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# Nitrogen Fixation Revisited on Iron(0) Dinitrogen Phosphine Complexes

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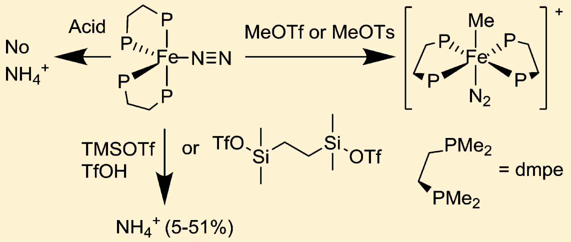
Supporting Information

**ABSTRACT:** A reinvestigation of the treatment of $[Fe(N_2)(PP)_2]$ (PP = depe, dmpe) with acid revealed no ammonium formation. Instead, rapid protonation at the metal center to give hydride complexes was observed. Treatment of $[Fe(N_2)(dmpe)_2]$ with methylating agents such as methyl triflate or methyl tosylate resulted in methylation of the metal center to afford $[FeMe(N_2)(dmpe)_2]^+$. Treatment of $[Fe(N_2)(dmpe)_2]$ with trimethylsilyl triflate, however, resulted in reaction at dinitrogen affording $NH_4^+$ on subsequent treatment with acid. The side-on bound hydrazine complex $[Fe(N_2H_4)(dmpe)_2]^{2+}$ and bis(ammonia) complex $[Fe(NH_3)_2(dmpe)_2]^{2+}$ were identified by $^{15}N$ NMR spectroscopy as other species formed in the reaction mixture.



## INTRODUCTION

Recent reviews into the mechanism of action of nitrogenases have highlighted the importance of iron as the key metal in the biological process of reducing dinitrogen to ammonia.[1] While the earliest reports of synthetic homogeneous well-defined catalysts for the reduction of dinitrogen primarily involved molybdenum,[2] recent advances in the conversion of dinitrogen to ammonia using iron complexes have been reported. In particular, the catalytic conversion of dinitrogen to tris(trimethylsilyl)amine in the presence of iron complexes such as $[Fe(CO)_5]$, $[Fe(SiMe_3)_2(CO)_4]$, $[CpFe(CO)_2]_2$ (Cp = cyclopentadienyl), $[Cp_2Fe]$, or $[\{\eta^5\text{-}C_5H_2(SiMe_3)_3\}_2Fe]$ has recently been demonstrated by Nishibayashi et al. where the tris(trimethylsilyl)amine product was hydrolyzed quantitatively to afford ammonia (up to 34 equiv based on Fe).[3] Reduction of dinitrogen to ammonia has also been demonstrated by Peters et al. using $[(TPB)Fe(N_2)]^-$ (TPB = $B(o\text{-}C_6H_4P^iPr_2)_3$), $[(CP^iPr_3)Fe(N_2)]^-$ ($CP^iPr_3$ = $C(o\text{-}C_6H_4P^iPr_2)_3^-$), or $[(CAAC)_2Fe]$ (CAAC = cyclic (alkyl)(amino)carbene) in the presence of acid and a strong reductant (potassium graphite).[4,5] Peters et al. have also reported other instances of dinitrogen functionalization on iron,[6−8] with electrophilic methylating reagents or silylating agents. Holland et al. reported that treatment of an iron β-diketiminate complex $[LFe(\mu\text{-}Cl)]_2$ (L = $MeC\{C(Me)N(2,6\text{-}Me_2C_6H_3)\}_2^-$) with potassium graphite under an atmosphere of nitrogen generated a tetrairon bis(nitride) complex, where the N−N triple bond of dinitrogen was completely cleaved. Subsequent treatment of the tetrairon dinitride complex with hydrogen gas afforded ammonia (42%).[9]

In some of the earliest reports of the conversion of coordinated dinitrogen to ammonia on iron complexes, Leigh et al. reported the in situ formation of Fe(0) dinitrogen complexes $[Fe(N_2)(PP)_2]$ [PP = depe = 1,2-bis(diethylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane] by deprotonation of the hydrido dinitrogen complexes *trans*-$[FeH(N_2)(PP)_2]^+BPh_4^-$ with a strong base such as potassium *tert*-butoxide.[10] Treatment of the Fe(0) dinitrogen complexes with common mineral acids such as HCl, $H_2SO_4$, and also $HBF_4$ afforded low yields of ammonia (3−20%). Leigh's results were different than those observed by Komiya et al., who reported that acid treatment of $[Fe(N_2)(depe)_2]$, synthesized by an alternative route, that is, the reduction of *trans*-$[FeCl_2(depe)_2]$ with sodium naphthalenide under an atmosphere of nitrogen, formed no ammonium.[11] In a related experiment, George and Zubieta et al. reported the formation of hydrazine and a very small amount of ammonia on reaction of $[Fe(N_2)(NP_3)]$ ($NP_3$ = $N(CH_2CH_2PPh_2)_3$) with HBr.[12] Tyler et al. have also reported that treatment of $[Fe(N_2)(DMeOPrPE)_2]$ (DMeOPrPE = 1,2-(bis(dimethoxypropyl)phosphine)ethane) with triflic acid afforded ammonium (up to 17%) and hydrazinium (2%).[13]

In this paper, we reinvestigate the reactions of Fe(0) dinitrogen complexes $[Fe(N_2)(PP)_2]$ (PP = depe, dmpe) with various acids and explore their reactivity with methylating and silylating agents.

## RESULTS AND DISCUSSION

We initially addressed the different results obtained by Leigh[10] and Komiya.[11] Both of these reports begin with Fe(0) dinitrogen complexes. Komiya's approach uses purified initial complexes, while Leigh generates the critical Fe(0) species in situ. When complexes are generated in situ, there is always the question as to whether the byproducts and/or residual reagents

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or some yet-to-be-identified species in solution could have a role in any reactions observed.

In both the Leigh and Komiya reports, ammonia was detected and quantified using the indophenol method—a colorimetric technique based on the reaction of ammonia with an oxidizing agent (such as hypochlorite) and phenol to form indophenol, which affords a blue color under alkaline conditions.[14] Interferences have been reported, both positive and negative, with nitrogen-containing compounds, metals, nonmetals (like sulfur and halogens), salt, and light.[15] While there have recently been reports of the use of $^1$H NMR spectroscopy to detect the presence of ammonium (where the resonance for ammonium appears at ~7 ppm as a relatively sharp 1:1:1 triplet with $^1J_{HN}$ 51 Hz due to coupling to $^{14}$N), the amount of ammonium formed was still determined by the indophenol method.[2a,4,13a,16] We used both $^1$H and $^{14}$N NMR spectroscopy for the detection of ammonium (Figure 1). $^{14}$N is 99.6% naturally abundant, and although the nucleus has a quadrupole moment, signals for ammonium are sharp due to the high electronic symmetry about the N atom. $^{14}$N NMR spectroscopy is particularly useful for samples that are only soluble in water (where the ammonium $^1$H cannot be detected due to exchange) or for samples where the relevant region in the $^1$H NMR (around 7 ppm) is obscured by other resonances. We are able to reliably detect ammonium at concentrations as low as 2 mmol/L (0.05 mg in 0.5 mL) using $^{14}$N NMR spectroscopy.

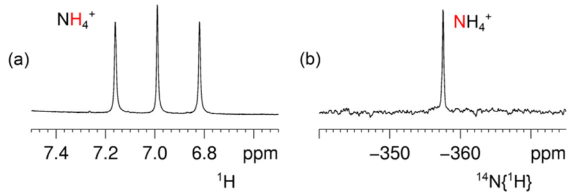


**Figure 1.** (a) $^1$H NMR spectrum and (b) $^{14}$N{$^1$H} NMR spectrum of ammonium triflate (DMSO-$d_6$, 300 MHz).

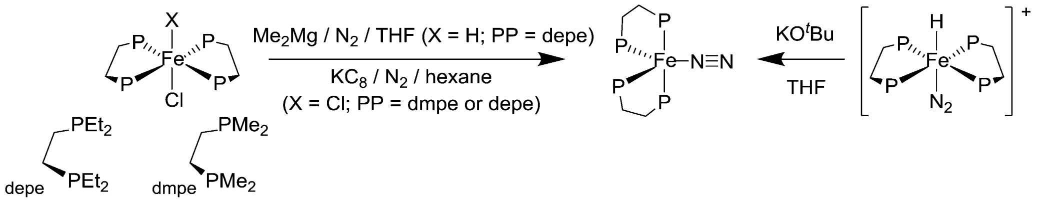
**Reaction of [Fe($N_2$)($PP)_2$] with HCl and with Triflic Acid.** The Fe(0) dinitrogen complex [Fe($N_2$)(depe)$_2$] was synthesized by treating the hydrido chloro complex [FeHCl(depe)$_2$] with dimethylmagnesium under an atmosphere of nitrogen (Scheme 1). In this case, methyl substitution of the chloride followed by elimination of methane affords a transient Fe(0) species,[17] which is presumably trapped by $N_2$. [Fe($N_2$)(dmpe)$_2$] was synthesized by reduction of the dichloro complex [$FeCl_2$(dmpe)$_2$] with potassium graphite under an $N_2$ atmosphere (Scheme 1). In this case, reduction of the dichloro complex gives the transient Fe(0) species that is presumably trapped by $N_2$. [Fe($N_2$)(depe)$_2$] can also be synthesized via potassium graphite reduction of the corresponding dichloride under $N_2$. These routes are modifications of Komiya's method and allow isolation of clean Fe(0)−$N_2$ products.

Both [Fe($N_2$)(dmpe)$_2$] and [Fe($N_2$)(depe)$_2$] dinitrogen complexes were also synthesized in situ by deprotonation of the corresponding hydrido dinitrogen compound, [FeH($N_2$)(PP)$_2$]$^+$, with potassium *tert*-butoxide (Leigh method). The $^{15}N_2$-labeled complexes were also synthesized using the above methods, and $^{15}$N NMR spectroscopy showed the complexes made by the different routes to be spectroscopically identical. We do not see any spectroscopic evidence for other dinitrogen complexes such as a bridging dinitrogen complex or a complex containing a dinitrogen bridging to $K^+$. On HCl treatment of [Fe($N_2$)(PP)$_2$] synthesized by the modified Komiya method, no ammonium was detected by NMR spectroscopy, and the main iron-containing products were identified as [FeH($N_2$)(PP)$_2$]$^+$ and [FeHCl(depe)$_2$]/[$FeCl_2$(dmpe)$_2$].

The reaction mixture after HCl treatment of [Fe($N_2$)(PP)$_2$] prepared in situ following Leigh's method exhibited a blue color when subjected to the indophenol test; however, no ammonium was detected by NMR spectroscopy. When the NMR samples were doped with 1 mg of ammonium chloride, a $^{14}$N signal at −356.8 ppm was readily detected, confirming that the samples do not contain anything that might obscure the detection of ammonium. Given our detection limit (see above), we would detect $NH_4^+$ if the yield was greater than 0.9% based on the concentration of [Fe($N_2$)(PP)$_2$]. The observed blue color from the indophenol test could arise from a false positive interference by iron[13b] or possibly from residual scraps of phosphine ligand in the reaction mixture. An authentic sample of dmpe·2HCl synthesized by treating dmpe with a solution of HCl in tetrahydrofuran does give rise to a blue color similar to that from a positive test when subjected to the standard indophenol test. While it is indeed inappropriate to conduct the indophenol test on a crude reaction mixture, we detected a broad $^{31}$P{$^1$H} NMR signal at 6.1 ppm for $H_2dmpe^{2+}$ in the $H_2SO_4$ solution used to collect the volatiles after base-distillation[10c] of a reaction mixture (after HCl treatment of [Fe($N_2$)(dmpe)$_2$] prepared by the Leigh method). This shows that the dmpe ligand is volatile enough to be distilled over and sufficiently robust to withstand treatment with base under these conditions. We cannot eliminate the possibility that the indophenol test may give a false positive under the reaction conditions particularly when detecting small amounts of $NH_4^+$. We also prepared HCl in situ by treatment of chlorotrimethylsilane with methanol[10b] and reacted the resulting solution with [Fe($N_2$)(dmpe)$_2$] prepared by $KC_8$ reduction of [$FeCl_2$(dmpe)$_2$] to find no ammonium formed.

Treatment of [Fe($N_2$)(dmpe)$_2$] with triflic acid afforded [Fe(dmpe)$_3$]$^{2+}$[18] as the main iron-containing byproduct, while reaction with 2,6-lutidinium triflate afforded [FeH($N_2$)(dmpe)$_2$]$^+$ and [{FeH(dmpe)$_2$}$_2$($\mu$-dmpe)]$^{2+}$ as the major products.[19] In our hands, neither the reaction of Fe($N_2$)-

**Scheme 1. Synthesis of Fe(0) Dinitrogen Complexes**

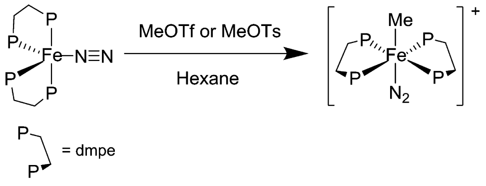


$(dmpe)_2$ with triflic acid nor lutidinium triflate afforded detectable amounts of $NH_4^+$.

While it is not possible to determine where initial reaction with $H^+$ might occur, apparently the products observed after reaction with acid show protonation at the metal center rather than protonation at dinitrogen. In this paper we report our investigation of the reaction of Fe(0) complexes with bulkier electrophiles.

**Reaction of $[Fe(N_2)(dmpe)_2]$ with Methyl Triflate or Methyl Tosylate.** Treatment of $[Fe(N_2)(dmpe)_2]$ with strongly electrophilic methylating agents such as methyl triflate (MeOTf) or methyl tosylate (MeOTs) at room temperature afforded the iron(II) methyl dinitrogen complex *trans*-$[FeMe(N_2)(dmpe)_2]^+$ (Scheme 2). This complex is unstable, especially in solution at room temperature, where after ~30 min the solution color darkens, a dark brown insoluble solid precipitates, and resonances for mainly $[Fe(dmpe)_3]^{2+}$[18] and other unidentified products are detected by NMR spectroscopy. The $^1H$ NMR spectrum of *trans*-$[FeMe(N_2)(dmpe)_2]^+$, acquired as soon as possible after dissolution of the sample, exhibits a pentet at −1.83 ppm, which collapses to a singlet on $^{31}P$ decoupling, and this resonance is characteristic of a metal-bound methyl group coupled to four equivalent phosphorus atoms, that is, a complex with an axial methyl group with four equivalent phosphorus nuclei in the equatorial plane of an octahedral complex. The $^1H$ NMR chemical shifts for the methyl groups in previously reported Fe−Me complexes range from 0.07 to −3.47 ppm.[20] The $^{13}C$ signal corresponding to the iron-bound methyl group was observed in the two-dimensional (2D) $^1H-^{13}C$ heteronuclear single quantum coherence (HSQC) NMR spectrum as a correlation at −15.3 ppm, which is within the range from −7.5 to −20 ppm reported for Fe−Me complexes.[20b] N≡N stretching frequencies were also observed at 2085 and 2068 $cm^{-1}$ in the IR spectrum—while we are uncertain of the reason for the presence of two bands for $\nu(N{\equiv}N)$, such a phenomenon has been previously reported.[21] While the molecular cation for $[FeMe(N_2)(dmpe)_2]^+$ was found at *m/z* 399.1087 at only 2% relative abundance in the mass spectrum, cations for $[Fe(N_2)(dmpe)_2\text{-}H]^+$ (*m/z* 383.0777) and $[FeMe(dmpe)_2]^+$ (*m/z* 371.1026) were found at 62 and 27% relative abundance, respectively. The isolated methyl complex $[FeMe(N_2)(dmpe)_2]^+$ is a rare example of a mononuclear methyl dinitrogen derivative.[22,23]

Scheme 2. Methylation of $[Fe(N_2)(dmpe)_2]$ to Afford $[FeMe(N_2)(dmpe)_2]^+$



So like reaction with $H^+$, the usual electrophilic methylating reagents “$Me^{+}$” also give products where the metal center has been methylated rather than products where the coordinated dinitrogen ligand in the Fe(0) dinitrogen complex has been methylated.

**Reaction of $[Fe(N_2)(dmpe)_2]$ with Trimethylsilyl Triflate.** Addition of the bulkier electrophile trimethylsilyl triflate (TMSOTf) to a solution of $[Fe(N_2)(dmpe)_2]$ in hexane, followed by evaporation of the volatiles under reduced pressure, afforded a brown solid, and $[FeH(N_2)(dmpe)_2]^+$ (40% yield) and $[Fe(dmpe)_3]^{2+}$ (44% yield) can be detected by NMR spectroscopy as components of the solid. The brown solid presumably also contains an N-trimethylsilylated species, and addition of triflic acid (TfOH) to the mixture afforded $NH_4^+$ (Scheme 3) as observed as a 1:1:1 triplet at ~ δ 7 ($^1J_{HN}$ 51 Hz, deuterated dimethyl sulfoxide (DMSO-$d_6$)) in the $^1H$ NMR spectrum. Further confirmation for the presence of ammonium was obtained by $^{14}N\{^1H\}$ NMR spectroscopy where a sharp singlet at δ −357.6 was observed (δ −358.6 for authentic sample of ammonium triflate in DMSO-$d_6$). On $^{15}N$-labeling, signals for $^{15}NH_4^+$ as well as $[FeH(^{15}N_2)(dmpe)_2]^+$ were observed by standard one-dimensional (1D) $^1H$ and $^{15}N$ NMR spectroscopy as well as by the 2D $^1H-^{15}N$ HSQC experiment (Figure 2).

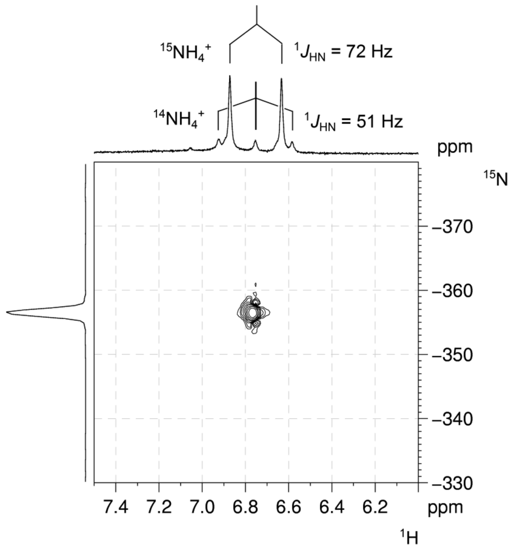
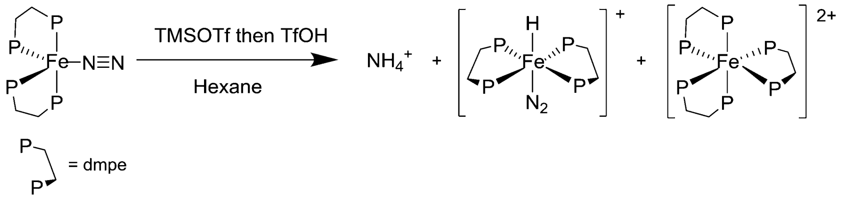


**Figure 2.** $^1H-^{15}N$ HSQC NMR spectrum (DMSO-$d_6$, 300 MHz) from the reaction of $[Fe(^{15}N_2)(dmpe)_2]$ with TMSOTf then TfOH.

Quantification of ammonium was performed by integration of the 1:1:1 triplet in the $^1H$ NMR spectrum against the signal of a known amount of dioxane as an internal standard. Yields of

Scheme 3. Reaction of $[Fe(N_2)(dmpe)_2]$ with Trimethylsilyl Triflate Then Trific Acid to Afford Ammonium



$NH_4^+$ ranged from 5 to 17% (yields calculated based on a 1:1 ratio of Fe complex/$NH_4^+$) under a variety of conditions (Table 1, entries 1 to 7)—the best yields of 17% were obtained when the reaction was performed under nitrogen in hexane with an excess of TMSOTf.

**Table 1. Yields of $NH_4^+$ from the Reaction of $[Fe(N_2)(dmpe)_2]$ with Trimethylsilyl Triflate Then with Triflic Acid**

| entry | reaction conditions | yield[a] (%) |
|---|---|---|
| 1 | Hexane solvent, 6−109 equiv TMSOTf, under nitrogen, room temperature | 17 ± 3[b] |
| 2 | 29 equiv TMSOTf added by diffusion | 11 |
| 3 | Reaction at −78 °C, 3 equiv TMSOTf | 11 |
| 4 | 103−1660 equiv TMSOTf added under vacuum | 7 ± 3[c] |
| 5 | Mixture of hexane and 1,4-dioxane solvent, 29 equiv TMSOTf | 6 |
| 6 | Mixture of hexane and dimethoxyethane solvent, 29 equiv TMSOTf | 5 |
| 7 | Mixture of hexane and diethyl ether solvent, 29 equiv TMSOTf | 6 |
| 8 | 17−26 equiv TMSOTf, 11−18 equiv KO$^t$Bu | 25 ± 6[d] |
| 9 | 9−19 equiv $(OTf)Me_2Si(CH_2)_2SiMe_2(OTf)$ | 23 ± 5[e] |
| 10 | 41−109 equiv TMSOTf, 8−10 equiv $CoCp^*_2$ | 37 ± 12[e] |
| 11 | 15−37 equiv TMSOTf, 9−22 equiv KO$^t$Bu, 9−13 equiv $CoCp^*_2$ | 51 ± 2[e] |

[a] Yields based on 1:1 ratio of Fe complex/$NH_4^+$. [b] Average of 13 runs. [c] Average of 2 runs. [d] Average of 4 runs. [e] Average of 3 runs.

Lowering the reaction temperature did not increase the yield of $NH_4^+$ (entry 3). The lower yield of $NH_4^+$ when TMSOTf was added under vacuum (entry 4) is probably due to degradation of the Fe(0) dinitrogen complex, which is unstable under vacuum. The lower yields of $NH_4^+$ when the reaction was performed in a range of solvents such as hexane and 1,4-dioxane, dimethoxyethane, or diethyl ether (Entries 5 to 7) may be due to a shift in the reaction profile toward the formation of more unwanted byproducts instead of the desired functionalized dinitrogen product in these solvents. The formation of $[FeH(N_2)(dmpe)_2]^+$ in this reaction is probably due to protonation of $[Fe(N_2)(dmpe)_2]$ by small amounts of acid formed by the reaction of TMSOTf with trace amounts of water. Given that $[FeH(N_2)(dmpe)_2]^+$ can be deprotonated with bases such as KO$^t$Bu to afford $[Fe(N_2)(dmpe)_2]$, it is no surprise that the yield of $NH_4^+$ formed increased to 25% when the reaction was performed in the presence of the KO$^t$Bu (entry 8). The type of silyl reagent is also important—a higher yield of $NH_4^+$ (23%) was obtained when the silyl reagent $(OTf)Me_2Si(CH_2)_2SiMe_2(OTf)$ was used (entry 9), while only a trace amount of $NH_4^+$ was detected when silyl reagents $^i$Pr$_3$SiOTf or $^t$BuMe$_2$SiOTf were used, indicating that increasing steric bulk on the silyl group did not improve the $NH_4^+$ yield.

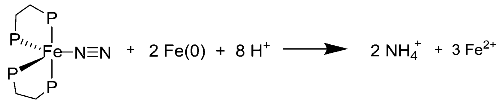
The Fe(0) oxidation state appears necessary for the formation of ammonia as in the reaction of the Fe(II) complex $[FeH(N_2)(dmpe)_2]^+$ with TMSOTf in a mixture of diethyl ether/tetrahydrofuran and then TfOH in DMSO-$d_6$, no ammonium was detected by $^{14}N$ NMR spectroscopy.

No $NH_4^+$ was formed when using chlorotrimethylsilane as the electrophilic silane indicating that either a more electrophilic silicon is required for the reaction to proceed or that the presence of chloride may facilitate an alternative reaction pathway.

The analogous depe complex $[Fe(N_2)(depe)_2]$, synthesized by reduction of $[FeCl_2(depe)_2]$ with potassium graphite, afforded $NH_4^+$ in a yield of 8% on treatment with TMSOTf then TfOH—a similar yield to that for the analogous dmpe complex.

It is important to recall that each molecule of dinitrogen requires six electrons and eight protons for the conversion to two molecules of $NH_4^+$ (Scheme 4). As there are no external sources of electrons in the reaction mixture, the Fe(0) must be sacrificially providing electrons to power the reaction, and this is probably one reason for the relatively low yields.

### Scheme 4



Assuming Fe(0) loses two electrons to form Fe(II), three molecules of Fe(0) dinitrogen complex are required to form two molecules of ammonia, that is, 1 equiv of Fe(0) dinitrogen complex can only afford a maximum of two-thirds of an equivalent of ammonia (or 67% yield). The Fe(0)/Fe(II) couple also sets a target zone for the redox potential that is required to provide reducing power to the reaction mixture. There is also the possibility that Fe(II) is further oxidized to Fe(III) as the reaction proceeds.

Reactions were performed with addition of an excess of $CoCp^*_2$ (where Cp* = pentamethylcyclopentadienyl) as an external electron source, and this increased the yield of ammonium to 37% (Table 1, entry 10). Reactions performed in the presence of both KO$^t$Bu and $CoCp^*_2$ increased the yield further to 51% (Table 1, entry 11). These yields must be taken in the context assuming that four electrons for the $N_2$ reduction are supplied by $CoCp^*_2$ so the maximum theoretical yield of ammonium is 200%. While the $NH_4^+$ yields reported here are sub-stoichiometric, the reduced yields are probably due, in part, to decomposition of the reactive $Fe(N_2)(dmpe)_2$ starting material and the formation of other products from competing reaction pathways.

We also attempted to characterize the "N-TMS product" formed after reaction with TMSOTf but before addition of TfOH. In particular, given Nishibayashi's report that Fe complexes in conjunction with sodium and TMSCl can facilitate the reduction of dinitrogen to tris(trimethylsilyl)amine ($N(TMS)_3$),[3] we looked for $N(TMS)_3$ by $^{29}Si$ NMR spectroscopy using both 1D and 2D techniques without success.

In one reaction of labeled $[Fe(^{15}N_2)(dmpe)_2]$ with TMSOTf, the $^{15}N$ NMR signatures of hydrazine complex $[Fe(^{15}N_2H_4)(dmpe)_2]^{2+}$ (−387.0 ppm) and bis(ammonia) complex $[Fe(^{15}NH_3)_2(dmpe)_2]^{2+}$ (−422.6 ppm) were detected (Figure 3)—the protons presumably arising from trace

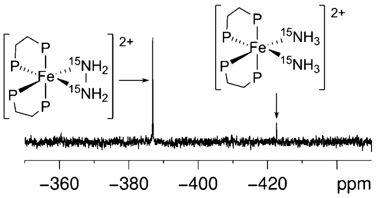
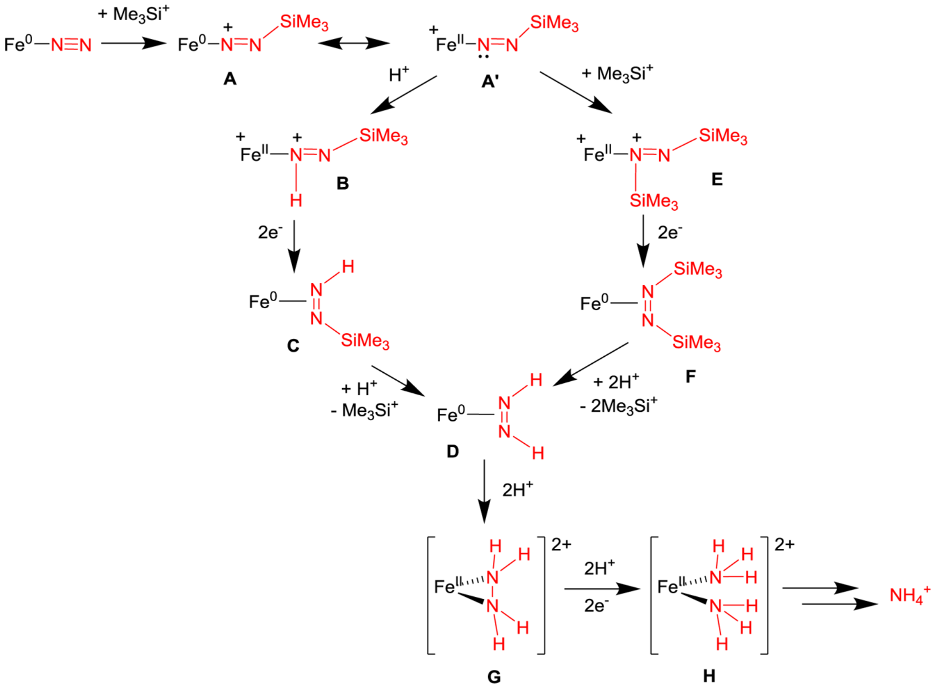


**Figure 3.** $^{15}N\{^1H\}$ NMR spectrum (DMSO-$d_6$, 51 MHz) from the reaction of $[Fe(^{15}N_2)(dmpe)_2]$ with TMSOTf and trace acid.

Scheme 5. A Possible Mechanism for the Trimethylsilyl-Mediated Conversion of Dinitrogen to Ammonia on Iron Containing the dmpe Ligand



amounts of water reacting with TMSOTf to form trace amounts of TfOH. A reaction with controlled addition of TfOH to the residue after reaction with TMSOTf also showed resonances for both the hydrazine and bis(ammonia) complexes, uncoordinated hydrazine, as well as a number of minor unidentified products. We have previously reported the synthesis and characterization of the hydrazine complex $[Fe(N_2H_4)(dmpe)_2]^{2+}$ where $\delta_N = -387.9$ ppm.[24] The bis(ammonia) complex $[Fe(NH_3)_2(dmpe)_2]^{2+}$ has not been reported previously and was synthesized independently by treatment of $[FeCl_2(dmpe)_2]$ with ammonia in methanol where the $^{15}N$ NMR signal was observed at −422.7 ppm. Both $[Fe(N_2H_4)(dmpe)_2]^{2+}$ and $[Fe(NH_3)_2(dmpe)_2]^{2+}$ are potential intermediates along the reaction cascade from Fe(0)−$N_2$ to ammonia. We have previously shown that the diazene complex $[Fe(N_2H_2)(dmpe)_2]$ can be protonated to afford the hydrazine complex $[Fe(N_2H_4)(dmpe)_2]^{2+}$;[25] thus, the diazene complex is also a possible intermediate in the reaction.

The mechanism for the trimethylsilyl-mediated conversion of dinitrogen to ammonia on an iron center coordinated by dmpe ligands is not clear; however, one possibility is that the reaction proceeds by initial trimethylsilylation of the terminal nitrogen atom to afford intermediate **A** containing a trimethylsilyldiazenido ligand (Scheme 5).

The intermediate labeled **A** is not an unreasonable species since the related trimethylsilyldiazenido Fe complex with the $SiP^iPr_3$ ligand has been isolated and characterized by Peters and co-workers.[7] Electron delocalization in **A**, from Fe(0) to the $N_2SiMe_3$, leads to the Fe(II) structure **A′**, and protonation of the diazenido ligand in **A′** at the metal-bound nitrogen and transfer of two electrons affords a side-on-bound Fe(0) trimethylsilyldiazene species **C**. Subsequent protodesilylation with acid affords the known side-on bound Fe(0) diazene complex **D**. Further reaction with acid and electrons affords the known side-on bound hydrazine complex $[Fe(N_2H_4)(dmpe)_2]^{2+}$ (**G**) and the bis(ammonia) complex $[Fe(NH_3)_2(dmpe)_2]^{2+}$ (**H**).

Alternatively, the species **A′** could react further with trimethylsilyl triflate as an electrophile at the metal-bound nitrogen to afford the bis(trimethylsilyldiazene) intermediate **E**, which on reduction could produce the side-on bound bis(trimethylsilylated) diazene **F**. Protodesilylation gives **D**, which then proceeds to form the hydrazine and ammonia complexes. While we did not observe the intermediates **C** or **F**, the analogous phenyl- and diphenyl-substituted diazenes $[Fe(HN{=}NPh)(dmpe)_2]$[26] and $[Fe(PhN{=}NPh)(dmpe)_2]$[24,25] (where protodesilylation is not possible) have been isolated and characterized previously.

In the reaction of $[Fe(N_2)(PP)_2]$ with electrophiles, clearly there are competing reaction pathways and smaller, weaker electrophiles tend to react at the metal center to provide products where the electrophile ($E^+$) is bonded to the metal center $[Fe(PP)_2E(N_2)]^+$. With TMS triflate, electrophilic attack appears to be on nitrogen, and this activation triggers electron transfer to the coordinated $N_2$ to start the reaction cascade that eventually leads to $NH_3$.

## ■ CONCLUSION

The reaction chemistry of $[Fe((N_2)(PP)_2]$ with acids was revisited. In our hands we could find no formation of $NH_4^+$ on treatment of Fe(0) dinitrogen complexes $[Fe(N_2)(PP)_2]$ with acid. Instead, protonation at the metal center was observed as the dominant reaction pathway to give the corresponding Fe(II) hydride complex.

Similarly, reaction of $[Fe(N_2)(PP)_2]$ with electrophilic methylating reagents (methyl triflate and methyl tosylate) again predominantly afforded products resulting from the methylation of the metal center with no reaction at the coordinated dinitrogen.

However, treatment of $[Fe(N_2)(PP)_2]$ with the sterically hindered strongly electrophilic reagent TMSOTf resulted in reaction at the coordinated dinitrogen ligand to produce $NH_4^+$ in yields of 5−52% after treatment with acid as detected and quantified by NMR spectroscopy. The side-on bound hydrazine complex $[Fe(N_2H_4)(dmpe)_2]^{2+}$ and bis(ammonia) complex $[Fe(NH_3)_2(dmpe)_2]^{2+}$ were also detected by $^{15}N$ NMR spectroscopy as products in the reaction mixture, and this suggests that these are possible intermediates in the reaction cascade from coordinated dinitrogen to ammonia.

As there are no external sources of electrons in the reaction mixture, we conclude that the Fe(0) must sacrificially provide electrons to power the reduction of coordinated dinitrogen.

## ■ EXPERIMENTAL SECTION

All manipulations of metal complexes and air-sensitive reagents were performed using standard Schlenk techniques or in nitrogen- or argon-filled gloveboxes. Solvents were dried and distilled under nitrogen or argon from sodium/benzophenone (tetrahydrofuran, hexane, benzene, 1,4-dioxane, dimethoxyethane), sodium/potassium alloy (hexane), diethoxymagnesium (ethanol), dimethoxymagnesium (methanol), and phosphorus pentoxide (dichloromethane). Tetrahydrofuran and diethyl ether were also dried and deoxygenated using a Pure Solv 400−4-MD (Innovative Technology) solvent purification system. DMSO was dried over activated molecular sieves, degassed via three freeze−pump−thaw cycles, and stored under nitrogen or argon. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Tetrahydrofuran-$d_8$ was dried over and distilled from sodium/benzophenone ketyl. DMSO-$d_6$ was dried over activated molecular sieves, while $D_2O$ was used without further purification. $^{15}N$-labeled dinitrogen was obtained from Cambridge Isotope Laboratories or Aldrich and used without further purification. Potassium *t*-butoxide was sublimed twice and stored under an inert atmosphere. Hydrochloric acid (4 M in dioxane or 2 M in diethyl ether) and triflic acid were purchased commercially and degassed via three freeze−pump−thaw cycles before use. Lutidinium triflate was prepared in quantitative yield by reaction of equimolar amounts of 2,6-lutidine and triflic acid in toluene. Chlorotrimethylsilane was distilled under argon before use. Methyl triflate, trimethylsilyl triflate, and *tert*-butyldimethylsilyl triflate were purchased from Aldrich and used without further purification. Triisopropylsilyl triflate was purchased from Alfa and used without further purification. Methyl tosylate was purified by benzene extraction before use. Dimethylmagnesium solution in tetrahydrofuran was prepared by the literature method.[27] Potassium graphite was prepared by the literature method.[28] The complexes *trans*-$[FeCl_2(depe)_2]$, *trans*-$[FeCl_2(dmpe)_2]$,[29] *trans*-$[FeHCl(depe)_2]$,[30] *trans*-$[FeHCl(dmpe)_2]$,[31] *trans*-$[FeH(N_2)(depe)_2]^+BPh_4^-$, and *trans*-$[FeH(N_2)(dmpe)_2]^+BPh_4^-$[32] were prepared using literature methods or slight modifications thereof. The $^{15}N$-labeled analogues of the dinitrogen complexes were prepared by direct exchange of the unlabeled coordinated dinitrogen with $^{15}N_2$.[33]

Air-sensitive NMR samples were prepared in an argon- or nitrogen-filled glovebox or on a high vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric Teflon valve. NMR spectra were recorded on Bruker Avance 300, 400, or 500 NMR spectrometers. $^1H$ NMR spectra were referenced to residual solvent resonances, while $^{31}P$ NMR spectra were referenced to external neat trimethyl phosphite at δ 140.85. $^{15}N$ and $^{14}N$ NMR spectra were referenced to external neat nitromethane at δ 0.00. $^{29}Si$ NMR spectra were referenced to external neat tetramethylsilane. In general, quantitative NMR experiments were conducted using the following parameters: 30° pulse, relaxation delay of 20 s, time domain size of 32 000 or 64 000 data points, sample temperatures of 25, 35, 45, or 60 °C ($^1H$); 90° pulse with inverse-gated proton decoupling, relaxation delay of 0.5 s, time domain size of 32 000 data points ($^{14}N$); 30° pulse with inverse-gated proton decoupling, relaxation delay of 40 s, time domain size of 64 000 data points ($^{31}P$).

Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer as nujol mulls unless otherwise stated. Mass spectrometric analyses were performed at the Bioanalytical Mass Spectrometry Facility, UNSW. Microanalyses were performed at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

**Preparation of $[Fe(N_2)(depe)_2]$.** *(i). From trans-[FeHCl(depe)$_2$].* A solution of $Me_2Mg$ in tetrahydrofuran (0.76 M with respect to $CH_3^-$, 30 μL, 23 μmol $CH_3^-$) was added to a solution of $[FeHCl(depe)_2]$ (10 mg, 20 μmol) in tetrahydrofuran (0.40 mL) under nitrogen. The mixture was shaken briefly and rapidly changed color from a bright orange to a pale orange with effervescence. This gave a solution that contained $[Fe(N_2)(depe)_2]$. The solvent was removed under reduced pressure, and the residue was extracted into hexane. The hexane was removed under reduced pressure to give $[Fe(N_2)(depe)_2]$ as an orange oil (6 mg, 63% with respect to $[FeHCl(depe)_2]$). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-$d_8$): δ 84.3 (s) (lit. δ 84.7, benzene-$d_6$; 89.3, toluene-$d_8$, 25 °C; 89.7, toluene-$d_8$, −55 °C). IR (nujol): 1976 $cm^{-1}$ (lit. 1978 $cm^{-1}$).[11b]

The $^{15}N$-labeled analogue $[Fe(^{15}N_2)(depe)_2]$ was prepared by performing the reaction described above under an atmosphere enriched with $^{15}N_2$. $^{15}N$ NMR (tetrahydrofuran-$d_8$, 41 MHz): δ −42.6 (d, $^1J_{N\alpha-N\beta}$ = 6.9 Hz, 1N, $\mathbf{N}_\beta$), −47.5 (d, 1N, $\mathbf{N}_\alpha$) (lit. δ −40.5 ($N_\beta$), −45.2 ($N_\alpha$), benzene-$d_6$).[11b]

*(ii). From trans-[FeH(N$_2$)(depe)$_2$]$^+$[BPh$_4$]$^-$.* A solution of $KO^tBu$ (30 mg, 0.27 mmol) in tetrahydrofuran (0.4 mL) was added to a solution of $[FeH(N_2)(depe)_2]^+[BPh_4]^-$ (50 mg, 71 μmol) in tetrahydrofuran (0.3 mL) under nitrogen. After the addition of $KO^tBu$, the reaction mixture darkened in color, and some white solid precipitated from the solution. NMR spectroscopy indicated that the reaction was complete after 2 d and that the solution contained $[Fe(N_2)(depe)_2]$. The product was not isolated and was used immediately in further reactions. This reaction was also performed using $Me_2Mg$ solution as the base—NMR spectroscopy indicated almost quantitative formation of the product after 16 h. $^{31}P\{^1H\}$ NMR (tetrahydrofuran-$d_8$, 162 MHz): δ 84.1 (s).

The in situ reaction mixture was placed under vacuum and then under an atmosphere of $^{15}N_2$ for 4 d. $^{31}P\{^1H\}$ NMR (tetrahydrofuran-$d_8$, 162 MHz): δ 84.0 (s). $^{15}N$ NMR (tetrahydrofuran-$d_8$, 41 MHz): δ −42.5 (d, $^1J_{N\alpha-N\beta}$ = 6.9 Hz, 1N, $\mathbf{N}_\beta$), −47.4 (d, 1N, $\mathbf{N}_\alpha$).

*(iii). From trans-[FeCl$_2$(depe)$_2$].* $[FeCl_2(depe)_2]$ (0.136 g, 0.252 mmol) and potassium graphite (0.162 g, 1.20 mmol, 4.8 equiv) were stirred in hexane (8 mL) under nitrogen at room temperature for 3 d. The reaction mixture was filtered through diatomaceous earth, and the pad of diatomaceous earth was washed with additional hexane to afford an orange solution (10.0 mL). The solution was used directly without further purification. *Quantification:* An aliquot of the solution (0.6 mL) was added to an NMR tube containing triethyl phosphate (27.2 mg, 0.149 mmol). Integration of the signals (δ 84.2 for $[Fe(N_2)(depe)_2]$, −0.15 for triethyl phosphate) in the $^{31}P$ NMR spectrum (run using parameters suitable for quantitative NMR) afforded the ratio of $[Fe(N_2)(depe)_2]$: triethyl phosphate 1:3.1. By calculating the amount of $[Fe(N_2)(depe)]$ in the NMR sample (12.2 μmol), the amount of $[Fe(N_2)(depe)_2]$ formed in total was determined to be 0.20 mmol (81% yield).

**Preparation of $[Fe(N_2)(dmpe)_2]$.** *(i). From trans-[FeH(N$_2$)(dmpe)$_2$]$^+$[BPh$_4$]$^-$.* A solution of $KO^tBu$ (20 mg, 0.18 mmol) in tetrahydrofuran (0.4 mL) was added to a solution of $[FeH(N_2)(dmpe)_2]^+[BPh_4]^-$ (50 mg, 71 μmol) in tetrahydrofuran (0.3 mL). After the addition of $KO^tBu$, the reaction mixture darkened in color, and a white solid started to precipitate. NMR spectroscopy indicated that the reaction was complete after 1 h and that the solution contained $[Fe(N_2)(dmpe)_2]$. The product was not isolated and was used immediately in further reactions. This reaction was repeated several times using up to 245 mg of $[FeH(N_2)(dmpe)_2]^+[BPh_4]^-$. The larger scale reaction mixtures were filtered through diatomaceous earth after addition of $KO^tBu$. NMR spectroscopy was used to monitor the conversion to $[Fe(N_2)(dmpe)_2]$, which took several hours to go to completion especially on larger scale. This reaction was also performed using $Me_2Mg$ solution as the base to form the product in situ. $^{31}P\{^1H\}$ NMR (tetrahydrofuran-$d_8$): δ 62.8 (s). IR (tetrahydrofuran): 1971 $cm^{-1}$ (lit. 1975 $cm^{-1}$).[10b]

The $^{15}N$-labeled analogue $[Fe(^{15}N_2)(dmpe)_2]$ was prepared by performing the reaction described above under an atmosphere enriched with $^{15}N_2$ using $[FeH(^{15}N_2)(dmpe)_2]^+[BPh_4]^-$ as the starting material. $^{15}N$ NMR (tetrahydrofuran-$d_8$): $\delta$ −45.1 (d, $^1J_{N\alpha\text{-}N\beta}$ = 5.9 Hz, 1N, $\mathbf{N}_\beta$), −49.1 (d, 1N, $\mathbf{N}_\alpha$).

*(ii). From trans-[FeCl$_2$(dmpe)$_2$].* $[FeCl_2(dmpe)_2]$ (0.148 g, 0.347 mmol) and potassium graphite (0.164 g, 1.21 mmol, 3.5 equiv) were stirred in hexane (8 mL) under nitrogen at room temperature for 3 d. The reaction mixture was filtered through diatomaceous earth to afford a dark orange-red solution (7.8 mL). The solution was used directly without further purification. *Quantification:* An aliquot of the solution (0.6 mL) was added to an NMR tube containing triethyl phosphate (28.1 mg, 0.154 mmol). Integration of the signals ($\delta$ 62.8 for $[Fe(N_2)(dmpe)_2]$, −0.15 for triethyl phosphate) in the $^{31}P$ NMR spectrum (run using parameters suitable for quantitative NMR) afforded the ratio of $[Fe(N_2)(dmpe)_2]$/triethyl phosphate 1:1.7. By calculating the amount of $[Fe(N_2)(dmpe)]$ in the NMR sample (22.3 $\mu$mol), the amount of $[Fe(N_2)(dmpe)_2]$ formed in total was determined to be 0.29 mmol (84% yield). Note: yields vary from 18 to 84%. $^{31}P\{^1H\}$ NMR (hexane): $\delta$ 63.0 (s). IR (hexane): 1994 $cm^{-1}$.

The $^{15}N$-labeled analogue $[Fe(^{15}N_2)(dmpe)_2]$ was prepared by freezing a hexane solution of $[Fe(N_2)(dmpe)_2]$ in liquid nitrogen, evacuating the headspace, backfilling with $^{15}N_2$, and then allowing the resulting solution to stand for several days to allow exchange to occur. $^{31}P\{^1H\}$ NMR (hexane, 162 MHz): $\delta$ 63.2 (s). $^{15}N$ NMR (hexane, 41 MHz): $\delta$ −47.2 (d, $^1J_{N\alpha\text{-}N\beta}$ = 5.9 Hz, 1N, $\mathbf{N}_\beta$), −48.8 (d, 1N, $\mathbf{N}_\alpha$) (lit. −47.2, −48.8). IR (hexane): 1928 $cm^{-1}$ (lit. 1928 $cm^{-1}$).[25]

**Reaction of Iron(0) Dinitrogen Complexes with HCl.** Excess HCl (7, 10, or 60 equiv) was added to a solution of the appropriate iron(0) dinitrogen complex in tetrahydrofuran under nitrogen. The reaction was monitored by NMR spectroscopy until it was complete. The solvent was removed under reduced pressure, and the residue was analyzed by NMR spectroscopy or by using the indophenol test.[34] In one specific example, a suspension of $[FeH(N_2)(dmpe)_2]^+BPh_4^-$ (0.245 g, 0.348 mmol) in tetrahydrofuran (4.5 mL) was filtered through diatomaceous earth then treated with a solution of KO$^t$Bu (0.080 g, 0.71 mmol) in tetrahydrofuran (1 mL) under nitrogen. After it was stirred for 1.5 h, the reaction mixture was filtered, and the filtrate was treated with a solution of HCl (2.0 M in diethyl ether, 1.2 mL, 7 equiv) then left to stir at room temperature overnight. The reaction mixture was evaporated to dryness under reduced pressure to afford 0.111 g of purple and green solid, of which 50 mg was extracted with $D_2O$ (0.7 mL). No ammonium was detected by $^{14}N$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($D_2O$, 162 MHz): $\delta$ 8.8 (br, $H_2dmpe^{2+}$). The expected yield of $NH_4Cl$ is reported to be 12−14% based on an $[FeH(N_2)(dmpe)_2]^+/NH_4^+$ ratio of 1:0.67 (1.5−1.7 mg in the whole reaction mixture or 0.7−0.8 mg in the 50 mg sample). $NH_4Cl$ (1.0 mg) was added to the NMR solution. $^{14}N$ NMR ($D_2O$, 29 MHz): $\delta$ −356.8 (m). The NMR solution containing 1.0 mg of $NH_4Cl$ was then diluted by a factor of 5 (0.1 mL with 0.4 mL of $D_2O$, 0.2 mg of $NH_4Cl$ in 0.5 mL) and 20 (0.025 mL with 0.475 mL of $D_2O$, 0.05 mg of $NH_4Cl$ in 0.5 mL) with both solutions showing visible $^{14}N$ signals as above. The remaining purple and green solid (0.061 g) and undissolved material after $D_2O$ extraction were suspended in aqueous KOH solution (10%, 20 mL), then distilled into an aqueous $H_2SO_4$ solution (0.5 M, 5 mL). An aliquot of the distillate (0.4 mL) with $D_2O$ (0.1 mL) was analyzed by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (162 MHz): $\delta$ 6.1 (br, $H_2dmpe^{2+}$).

**Reaction of $[Fe(N_2)(dmpe)_2]$ with HCl Generated by Reaction of TMSCl and Methanol.**

(i) Methanol (0.05 mL, 1 mmol) was added to a solution of chlorotrimethylsilane (0.1 mL, 0.8 mmol) in $C_6D_6$ (0.4 mL) under nitrogen to form a solution of HCl in situ. A solution of $[Fe(dmpe)_2(N_2)]$ in hexane (0.6 mL, 0.2 $\mu$mol), generated by $KC_8$ reduction of $[Fe(dmpe)_2Cl_2]$, was then added by syringe to the HCl solution. On mixing, some gas evolution was observed, and the orange color of $[Fe(dmpe)_2(N_2)]$ disappeared to form a pale green solution with a separate pale pink layer at the bottom. On standing, a white solid precipitated, and the pale pink layer turned dark brown. After standing overnight, the volatiles were removed under reduced pressure, the residue dissolved partially in DMSO-$d_6$, and TfOH was added (three drops). No $NH_4^+$ was detected by $^1H$ NMR spectroscopy.

(ii) A solution of $[Fe(dmpe)_2(N_2)]$ in hexane (0.6 mL, 0.1 $\mu$mol), generated by $KC_8$ reduction of $[Fe(dmpe)_2Cl_2]$, was added by syringe to an NMR tube containing chlorotrimethylsilane (0.2 mL, 2 mmol), and the mixture remained orange in color. Methanol (0.05 mL) was added, and gas was evolved immediately, while the solution turned pale blue-green and a separate dark brown layer formed at the bottom. On standing, the solution turned nearly colorless, and a white solid formed, while the separate layer at the bottom turned purple and then pink. The volatiles were removed under reduced pressure, the residue dissolved partially in DMSO-$d_6$, and TfOH added (two drops). No $NH_4^+$ was detected by $^1H$ NMR spectroscopy.

**Reaction of $[Fe(N_2)(dmpe)_2]$ with Triflic Acid.**

(i) Triflic acid (1 M in diethyl ether, 26 mL, 0.026 mol) was added to a solution of $[Fe(N_2)(dmpe)_2]$ (prepared in situ from $[FeH(N_2)(dmpe)_2][BPh_4]$ (0.30 g, 0.43 mmol) and KO$^t$Bu (0.096 g, 0.85 mmol)) in tetrahydrofuran (15 mL) under nitrogen. A color change from orange to dark brown then to pale orange was observed. The pale yellow precipitate formed was collected by filtration, and the filtrate was reduced in volume under reduced pressure. Both precipitate (extracted with $D_2O$) and residue from the filtrate (one drop $D_2O$ added for lock) were analyzed by $^{14}N$ NMR spectroscopy, and no $NH_4^+$ was detected.

(ii) $[FeCl_2(dmpe)_2]$ (0.207 g, 0.485 mmol) and $KC_8$ (0.221 g, 1.63 mmol) were stirred in hexane (4 mL) under nitrogen overnight. The reaction mixture was filtered through diatomaceous earth, and half of the filtrate was treated with triflic acid (0.06 mL, 0.7 mmol). The pink precipitate was collected by filtration and identified as $[Fe(dmpe)_3]^{2+}$ (74 mg, 92 $\mu$mol, 38% based on $[FeCl_2(dmpe)_2]$). No $NH_4^+$ was detected by $^1H$ NMR spectroscopy. $^1H$ NMR (DMSO-$d_6$, 300 MHz): $\delta$ 2.17−1.67 (br m, 12H, $\mathbf{CH}_2$), 1.56 (br s, 18H, $\mathbf{CH}_3$), 1.50 (br s, 18H, $\mathbf{CH}_3$). $^1H\{^{31}P\}$ NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.98 (m, 6H, $\mathbf{CH}_2$), 1.81 (m, 6H, $\mathbf{CH}_2$), 1.56 (s, 18H, $\mathbf{CH}_3$), 1.50 (s, 18H, $\mathbf{CH}_3$). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 122 MHz): $\delta$ 48.9 (s).

(iii) Triflic acid (0.191 g, 1.27 mmol) was added to a solution of $[Fe(N_2)(dmpe)_2]$ in hexane (0.8 mL, 0.1 $\mu$mol), which had been generated by $KC_8$ reduction of $[Fe(dmpe)_2Cl_2]$. Gas evolution was observed, and the solution turned pale yellow. After standing overnight, the volatiles were removed under reduced pressure, and the residue was dissolved in DMSO-$d_6$. No $NH_4^+$ was detected by $^1H$ NMR spectroscopy, and the main product formed was $H_2dmpe^{2+}$. $^1H$ NMR (DMSO-$d_6$, 500 MHz): $\delta$ 6.30 (br d, $^1J_{HP}$ = 525 Hz, 2H, P$\mathbf{H}$), 2.36 (br s, 4H, $\mathbf{CH}_2$), 1.68 (br s, 12H, $\mathbf{CH}_3$). $^1H\{^{31}P\}$ NMR (DMSO-$d_6$, 500 MHz): $\delta$ 6.30 (br, 2H, P$\mathbf{H}$), 2.36 (s, 4H, $\mathbf{CH}_2$), 1.68 (s, 12H, $\mathbf{CH}_3$). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 202 MHz): $\delta$ 8.6 (br).

**Reaction of $[Fe(N_2)(dmpe)_2]$ with 2,6-Lutidinium Triflate.** Lutidinium triflate (20 mg, 77 $\mu$mol) was added to a solution of $[Fe(N_2)(dmpe)_2]$ in hexane (5 mL, 77 $\mu$mol), which had been generated by $KC_8$ reduction of $[Fe(dmpe)_2Cl_2]$. Tetrahydrofuran (0.1 mL) was added to aid dissolution of the lutidinium triflate. The brown solid was collected by filtration, and the orange filtrate was further treated with a solution of lutidinium triflate (23 mg, 89 $\mu$mol) in ethanol (0.4 mL). Rapid decolorization to pale yellow was observed, and a yellow solid precipitated, which was collected by filtration. Both solids were dissolved in DMSO-$d_6$ and analyzed by $^1H$ NMR spectroscopy to show no $NH_4^+$. $^1H$ NMR (DMSO-$d_6$, 400 MHz, high field only): $\delta$ −17.87 (m, $[\{Fe\mathbf{H}(dmpe)_2\}_2(\mu\text{-dmpe})]^{2+}$, −19.48 (m, $[Fe\mathbf{H}(N_2)(dmpe)_2]^+$). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 162 MHz): $\delta$ 69.8 (br, $[\{FeH(\mathbf{dmpe})_2\}_2(\mu\text{-dmpe})]^{2+}$, 66.6 (s, $[FeH(N_2)(\mathbf{dmpe})_2]^+$), 15.8 (m, $[\{FeH(dmpe)_2\}_2(\mu\text{-}\mathbf{dmpe})]^{2+}$).

**Preparation of *trans*-$[FeMe(N_2)(dmpe)_2]^+OTf^{-2}$.** Methyl triflate (0.282 g, 1.72 mmol) was added to a dark orange hexane solution of $[Fe(N_2)(dmpe)_2]$ (2.57 mL, 0.109 mmol) under nitrogen. A pale orange precipitate formed immediately, and after about a minute, the supernatant liquid was nearly colorless. The precipitate was collected by filtration, washed with hexane several times, washed with benzene several times, and then dried in vacuo (42 mg, 0.077 mmol, 70% yield). Anal. Calcd for $C_{14}H_{35}F_3FeN_2O_3P_4S$ (548.24): C, 30.67; H, 6.44; N, 5.11. Found: C, 30.44; H, 6.48; N, 4.49%. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 1.85 (m, 8H, PC**H**$_2$), 1.47 (br s, 12H, PC**H**$_3$), 1.35 (br s, 12H, PC**H**$_3$), −1.83 (p, $^3J_{HP}$ 8.7 Hz, 3H, FeC**H**$_3$). $^1$H{$^{31}$P} NMR (DMSO-$d_6$, 400 MHz): $\delta$ 1.85 (s, 8H, PC**H**$_2$), 1.47 (s, 12H, PC**H**$_3$), 1.35 (s, 12H, PC**H**$_3$), −1.83 (s, 3H, FeC**H**$_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 101 MHz, from $^1$H−$^{13}$C HSQC): $\delta$ 27.8 (P**C**H$_2$), 12.7 (P**C**H$_3$), 11.0 (P**C**H$_3$), −15.3 (Fe**C**H$_3$). $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 162 MHz): $\delta$ 65.0 (s). IR (nujol): 2085 s, 2068 s, 1428 m, 1307 m, 1289 m, 1263 s, 1240 m, 1223 m, 1151 s, 1072 w, 1031 s, 990 w, 943 s, 931 s, 894 m, 870 w, 843 w, 800 w, 752 w, 738 m, 710 m, 649 m, 638 s, 571 s cm$^{-1}$. MS (ESI, acetonitrile): *m*/*z* 655.1036 (10%, $[Fe(dmpe)_3(OTf)]^+$), 587.0839 (20, $[Fe(dmpe)_2(CH_3CN)_2(OTf)]^+$), 546.0573 (19, $[Fe(dmpe)_2(CH_3CN)(OTf)]^+$), 523.1542 (75), 505.0308 (100, $[Fe(dmpe)_2(OTf)]^+$), 491.1001 (17), 415.0921 (12), 399.1087 (2, $[FeMe(N_2)(dmpe)_2]^+$), 391.0477 (100), 383.0777 (62, $[Fe(N_2)(dmpe)_2\text{-}H]^+$), 371.1026 (27, $[FeMe(dmpe)_2]^+$), 355.0713 (94, $[Fe(dmpe)_2\text{-}H]^+$), 341.0276 (11), 261.0728 (22), 239.0042 (21), 205.0513 (72, $[Fe(dmpe)\text{-}H]^+$), 186.0366 (53), 178.0392 (29).

**Reaction of $[Fe(N_2)(dmpe)_2]$ with Trimethylsilyl Triflate.** Trimethylsilyl triflate (0.108 g, 0.486 mmol) was added dropwise to a solution of $[Fe(N_2)(dmpe)_2]$ in hexane (6.6 mL, 79.2 $\mu$mol) to form a dark brown suspension, which was left to stand at room temperature overnight. The brown precipitate was collected by filtration, and the filtrate was evaporated to dryness under reduced pressure. Samples of the solid and residue from the filtrate were dissolved in DMSO-$d_6$, then analyzed by NMR spectroscopy. Alternatively, the volatiles were removed under reduced pressure, and the residue was dissolved in DMSO-$d_6$ for NMR analysis. $^1$H{$^{31}$P} NMR (DMSO-$d_6$, 400 MHz, high-field region only): $\delta$ −19.37 (s, [Fe**H**$(N_2)(dmpe)_2]^+$), −19.63 (s, [Fe**H**(DMSO-$d_6$)$(dmpe)_2]^+$). $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 162 MHz): $\delta$ 66.0 (s, $[FeH(N_2)(dmpe)_2]^+$), 65.5 (s, [FeH(DMSO-$d_6$)$(dmpe)_2]^+$), 49.0 (s, $[Fe(dmpe)_3]^{2+}$). $^{29}$Si{$^1$H} NMR (DMSO-$d_6$, 99 MHz, from $^1$H−$^{29}$Si HMBC): $\delta$ 7.9 (TMS-O-TMS). IR: 2091s ($\nu$(N≡N) for $[FeH(N_2)(dmpe)_2]^+$), 1866 w, 1425 s, 1261 s, 1223 s, 1147 s, 1031 s, 934 s, 895 s, 862 m, 845 m, 802 m, 752 m, 738 m, 721 m, 708 m, 651 m, 637 s, 572 m cm$^{-1}$. MS (ESI, acetonitrile): *m*/*z* 523.1546 (55%), 385.0931 (55, $[Fe(H)(N_2)(dmpe)_2]^+$), 372.0742 (11), 355.0714 (42, $[Fe(dmpe)_2\text{-}H]^+$), 253.0755 (49), 239.0043 (100), 178.0393 (29, $[Fe(dmpe)_2]^{2+}$).

A known amount of 1,4-dioxane and a drop of triflic acid were added to each NMR sample. Integration of the $NH_4^+$ and 1,4-dioxane $^1$H NMR signals at $\delta$ 7.06 and 3.56, respectively, allowed the total yield of $NH_4^+$ to be determined (16% yield based on $[Fe(N_2)(dmpe)_2]$).

The reaction was also performed in a similar manner on a $^{15}$N-labeled sample with a solution of $[Fe(^{15}N_2)(dmpe)_2]$ in hexane (0.8 mL, 20 $\mu$mol) and trimethylsilyl triflate (40 mg, 0.18 mmol). $^1$H{$^{31}$P} NMR (DMSO-$d_6$, 300 MHz, high-field region only): $\delta$ −19.53 (br). $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 122 MHz): $\delta$ 65.8 (br), 49.0 (br, $[Fe(dmpe)_3]^{2+}$). $^{15}$N{$^1$H} NMR (DMSO-$d_6$, 30 MHz): $\delta$ −50.2 ($\mathbf{N}_\beta$ for $[FeH(N_2)(dmpe)_2]^+$), −62.5 ($\mathbf{N}_\alpha$ for $[FeH(N_2)(dmpe)_2]^+$). $^{29}$Si{$^1$H} NMR (DMSO-$d_6$, 99 MHz, from $^1$H−$^{29}$Si HMBC): $\delta$ 8.0 (TMS-O-TMS), 10.8 (TMS−OH). IR: 2094 w, 2039 m, 1974 m, 1862 w, 1263 s, 1223 m, 1148 s, 1031 s, 934 s, 893 m, 843 m, 753 m, 737 m, 719 m, 637 s cm$^{-1}$. MS (ESI, acetonitrile): *m*/*z* 523.1547 (67%), 507.1598 (60, $[Fe(dmpe)_3{+}H]^+$), 423.1233 (10), 391.0480 (51), 385.0933 (65, $[Fe(H)(N_2)(dmpe)_2]^+$), 355.0715 (41, $[Fe(dmpe)_2\text{-}H]^+$), 341.1068 (24), 253.0756 (100, $[Fe(dmpe)_3]^{2+}$), 239.0044 (89), 186.0368 (30), 178.0393 (61, $[Fe(dmpe)_2]^{2+}$).

The yields of $[FeH(N_2)(dmpe)_2]^+$ (0.90 $\mu$mol, 40%) and $[Fe(dmpe)_3]^{2+}$ (0.98 $\mu$mol, 44%) were determined in a separate experiment, where TMSOTf (0.081 g, 0.36 mmol) was added to a solution of $[Fe(N_2)(dmpe)_2]$ in hexane (0.8 mL, 2.2 $\mu$mol), by adding a known amount of triethyl phosphate into the NMR sample in DMSO-$d_6$ and integrating the respective $^{31}$P resonances. On the basis of the yield of $[FeH(N_2)(dmpe)_2]^+$, the amount of water/TfOH in TMSOTf was estimated at 0.2%.

**Reaction of $[Fe(^{15}N_2)(dmpe)_2]$ with Trimethylsilyl Triflate and Trace Acid.** A solution of $[Fe(N_2)(dmpe)_2]$ in hexane (0.5 mL, 50 $\mu$mol) was placed under an atmosphere of $^{15}N_2$ then left to stand for several days. Trimethylsilyl triflate (0.12 g, 0.55 mmol) was then added under nitrogen. After the solution stood overnight, the volatiles were removed under reduced pressure. $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 162 MHz): $\delta$ 70.3 (t, $[Fe(N_2H_4)(dmpe)_2]^{2+}$ and $[Fe(NH_3)_2(dmpe)_2]^{2+}$), 66.0 (s, $FeH(N_2)(dmpe)_2]^+$), 65.5 (s, FeH(DMSO-$d_6$)$(dmpe)_2]^+$), 60.0 (t, $[Fe(N_2H_4)(dmpe)_2]^{2+}$ and $[Fe(NH_3)_2(dmpe)_2]^{2+}$), 49.0 (s, $[Fe(dmpe)_2]^{2+}$). $^{15}$N{$^1$H} NMR (DMSO-$d_6$, 51 MHz): $\delta\delta$ −69.9 (s, $^{15}N_2$), −387.0 (s, $[Fe(N_2H_4)(dmpe)_2]^{2+}$), −422.6 (s, $[Fe(NH_3)_2(dmpe)_2]^{2+}$).

**Reaction of $[Fe(^{15}N_2)(dmpe)_2]$ with Trimethylsilyl Triflate and then Controlled Addition of TfOH.** A solution of $[Fe(N_2)(dmpe)_2]$ in hexane (0.8 mL, 20 $\mu$mol) was placed under an atmosphere of $^{15}N_2$ then left to stand for several days. Trimethylsilyl triflate (36 mg, 0.16 mmol) was then added under nitrogen. After the solution stood overnight, the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-$d_6$ and treated drop by drop with a 0.1 M solution of TfOH in DMSO-$d_6$. $^{15}$N NMR (DMSO-$d_6$, 41 MHz, from $^1$H−$^{15}$N HSQC, after addition of 0.15 equiv of TfOH): $\delta$ −277.2 (unidentified), −335.9 ($^{15}N_2H_4$), −416.3 ($[FeCl(^{15}NH_3)(dmpe)_2]^+$), −423.1 ($[Fe(^{15}NH_3)_2(dmpe)_2]^{2+}$). $^{15}$N NMR (DMSO-$d_6$, 41 MHz, from $^1$H−$^{15}$N HSQC, after addition of 0.54 equiv of TfOH): $\delta$ −361.2 (unidentified), −387.7 ($[Fe(^{15}N_2H_4)(dmpe)_2]^{2+}$), −416.1 ($[FeCl(^{15}NH_3)(dmpe)_2]^+$). $^{15}$N NMR (DMSO-$d_6$, 41 MHz, from $^1$H−$^{15}$N HSQC, after addition of 0.66 equiv of TfOH): $\delta$ −358.4 ($^{15}NH_4^+$), −361.4 (unidentified), −381.9 (unidentified), −387.3 ($[Fe(^{15}N_2H_4)(dmpe)_2]^{2+}$). $^{15}$N NMR (DMSO-$d_6$, 51 MHz, from $^1$H−$^{15}$N HSQC, after addition of 0.79 equiv of TfOH): $\delta$ −358.2 ($^{15}NH_4^+$), −361.3 (unidentified). $^{15}$N NMR (DMSO-$d_6$, 41 MHz, from $^1$H−$^{15}$N HSQC, after addition of 6.6 equiv of TfOH): $\delta$ −358.2 ($^{15}NH_4^+$).

**Reaction of $[FeH(N_2)(dmpe)_2]^+BPh_4^-$ with Trimethylsilyl triflate.** A solution of trimethylsilyl triflate (0.135 g, 0.607 mmol) in diethyl ether (3 mL) was added to a suspension of $[FeH(N_2)(dmpe)_2]^+BPh_4^-$ in tetrahydrofuran (1 mL) under nitrogen, and the reaction mixture was stirred at room temperature overnight. No obvious change in the appearance of the reaction mixture was observed. The pale orange solid (0.109 g) was collected by filtration and washed with diethyl ether. The filtrate was evaporated to dryness under reduced pressure to afford a pale yellow solid (0.066 g). Portions of both solids were partially dissolved in DMSO-$d_6$, treated with a drop of TfOH each and analyzed by $^{14}$N NMR spectroscopy, which showed no signal for $NH_4^+$ in both samples.

**Preparation of cis-$[Fe(NH_3)_2(dmpe)_2]^{2+}(Cl^-)(BPh_4^-)$.** Ammonia gas was bubbled through methanol (80 mL) for 45 min to afford a saturated solution. $[FeCl_2(dmpe)_2]$ (0.204 g, 0.478 mmol) was dissolved in ammonia-saturated methanol (10 mL) to afford a dark purple-red solution, which turned to an orange suspension over the course of 45 min. The reaction mixture was filtered, and the filtrate was added directly to a solution of sodium tetraphenylborate (0.23 g, 0.67 mmol) in ammonia-saturated methanol (5 mL). The orange precipitate formed was collected by filtration, washed with ammonia-saturated methanol (10 mL), and then dried in vacuo (0.195 g, 0.262 mmol, 55% yield). Anal. Calcd for $C_{36}H_{58}BClFeN_2P_4$ (744.87): C, 58.05; H, 7.85; N, 3.76. Found: C, 57.88; H, 7.82; N, 3.77%. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.18 (m, 8H, *o*-**Ph**), 6.92 (m, 8H, *m*-**Ph**), 6.79 (m, 4H, *p*-**Ph**), 2.22−1.82 (m, 6H, PC**H**$_2$), 1.97 (br s, 6H, N**H**$_3$), 1.61 (br s, 6H, PC**H**$_3$), 1.51 (br s, 6H, PC**H**$_3$), 1.48−1.36 (m, 2H, PC**H**$_2$), 1.20 (br s, 6H, PC**H**$_3$), 1.04 (br s, 6H, PC**H**$_3$). $^1$H{$^{31}$P} NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.18 (m, 8H, *o*-**Ph**), 6.92 (m, 8H, *m*-**Ph**), 6.79 (m, 4H, *p*-**Ph**), 2.15−1.82 (m, 6H, PC**H**$_2$), 1.97 (s, 6H, N**H**$_3$), 1.61 (s, 6H, PC**H**$_3$), 1.51 (s, 6H, PC**H**$_3$), 1.44 (m, 2H, PC**H**$_2$), 1.20 (s, 6H, PC**H**$_3$), 1.04 (6H, PC**H**$_3$). $^{15}$N{$^1$H} NMR (DMSO-$d_6$, 51 MHz, from $^1$H−$^{15}$N HSQC): $\delta$ −422.7 (**N**H$_3$). $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 202 MHz): $\delta$ 67.6 (app. t, splitting 37 Hz, 2P), 60.7 (app. t, 2P). IR (nujol): 3323 m, 3288 w, 3272 w, 3236 w, 3193 m, 3145 m, 3050 m, 3038 m, 1627 m, 1580 m, 1427 s, 1344 w, 1311 s, 1298 m, 1270 w, 1184 w, 1165 w, 1130 w, 1076 w, 1068 w, 1028 w, 946 m, 929 s, 913 w, 892 m, 837 m, 796 w, 769 w, 748 m, 738 s, 727 s, 707 s, 652 m, 626 m, 615 m, 603 m $cm^{-1}$.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Discussion of reaction byproduct in the presence of DMSO, experimental details including preparations of dmpe·2HCl, ammonium triflate, $(OTf)Me_2Si(CH_2)_2SiMe_2(OTf)$, and *trans*-$[FeH(DMSO)(dmpe)_2]^+BPh_4^-$. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00211.

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### Notes

The authors declare no competing financial interest. A portion of the work reported here was carried out while the authors were based at the School of Chemistry, University of Sydney, Australia.

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