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## Catalytic conversion of nitrogen to ammonia by a molecular Fe model complex

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### Abstract

The reduction of  $N_2$  to  $NH_3$  is a requisite transformation for life.<sup>1</sup> While it is widely appreciated that the iron-rich cofactors of nitrogenase enzymes facilitate this transformation,<sup>2–5</sup> how they do so remains poorly understood. A central element of debate has been the exact site(s) of nitrogen coordination and reduction.<sup>6,7</sup> The synthetic inorganic community placed an early emphasis on Mo<sup>8</sup>, because Mo was thought to be an essential element of nitrogenases<sup>3</sup> and because pioneering work by Chatt and coworkers established that well-defined Mo model complexes could mediate the stoichiometric conversion of  $N_2$  to  $NH_3$ .<sup>9</sup> This chemical transformation can be performed in a catalytic fashion by two well-defined molecular systems that feature Mo centres.<sup>10,11</sup> However, it is now thought that Fe is the only transition metal essential to all nitrogenases,<sup>3</sup> and recent biochemical and spectroscopic data has implicated Fe instead of Mo as the site of  $N_2$  binding in the FeMo-cofactor.<sup>12</sup> In this work, we describe a tris(phosphine)borane-supported Fe complex that catalyzes the reduction of  $N_2$  to  $NH_3$  under mild conditions, wherein >40% of the  $H^+/e^-$  equivalents are delivered to  $N_2$ . Our results indicate that a single Fe site may be capable of stabilizing the various  $N_xH_y$  intermediates generated en route to catalytic  $NH_3$  formation. Geometric tunability at Fe imparted by a flexible Fe-B interaction in our model system appears to be important for efficient catalysis.<sup>13–15</sup> We propose that the interstitial light C-atom recently assigned in the nitrogenase cofactor may play a similar role,<sup>16,17</sup> perhaps by enabling a single Fe site to mediate the enzymatic catalysis via a flexible Fe-C interaction.<sup>18</sup>

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Nitrogen is fixed on a staggering scale by the industrial Haber-Bosch process using a solid-state Fe catalyst at very high temperatures and pressures, and in Nature by nitrogenase enzymes under ambient conditions.<sup>1</sup> These enzymes feature active site cofactors rich in S and Fe (FeFecofactor), and can additionally contain a Mo (FeMo-cofactor; Figure 1) or V (FeV-cofactor) site.<sup>2,3</sup>

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The intimate mechanism of biological nitrogen fixation is a topic that has fascinated chemists, biochemists, and biologists alike.<sup>4,5,6,7</sup> Synthetic chemists have searched for decades for well-defined complexes that can catalyze N<sub>2</sub> reduction to NH<sub>3</sub>.<sup>19,20,21,22</sup> Chatt's early work with low-valent Mo complexes provided a mechanistic outline for approaching this problem now commonly called the "Chatt" or "distal" mechanism, wherein a terminal nitride intermediate is generated upon liberation of the first NH<sub>3</sub> equivalent (Figure 1, bottom).<sup>9</sup> Other mechanisms, including an "alternating" scenario (Figure 1, top), have also received attention.<sup>6</sup> To date, even modest catalysis of NH<sub>3</sub> production directly from N<sub>2</sub> by a well-defined model complex is still limited to the original tri(amido)amine Mo systems of Schrock and coworkers, and the more recently discovered phosphine-pincer Mo system of Nishibayashi and coworkers.<sup>10,11</sup> Earlier work by Pickett had established the electrochemical feasibility of an NH<sub>3</sub> production cycle with W.<sup>19</sup>

Synthetic efforts to establish whether one or more Fe sites can catalyze N<sub>2</sub> reduction to NH<sub>3</sub> in a well-defined model complex have progressed more slowly. For example, previous Fe-N<sub>2</sub> model complexes have not afforded more than ca. 10% of NH<sub>3</sub> per Fe equivalent upon treatment with proton sources.<sup>7,23,24</sup> Despite significant advances,<sup>24</sup> which have most recently included reductive N<sub>2</sub> cleavage at iron<sup>22</sup> and the catalytic reductive silylation of N<sub>2</sub> facilitated by unknown Fe species derived from Fe precursors such as ferrocene and iron pentacarbonyl,<sup>25</sup> the delivery of protons and electrons to N<sub>2</sub> to catalytically generate NH<sub>3</sub> at a synthetic Fe complex has remained an unsolved challenge. Here we show that a recently reported mononuclear Fe complex, [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] (TPB = tris(phosphine)borane; see Figure 2A),<sup>13,14</sup> can catalyze the reduction of N<sub>2</sub> to NH<sub>3</sub> by protons and electrons in solution at -78 °C under one atmosphere of N<sub>2</sub>.

The Fe center of the "(TPB)Fe" fragment readily binds dinitrogen as evidenced by the featured 5-coordinate complex [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] and the previously reported neutral N<sub>2</sub> adduct, (TPB)Fe(N<sub>2</sub>).<sup>14</sup> The same scaffold also accommodates a variety of other nitrogenous ligands relevant to NH<sub>3</sub> generation, including terminally bonded NH<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub>H<sub>4</sub> ligands.<sup>15</sup> Both the substrate-free complex, [(TPB)Fe][BAr<sup>F</sup><sub>4</sub>] (where [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> represents the weakly coordinating anion [B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>-</sup>),<sup>15</sup> and (TPB)Fe(N<sub>2</sub>) may be reduced to [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] by Na/Hg reduction under 1 atm N<sub>2</sub> followed by the addition of two equivalents of 12-crown-4 to encapsulate the sodium cation (Figure 2A). Model reactions with silyl electrophiles have also shown that the β-N of the coordinated N<sub>2</sub> ligand can be mono- or difunctionalized with concomitant lengthening of the Fe-B distance.<sup>13</sup> Furthermore, starting from (TPB)Fe(NH<sub>2</sub>), a reductive protonation sequence has been established (Figure 2B) that liberates NH<sub>3</sub> and affords (TPB)Fe(N<sub>2</sub>).<sup>15</sup> This reaction sequence demonstrates the synthetic viability of reductive release of NH<sub>3</sub> from an Fe-NH<sub>2</sub> intermediate with simultaneous uptake of N<sub>2</sub>. In sum, the rich reaction chemistry of the (TPB)Fe scaffold with nitrogenous ligands motivated us to more closely examine the possibility that it might catalyze N<sub>2</sub> fixation.

The addition of excess acid to [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] at -78 °C was investigated. When [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] was dissolved in THF, cooled to -78 °C, and exposed to six equivalents of H<sup>+</sup> in the form of HBar<sup>F</sup><sub>4</sub>·2 Et<sub>2</sub>O, a previously unobserved yellow solution resulted that, upon warming followed by addition of proton sponge (1,8-

bis(dimethylamino)naphthalene), was shown by  $^1\text{H}$  NMR analysis to contain the previously characterized complex  $[(\text{TPB})\text{Fe}(\text{NH}_3)][\text{BAr}^{\text{F}}_4]$  (ca. 30-35% of the total Fe),<sup>15</sup> along with resonances consistent with  $[(\text{TPB})\text{Fe}][\text{BAr}^{\text{F}}_4]$  (ca. 40-45% of the total Fe) and two other minor and as yet unidentified paramagnetic (TPB)Fe-species (see SI). An independent EPR study of this low temperature protonation reaction in 2-methyltetrahydrofuran revealed a new rhombic  $S = \frac{1}{2}$  signal (see SI) that we speculate may be  $(\text{TPB})\text{Fe}(=\text{N}-\text{NH}_2)^+$  or an alternative structural isomer such as  $(\text{TPB})\text{Fe}(\text{NH}=\text{NH})^+$ . Spin quantification of this species shows it to represent >85% of the Fe species in solution, and its rhombic EPR spectrum is highly similar to the rhombic EPR signature that is obtained upon oxidation of  $(\text{TPB})\text{Fe}=\text{N}(p\text{-tolyl})$  to generate  $(\text{TPB})\text{Fe}=\text{N}(p\text{-tolyl})^+$  (SI). Subsequent low temperature reduction of a similarly prepared mixture regenerates  $[(\text{TPB})\text{FeN}_2][\text{Na}(12\text{-crown-4})_2]$ , as determined by IR spectroscopy, suggesting the possibility of cycling protonation and reduction with this Fe system.

To explore the possibility of  $\text{N}_2$  reduction catalysis using this (TPB)Fe system, we canvassed several reductants (e.g.,  $\text{Na}[\text{naphthalenide}]$ ,  $\text{Mg}(\text{THF})_3(\text{anthracene})$ ,  $\text{Na}/\text{Hg}$ ,  $\text{KC}_8$ ) and acids (e.g.,  $\text{HCl}$ , trifluoromethanesulfonic acid,  $\text{HBAr}^{\text{F}}_4 \cdot 2 \text{Et}_2\text{O}$ ) in a variety of solvents and solvent mixtures (e.g., tetrahydrofuran, dimethoxyethane, diethyl ether, toluene). When carried out at  $-78^\circ\text{C}$  numerous reaction conditions showed unusually high yields of  $\text{NH}_3$  relative to the number of Fe equivalents in the reaction vessel, and the combination of  $\text{KC}_8$ ,  $\text{HBAr}^{\text{F}}_4 \cdot 2 \text{Et}_2\text{O}$ , and  $\text{Et}_2\text{O}$  solvent enabled the catalytic generation of  $\text{NH}_3$ .

In a representative catalytic run, red  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  was suspended in diethyl ether in a reaction vessel at  $-78^\circ\text{C}$ , followed by the sequential addition of excess acid and then excess reductant. Ammonia analysis followed the indophenol protocol (see Methods and SI) and the independent identification of ammonium salts by  $^1\text{H}$  NMR spectroscopy in DMSO by comparison with an authentic sample of  $[\text{NH}_4][\text{Cl}]$  (Figure 3A). An experiment performed using the  $[(\text{TPB})\text{Fe}(^{14}\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  catalyst under an  $^{15}\text{N}_2$  atmosphere, followed by  $^1\text{H}$  NMR analysis (Figure 3A) of the volatile reaction products, confirmed the production of  $^{15}\text{NH}_4[\text{Cl}]$ , as expected, with only trace  $^{14}\text{NH}_4[\text{Cl}]$ . This overall procedure has been repeated many times, and Table 1 includes data averaged from 16 independent runs (entry 1) wherein yields were, on average, 7.0 equiv  $\text{NH}_3$  per Fe equiv. Using 7.0 equiv  $\text{NH}_3$  as the product stoichiometry, 44% of the added protons are reliably delivered to  $\text{N}_2$  to produce  $\text{NH}_3$ . Individual runs have in our hands reached a maximum of 8.5 equiv  $\text{NH}_3$  per Fe equiv under these standard conditions.  $[(\text{TPB})\text{Fe}][\text{BAr}^{\text{F}}_4]$  is also an effective catalyst and afforded  $6.2 \pm 0.7$  equiv  $\text{NH}_3$  per added Fe equivalent (Table 1, entry 2). For comparison, the Mo systems of Schrock and Nishibayashi have afforded between 7-12 equiv  $\text{NH}_3$  per Mo equiv.<sup>10,11</sup> The current Fe system appears to be active at an unusually low temperature ( $-78^\circ\text{C}$ ) but benefits from a strong reductant ( $\text{KC}_8$ ). We do not yet know if conditions can be found that will tolerate a milder reductant, for example by circumventing the need to generate the  $(\text{TPB})\text{Fe}(\text{N}_2)^-$  anion during catalysis.

Table 1 lists several sets of conditions (entries 10-15) other than the standard conditions described above that were canvassed. Several of these alternative conditions showed  $\text{NH}_3$  generation, though not in catalytic or even in high yields.  $\text{N}_2\text{H}_4$  was not detected (SI) as an

additional product when using the standard catalytic protocol for  $\text{NH}_3$  generation with  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  (SI). If two equivalents  $\text{N}_2\text{H}_4$  (per Fe) are added to  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  in diethyl ether, followed by subjecting the mixture to the standard catalytic conditions and work-up, only trace  $\text{N}_2\text{H}_4$  remains (SI). This result suggests that if  $\text{N}_2\text{H}_4$  is generated as an intermediate during catalysis it would not likely be detectable upon work-up and analysis. Worth noting is that  $\text{HBAr}^{\text{F}}_4 \cdot 2 \text{Et}_2\text{O}$  and  $\text{KC}_8$  reacts in the absence of an Fe precursor, under the standard catalytic conditions at  $-78^\circ\text{C}$ , to generate  $\text{H}_2$  but not  $\text{NH}_3$  ( $>75\%$  yield of  $\text{H}_2$  after 40 minutes). That  $\text{H}_2$  generation is kinetically feasible without the addition of an Fe precursor, and yet  $\text{NH}_3$  can nonetheless be generated upon the addition of  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  or  $[(\text{TPB})\text{Fe}][\text{BAr}^{\text{F}}_4]$ , underscores the facility by which this Fe system mediates overall H-atom delivery to  $\text{N}_2$ .

To further explore whether a (TPB)Fe containing precursor is needed to facilitate the overall catalysis, beyond the stoichiometric model reactions summarized above, we canvassed several Fe complexes under analogous conditions. Of most interest is the complex  $[(\text{Si}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$ , which is isostructural to  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  but replaces the B atom of TPB by a Si atom.<sup>26</sup> A central difference between (TPB)Fe and  $(\text{Si}^{\text{iPr}}_3)\text{Fe}$  complexes is the far greater flexibility of the Fe-B versus the Fe-Si bond that is positioned *trans* to the apical ligand.<sup>13,14,15,26</sup> While some  $\text{NH}_3$  generation was observed for  $[(\text{Si}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  when subjected to the standard catalytic reaction conditions described above, sub-stoichiometric yields of  $\text{NH}_3$  relative to Fe were obtained ( $0.7 \pm 0.5$  equiv  $\text{NH}_3$  per Fe equiv; entry 3). We also conducted additional control experiments under the standard catalytic conditions with  $\text{FeCl}_2 \cdot 1.5 \text{THF}$ ,  $\text{FeCl}_3$ ,  $\text{Cp}_2\text{Fe}$ ,<sup>25</sup> and  $\text{Fe}(\text{CO})_5$ <sup>25</sup> (entries 5-8) and found that only trace amounts of  $\text{NH}_3$  ( $<0.2$  equiv in all cases on average; 4 runs) were produced by these Fe precursors (SI).<sup>27</sup> The known phosphine-supported Fe(0)- $\text{N}_2$  complex  $\text{Fe}(\text{depe})_2(\text{N}_2)$ <sup>28</sup> was also subjected to the standard conditions and afforded sub-stoichiometric yields of  $\text{NH}_3$  per Fe equivalent (see SI).

In separate work, the addition of an atmosphere of  $\text{H}_2$  to (TPB)Fe( $\text{N}_2$ ) was shown to generate (TPB)( $\mu\text{-H}$ )Fe( $\text{N}_2$ )(H) as a stable product (Figure 3C).<sup>29</sup> We hence suspected that catalyst poisoning might occur in part via the formation of (TPB)( $\mu\text{-H}$ )Fe( $\text{N}_2$ )(H) under the catalytic reaction conditions. In accord with this idea, when  $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})_2]$  was exposed to 10 equiv  $\text{HBAr}^{\text{F}}_4 \cdot 2 \text{Et}_2\text{O}$  and 12 equiv  $\text{KC}_8$  at low temperature, IR and  $^{31}\text{P}$  NMR analysis of the resulting mixture showed the presence of (TPB)( $\mu\text{-H}$ )Fe( $\text{N}_2$ )(H) via its signature spectroscopic features (30% of total Fe by  $^{31}\text{P}$  NMR integration; SI).<sup>29</sup> (TPB)( $\mu\text{-H}$ )Fe( $\text{N}_2$ )(H) is stable for short periods to both  $\text{HBAr}^{\text{F}}_4 \cdot 2 \text{Et}_2\text{O}$  and also  $\text{KC}_8$  in  $\text{Et}_2\text{O}$  at room temperature, and when subjected to the standard catalytic conditions for  $\text{NH}_3$  production liberates only  $0.5 \pm 0.1$  equiv  $\text{NH}_3$  per Fe equiv (Table 1 entry 4).

The general absence of a functional, catalytic Fe model system over the past few decades has often led to an emphasis on  $\text{Mo}^{30}$  as a plausible site of  $\text{N}_2$  uptake and reduction at the most widely studied FeMo-cofactor. While this may yet prove to be true, recent spectroscopic and biochemical evidence has sharpened the focus on an Fe center as the  $\text{N}_2$  binding site.<sup>12</sup> The results reported here establish that it is possible to catalyze the conversion of  $\text{N}_2$  to  $\text{NH}_3$  by protons and electrons using a well-defined mononuclear Fe- $\text{N}_2$

complex, and suggests the possibility that a single Fe-binding site of the cofactor could in principle mediate  $N_2$  reduction catalysis.<sup>18</sup> To achieve this catalytic behavior, geometric flexibility at the Fe- $N_2$  binding site would be beneficial as it would stabilize  $N_xH_y$  intermediates of different electronic demands. Such geometric and redox flexibility, under the local three-fold symmetry presented by an Fe center, its three neighboring sulfides, and the interstitial light atom of the FeMo-co,<sup>16,17</sup> may at least in part be achieved by attributing a hemi-labile role to the interstitial C-atom (Figure 1). Such a role could serve to expose an initial Fe- $N_2$  binding site by Fe-C elongation. Subsequent modulation of the Fe-C interaction and hence the local Fe geometry as a function of the  $N_2$  reduction state would enable the Fe center to stabilize the various  $N_xH_y$  intermediates along a pathway to  $NH_3$ . While inherently speculative, this hypothesis is rooted in the functional (TPB)Fe catalysis discussed herein, along with the types of (TPB)Fe complexes and stoichiometric transformations described previously for this scaffold.<sup>13,14,15</sup>

The mechanistic questions that arise from the present Fe catalyst system are rich. While all of the model complexes relevant to the (TPB)Fe- $N_xH_y$  system are mononuclear, we cannot exclude the possibility of bimolecular reaction intermediates. We more generally don't know whether the  $N_2$  reduction catalysis proceeds along a distal pathway via a terminal nitride intermediate, such as (TPB)Fe(N) or (TPB)Fe(N)<sup>+</sup>, via intermediates along an alternating pathway, such as (TPB)Fe-NH-NH<sub>2</sub> or (TPB)Fe-NH<sub>2</sub>-NH<sub>2</sub><sup>+</sup>, or via some hybrid pathway. The tentatively assigned (TPB)Fe=N-NH<sub>2</sub><sup>+</sup> species that can be observed by EPR spectroscopy provides us a useful starting point for such studies. In light of the identification of C as the interstitial light atom of the cofactor, it is also of interest to develop and compare synthetic model systems that feature a C-atom in the ligand backbone instead of a B-atom.

## Methods Summary

### General considerations

All complexes and reagents were prepared according to literature procedures referenced in the Supplemental Information (SI) unless otherwise noted. Manipulations were carried out under an  $N_2$  atmosphere utilizing standard dry glove-box or Schlenk-line techniques. All solvents used were deoxygenated and dried by an argon sparge followed by passage through an activated alumina column.

### Spectroscopy

NMR measurements were obtained on Varian 300 MHz spectrometers. Deuterated solvents for these measurements were obtained from Cambridge Isotope Laboratories and were dried and degassed prior to use. All <sup>1</sup>H NMR spectra were referenced to residual solvent peaks. EPR X-band spectra were obtained on a Bruker EMX spectrometer with the aid of the Bruker Win-EPR software suite version 3.0. The EPR spectrometer was equipped with a rectangular cavity that operated in the TE<sub>102</sub> mode. Temperature control was achieved with a liquid- $N_2$ -filled quartz-dewar in which the sample was submerged during data collection. UV-Vis spectra were acquired on a Cary 50 spectrometer from 1100 nm to 200 nm in the fast scan mode. IR spectra were obtained via KBr pellets on a Bio-Rad Excalibur FTS 3000 spectrometer using Varian Resolutions Pro software set at 4 cm<sup>-1</sup> resolution.

## Catalysis and ammonia collection and quantification

The standard catalysis protocol involved the addition first of acid, followed by reductant, to a suspension of the precatalyst in diethyl ether at  $-78\text{ }^{\circ}\text{C}$  in a closed vessel under 1 atm  $\text{N}_2$ . Ammonia produced during each catalytic run was collected by vacuum transfer of the reaction volatiles onto anhydrous HCl in diethyl ether. The resulting slurry was dried and extracted into water and aliquots were then tested for the presence of ammonia via the indophenol method.

A Methods section, associated references, and a detailed Supplemental Information are available in the online version of this paper.

## Methods

### General Considerations

$[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-}4)_2]$ ,<sup>14</sup>  $[(\text{TPB})\text{Fe}][\text{BAr}^{\text{F}}_4]$ ,<sup>15</sup>  $(\text{TPB})(\mu\text{-H})\text{Fe}(\text{H})(\text{N}_2)$ ,<sup>29</sup>  $[\text{Lutidinium}][\text{BAr}^{\text{F}}_4]$ ,<sup>31</sup>  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$ ,<sup>32</sup>  $[(\text{Si}^{\text{iPr}}_3)\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-}4)_2]$ ,<sup>26</sup>  $\text{FeCl}_2 \cdot (\text{THF})_{1.5}$ ,<sup>33</sup>  $\text{KC}_8$ ,<sup>34</sup>  $[(\text{TPB})\text{Fe}(\text{NH}_3)][\text{BAr}^{\text{F}}_4]$ ,<sup>15</sup>  $[(\text{TPB})\text{Fe}(\text{N}_2\text{H}_4)][\text{BAr}^{\text{F}}_4]$ ,<sup>15</sup> and  $\text{Fe}(\text{depe})_2\text{N}_2$ <sup>28</sup> were prepared according to literature procedures. Note:  $[\text{Lutidinium}] = 2,6\text{-dimethylpyridinium}$ ;  $[\text{BAr}^{\text{F}}_4] = [\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]^-$ . Labeled  $^{15}\text{N}_2$  (98% purity) was obtained from Cambridge Isotope Laboratories. Solvents used for catalytic runs were additionally stirred for more than 2 hours over Na/K alloy and then filtered prior to use, in addition to standard sparging (Ar gas) and passage through an activated alumina column.

### Ammonia Quantification

A Schlenk tube was charged with HCl (3 mL of a 2.0 M solution in  $\text{Et}_2\text{O}$ , 6 mmol). Reaction mixtures were vacuum transferred into this collection flask. Residual solid in the reaction vessel was treated with a solution of  $[\text{Na}][\text{O-}t\text{-Bu}]$  (40 mg, 0.4 mmol) in 1,2-dimethoxyethane (1 mL) and sealed. The resulting suspension was allowed to stir for 10 minutes before all volatiles were again vacuum transferred into the collection flask. After completion of the vacuum transfer, the flask was sealed and warmed to room temperature. Solvent was removed *in vacuo* and the remaining residue was dissolved in  $\text{H}_2\text{O}$  (1 mL). An aliquot of this solution (20 or 40  $\mu\text{L}$ ) was then analyzed for the presence of  $\text{NH}_3$  (trapped as  $[\text{NH}_4][\text{Cl}]$ ) via the indophenol method.<sup>35</sup> Quantification was performed with UV-Vis spectroscopy by analyzing absorbance at 635 nm. The tables shown in the SI indicate the raw data for the runs. Runs with small absorbance levels ( $< 0.02$  absorbance units) suffer from a large degree of error due to a small signal-to-noise ratio. Catalytic runs that used a 40  $\mu\text{L}$  aliquot are denoted with an asterisk, accounting for larger relative absorbances.

### Standard Catalytic Protocol

$[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-}4)_2]$  (2 mg, 0.002 mmol) was suspended in  $\text{Et}_2\text{O}$  (0.5 mL) in a 20 mL scintillation vial equipped with a stir bar. This suspension was vigorously stirred and cooled to  $-78\text{ }^{\circ}\text{C}$  in a cold well inside of the glove box. A similarly cooled solution of  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  (93 mg, 0.092 mmol) in  $\text{Et}_2\text{O}$  (1.5 mL) was added to the suspension in one portion with rapid stirring. Any remaining acid was dissolved in cold  $\text{Et}_2\text{O}$  (0.25 mL) and added subsequently. The reaction mixture turned light yellow-orange and homogeneous

upon addition of acid and the resulting solution was allowed to stir for 5 minutes before being transferred into a pre-cooled Schlenk tube equipped with a stirbar. The original reaction vial was washed with cold Et<sub>2</sub>O (0.25 mL) and was subsequently transferred to the Schlenk tube. Solid KC<sub>8</sub> (15 mg, 0.100 mmol) was suspended in cold Et<sub>2</sub>O (0.75 mL) and added dropwise to the rapidly stirred solution in the Schlenk tube and was then tightly sealed. The reaction was allowed to stir for 40 minutes at -78 °C before being warmed to room temperature and stirred for 15 minutes.

Detailed experimental procedures and data for all experiments can be found in the Supplemental Information.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

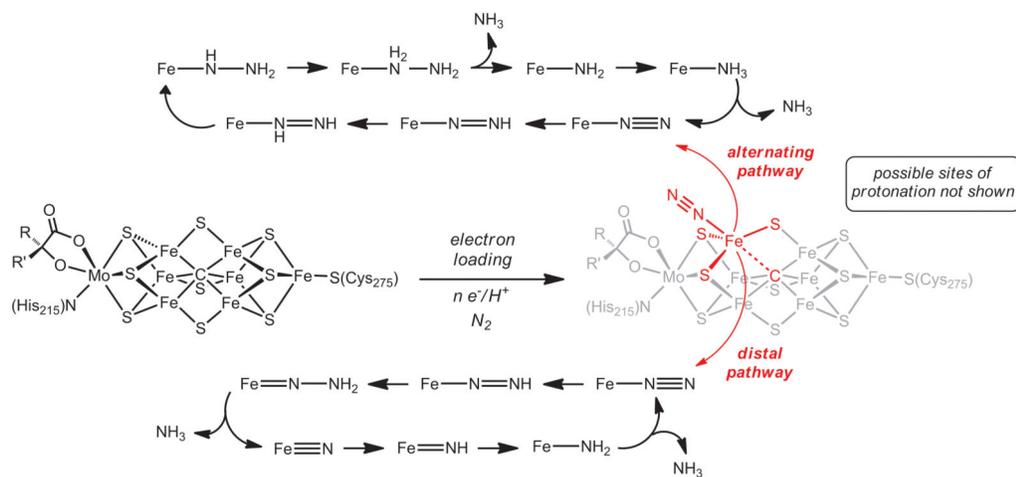
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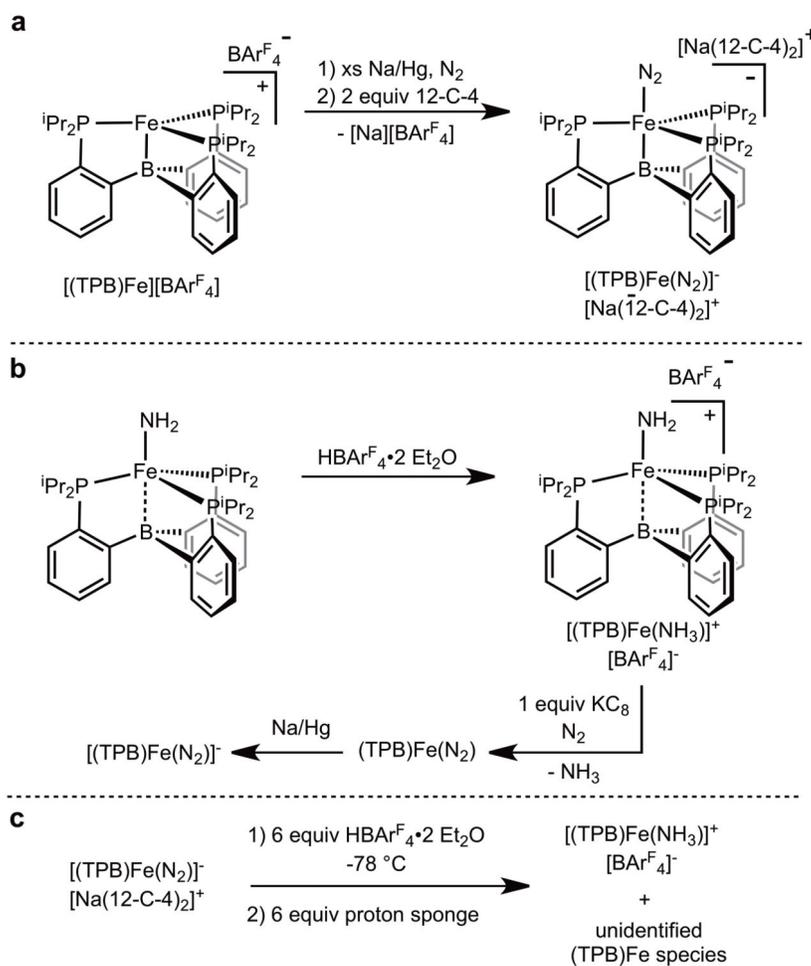
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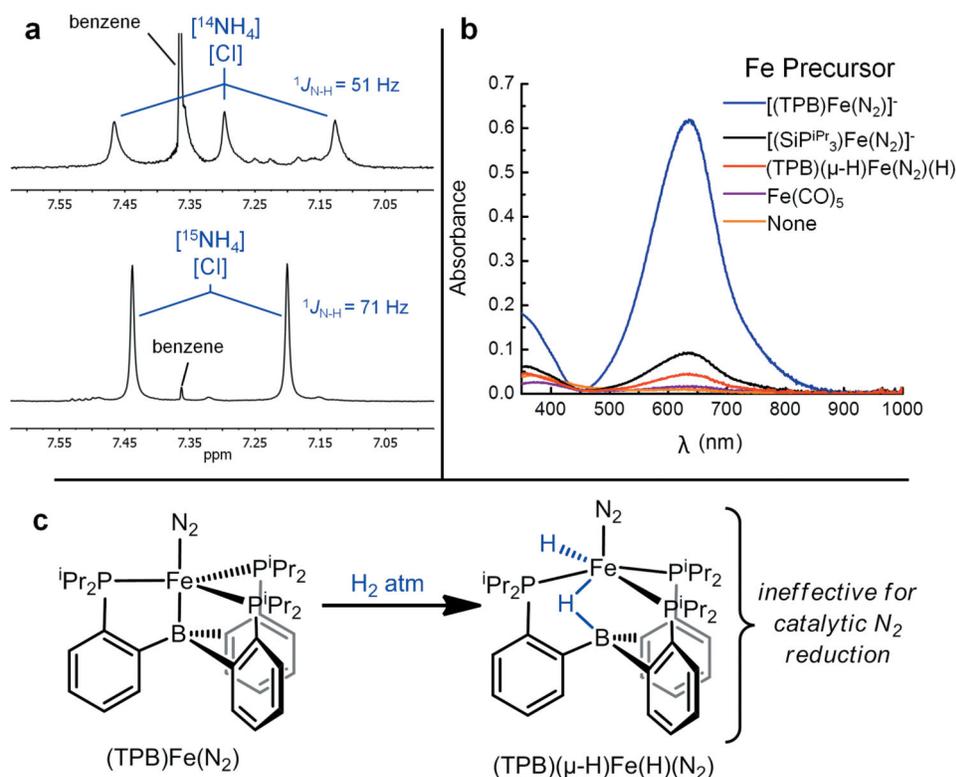
**Fig. 1. Chemical line representations of the FeMo-cofactor of nitrogenase**

A schematic depiction of postulated  $N_2$  binding and reduction at an Fe site *via* limiting alternating (top) and distal (bottom) mechanisms. The drawing emphasizes a possible hemi-labile role for the interstitial C-atom with respect to an Fe- $N_2$  binding site.



**Fig. 2. Stoichiometric (TPB)Fe-N<sub>2</sub> model reactions**

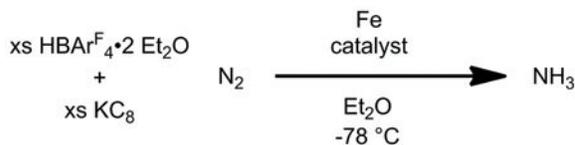
(a) N<sub>2</sub> binding to [(TPB)Fe][BARF<sub>4</sub>] under electron-loading to generate [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>]. (b) Reductive protonolysis of (TPB)Fe(NH<sub>2</sub>) to release NH<sub>3</sub> with concomitant N<sub>2</sub> uptake. (c) Generation of [(TPB)Fe(NH<sub>3</sub>)] [BARF<sub>4</sub>]<sup>-</sup> and other (TPB)Fe-species upon addition of acid to [(TPB)Fe(N<sub>2</sub>)] [Na(12-crown-4)<sub>2</sub>] at low temperature, followed by warming and then addition of base. 12-C-4 is an abbreviation for 12-crown-4. *Note:* TPB = tris(phosphine)borane.



**Fig. 3. Spectral data for ammonia analysis, and catalyst poisoning**

(a)  $^1\text{H}$  NMR spectrum (300 MHz) of  $[\text{}^{14}\text{NH}_4][\text{Cl}]$  in  $\text{DMSO-}d_6$  produced from a catalytic run under  $^{14}\text{N}_2$  (top) and of  $[\text{}^{15}\text{NH}_4][\text{Cl}]$  in  $\text{DMSO-}d_6$  produced from an independent catalytic run under 1 atm  $^{15}\text{N}_2$ . (b) Representative optical data for  $\text{NH}_3$  product analysis using the indophenol method from catalytic runs using the standard conditions with the precursors indicated. (c)  $\text{H}_2$  binds to  $(\text{TPB})\text{Fe}(\text{N}_2)$  to generate  $(\text{TPB})(\mu\text{-H})\text{Fe}(\text{H})(\text{N}_2)$ , which itself is ineffective for the catalytic generation of  $\text{NH}_3$  from  $\text{N}_2$  under the standard conditions. *Note:* TPB = tris(phosphine)borane; DMSO = dimethylsulfoxide.

**Table 1**  
**Catalytic ammonia generation from N<sub>2</sub> mediated by Fe precursors**



Using standard catalytic conditions as described in the text		
Entry	Fe precursor	NH <sub>3</sub> equiv/Fe <sup>a,b,c</sup>
1	[(TPB)Fe(N <sub>2</sub> )] [Na(12-crown-4) <sub>2</sub> ]	7.0 ± 1 <sup>d</sup>
2	[(TPB)Fe][BAR <sup>F</sup> <sub>4</sub> ]	6.2
3	[(Si <sup>iPr</sup> <sub>3</sub> )Fe(N <sub>2</sub> )] [Na(12-crown-4) <sub>2</sub> ]	0.7
4	(TPB)(μ-H)Fe(N <sub>2</sub> )(H)	0.5
5	FeCl <sub>2</sub> · 1.5 THF	<0.1
6	FeCl <sub>3</sub>	<0.1
7	Cp <sub>2</sub> Fe	<0.2
8	Fe(CO) <sub>5</sub>	<0.1
9	none	<0.1
Variations on standard conditions using [(TPB)FeN <sub>2</sub> ] [Na(12-crown-4) <sub>2</sub> ]		
Entry	Variation	NH <sub>3</sub> equiv/Fe <sup>a,b,c</sup>
10	HOTf as acid <sup>e</sup>	0.4
11	[Lutidinium][BAR <sup>F</sup> <sub>4</sub> ] as acid	<0.1
12	HCl as acid	<0.1
13	Cp* <sub>2</sub> Co as reductant	0.6
14	Cp* <sub>2</sub> Cr as reductant	<0.2
15	K metal as reductant	0.4

<sup>a</sup> NH<sub>3</sub> was collected by vacuum transfer of the reaction volatiles into HCl in diethyl ether. A dimethoxyethane solution of [Na][O<sup>t</sup>Bu] (20 equiv relative to Fe) was added to the reaction vessel residue, followed by an additional vacuum transfer, to ensure complete liberation of all NH<sub>3</sub>. The [NH<sub>4</sub>][Cl] precipitate formed in the acidic Et<sub>2</sub>O collection vessel was reconstituted in deionized H<sub>2</sub>O, from which an aliquot was taken for indophenol quantification. Analysis of the [NH<sub>4</sub>][Cl] formed by <sup>1</sup>H NMR spectroscopy in DMSO, compared with an authentic sample, provided independent confirmation of NH<sub>3</sub> generation.

<sup>b</sup> Data for individual experimental runs, and additional runs using potential precatalysts that are not presented in this table, are provided in the SI.

<sup>c</sup> Unless noted otherwise, all yields are reported as an average of 4 runs.

<sup>d</sup> Average of 16 runs.

<sup>e</sup> HOTf = trifluoromethanesulfonic acid.