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Journal

Journal of the American Chemical Society, 137(24)

ISSN

0002-7863

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Publication Date

2015-06-24

DOI

10.1021/jacs.5b03432

Peer reviewed



Published in final edited form as:

J Am Chem Soc. 2015 June 24; 137(24): 7803–7809. doi:10.1021/jacs.5b03432.

Characterization of an $\text{Fe}\equiv\text{N-NH}_2$ Intermediate Relevant to Catalytic N_2 Reduction to NH_3

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Abstract

The ability of certain transition metals to mediate the reduction of N_2 to NH_3 has attracted broad interest in the biological and inorganic chemistry communities. Early transition metals such as Mo and W readily bind N_2 and mediate its protonation at one or more N atoms to furnish $\text{M}(\text{N}_x\text{H}_y)$ species that can be characterized and, in turn, extrude NH_3 . By contrast, the direct protonation of Fe- N_2 species to $\text{Fe}(\text{N}_x\text{H}_y)$ products that can be characterized has been elusive. Herein we show that addition of acid at low temperature to $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})]$ results in a new $S = 1/2$ Fe species. EPR, ENDOR, Mössbauer, and EXAFS analysis, coupled with a DFT study, unequivocally assign this new species as $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$, a doubly protonated hydrazido(2-) complex featuring an Fe-to-N triple bond. This unstable species offers strong evidence that the first steps in Fe-mediated nitrogen reduction by $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(12\text{-crown-4})]$ can proceed along a distal or 'Chatt-type' pathway. A brief discussion of whether subsequent catalytic steps may involve early or late stage cleavage of the N-N bond, as would be found in limiting distal or alternating mechanisms, respectively, is also provided.

Since the discovery¹ and crystallographic characterization² of the FeMo-cofactor as the active site of FeMo-nitrogenase, there has been substantial interest in elucidating the mechanism of biological nitrogen reduction.³ While synthetic model chemistry cannot provide direct mechanistic information regarding enzymatic N_2 reduction, it can play a crucial role in exploring the chemical viability of proposed pathways and in exposing new reactivity patterns that help stimulate, frame, and constrain various hypotheses. Early synthetic model work by Chatt, Hidai and others⁴ as well as recent examples of molecular Mo catalysts for N_2 reduction⁵ lent credibility to the early proposal that the Mo center in the FeMo-cofactor could in principle serve as the site of N_2 binding and reduction via a distal or

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Supporting Information. Detailed experimental and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

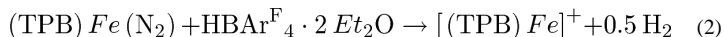
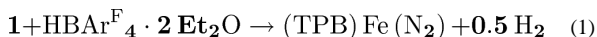
Chatt-type mechanism.^{4a,6} More recent spectroscopic, biochemical, and structural studies of FeMo-nitrogenase have suggested that iron is the more likely site for N₂ binding and reduction in the FeMo-cofactor.⁷ This hypothesis also reflects that, to date, iron is the only transition metal known to be essential to nitrogenase activity, underscored by the characterization of Fe-only nitrogenases.^{3b,8} This state of affairs has motivated studies towards the synthesis of Fe complexes that mimic steps in proposed N₂ reduction schemes and/or stabilize candidate iron intermediates of biological nitrogen fixation.⁹

Indeed, numerous synthetic studies underscore the idea that an Fe-N₂ binding site(s) may be mechanistically relevant to biological N₂ fixation.¹⁰ We have been interested in the postulate that a single Fe center can mediate N₂ reduction via a flexible ligand environment that enables N₂ coordination at Fe and facilitates the stabilization of intermediates exhibiting Fe-N multiple bonding *en route* to NH₃ formation.¹¹ Isolated synthetic Fe complexes of a tris(phosphine)borane (TPB) scaffold (Scheme 1) with bound N₂ or imido (NR²⁻) ligands demonstrate important aspects of this single-site hypothesis.^{11e,f} Moreover, through the use of chlorosilanes, this scaffold permits the conversion of Fe-N₂ to Fe≡N-NR₂, modeling the first two steps in a Chatt-type mechanism. The generation and characterization of a parent Fe≡N-NH₂ unit, either directly from Fe-N₂ or otherwise, proved more challenging.

Recently, three Fe-based catalysts for N₂ reduction to NH₃ were reported by our laboratory.¹² These catalysts appear to be single-site^{12a,13} and provide functional Fe-N₂ reduction systems for which systematic mechanistic studies can be conducted. In our original report,^{12a} a new *S* = 1/2 species was generated by the low temperature addition of excess acid to [(TPB)Fe(N₂)] [Na(12-crown-4)₂] (**1**) in the absence of exogenous reductant. This doublet species was tentatively postulated to be the hydrazido(2-) complex [(TPB)Fe≡N-NH] [BAr^F₄] (BAr^F₄ = (3,5-(CF₃)₂C₆H₃)₄B⁻) (**2**),^{12a} but several alternative structures such as those candidates depicted in Scheme 1 could not be excluded. Because **2** is a likely intermediate of catalytic nitrogen reduction by **1** (*vide infra*), its characterization is of primary interest.

Herein we report combined EPR, ENDOR, and EXAFS spectroscopic studies that assign **2** as the parent hydrazido(2-) complex [(TPB)Fe≡N-NH₂] [BAr^F₄]. ⁵⁷Fe Mössbauer studies indicate that this species constitutes a significant portion of the Fe-containing material upon exposure of **1** to acid. Finally, the geometric constraints provided by the spectroscopic data are corroborated by the optimized geometry of **2** obtained from Density Functional Theory (DFT) methods.

Mixing of pre-catalyst **1** and 10 equivalents of HBAr^F₄ · 2 Et₂O in thawing 2-MeTHF solutions at -136 °C (Scheme 1) resulted in the disappearance of the dark red color characteristic of **1** and the formation of a brown-yellow solution. Analysis by CW X-band EPR indicates complete consumption of **1** and appearance of a new, more rhombic, *S* = 1/2 signal at 77 K (Figure 1B). Indeed, spin integration of the signal of **2** suggests a yield of 87(8)%. If stoichiometric acid is added to **1** at low temperature, rapid oxidation to neutral *S* = 1 (TPB)Fe(N₂) with loss of 0.5 equiv H₂ occurs instead (eqn 1) and no EPR signal is observed (SI).^{12a}



The signal for **2** can be generated, albeit at lower intensity, with as little as 2 equivalents of acid. EPR spectra collected at 10 K reveal weak, complicated signals at low field that are consistent with one or more $S = 3/2$ species (SI), in addition to those stemming from **2**. The EPR spectrum of **2** is distinct from the more axial signature of **1** (Figure 1A) and it is also distinct from the previously reported EPR spectrum for (TPB)Fe(N₂SiMe₃) (**3**).^{11g} The fact that structurally characterized **3**, a model complex of the as yet uncharacterized complex '(TPB)FeN₂H', displays a more axial EPR spectrum than that of **2** suggests that **2** is electronically distinct from **3**, and by extension is unlikely to be the parent (TPB)FeN₂H diazenido species (candidate **2'**-E in Scheme 1). Moreover, the requirement of 2 equiv of acid strongly suggests an alternative structure to **2'**-E.

Metal hydrazido(2-) complexes typically display substantial M-N multiple bonding, and are thus electronically similar to metal imido complexes.^{5b,14} The cationic imido complex [(TPB)Fe≡N-Ad][BAr^F₄] (**4**) is isoelectronic to [(TPB)Fe≡N-NH₂][BAr^F₄], but was found to be thermally stable. This imido complex has been crystallographically characterized (SI) and also displays a rhombic EPR spectrum (Figure 1C). The rhombic EPR spectrum of **4** reflects a pseudotetrahedral iron center resulting from Fe-B elongation (Fe-B = 2.770 Å) as the iron center slips above the P₃ plane. This geometry should place an unpaired spin in a relatively nonbonding orbital arising from a ²E_{dx²-y²,xy state. This electronic structure is reminiscent of the ferrocenium cation and is also similar to various low spin L₃Fe^{III}≡NR imides that have been previously described.^{15,9d}}

Fe-N triply bonded species supported by the TPB scaffold include [(TPB)Fe≡N-Ad][BAr^F₄] (this work) and (TPB)Fe≡N(4-OMe-Ph).^{11e} These species have characteristically short Fe-N distances of 1.660 Å and 1.668 Å respectively. Structural data was sought for **2** to probe for an anticipated short Fe≡N-NH₂ triple bond. Iron K-edge X-ray extended X-ray absorption fine structure (EXAFS) data were collected and allowed for the observation of Fe-ligand distances in solution samples. These data were collected on frozen preparations (SI) of **2** in 2-MeTHF and are shown in Figure 2. Three pronounced peaks are observed in the Fourier transform spectrum, including one peak much shorter than expected for a singly-bonded Fe-N pair. Indeed the EXAFS and Fourier transform spectra can be best fit with a short Fe-N distance of 1.64 Å and two Fe-P distances of 2.28 Å and 2.42 Å in a 1:2 ratio. Additionally, an Fe-B scattering path may be included in the fit at a distance of 2.67 Å, although convolution from the Fe-P scatterers makes this assignment tentative.

The observation of two different Fe-P scatterers for a complex with three phosphorous ligands can arise from various scenarios. If one assumes the EXAFS sample contains a single species, the two distances observed could correspond to a distorted structure with two long Fe-P distances and one short distance. A similar, though substantially lessened, distortion is observed in [(TPB)Fe≡N-Ad][BAr^F₄]. Alternatively, these disparate distances

could arise from the presence of more than one species in the sample, each with a narrow distribution of Fe-P distances, a scenario that seems more likely based on the observation that oxidation of **1** by acid is a competing side reaction (eqn 1). The apparently larger than expected Debye-Waller factor in the fitting for the Fe-N scatterer would thereby result from the presence of multiple species; the short and long Fe-P distances correspond closely to those observed in low-spin and high-spin iron complexes of the (TPB) ligand scaffold, which display variable Fe-N distances.^{11f-h}

To further probe the possible presence of multiple iron species generated on addition of acid to **1** at low temperature, Mössbauer analysis of in-situ generated solutions of **2** was undertaken. In brief, an ethereal solution of ⁵⁷Fe-enriched [(TPB)⁵⁷Fe(N₂)]Na(Et₂O)_x was frozen and then layered with excess HBAr^F₄ · 2 Et₂O in Et₂O that was then also frozen. This sample was then allowed to thaw to ~-110 °C and then mechanically stirred. The sample was then transferred to a Mössbauer cup chilled at 77 K for analysis. The Mössbauer spectrum of a representative sample is shown in Figure 3 and suggests the presence of three primary iron-containing species. Similarly prepared samples showed the same features but in variable ratios and hence caution must be exercised with respect to extrapolating the population of **2** in this specific Mössbauer sample relative to the population of **2** in independently prepared EXAFS and EPR samples. Nevertheless, the Mössbauer data confirm the presence of three (TPB)Fe-species generated under relatively comparable conditions. One of the three species present in the representative Mössbauer spectrum shown (~20% of total Fe present; SI) can be definitively assigned as the neutral *S* = 1 Fe-N₂ adduct (TPB)Fe(N₂) by comparison with an authentic sample (δ = 0.56 mm/s; E_Q = 3.34 mm/s). The two other species are present in approximately equal amounts (40% each of total Fe). These two components can be simulated in multiple ways (see SI for a detailed discussion), but comparison of the simulation parameters with those of independently characterized, pure (TPB)Fe complexes suggests the simulation of Figure 3 to be the most reasonable. The simulation parameters suggest one of them is the previously characterized *S* = 3/2 cation [(TPB)Fe]⁺ (δ = 0.75 mm/s; E_Q = 2.55 mm/s);¹⁶ the other by default is therefore the iron hydrazido(2-) cation **2** (δ = 0.35 mm/s; E_Q = 1.02 mm/s).

The presence of (TPB)Fe(N₂) and [(TPB)Fe]⁺ in the sample is consistent with our previous finding that the addition of HBAr^F₄ · 2 Et₂O to **1** leads to net oxidation of the complex to generate (TPB)Fe(N₂) via loss of H₂.^{12a} Likewise, (TPB)Fe(N₂) can be further oxidized to [(TPB)Fe]⁺ via addition of HBAr^F₄ · 2 Et₂O (eqn 2, SI). In sum, the available Mössbauer data predicts that variously prepared samples of **2** may contain (TPB)Fe(N₂) and [(TPB)Fe]⁺ and this fact helps explain the additional P scatterer in the EXAFS data, as well as the larger than expected Fe-N Debye-Waller factor. As (TPB)Fe(N₂) is EPR-silent, and [(TPB)Fe]⁺ does not display EPR signals at 77 K, this Fe speciation is fully consistent with the clean spectrum observed by CW X-band EPR (Figure 1B).

While the aforementioned characterization data are most consistent with [(TPB)Fe≡N-NH₂][BAr^F₄], the techniques used are not sensitive to the presence or location of the protons. As a direct probe of these protons, as well as other nuclei in **2**, we turned to electron nuclear double resonance (ENDOR) spectroscopy. This technique is particularly attractive because it

selectively monitors $S = 1/2$ **2** regardless of the presence of the other species that complicate the EXAFS and Mössbauer analysis.

Figure 4 presents a 2D field-frequency pattern of ^1H Davies pulsed Q-band ENDOR spectra collected across the EPR envelope of **2**. In addition to ancillary ligand signals from weakly-coupled protons with $A < 4$ MHz, the spectra show strongly-coupled signals that arise from protonation of the N_2 ligand (Figure 4). The spectra collected at the 'crystal-like' fields, g_1 and g_3 , show two distinct ^1H doublets, $A_{g_1}(^1\text{H}\alpha) \sim 16$ MHz, and $A_{g_1}(^1\text{H}\beta) \sim 10$ MHz (Figure 4, blue and red, respectively), indicating the presence of two well-defined, inequivalent protons, consistent with assignment of **2** as exhibiting an unsymmetrically bound di-protonated ($-\text{N}-\text{NH}_2$) species, inconsistent with the proposed structures **2'-B** and **2'-E** (Scheme 1). Structure **2'-B** has two protons which are anticipated to be approximately equivalent with couplings substantially larger than observed (see below), and structure **2'-E** should only have one proton signal.

As the magnetic field is increased, the $^1\text{H}\alpha$ feature splits, with the outer peak reaching a maximum ^1H coupling between g_1 and g_2 (11661 G), $A_{\text{max}} = 18$ MHz for $^1\text{H}\alpha$; with further increase in field the pattern coalesces into the single doublet at g_3 . The maximum coupling for a metal-bound hydride ($A_{\text{max}} \sim 40$ MHz) is much larger,¹⁷ inconsistent with structures **2'-C** and **2'-D**, Scheme 1. The $^1\text{H}\alpha$ pattern resembles that of a heme hydroperoxy Fe-O-OH proton,¹⁸ an appealing analogy to the Fe-N-NH₂ unit in **2**, and those analyses provide a good starting point for analysis of the $^1\text{H}\alpha$ hyperfine tensor; simulation of the $^1\text{H}\alpha$ pattern (Figure 4, blue) yields a slightly rhombic tensor of $\mathbf{A} = +[18.0, 10.5, 8.0]$ MHz (see Fig 4 caption), whose anisotropic contribution corresponds to an Fe-H α distance of $d > 3.1$ Å, with the Fe-H α vector rotated away from g_1 , which coincides approximately with the Fe-N bond and the molecular pseudo C_3 axis.¹⁹ In short, the analysis requires a non-linear Fe-N-N geometry (Fig S8).

The smaller $^1\text{H}\beta$ coupling (Fig 4, red) exhibits a 2D pattern that can be described by a hyperfine tensor whose anisotropic contribution corresponds to an Fe-H β distance of $d > 3.5$ Å, with the Fe-H β vector along g_1 (the Fe-N bond). The absolute signs of the $^1\text{H}\alpha$, $^1\text{H}\beta$, couplings are implied by the assumption that the dominant anisotropic component is determined by through-space dipolar coupling, and were confirmed by the Variable Mixing Time (VMT) Pulsed ENDOR Saturation and Recovery (PESTRE) protocol (SI). The estimated Fe- $^1\text{H}\alpha$ / $^1\text{H}\beta$ distances, along with the orientations of the hyperfine coupling tensors relative to \mathbf{g} , imply that both protons have been added to the β -N of a bound N_2 , to generate a bent $\text{Fe}\equiv\text{N}-\text{NH}_2$ moiety, with a Fe-N-N bond angle $\delta \sim 150^\circ$ (SI). Notably, as indicated above, the metrical parameters for the two protons are inconsistent with *every* other model visualized in Scheme 1.

Q-band $^{14/15}\text{N}$ ENDOR data was also acquired to further characterize the hydrazido ligand of **2** (Figure 5). A ^{15}N ENDOR response is observed as a peak at $\nu_+ = +9.8$ MHz (Figure 5), corresponding to $A_2(\text{2-}^{15}\text{N}) = +9.0$ MHz, $A_2(\text{2-}^{14}\text{N}) = -6.4$ MHz for the coordinated nitrogen (upon scaling by the gyromagnetic ratios of ^{14}N and ^{15}N ($\gamma \equiv g_n(^{14}\text{N})/g_n(^{15}\text{N}) \equiv A(^{14}\text{N})/A(^{15}\text{N}) = -0.71$)). The $\text{2-}^{14}\text{N}$ ENDOR response has a quadrupole splitting of $3P = 2.7$ MHz at g_2 . Furthermore, the isotopically labeled $\text{2-}(^{15}\text{N})$ sample has a resolved

hyperfine coupling of $A_3(^{15}\text{N}) = +8.0$ MHz near g_3 . The corresponding ^{14}N ENDOR response of **2**-(^{14}N) is expected to have a coupling of $A_3(^{14}\text{N}) = -5.7$ MHz, but is not observed. The additional quadrupole splitting of the ^{14}N at g_3 may orient **A** and **P** in such a manner that the quadrupole ENDOR response is too broad at g_3 and sharpest at g_2 . No distinguishable nitrogen ENDOR features were observed at fields below g_2 for either **2**-(^{14}N) and **2**-(^{15}N), but the single-field three-pulse ESEEM spectrum of **2**-(^{14}N) (SI) is well simulated with a single ^{14}N tensor of $\mathbf{A}(\mathbf{2}\text{-}^{14}\text{N}) = -[4.34, 7.18, 6.22]$ MHz and quadrupole parameters of $e^2qQ/h = 1.76$ ($P = 0.88$ MHz) and rhombicity factor, $\eta = 0.64$, in excellent agreement with the observed $P_2 = 0.90$ MHz from ENDOR spectroscopy. The presence of quadrupole coupling with high rhombicity supports the idea of a non-linear Fe-N-N linkage.

^{11}B ENDOR spectra of **2** (SI, Fig. S10 and S11) show a coupling of $a_{iso} \sim -8.8$ MHz, completing the characterization of the axial ligands to Fe. As shown in Figure S11, the ^{11}B nuclei exhibits a VMT-PESTRE response, typical of a nuclei with negative spin density and a negative **A**. Using the ^{11}B as a 'reference,' the observed ^{14}N nuclei possesses negative spin density and $^1\text{H}\alpha$ and $^1\text{H}\beta$ both exhibit positive spin density. The negative spin density observed on the ^{11}B and ^{14}N nuclei is a result of the spin-polarization of the Fe-B bond by the positive-spin density of the Fe center.

Finally, a nearly isotropic ^{31}P ENDOR signal from the phosphine ligand is simulated with $\mathbf{A}(\mathbf{31}\text{P}\alpha) = [43, 42, 40]$ MHz (Figure 4, green). Features of a second phosphine are observed in Figure 5, around 10.0–10.5 MHz and assigned as the ν_- transitions of ^{31}P doublet with $A \sim 60$ MHz; the ν_+ partner of this ^{31}P response unfortunately falls underneath the intense ENDOR response of weakly coupled solvent protons (^1H) (~ 55 MHz) (Figure S12). This observation of two ^{31}P couplings, one with $A_3(^{31}\text{P}\beta) \sim 64$ MHz the other with $A_3(^{31}\text{P}\alpha) = 40$ MHz by ENDOR spectroscopy correlates well with the simulation of the X-band EPR spectrum (Figure 1).

Computational studies were undertaken to compare the parameters of the theoretically predicted structure with those obtained spectroscopically. An optimized geometry (SI) of $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$ was found, utilizing the core of $[(\text{TPB})\text{Fe}\equiv\text{NAd}]^+$ for an initial guess. This geometry shows similar bonding metrics to those observed by EXAFS and ENDOR analysis. Thus, ENDOR requires di-protonation of the remote N2, while EXAFS requires a short Fe-N1 distance consistent with the calculated value 1.70 Å, and calculated Fe-P distances of 2.29, 2.31, and 2.36 Å (Figure 6A). The characteristically short Fe-N distance (i.e. 1.7 Å) is consistently found when exploring a variety of functionals while the Fe-P distances show slightly more variation (SI). In addition, the bending at N α required for the interpretation of the ENDOR data is observed in the calculated gas-phase structure. Figure 6B depicts the predicted spin distribution in $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$ suggesting that the majority of spin is carried by Fe with leakage to the NNH $_2$ ligand and B also evident. Other candidate structures for **2** were similarly optimized and found to be higher energy isomers. For example, a comparison of the energies of the hydrazido(2-) species versus a diazene isomer (Scheme 1, **2**'-A) shows that the assigned $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$ isomer is lower in energy by 17.0 (BP86) or 8.2 (M06L) kcal/mol (SI). Taken together the computational work is also consistent with the assignment of **2** as $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$.

While **2** has been generated herein with excess acid at $-136\text{ }^{\circ}\text{C}$ in 2-MeTHF, N_2 reduction catalysis by **1** was originally carried out at $-78\text{ }^{\circ}\text{C}$ in Et_2O by addition of acid followed by addition of reductant.^{12a} As such, we sought to determine whether **2** could be detected in mixtures more relevant to catalysis, prior to the addition of the reductant. X-band EPR spectra of solutions prepared from the addition of acid to **1** at either $-136\text{ }^{\circ}\text{C}$ in 2-MeTHF or at $-78\text{ }^{\circ}\text{C}$ in Et_2O indicate that **2** is present in both preparations (SI, Fig. S15). Furthermore, upon warming to $-40\text{ }^{\circ}\text{C}$ or to room temperature, both preparations show the growth of $S = 3/2$ signals concomitant with the decay of the signals of **2**. The identity of these $S = 3/2$ species is hard to determine due to convolution of the quartet signals. One such $S = 3/2$ species, $[(\text{TPB})\text{Fe}(\text{NH}_3)]^+$, has been definitively assigned by inspection of the ^1H NMR spectrum of a similarly-prepared mixture following warming to room temperature.^{12a} Therefore, **2** decays at least in part to $[(\text{TPB})\text{Fe}(\text{NH}_3)]^+$ upon warming even without exogenous reductant.

The combined spectroscopic data presented herein confirm the assignment of **2** as a $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$ hydrazido(2-) complex. All of the likely alternative formulations for **2** can be conclusively excluded by presented data. The observation of a short Fe-N distance by EXAFS spectroscopy conclusively excludes the two diazene formulations, **2'-A**, **B**, as well as **2'-E**. In addition, an η^1 diazene adduct (**2'-A**) should have two ^1H hyperfine couplings, but with one much stronger than the two observed. An η^2 diazene adduct (**2'-B**), is expected to have two ^1H couplings larger than observed. Hydride formulations (**2'-C**, **2'-D**) are ruled out by the ^1H couplings and metric parameters already discussed. Finally, **2'-E** would have only one coupled proton.

To summarize, double protonation at the distal nitrogen, as invoked in a distal or Chatt type mechanism, is viable for this iron catalyst and likely occurs in the Fe-mediated N_2 fixation cycle catalyzed by **1** (Scheme 2). One or more downstream species arising from the decomposition of **2** involve higher spin ($S = 3/2$) species based on X-band EPR data (see SI). Plausible candidates for these $S = 3/2$ species include $[(\text{TPB})\text{Fe}(\text{NH}_3)]^+$, $(\text{TPB})\text{Fe}(\text{NH}_2)$, and $[(\text{TPB})\text{Fe}]^+$; these species, each of which is shown in blue in Scheme 2, are compatible with both distal and alternating scenarios. Another candidate $S = 3/2$ species is the hydrazine complex that would form on the alternating pathway, $[(\text{TPB})\text{Fe}(\text{N}_2\text{H}_4)]^+$, which was previously characterized and shown to decompose to $[(\text{TPB})\text{Fe}(\text{NH}_3)]^+$.^{11h} A branching scenario whereby the distal intermediate **2** isomerizes to an alternate diazene structure, such as either **2'-A** or **2'-B** in Scheme 1, that then proceeds to $(\text{TPB})\text{Fe-N}_2\text{H}_4^+$ as a later-stage intermediate of the alternating pathway, remains a mechanistic possibility.⁷ Likewise, formal H-atom addition to **2** at the α N-atom (Scheme 1) provides an alternative possible branching point from the distal to the alternating pathway. The key point we wish to underscore is that the observation of **2** is not incompatible with late stage N-N cleavage via a hydrazine intermediate.

Sorting out further mechanistic details for the present system warrants additional studies. But one conclusion is clear: an imide-like $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2]^+$ species can be directly generated at low temperature by protonation of the Fe- N_2 catalyst precursor, and solutions of this species are known to decay to $[(\text{TPB})\text{Fe}(\text{NH}_3)]^+$. This is a satisfying conclusion as it

links the chemistry of iron-to-nitrogen multiple bonding to an N₂ fixation cycle. In this context a conceptual parallel can be drawn to catalytic O₂ reduction wherein iron-to-oxygen multiply bonded species (e.g., Fe=O) are generated as intermediates.²⁰

Supplementary Material

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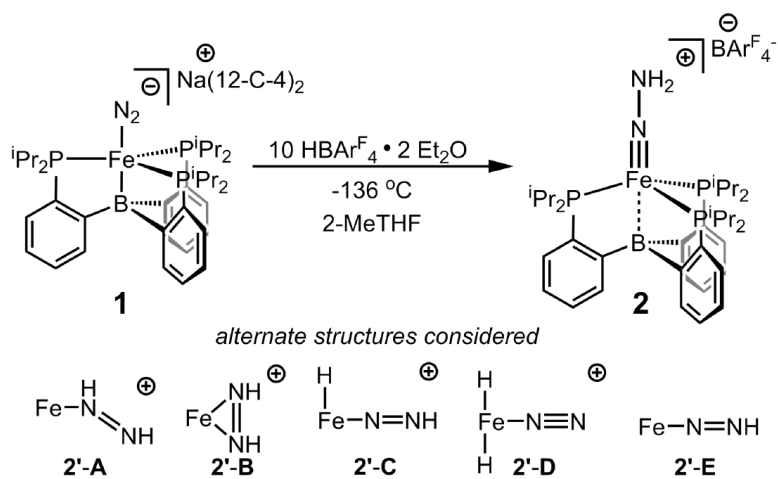
ACKNOWLEDGMENT

This work was supported by the NIH (GM 070757 to JCP, GM 111097 to BMH), the NSF (MCB-1118613 to BMH, DGE-0824162 to GEC), an NSERC fellowship (to LZ), a Caltech Center for Environmental Microbial Interactions fellowship (to LZ), and the Gordon and Betty Moore Foundation. We thank the staff at Beamline 9–3, Stanford Synchrotron Radiation Lightsource (SSRL). SSRL is operated for the DOE and supported by OBER and by the NIH, NIGMS (P41GM103393) and the NCRR (P31RR001209).

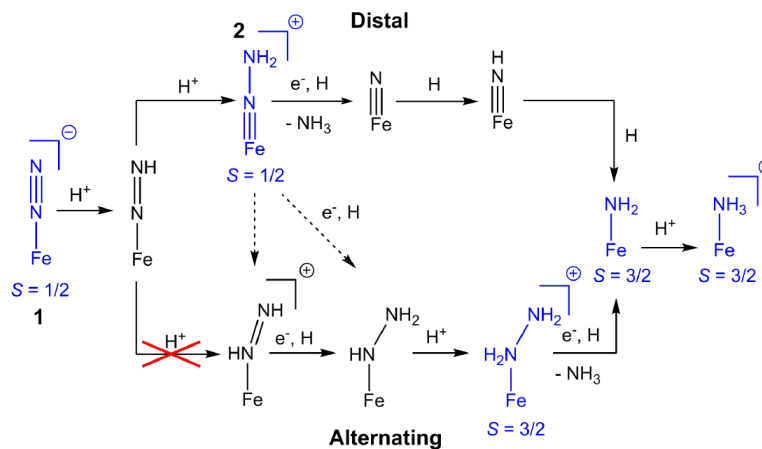
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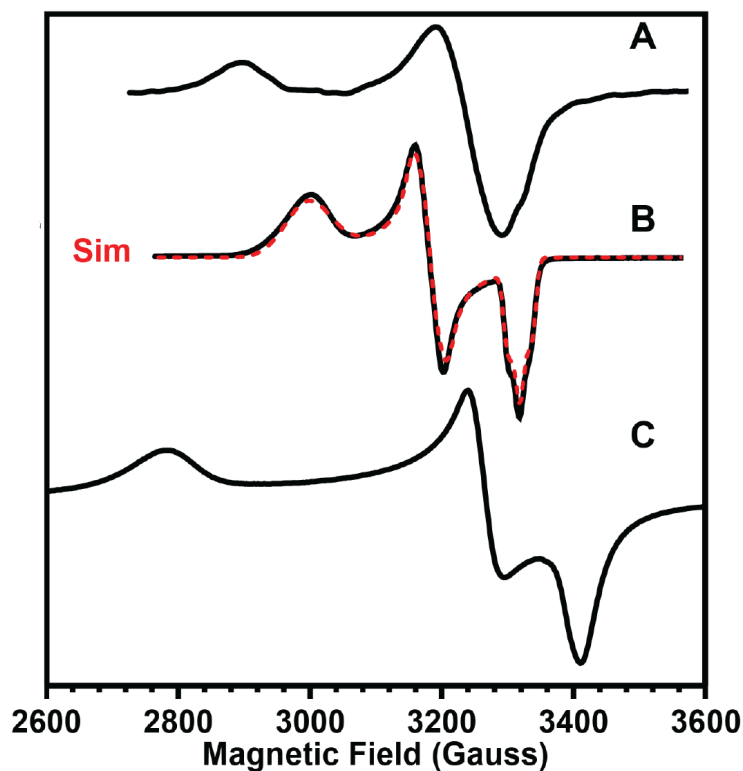
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SCHEME 1.

**SCHEME 2.**

Plausible scenarios that would transform $[\text{Fe-N}_2]^-$ catalyst **1** to $[\text{Fe-NH}_3]^+$ where $[\text{Fe}\equiv\text{N-NH}_2]^+$, **2**, is a key intermediate. Species shown in blue (along with spin states) have been experimentally characterized. *Top path* illustrates a limiting distal mechanism, *bottom path* an alternating mechanism, and the dotted arrows illustrate hybrid paths that could shuttle distal intermediate **2** to an alternating pathway that features late stage N-N cleavage. The order of protons, electrons, and/or H-atoms are provided for bookkeeping purposes only.

**FIGURE 1.**

(A) 77 K X-Band (9.388 GHz) EPR of [(TPB)Fe(N₂)] [Na(12-crown-4)]₂ (**1**). (B) 77 K X-Band (9.409 GHz) EPR after addition of 10 equivalents of HBAr^F₄ · 2 Et₂O to **1** to generate [(TPB)Fe≡N-NH₂] [BAr^F₄] (**2**). The parameters for the simulation of the spectrum are: $g_1 = 2.222$, $g_2 = 2.091$, $g_3 = 2.006$, two ³¹P nuclei coupling $A_3(^{31}\text{P}\alpha) = 64$ MHz, $A_3(^{31}\text{P}\beta) = 40$ MHz determined from ENDOR spectroscopy and third phosphorus of $A_3(^{31}\text{P}\lambda) = 20$ MHz; line broadening = 256, 113, and 41 MHz for g_1 , g_2 , and g_3 respectively. (C) 77 K X-Band (9.399 GHz) EPR of [(TPB)Fe≡N-Ad] [BAr^F₄] (**4**).

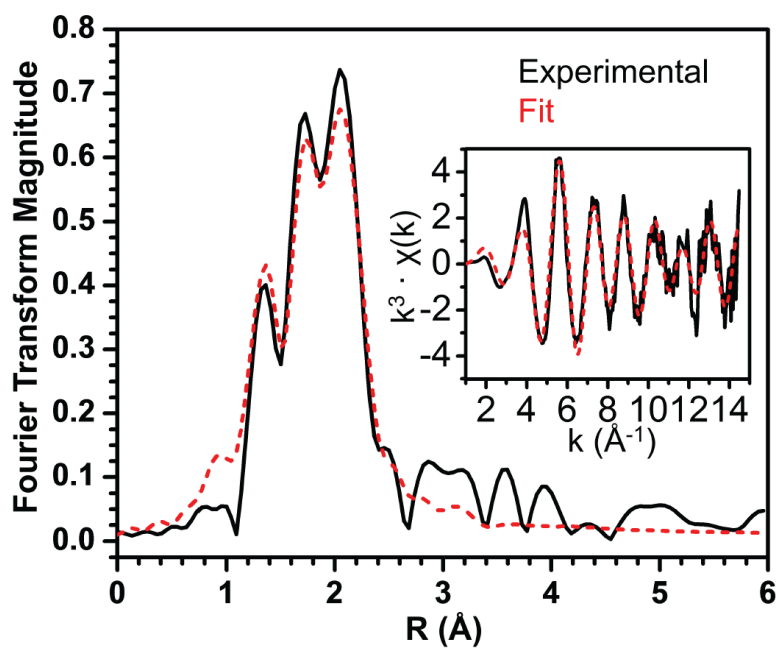


FIGURE 2.

Fe K-edge Fourier transform of the EXAFS spectrum collected on a sample of **2**. Inset shows the EXAFS oscillations. Scatterer distances (\AA) are Fe-P = 2.28, Fe-P = 2.42, Fe-N = 1.64, and Fe-B = 2.67 with the phosphines present in a 1:2 ratio. Full fit parameters may be found in the SI.

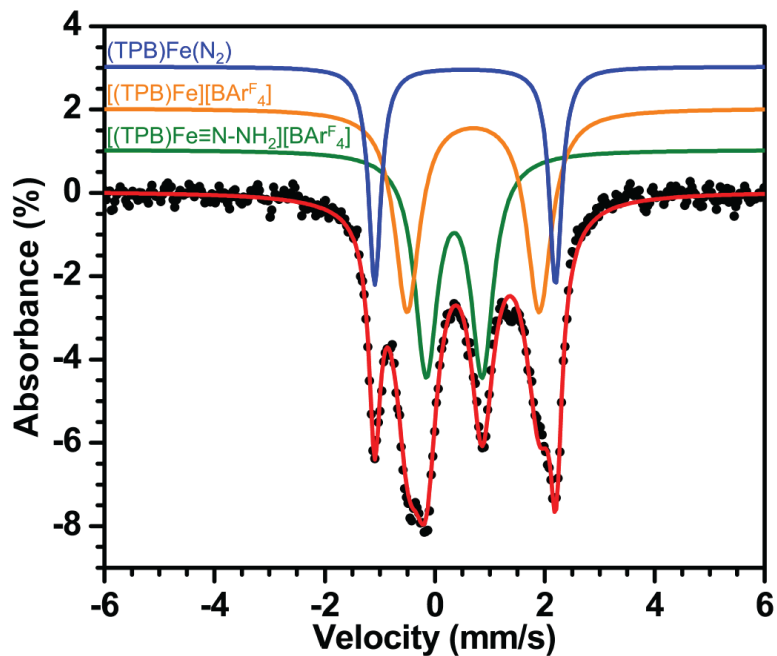


FIGURE 3.

^{57}Fe Mössbauer spectrum obtained by the reaction of ^{57}Fe -enriched $[(\text{TPB})^{57}\text{Fe}(\text{N}_2)]$ $[\text{Na}(\text{Et}_2\text{O})_x]$ with 5 equiv $\text{HBAr}^{\text{F}_4} \cdot 2 \text{Et}_2\text{O}$ in Et_2O at -110°C . Data is shown as black dots and the combined simulation is shown in red. The individual sub-spectra representing $(\text{TPB})\text{Fe}(\text{N}_2)$, $[(\text{TPB})\text{Fe}][\text{BAr}^{\text{F}_4}]$, and $[(\text{TPB})\text{Fe}\equiv\text{N-NH}_2][\text{BAr}^{\text{F}_4}]$ (**2**) are shown in blue, orange, and green respectively and are offset for clarity. The spectrum was collected at 80 K in the presence of a 50 mT applied magnetic field to minimize line broadening (fast relaxation regime). Refer to the SI for simulation parameters and more detailed discussion.

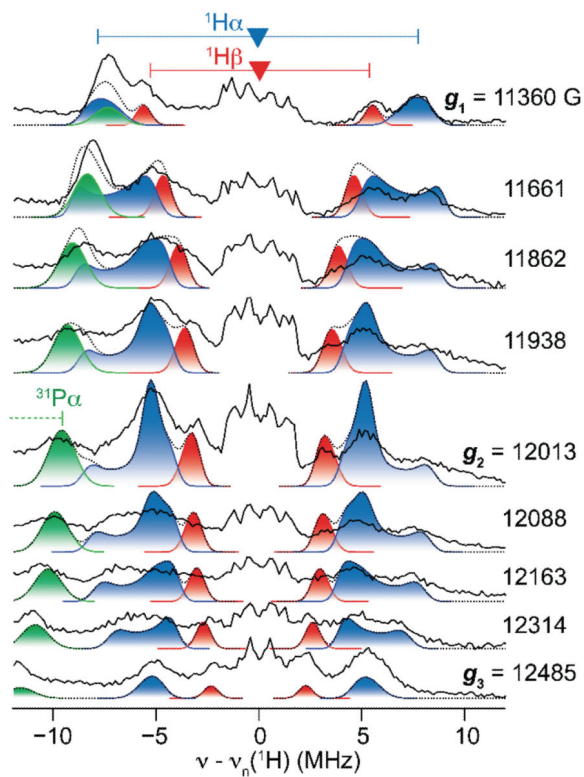
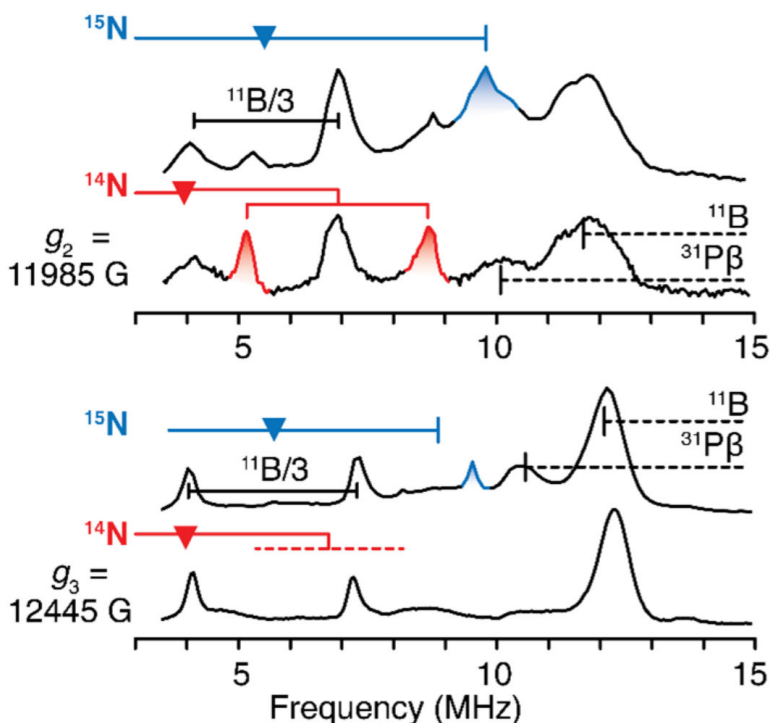


FIGURE 4.

2D field-frequency 35.049 GHz Davies ENDOR pattern of **2** (black solid) collected at 2 K. $^1\text{H}\alpha$, blue, $A = [18.0, 10.5, 8.0]$ MHz, $\beta = 30^\circ$; $^1\text{H}\beta$, red, $A = [11.5, 6.0, 4.5]$ MHz, $\beta = 0^\circ$; $^{31}\text{P}\alpha$, green, $A = [43, 42, 40]$ MHz. Summed ENDOR simulation of $^1\text{H}\alpha$, $^1\text{H}\beta$, and $^{31}\text{P}\alpha$ is in black dashed line. Conditions: $\pi = 60$ ns; $\tau = 600$ ns; $T_{\text{RF}} = 30$ μs ; repetition time = 20 ms; RF frequency randomly hopped.

**FIGURE 5.**

Davies pulsed ENDOR spectra of **2** collected at 2 K for each ^{14}N and ^{15}N isotopologues in red and blue, respectively. Observed 14/15N couplings are Larmor centered (triangles) split by *A* and *P* for ^{14}N (goalposts). A stronger nitrogen coupling is observed in **2** following protonation of **1**. At g_2 : $A_2(\mathbf{2}\text{-}^{15}\text{N}) = +9.0$ MHz; $A_2(\mathbf{2}\text{-}^{14}\text{N}) = -6.4$ MHz; $3P(\mathbf{2}\text{-}^{14}\text{N}) = 2.7$ MHz. At g_3 : $A_3(\mathbf{2}\text{-}^{15}\text{N}) = +8.0$ MHz but the corresponding $A_3(\mathbf{2}\text{-}^{14}\text{N}) = -5.7$ MHz is possibly further quadrupole split and not observed. The ν_- feature of $a_{iso}(\mathbf{2}\text{-}^{11}\text{B}) = -8.7$ MHz at ~11 to 12 MHz. The features observed at 10.0 and 10.5 MHz at g_2 and g_3 , respectively, is the ν of $a_{iso}(\mathbf{2}\text{-}^{31}\text{P}\beta) = 60$ MHz. $^{11}\text{B}/3$: peaks at $\nu_{\text{B}}/3$, the third harmonic of ^{11}B nuclear Larmor frequency. Parameters: microwave frequency = 34.88 GHz; $\pi/2 = 100$ ns; $\tau = 600$ ns; $T_{\text{RF}} = 60$ μs ; repetition time = 20 ms.

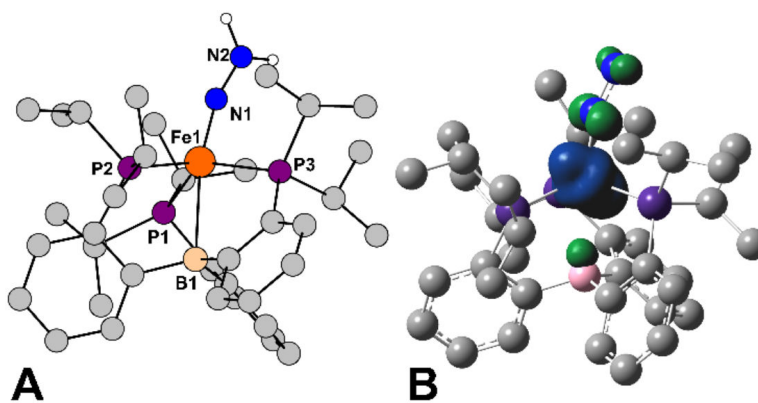


FIGURE 6. (A) Computed geometry for $[(\text{TPB})\text{Fe}\equiv\text{N}-\text{NH}_2]^+$ and (B) spin density plot for $[(\text{TPB})\text{Fe}\equiv\text{N}-\text{NH}_2]^+$. Both plots generated with the M06L functional with TZVP, SVP, and 6-31G(d) basis sets on Fe, P B N, C, and H respectively.