)H][BPh_4] (9). A N_2H_4/THF solution (1.7 mL, 0.072 M) was added to a stirring THF solution of *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4] (0.14 g, 0.120 mmol) under argon. The reaction was stirred for 12 h, during which time the solution color changed from brown to bright yellow. The solvent was allowed to evaporate, yielding an orange-yellow oil. The ^{15}N isotopologue was synthesized in the same manner using $^{15}N_2H_4$. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 81.3 (s). ^{31}P NMR (THF-d_8): δ 81.3 (d, $^2J_{PH}$ = 49 Hz). ^1H NMR (THF-d_8) of the hydride region: δ −29.3 (quintet, $^2J_{HP}$ = 49 Hz). $^{15}N\{^1H\}$ NMR (THF-d_8): δ −317 (d, $^1J_{NN}$ = 5 Hz), −383 (d, $^1J_{NN}$ = 5 Hz). ^{15}N NMR (THF-d_8): δ −317 (td, $^1J_{NH}$ = 63 Hz, $^1J_{NN}$ = 5 Hz), −383 (td, $^1J_{NH}$ = 69 Hz, $^1J_{NN}$ = 5 Hz). ^1H−^{15}N HMQC (THF-d_8): δ 3.7 (d, $^1J_{HN}$ = 68 Hz), 2.9 (d, $^1J_{HN}$ = 59 Hz). MS analysis showed that the complex reacted with the N_2 purge gas to form [Fe(DMeOPrPE)$_2$(N_2)H]$^+$ in the mass spectrometer. Calcd for [Fe(DMeOPrPE)$_2$(N_2)H]$^+$: *m/z* 849.43. Found: *m/z* 849.33 [M$^+$]. Using a liquid IR cell, ν_{FeH} was observed at 1962 cm^{-1}.

Synthesis of *trans*-Fe(DMeOPrPE)$_2$(Cl)H. An excess of tetraethylammonium chloride was added to a stirring THF solution of *trans*-[Fe(DMeOPrPE)$_2$(N_2)H][BPh_4] under argon. The reaction was stirred for 2 h and filtered through Celite to remove [NEt_4][BPh_4], and then the solvent was allowed to evaporate, yielding a bright-orange oil. The product contained uncoordinated DMeOPrPE as an impurity. The free ligand was removed by running the pentane solution through a column of basic alumina and then washing the column with pentane several times. The product, still bound to the alumina, was then isolated by washing the column with diethyl ether. As discussed in the text, the product was readily soluble in all organic solvents and thus could only be obtained as an oil. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 83.0 (s). ^{31}P NMR (C_6D_6): δ 83.0 (d, $^2J_{PH}$ = 49 Hz). ^1H NMR (C_6D_6) of the hydride region: δ −32.5 (quintet, $^2J_{HP}$ = 49 Hz).

Alternative Synthesis of *trans*-[Fe(DMeOPrPE)$_2$(N_2H_4)H][BPh_4]. To a stirring solution of *trans*-Fe(DMeOPrPE)$_2$(Cl)H in THF (0.033 g, 0.038 mmol) was added a solution of hydrazine in THF (65 μL, 0.603 M, 0.039 mmol). $NaBPh_4$ (0.013 g, 0.039 mmol) was immediately added, and the mixture was allowed to stir for 1 h. The bright-yellow solution was filtered through Celite. The NMR spectra of the product synthesized by this route were identical with those described above.

Reaction of *trans*-Fe(DMeOPrPE)$_2$(Cl)H with $^{15}N_2H_4$. $TlPF_6$ was added to a THF-d_8 solution of *trans*-Fe(DMeOPrPE)$_2$(Cl)H under argon, and the solution was filtered through Celite directly into a J. Young tube. To this NMR tube was added a 10-fold excess of $^{15}N_2H_4$. The initial $^{31}P\{^1H\}$ NMR spectrum showed a mixture of **9** and **10**. Because of the addition of excess hydrazine, a clean ^1H NMR spectrum could not be obtained. The tube was allowed to stand overnight. Hexane and pentane were then used to precipitate the products, and the resulting oil was washed twice with pentane. The oil was then redissolved in toluene-d_8 and filtered through Celite into another J. Young NMR tube. The $^{31}P\{^1H\}$ NMR spectrum showed seven different iron phosphine species. By a comparison of the integrations in the $^{31}P\{^1H\}$ and ^1H NMR spectra, five of the species could be assigned because they had been previously synthesized. The other two species were assigned as **8** and **8b** (see the Results and Discussion section). Only the NMR data for these two species are listed here. **8**. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 79.6 (s). ^{31}P NMR (toluene-d_8): δ 79.6 (d, $^2J_{PH}$ = 49 Hz). ^1H NMR (toluene-d_8): δ 15.0 (dd, $^1J_{HN}$ = 60 Hz, $^3J_{HH}$ = 24 Hz), 14.1 (ddt, $^1J_{HN}$ = 48 Hz, $^3J_{HH}$ = 24 Hz, $^3J_{HP}$ = 5 Hz), −17.8 (quintet, $^2J_{HP}$ = 49 Hz). **8b**. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 80.8 (s). ^{31}P NMR (toluene-d_8): δ 80.8 (d, $^2J_{PH}$ = 49 Hz). ^{1}H NMR (toluene-d_8): δ 13.8 (d, $^1J_{HN}$ = 58 Hz), −19.2 (quintet, $^2J_{HP}$ = 49 Hz).

Acetate Binding Control Experiments. Excess sodium acetate was added to a THF solution of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)H]-[BPh$_4$]. There was no change in the ^{31}P{^{1}H} NMR spectrum over 24 h (singlet at 79.3 ppm). The same result was achieved with excess lithium acetate.

Lead Acetate Oxidation of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)H]-[BPh$_4$]. A solution of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)H][BPh$_4$] in an NMR tube fitted with a septum was cooled to −78 °C. The slow addition of excess 99.99% Pb(OAc)$_4$ dissolved in THF using a syringe resulted in a mixture of products, most of which could be assigned (see the Results and Discussion section). One peak of interest in the ^{31}P{^{1}H} NMR spectrum corresponded to *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$. ^{31}P{^{1}H} NMR (THF): δ 78.8 (s).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{15}N NMR spectra of **10**, ^{1}H and ^{1}H HMQC spectra of **9**, decomposition of **9**, ^{31}P NMR spectra of *trans*-Fe-(DMeOPrPE)$_2$(Cl)H, and calculated ^{1}H NMR spectrum of *trans*-[Fe(DMeOPrPE)$_2$(N$_2$H$_2$)H]$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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