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Characterization of the earliest intermediate of Fe-N₂ protonation: CW and Pulse EPR detection of an Fe-NNH species and its evolution to Fe-NNH₂⁺

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Abstract

Iron diazenido species (Fe(NNH)) have been proposed as the earliest intermediates of catalytic N₂-to-NH₃ conversion (N₂RR) mediated by synthetic iron complexes, and relatedly as intermediates of N₂RR by nitrogenase enzymes. However, direct identification of such iron species, either during or independent of catalysis, has proven challenging owing to their high degree of instability. The isolation of more stable silylated diazenido analogs, Fe(NNSiR₃), and also of further downstream intermediates (e.g., Fe(NNH₂)), nonetheless points to Fe(NNH) as the key first intermediate of protonation in synthetic systems. Herein we show that low temperature protonation of a terminally bound Fe-N₂⁻ species, supported by a bulky trisphosphinoborane ligand (ArP₃^B), generates an *S* = 1/2 terminal Fe(NNH) species that can be detected and characterized by continuous-wave (CW) and pulse EPR techniques. The ¹H-hyperfine for ArP₃^BFe(NNH) derived from the presented ENDOR studies is diagnostic for the distally-bound H-atom (*a*_{iso} = 16.5 MHz). The Fe(NNH) species evolves further to cationic [Fe(NNH₂)]⁺ in the presence of additional acid, the latter being related to a previously characterized [Fe(NNH₂)]⁺ intermediate of N₂RR mediated by a far less encumbered iron tris(phosphine)borane catalyst. While catalysis is suppressed in the present sterically very crowded system, N₂-to-NH₃ conversion can nevertheless be demonstrated. These observations in sum add support to the idea that Fe(NNH) plays a central role as the earliest intermediate of Fe-mediated N₂RR in a synthetic system.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Procedures and characterization data (PDF)

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INTRODUCTION

The mechanism of nitrogen fixation in nitrogenase enzymes has fascinated researchers since the discovery and characterization of the iron-molybdenum-cofactor (FeMoco), which is the active site for substrate binding and reduction in FeMo-nitrogenase.^{1,2,3} While a host of scenarios continue to be considered, hypotheses surrounding the mechanism of the key bond breaking and making steps are often framed in the context of two limiting pathways.⁴ One is the distal pathway, where successive delivery of H-atom equivalents occurs at N_β, leading to an early N-N bond cleavage step with liberation of the first ammonia equivalent. The second is an alternating pathway, wherein the delivery of H-atom equivalents alternates between N_β and N_α and late-stage N-N cleavage leads to the first NH₃ equivalent (Figure 1).

Model chemistry from Chatt, Hidai, and others on group VI coordination complexes focused early attention on the distal mechanism, and seminal studies of a well-defined molybdenum tris(amido)amine catalyst system by Schrock cemented the viability of such a pathway for a single Mo active site.^{5,6,7,8} The development of improved Mo catalysts continues at a robust pace.⁹

Structural and spectroscopic studies of nitrogenase enzymes have, however, implicated one or two iron centers as the initial site/s of N₂ binding and subsequent reduction steps,^{4,10} consistent with the fact that molybdenum is not an essential metal for nitrogenase activity.² In this context, several iron model systems have shown catalytic activity for N₂-to-NH₃ conversion (N₂RR).¹¹

Recent mechanistic studies from our lab using a tris(phosphine)borane iron (P₃^BFe) catalyst system have established the viability of a distal iron pathway for NH₃ generation, releasing a terminal nitride intermediate ([P₃^BFe^{IV}≡N]⁺).¹² However, related mechanistic studies we have undertaken have revealed the possibility that multiple pathways may be operative in the iron catalyst systems, including hybrid crossover pathways.¹³ This idea is consistent with the competitive generation of N₂H₄ in both stoichiometric and catalytic yields.^{11e,13,14}

These complexities notwithstanding, a critical first intermediate that serves as the linchpin to later stage intermediates along various trajectories is the terminal diazenido, Fe-NNH (Figure 1). This type of species may be regarded as a nitrogenous analogue of an iron hydroperoxo, Fe-OOH, the latter playing a central role in enzymes such as cytochrome P450's and bleomycin via reductive protonation of O₂.¹⁵ Fe-NNH species are expected to be even less stable, and current precedent for their reliable characterization using any transition metal is limited to three examples featuring either Mo or W.

Schrock and Yandulov unambiguously identified, based on ¹H NMR, ¹⁵N NMR, IR, and X-ray crystallographic data, examples of comparatively stable Mo- and W-NNH species.¹⁶ Earlier evidence for such species was first reported by Chatt and coworkers,¹⁷ which was later validated by more careful vibrational studies from Lehnert and Tuzek for the complex (dppe)W(F)(NNH) (dppe = bis(diphenyl)phosphinoethane).¹⁸ Lehnert and Tuzek also showed that some of the early assignments of "M-NNH" (M = Mo/W) species were misleading, owing to alternative M(H)(N₂) isomers being highly favored, or in equilibrium with the M-NNH form, and also due to misinterpretation of complex vibrational data.

Indeed, there have been long standing challenges associated with the use of vibrational data to reliably assign terminal M-NNH species, and their N-H vibrations in particular.¹⁸

There is also the mention of a cationic *trans*-(H)(DMeOPrPE)₂Fe(HN=NH)⁺ species formed as part of a reaction mixture by Tyler and coworkers from the addition of hydrazine to (H)(DMeOPrPE)₂Fe(Cl)⁺; within the same mixture, it is speculated that a resonance observed at 13.8 ppm in the ¹H NMR spectrum may be attributable to (H)Fe(NNH), possibly generated via deprotonation of (H)Fe(HN=NH)⁺ by available hydrazine.¹⁹ Further data are not available.²⁰

We have previously shown that the addition of stoichiometric acid, even at low temperature (−135 °C to −78 °C), to P₃^EFe-N₂[−] species (E = B, Si, C) known to be active for NH₃ generation, leads instead to net oxidation and liberation of 0.5 equiv of H₂ (Eqn 1). Given that Fe-NNH species are predicted to have extremely weak N-H bonds,^{11g,21,22} such reactivity is perhaps unsurprising. The presence of additional acid can lead to the formation of P₃^EFe-NNH₂⁺ (established for E = B, Si),^{11a,13,23} presumably via trapping of Fe-NNH prior to bimolecular H₂ release (Eqn 2). This observation, along with related studies preparing kinetically stabilized, terminal Fe-NNR species (R = alkyl, silyl) by alkylation/silylation of Fe-N₂[−] precursors,^{24,25} strongly implicates Fe-NNH intermediates.

To overcome the inherent challenges posed by direct detection of an Fe-NNH species in a system active for NH₃ generation from N₂, one with a comparatively very weak and therefore highly reactive N-H bond,²⁶ we have undertaken the design of a sterically encumbered trisphosphine(borane)-iron system and have studied the protonation of its Fe-N₂[−] derivative at extremely low temperature by continuous wave (CW) and pulse EPR spectroscopy, including electron-nuclear double resonance (ENDOR) and hyperfine sublevel correlation (HYSCORE) spectroscopies.²⁷ Herein we describe the direct characterization of ArP₃^BFe-NNH (where Ar = 3,5-diisopropyl-4-methoxyphenyl), and its evolution to the next intermediate state, ArP₃^BFe-NNH₂⁺. In addition to bearing on the mechanism of Fe-mediated nitrogen fixation by synthetic systems, these data provide the first detailed EPR signatures for an Fe-NNH species, using methods similar to those being employed to probe for intermediates of the FeMoco. These data should therefore prove valuable in constraining future assignments of plausible intermediates within the enzymatic system/s.

RESULTS AND DISCUSSION

To attenuate the rate of bimolecular degradation of a terminal Fe-NNH species, we targeted an electron rich, tris(diarylphosphino)borane system (ArP₃^B) (where Ar = 3,5-diisopropyl-4-

methoxyphenyl) as a ligand framework that might provide sufficient vertical steric bulk to create a protective binding pocket for an NNH ligand. While aryl (instead of alkyl) substituents on the tris(phosphine)borane-iron system have not been compatible with N_2RR catalysis, we reasoned that inclusion of isopropyl and methoxy substituents on the aryl rings would render the phosphines sufficiently electron-donating to be able to observe successful N_2 protonation, and possibly even NH_3 formation.

The new ArP_3^B ligand was assembled from previously reported orthobromophenyldichlorophosphine, 4-bromo-2,6-diisopropyl-1-methoxybenzene, and $B(OMe)_3$ (Scheme 1).^{28,29} Metalation of ArP_3^B with $FeBr_2$ in THF followed by sodium-mercury amalgam reduction in benzene afforded, following work-up, dark brown iron(I) ArP_3^BFeBr as an $S = 3/2$ dark brown microcrystalline solid (58.9 %, Scheme 1). The solid-state X-ray crystal structure of ArP_3^BFeBr is shown in Figure 2 (top), revealing a pseudo three-fold symmetric environment with the ligand binding in the expected tetrapodal fashion. Further reduction of ArP_3^BFeBr with sodium-mercury amalgam in benzene produced diamagnetic iron(0) $ArP_3^BFe-N_2$, isolated as a dark green solid in 79.5 % yield. The diamagnetic nature of $ArP_3^BFe-N_2$, compared with the $S = 1$ spin state of $P_3^BFe-N_2$, derives from an additional interaction of the iron center with pi-density from one of the phenylene linkers (Figure 2, bottom), leading to a closed-shell 18-electron configuration.³⁰ Access to the desired $S = 1/2$ anion $ArP_3^BFe-N_2^-$ proceeded smoothly by additional reduction of $ArP_3^BFe-N_2$ over sodium-mercury amalgam in THF.

Treatment of the solution with two equivalents of 12-crown-4 (12-C-4) and work-up provided $[ArP_3^BFe(N_2)][Na(12-C-4)_2]$ in 90% yield as a red solid. While we were unable to obtain single crystals of $[ArP_3^BFe(N_2)][Na(12-C-4)_2]$ suitable for solid-state XRD analysis, a DFT optimized geometry for $ArP_3^BFe-N_2^-$ is shown in Figure 3 that illustrates the high degree of steric shrouding of the coordinated N_2 ligand. Isostructural and isoelectronic $iPrP_3^BFe-N_2^-$ has been characterized in the solid state.³¹ The N_2 stretching frequency observed for $ArP_3^BFe(N_2)$ of 2014 cm^{-1} is very similar to that of the parent $iPrP_3^BFe(N_2)$ system (2011 cm^{-1}) with isopropyl substituents on the phosphines. However, comparison of the N_2 stretching frequencies of $[ArP_3^BFe(N_2)][Na(12-C-4)_2]$ and $[iPrP_3^BFe(N_2)][Na(12-C-4)_2]$ (1937 cm^{-1} and 1905 cm^{-1} , respectively) qualitatively suggests that the bulky arylphosphine ligand does not facilitate activation of the N_2 ligand to quite the same extent that the parent ligand ($iPrP_3^B$) does at the redox state poised for protonation ($[Fe-N_2]^-$).³¹

To assess the value of the ArP_3^BFe -system as a model for probing intermediates of catalytic N_2 -to- NH_3 conversion, we examined whether NH_3 could be generated by the addition of acid to $[ArP_3^BFe(N_2)][Na(12-C-4)_2]$ in the absence of reductant. The NH_3 yields obtained established the viability of N_2 -to- NH_3 conversion (~ 0.25 equiv in the presence of 2 – 5 equiv acid) and show that early stage protonation is likely feasible. Nevertheless, the bulky ArP_3^BFe -system is inactive as a catalyst when both acid and reductant are present (using either $HBArF_{24}$ in combination with KC_8 , or $CoCp^*_2$ with $[Ph_2NH_2][OTf]$). This is not unexpected. The extreme degree of steric bulk, and the fact that a phenyl-derivative of the parent system, $[PhP_3^BFe(N_2)][Na(12-C-4)_2]$, is also inactive as a catalyst, suggest the ArP_3^BFe -system would be unlikely to be catalytically competent.³²

We next investigated the reactivity of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ with $\text{HBAr}_{24}^{\text{F}} \cdot 2\text{Et}_2\text{O}$ ($\text{BAr}_{24}^{\text{F}}$ = tetra-(3,5-bistrifluoromethylphenyl)borate) by continuous-wave (CW) X-band (~ 9.4 GHz) EPR spectroscopy (Figure 4).

Reactions between $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$, whose X-band EPR spectrum is shown in Figure 4A, and $\text{HBAr}_{24}^{\text{F}} \cdot 2\text{Et}_2\text{O}$ were performed in EPR tubes in thawing 2-Me-THF solutions and mechanically mixed with a stainless steel needle. Mixing of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ with one equivalent of $\text{HBAr}_{24}^{\text{F}} \cdot 2\text{Et}_2\text{O}$ in thawing 2-Me-THF for 15 minutes generated a new $S = 1/2$ species with a nearly axial signal with $g = [2.021, 2.023, 2.177]$ (Figure 4B), assigned as the desired $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$. Mixing instead for 30 minutes, or mixing for 15 minutes but with an excess of acid (2.3 equiv), produces a clean $S = 1/2$ signal for $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ (Figure 4C). This signal decays rapidly upon warming to -78 °C to generate a mixture of species, of which the major product is $\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)$.

Warming *in situ* generated $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ to -78 °C for 30 seconds in the presence of excess acid, followed by re-cooling the sample resulted in the growth of a new and more rhombic $S = 1/2$ signal with $g = [2.004, 2.086, 2.176]$ (Figure 4D), corresponding to the doubly protonated species, $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}_{24}^{\text{F}}]$. Warming for 90 instead of 30 seconds produces this signal cleanly, with full decay of the signal for $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ (Figure 4E). Hence, the X-band EPR spectra collected in Figure 4 show the progression of the earliest stages of protonation of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)]^-$ via $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)]^+$.

To further corroborate these assignments, and to obtain more detailed information regarding the electronic structures of $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}_{24}^{\text{F}}]$, pulse ENDOR and HYSCORE were applied to samples of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)]^-$, $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$, and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}_{24}^{\text{F}}]$, as well as their isotopically enriched analogs generated using $\text{DBAr}_{24}^{\text{F}} \cdot 2\text{Et}_2\text{O}$, or beginning from the ^{15}N -labelled anion $[\text{ArP}_3^{\text{B}}\text{Fe}(^{15}\text{N}_2)]^-$. We also prepared and similarly characterized $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$ as a stable isoelectronic and isostructural analogue of $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$.

For comparison to the protonated species of interest, the field-dependent Q-band ENDOR spectra of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ were collected. They are well simulated with hyperfine coupling to ^{11}B and three unique ^{31}P environments (Figure 5A and 5B, Table 1). The electron-spin-echo (ESE)-detected EPR spectrum is shown in Figure 5C.

In order to determine hyperfine couplings to $^{14/15}\text{N}$, we undertook HYSCORE studies, which generally are quite sensitive to highly anisotropic hyperfine couplings and quadrupolar nuclei, and offer equivalent information on hyperfine couplings and nuclear quadrupole coupling parameters for $^{14/15}\text{N}$ in comparison to ENDOR spectroscopy. Isotopic labelling with $^{15}\text{N}_2$ aided in independent determination of the hyperfine coupling constants for $^{15/14}\text{N}$ and quadrupole parameters for ^{14}N via HYSCORE spectroscopy at X-band (Figure 6; also see SI for other field positions). The combined HYSCORE data sets for natural abundance and ^{15}N -enriched $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ were well simulated by a single class of $^{14/15}\text{N}$, with $A(^{14}\text{N}) = [-1.4, -2.3, 0.7]$ MHz, nuclear quadrupole coupling constant $e^2Qq/h = 3.4$ MHz, and very low estimation of the electric field gradient (e.f.g.) asymmetry parameter $\eta = 0.1$, consistent with the presence of axially symmetric charge

density about N expected for an Fe-N≡N moiety. It is important to note that we do not have direct experimental evidence from the data for the absolute sign of the $^{14/15}\text{N}$ hyperfine, but the experimental data and simulations are sensitive to the relative sign of the principle components of the hyperfine tensor.

Pulse EPR characterization of the proposed $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ intermediate was pursued next. The viscous nature of the thawing 2-Me-THF and significant thermal sensitivity of the reaction precluded generation of this species in the relatively fragile, small diameter tubes used for Q-band ENDOR spectroscopy (O.D. = 1.6 mm), and X-band ENDOR spectroscopy was therefore employed instead. The field-dependent X-band ENDOR spectra of the Fe(NNH) species are well-simulated with hyperfine coupling to ^{11}B , two unique ^{31}P environments (one strongly coupled, and two equivalent, more weakly coupled nuclei), and a single acid-derived ^1H nucleus (see Figure 7 and Table 2). Isotopic labelling using ^2H -enriched $\text{HBAr}^{\text{F}}_{24} \cdot 2\text{Et}_2\text{O}$ as the acid gave $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NND})$, which appears identical to $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ by CW X-band EPR; however, subtraction of the ENDOR spectra of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NND})$ from those of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ reveals coupling to a single acid-derived ^1H nucleus with $A(^1\text{H}) = [19.3, 18.3, 12]$ MHz, (Figure 7B). X-band HYSCORE spectra of analogously prepared $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ and $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NND})$ samples confirm the presence of this single class of acid-derived ^1H (see SI). Specifically, the features from this acid-derived ^1H that are well simulated using the same parameters determined from ENDOR are absent in the HYSCORE of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NND})$. Additionally, ^2H - ^1H difference spectra exhibit features arising from a single class of ^2H coupling that is well simulated by scaling the previously determined ^1H HFI by the proportion of $^2\text{H}/^1\text{H}$ gyromagnetic ratios ($^2\text{H}\gamma/^1\text{H}\gamma = 0.154$) such that $A(^2\text{H}) = [2.97, 2.82, 1.85]$ MHz, and relatively small ^2H nuclear quadrupole parameters, $e^2Qq/h = 0.25$ MHz and $\eta = 0.1$, as expected for deuterium in N-H bonds.³³

The ^1H hyperfine coupling derived from ENDOR and HYSCORE spectroscopy can be decomposed into its isotropic (a_{iso}) and anisotropic components (A_{aniso}), giving $a_{\text{iso}} = 16.5$ MHz and $A_{\text{aniso}} = [2.8, 1.8, -4.5]$. Utilizing the point-dipole approximation, the minimum distance of the ^1H nucleus from the unpaired spin can be estimated using equation 3 and solving for r by taking the largest value of A_{aniso} as twice the dipolar component t of the ^1H hyperfine, such that $A_{\text{aniso}} = [-T(1-\delta), -T(1+\delta), 2T]$, where δ represents the rhombicity of A_{aniso} . This places the lower limit for the distance of the ^1H from the metal center at $3.31 \text{ \AA}$ (i.e. $r \geq 3.31 \text{ \AA}$). To evaluate whether this distance is consistent with the assignment of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$, we performed a DFT geometry optimization on a model structure using the TPSS functional, the def2-TZVP basis set for Fe, and def2-SVP for all other atoms (see SI). This combination of functional and basis set have been previously used by our group in the study of the related $\text{P}_3^{\text{B}}\text{Fe}$ systems.^{11g,22} The distance between Fe and the proton on the β -nitrogen, predicted by the optimized structure, is $\sim 3.52 \text{ \AA}$, consistent with the estimated r $3.31 \text{ \AA}$ using Eqn 3.

$$T = \frac{\mu_0}{4\pi} \cdot \frac{g_{\text{avg}}g_n\mu_B\mu_N}{hr^3} \quad (\text{Eqn 3})$$

The relatively large value of $a_{\text{iso}} = 16.5$ for this Fe-NNH proton, in comparison to the aforementioned structurally analogous iron hydroperoxo (Fe-OOH) intermediate in Cytochrome P450 ($A_1 \approx 8.2$ MHz via Q-band ENDOR)^{15c} can likely be rationalized by the presence of spin density in Fe-N $_{\alpha}$ pi-bonds, facilitating polarization of the ^1H s-orbital through hyperconjugation.

X-Band HYSCORE spectra of natural abundance $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ and ^{15}N -enriched $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$, along with corresponding simulations, are provided in Figure 8 (vide infra). In this case, simulations of the combined HYSCORE data of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ required consideration of two distinct classes of $^{14/15}\text{N}$ nuclei, with $A(^{14}\text{N}_{\alpha}) = [-2.5, -7.1, -1.8]$ and $A(^{14}\text{N}_{\beta}) = [-2.9, -1.8, 0.7]$ MHz. Assignments of these couplings as N_{α} and N_{β} is made on the basis of the magnitude of their isotropic hyperfine (a_{iso}), which is generally sensitive to bonding covalency with the center of spin density. Simulations indicate these two nitrogens exhibit similar nuclear quadrupole parameters, with $e^2Qq/h(^{14}\text{N}_{\alpha}) = 2.0$ MHz, $e^2Qq/h(^{14}\text{N}_{\beta}) = 1.8$ MHz, and $\eta(^{14}\text{N}_{\alpha}) = \eta(^{14}\text{N}_{\beta}) = 0.6$.

As noted above, we also undertook the generation of the stable silylated complex $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$ by analogy to derivatives prepared previously.²⁴ Vigorously stirring $^{\text{Ar}}\text{P}_3^{\text{B}}\text{FeBr}$ in the presence of 1 equiv Me_3SiCl and 3 equiv Na/Hg amalgam in THF followed by work-up afforded $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$ as a greenish-brown solid ($\nu_{\text{NN}} = 1717$ cm^{-1} ; thin film). In a manner similar to $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$, the CW X-band EPR spectrum of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$ features a near axial g -tensor with well-resolved hyperfine coupling to a single ^{31}P atom evident at the high-field edge of the spectrum (see SI). Likewise, comparative ENDOR (Figure 9) and HYSCORE (Figure 10) data confirm similar trends in the ^{31}P , ^{11}B and ^{14}N hyperfine coupling tensors to $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$; two weakly coupled ^{31}P nuclei, with one more strongly coupled, and rather isotropic ^{11}B and two distinct ^{14}N nuclei (Table 3). Q-band HYSCORE was also performed on this species, confirming the presence of these two distinct ^{14}N couplings (see SI).

Importantly, simulations of the ^{14}N HYSCORE data for these two complexes indicate that the nuclear quadrupole coupling constant and electric field gradient asymmetry parameters of the two classes of detected ^{14}N nuclei of $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$ and $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$ are the same, with $e^2Qq/h(^{14}\text{N}_{\alpha}) = 2.0$ MHz, $e^2Qq/h(^{14}\text{N}_{\beta}) = 1.8$ MHz, and $\eta(^{14}\text{N}_{\alpha}) = \eta(^{14}\text{N}_{\beta}) = 0.6$, corroborating similarity in bonding environments and symmetry of charge about the N nuclei in each complex. This confirms that the silyl-diazenido analog is an appropriate electronic structure model for the more reactive $^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$.

To confirm the assignment of $[^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ as the product of the reaction of $[^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-4})_2]$ with excess acid, we collected Q-band ENDOR spectra to probe the ^{11}B , ^{31}P and ^1H hyperfine interactions. For the assignment of this species, we benefit from comparative EPR spectral data already available for the parent $[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$.²³

The field-dependent Q-Band ENDOR spectra of $[^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ are well modeled with hyperfine couplings to ^{11}B , three nearly equivalent ^{31}P nuclei, and two ^1H nuclei, with one being strongly coupled and one more weakly coupled (Figures 11 and Table

4). X-band HYSCORE spectra of the similarly prepared $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NND}_2)][\text{BAr}^{\text{F}}_{24}]$ samples confirm the presence of these two classes of acid-derived ^1H (see SI).

These parameters are similar to those for the analogous $[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ previously characterized by similar methods; however, the H-atoms on N_β in $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ exhibit somewhat larger isotropic hyperfine couplings²³, potentially due to a greater extent of polarization of the ^1H s-orbitals via hyperconjugation with spin density localized in Fe- N_α pi-symmetry orbitals in-plane with the N_β -H bonds. Decomposition of the observed ^1H hyperfine couplings into their isotropic and anisotropic components provides $a_{\text{iso}} = 21.3$ MHz, $A_{\text{aniso}} = [-5.3, -0.3, 5.7]$ MHz for the more strongly coupled ^1H , and $a_{\text{iso}} = 12.8$ MHz, $A_{\text{aniso}} = [-2.8, 0.7, 2.2]$ for the more weakly coupled ^1H .

Again from equation 3, the estimated minimum distances r for the two protons are: $r_{(1)} = 3.07$ Å for the more strongly coupled ^1H , and $r_{(2)} = 3.89$ Å for the more weakly coupled ^1H . These distances are consistent with both protons being localized on N_β , and are in reasonably good agreement with the predicted Fe-H distances from a DFT optimized structure of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$: 3.20 Å and 3.73 Å, respectively. In a manner similar to the previously characterized $[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$, an Euler rotation ($\beta = 35^\circ$) of the hyperfine tensor of the more strongly coupled proton was necessary to simulate the ENDOR spectra, consistent with a non-linear Fe-N-NH₂ moiety with an Fe-N-N bond angle of $\sim 140^\circ$, also consistent with the DFT optimized structure.

X-Band HYSCORE spectra of natural abundance $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ and its ^{15}N -enriched derivative, along with corresponding simulations are provided in Figure 12. For this species, only a single coupling to $^{14/15}\text{N}$ with $A(^{14}\text{N}_\alpha) = [-0.9, 7.1, 0.1]$ MHz, $e^2Qq/h(^{14}\text{N}_\alpha) = 1.7$ MHz, and $\eta(^{14}\text{N}_\alpha) = 0.7$ is necessary to simulate the experimental data. This was also the case for the previously characterized $[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$, with only a single class of nitrogen detected via Q-band ENDOR and electron spin echo envelope modulation (ESEEM).²³ Q-band HYSCORE was also performed on natural abundance $[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ in order to evaluate the possibility of coupling to a second class of ^{14}N , but this data was also well simulated using the same ^{14}N simulation parameters derived from X-band HYSCORE (see SI).

Information about the electronic structure of the NNH_x ($x = 0, 1, 2$) moiety can be gleaned from examination of the nuclear hyperfine couplings, nuclear quadrupole couplings (e^2Qq/h) and electric field gradient asymmetry parameters (η) for N_α across the series of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)]^-$, $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$ and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)]^+$. These parameters are of particular interest because of the scarcity of data on these types of iron compounds, and their potential value in the identification of catalytically relevant intermediates in synthetic and biological nitrogen fixation systems.

To determine the hyperfine couplings to nitrogen, as well as the nuclear quadrupole parameters e^2Qq/h and η for the ^{14}N atoms in the N_2 , NNH , and NNH_2 ligands, we relied on comparison of the X-Band HYSCORE spectra of samples of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$, $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$, and $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH}_2)][\text{BAr}^{\text{F}}_{24}]$ with that of their ^{15}N -labeled samples

(Figures 6, 8, 10, and 12, and Tables 5 and 6). Simulation of the ^{15}N HSCORE allowed for the ^{15}N HFI to be determined in the absence of any complications from the influence of nuclear quadrupole interactions. Accounting for the ratio of $^{14}/^{15}\text{N}$ gyromagnetic ratios ($^{14}\text{N}\gamma/^{15}\text{N}\gamma = -0.7219$), the ^{14}N HFI could be fixed, allowing the nuclear quadrupole interactions to be estimated independently via simulation of the ^{14}N HSCORE spectra. The combined HSCORE data sets reveal that the hyperfine tensors assigned to N_α in each case exhibit significant anisotropy, comparable in magnitude to the isotropic component in each complex. Specifically, $a_{\text{iso}} = -1.0$ MHz for $[\text{ArP}_3\text{BFe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$; $a_{\text{iso}} = -3.8$ MHz for $\text{ArP}_3\text{BFe}(\text{NNH})$; $a_{\text{iso}} = -2.6$ MHz for $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BArF}_{24}]$.

The magnitude of the anisotropic contributions to the ^{14}N hyperfine increases as a function of degree of protonation. Additionally, for each of the complexes measured in this series, A_{aniso} exhibits significant rhombic symmetry, and in the case of the $\text{ArP}_3\text{BFe}(\text{NNH})$, $\text{ArP}_3\text{BFe}(\text{NNSiMe}_3)$, and $[\text{ArP}_3\text{BFe}(\text{NNH}_2)]^+$ species, is too large to be purely accounted for by the through-space dipolar interaction between N_α and the spin density localized on Fe. Utilizing the point dipole approximation and Fe-N distances from the geometry-optimized DFT structures, the estimated $^{14}\text{N}_\alpha$ dipolar hyperfine magnitudes for the FeNNx series of complexes examined here are all within the range of $1.01 < t < 1.188$ MHz. The higher magnitude of A_{aniso} values for the $\text{ArP}_3\text{BFe}(\text{NNH})$ and $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BArF}_{24}]$ indicates at least partial, if modest, delocalization of spin onto p-orbitals at N_α upon protonation. The significant rhombicity of the hyperfine tensors for all species examined here suggests modest localization of unpaired spin density in multiple orthogonal p-orbitals at N_α , which increases as a function of protonation.

The ^{14}N nuclear quadrupole interaction measured through HSCORE arises from the interaction between the ^{14}N quadrupole moment with the inhomogeneous electric field produced by electrons in p-orbitals localized at the nucleus. As such, this interaction provides a point-specific measure of the axial electric field gradient magnitude (parametrized by $e^2Qq/\hbar$) and its symmetry, parametrized by η , which ranges from 0 for pure axial symmetry to 1 for full rhombic symmetry. Starting from $[\text{ArP}_3\text{BFe}(\text{N}_2)]^-$, the trend in the observed $^{14}\text{N}_\alpha$ quadrupole parameters for the series can be discussed in terms of the Townes-Dailey model,³⁴ in which these quadrupole parameters are primarily determined by differences in the relative electron occupancy in the nitrogen $2p\sigma$ orbital (denoted N_3) and the average of the densities in the two orthogonal $2p\pi$ orbitals (N_1 , N_2), such that $|e^2qQ/e^2qQ_0| = |\text{N}_3 - (\text{N}_1 + \text{N}_2)/2|$, where $e^2qQ_0 = -(8-10)$ MHz for a single electron in a $2p$ orbital for the sp hybridized N_α . Differences in the relative charge densities of the two orthogonal $2p\pi$ orbitals at $^{14}\text{N}_\alpha$ contributes to the electric field gradient asymmetry η . With this simple picture in mind, the downward trend (Table 6) in the magnitude of $e^2Qq/\hbar$ as a function of protonation of the terminal N atom can be rationalized by a decrease in N-N sigma bonding relative to Fe-N sigma-bonding and/or Fe-N pi bonding. The subsequent increase in η suggests a significant imbalance between the charge density in the two orthogonal $^{14}\text{N}_\alpha$ $2p\pi$ orbitals, as would be expected to accompany loss of a single Fe-N pi-bond upon protonation, though a loss of linearity of the Fe-N-N moiety would also be expected to contribute significantly.

Interestingly, the most significant change in the $^{14}\text{N}_\alpha$ quadrupole interaction occurs after the first protonation, with a reduction of e^2Qq/h by $\sim 40\%$ and a significant increase in η from 0.1 to 0.6, with a much more modest reduction of e^2Qq/h and increase in η upon the second protonation. This observation suggests that there is fairly little change in the bonding environment at N_α in going from NNH to NNH_2 in comparison to the initial protonation. Also, the measured ^{14}N quadrupole coupling parameters for $(\text{ArP}_3\text{BFe}(\text{NNH}))$ and the silyl-diazenido analogue $\text{ArP}_3\text{BFe}(\text{NNSiMe}_3)$ are identical, reflecting very similar bonding environment at N_α and N_β for these two species, respectively. Finally, the similarity of $e^2Qq/h = 1.7$ MHz and $\eta = 0.7$ for $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BARF}_{24}]$ to the previously reported values of $e^2Qq/h = 1.74$ MHz and $\eta = 0.64$ for N_α in $[\text{P}_3\text{BFe}(\text{NNH}_2)][\text{BARF}_{24}]$, suggests that the bonding character/electronic structure at N_α is comparable in both compounds, further cementing the assignment of $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BARF}_{24}]$ (Table 6).^{23,35}

CONCLUSIONS

We have described the first characterization of a terminally bonded $\text{Fe}(\text{NNH})$ species, generated by protonation of Fe-N_2^- . Fe-NNH intermediates provide a linchpin between the limiting mechanisms of Fe -mediated N_2 -to- NH_3 conversion, and feature unusually weak and hence reactive N-H bonds, with estimated $\text{BDFE}_{\text{N-H}}$ values less than 35 kcal/mol for the types species discussed here. As a result, $\text{Fe}(\text{NNH})$ species had proven very difficult to detect up to now. CW and pulse EPR methods have been shown to be highly effective in the characterization of reactive $S = 1/2$ states of the FeMoco , and such tools, coupled with a sterically encumbering tris(phosphine)borane ligand and very low temperatures, enabled us to detect and assign $\text{ArP}_3\text{BFe}(\text{NNH})$ and observe its evolution to doubly protonated $\text{ArP}_3\text{BFe}(\text{NNH}_2)^+$. The latter species is a presumed on-path intermediate for the structurally related and catalytically active P_3BFe system. The synthesis and characterization of a stable $\text{ArP}_3\text{BFe}(\text{NNSiMe}_3)$ complex, which serves as an isoelectronic and kinetically stabilized relative of $\text{ArP}_3\text{BFe}(\text{NNH})$, adds additional support our assignment.

The ^1H -hyperfine for $\text{ArP}_3\text{BFe}(\text{NNH})$ derived from the presented ENDOR studies is diagnostic for the distally-bound H-atom ($a_{\text{iso}} = 16.5$ MHz). The $^{14}\text{N}_\alpha$ quadrupole interaction, extracted from HSCORE data for each species discussed, shows significant change in bonding at N_α upon the first protonation step ($\text{Fe-N}_2^- \rightarrow \text{Fe}(\text{NNH})$) with a $\sim 40\%$ decrease in e^2Qq/h consistent with loss of N-N sigma-bonding and increase in Fe-N sigma bonding, and the significant increase in the electric field gradient asymmetry η with differential charge densities in $2p_{x,y}$ orbitals at C and loss of Fe-N-N linearity. This bonding symmetry at N_α appears to be largely maintained at the second protonation step that produces $\text{Fe}(\text{NNH}_2)^+$.

By analogy to the better studied reductive protonation of oxygen at iron introduced earlier, the $S = 1/2$ $\text{Fe}(\text{NNH})$ species can be considered as an N_2 -derived analogue of iron(III) hydroperoxide species, $\text{Fe}^{\text{III}}(\text{OOH})$, well known in heme and non-heme iron systems in the context of oxygen binding and reductive protonation. EPR methods were also crucial to the characterization these $\text{Fe}^{\text{III}}(\text{OOH})$ species, and in particular in identifying the H-atom bound to the the distal O-atom.¹⁵ While the $S = 1/2$ iron center in $\text{ArP}_3\text{BFe}(\text{NNH})$ can be most simply formulated as monovalent (ignoring the sigma backbond to boron), it can also be

regarded as trivalent (including the sigma backbond to boron).³⁰ The latter description underscores the analogy with Fe^{III}(OOH). The present Fe(NNH) system is highly covalent and hence valence assignments, while helpful in considering this conceptual analogy, need to be interpreted with caution. Additional studies are of interest to map the electronic structures of Fe(NNH) species as a function of coordination number, geometry, and ligand field strength.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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distinct from $P_3^BFe(N_2)$, owing to the additional arene interaction (Figure 2). This is manifest in an irreversible $^{Ar}P_3^BFe-N_2/^{Ar}P_3^BFe-N_2^-$ reduction event (see SI), which may also short-circuit catalytic N_2 -to- NH_3 conversion in preference to HER.

33. From a linear correlation of $^2H\ e^2Qq/h$ for deuterium nuclei in $N^+-D...O$ bonds with the hydrogen bond strength (parametrized by $1/R(D...O)^3$), Hunt et al. estimated that the $^2H\ e^2Qq/h$ for an isolated (non-hydrogen bonded) N^+-D group should be ~ 0.25 MHz, in good agreement with the values estimated from the 2H HYSCORE simulations for the $N\beta$ -D nuclei in this study. See: Hunt MJ; Mackay AL Deuterium and Nitrogen Pure Quadrupole Resonance in Deuterated Amino Acids. *Journ. Mag. Res* 1973, 15, 402–414.
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Figure 1.
Outline of limiting pathways for distal and alternating scenarios for N_2 -to- NH_3 conversion.

Figure 2. ORTEP representation of (top) $^{Ar}P_3^BFeBr$ (H atoms omitted for clarity), and (bottom) $^{Ar}P_3^BFe(N_2)$. Thermal ellipsoids are drawn at the 50% probability level.

Figure 3. Space-filling model of the DFT optimized structure of $\text{ArP}_3\text{BFe-N}_2^-$, using the full ArP_3B ligand (TPSS, def2-TZVP on Fe, def2-SVP on C, H, P, B, O, N).

Figure 4.

Reaction progress of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-}4)_2]$ with excess $\text{HBarF}_{24}\bullet 2\text{Et}_2\text{O}$ in 2-Me-THF, as monitored by CW X-band EPR. Simulations for discrete species are shown in red. Spectra show the progression from: (A) Pure $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-}4)_2]$. (B) Mixture of $[\text{ArP}_3^{\text{B}}\text{Fe}(\text{N}_2)][\text{Na}(12\text{-C-}4)_2]$ and $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$, on addition of 1 equiv $\text{HBarF}_{24}\bullet 2\text{Et}_2\text{O}$ for 15 min at 138 K. (C) Same as in spectrum B, but instead with 2.3 equiv $\text{HBarF}_{24}\bullet 2\text{Et}_2\text{O}$ present, showing full conversion to $\text{ArP}_3^{\text{B}}\text{Fe}(\text{NNH})$. An identical spectrum was obtained on mixing for 30 minutes in the presence of 1 equiv $\text{HBarF}_{24}\bullet 2\text{Et}_2\text{O}$. (D) Reaction mixture

from trace C, after warming to 195 K for 30 seconds and then rapidly freeze quenching in liquid N₂. Trace shows a mixture of ^{Ar}P₃^BFe(NNH) and [^{Ar}P₃^BFe(NNH₂)] [^BAr^F₂₄]. (E) Reaction mixture from trace D after warming to 195 K for 90 seconds, showing complete conversion to [^{Ar}P₃^BFe(NNH₂)] [^BAr^F₂₄]. Reactions with up to 5 equiv H^BAr^F₂₄•2Et₂O provided identical spectra. See Tables 1, 2, and 4 for relevant simulation parameters. Acquisition parameters for all spectra: temperature = 77 K; MW frequency = 9.44 GHz; MW power = 6.44 mW; modulation amplitude = 0.1 mT; conversion time = 5.12 ms. Simulations parameters for the signals in A C and E (with broadening parameters HStrain = [50 50 170] MHz and gStrain = [0.001, 0.02, 0.03]) can be found in Tables 1, 2, and 4, respectively.

Figure 5.

(A) Field-dependent Q-Band ^{11}B -Davies ENDOR spectra of $[\text{ArP}_3\text{BFe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ with simulation of ^{11}B features (red). (B) Field-dependent Q-Band ^{31}P -Davies ENDOR spectra of $[\text{ArP}_3\text{BFe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ with simulation of individual ^{31}P hyperfine couplings. Intense features near c.a. 50 MHz arise from weakly coupled ligand/solvent protons. (C) Electron-spin-echo(ESE)-detected EPR spectrum with ENDOR field positions marked in red. Acquisition parameters: temperature = 15 K; MW frequency = 34.124 GHz; τ = 300 ns; MW pulse length ($\pi/2$, π) = 40 ns, 80 ns; RF pulse length = 40 μs ; shot repetition time (srt) = 5 ms.

Figure 6.

X-Band HYSCORE spectra (top) of natural abundance (left) and ^{15}N enriched (right) $[\text{ArP}_3\text{BFe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$ with comparison (bottom) of experimental data (grey) to simulations of hyperfine couplings to $^{14/15}\text{N}_\alpha$ (red) using parameters in Table 1. Acquisition parameters: temperature = 20 K; magnetic field = 325.3 mT; microwave frequency = 9.411 GHz (^{14}N), 9.424 GHz (^{15}N); MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 142 ns; $t_1 = t_2 = 100$ ns; $t_1 = t_2 = 16$ ns; shot repetition time (srt) = 1 ms).

Figure 7.

(A) Field-Dependent X-Band Davies ENDOR spectra of $\text{ArP}_3\text{BFe(NNH)}$ with simulation of individual hyperfine couplings. Acquisition parameters: temperature = 10 K; MW frequency = 9.72 GHz; $\tau = 240$ ns; MW pulse length ($\pi/2$, π) = 20 ns, 40 ns; RF pulse length = 15 μs ; $\text{srt} = 5$ ms. (B) Difference spectra of $\text{ArP}_3\text{BFe(NNH)}$ and $\text{ArP}_3\text{BFe(NND)}$ (black), with simulations of the acid-derived ^1H hyperfine coupling (red). Difference spectra presented were smoothed using a 3-point Savitzky-Golay filter. The narrow peak at c.a. 10 MHz in these difference spectra are due to residual intensity from the ^{11}B ENDOR signal. (C) X-band ESE-detected EPR spectrum with ENDOR field positions marked in red.

Figure 8.

X-Band HYSCORE spectra (top) of natural abundance (left) and ^{15}N enriched (right) $\text{ArP}_3\text{BFe}(\text{NNH})$ with comparison (bottom) of experimental data (grey) to simulations of hyperfine couplings to $^{14/15}\text{N}_\alpha$ (red), $^{14/15}\text{N}_\beta$ (blue) and ^{11}B (green) using parameters in Table 2. Acquisition parameters: temperature = 20 K; magnetic field = 330.1 mT; microwave frequency = 9.392 GHz; MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 142 ns; $t_1 = t_2 = 100$ ns; $t_1 = t_2 = 16$ ns; shot repetition time (srt) = 1 ms).

Figure 9.

Field-Dependent Q-Band Davies ENDOR spectra of $\text{ArP}_3\text{BFe}(\text{NNSiMe}_3)$. (A) Simulation of the ^{11}B hyperfine coupling simulated in red. Asterisks indicate features arising from the 3rd harmonic of the higher frequency ^{11}B ENDOR peak. (B) Simulation of individual ^{31}P hyperfine couplings. Intense features near c.a. 49-52 MHz stem from weak ^1H couplings from ligand or solvent protons. (C) Q-band ESE-detected field sweep with field positions at which the ENDOR spectra were acquired marked in red. Acquisition parameters: temperature = 15 K; MW frequency = 34.040 GHz; MW pulse length ($\pi/2$, π) = 20 ns, 40 ns; τ = 132 ns; RF pulse length = 15 μs ; srt = 5 ms).

Figure 10.

(top) X-Band HYSCORE spectrum of $^{41}\text{P}_3\text{BFe}(\text{NNSiMe}_3)$, with comparison (bottom) of experimental data to simulations (grey) of $^{14}\text{N}_\alpha$ (red), $^{14}\text{N}_\beta$ (blue) and ^{11}B (green), using the simulation parameters in Table 3. Acquisition parameters: temperature = 20 K; magnetic field = 334.0 mT; microwave frequency = 9.392 GHz; MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 140 ns; $t_1 = t_2 = 100$ ns; $t_1 = t_2 = 16$ ns; shot repetition time (srt) = 1 ms).

Figure 11.

Field-Dependent Q-Band Davies ENDOR spectra of $[\text{ArP}_3\text{BF}_2\text{Fe}(\text{NNH}_2)][\text{BArF}_{24}]$. (A) Simulations of the ^{11}B hyperfine coupling in red using simulation parameters in Table 4. (B) Simulations of the individual ^{31}P and ^1H hyperfine couplings, using simulation parameters in Table 4. (C) Difference spectra of ^1H and ^2H $[\text{ArP}_3\text{BF}_2\text{Fe}(\text{NNH}_2)][\text{BArF}_{24}]$ (black) with individual simulations of the two acid-derived ^1H hyperfine couplings. Difference spectra presented were smoothed using a 3 point Savitzky-Golay filter. (D) Q-band ESE-detected EPR spectrum with ENDOR field positions marked in red. The asterisk indicates a small background signal arising from a component of the EPR cavity. Acquisition parameters: temperature = 10 K; MW Frequency = 34.121 GHz; τ = 240 ns; MW pulse length ($\pi/2$, π) = 20 ns, 40 ns; RF pulse length = 15 μs ; srt = 5ms).

Figure 12.

X-Band HSCORE spectra (top) of natural abundance (left) and ^{15}N enriched $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BArF}_{24}]$ with comparison (bottom) of experimental data (grey) to simulations of $^{14/15}\text{N}_\alpha$ (red), and ^{11}B (green) using parameters in Table 4. Acquisition parameters: temperature = 20 K; magnetic field = 324.1 mT; microwave frequency = 9.424 GHz (^{14}N), 9.423 GHz (^{15}N); MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 142 ns; $t_1 = t_2 = 100$ ns; $t_1 = t_2 = 16$ ns; shot repetition time (srt) = 1 ms.

Scheme 1.
Synthesis of ArP_3B , metalation, and generation of $\text{ArP}_3\text{BFe-N}_2^{0/-}$

Table 1.

g-Values and Nuclear hyperfine couplings (in MHz) derived from CW-EPR, ENDOR and HYSCORE for $[\text{ArP}_3\text{BFe}(\text{N}_2)][\text{Na}(\text{12-C-4})_2]$. *

g	2.014	2.074	2.144	
Nucleus	A_1	A_2	A_3	a_{iso}
^{11}B	15.2	15.3	15.3	15.3
$^{31}\text{P}_{(1)}$	41	20	18	26.3
$^{31}\text{P}_{(2)}$	63	48	42	51
$^{31}\text{P}_{(3)}$	123	111	110	115
$^{14}\text{N}_a$	-1.4	-2.3	0.7	-1.0

* See figures 5, 6. Approximate error estimates for A values determined from simulations are: ^{11}B ($A \pm 2\%$); ^{31}P ($A \pm 10\%$); $^{14/15}\text{N}$ ($A \pm 10\%$).

Table 2.

g-Values and Nuclear Hyperfine Couplings (in MHz) Derived from CW- EPR, ENDOR and HYSCORE for $(\text{ArP}_3\text{B})\text{Fe}(\text{NNH})$.*

g	2.021	2.023	2.177	
Nucleus	A_1	A_2	A_3	a_{iso}
^1H	19.3	18.3	12.0	16.5
^{11}B	12	11.3	10.5	11.3
$^{31}\text{P}_{(1,2)}$	22	17	17	18.7
$^{31}\text{P}_{(3)}$	85	65	72	74
$^{14}\text{N}_\alpha$	-2.5	-7.1	-1.8	-3.8
$^{14}\text{N}_\beta$	-2.9	-1.8	0.7	-1.3

* see figures 7, 8. Approximate error estimates for A values determined from simulations are: ^1H ($A \pm 5\%$); ^{11}B ($A \pm 2\%$); ^{31}P ($A \pm 10\%$); $^{14}\text{N}_\alpha$ ($A \pm 10\%$); $^{14}\text{N}_\beta$ ($A \pm 20\%$).

Table 3.

g-Values and Nuclear Hyperfine Couplings (in MHz) Derived from CW-EPR, ENDOR and HYSCORE for $\text{ArP}_3\text{BFe}(\text{NNSiMe}_3)$. *

g	2.009	2.030	2.234	
Nucleus	A_I	A_2	A_3	a_{iso}
^{11}B	12.5	12.7	13.5	12.9
$^{31}\text{P}_{(1)}$	25	16	26	22.3
$^{31}\text{P}_{(2)}$	36	26	26	29.3
$^{31}\text{P}_{(3)}$	111	90	92	97.7
$^{14}\text{N}_\alpha$	-5.5	-7.6	-1.6	-4.9
$^{14}\text{N}_\beta$	-4.0	-4.5	-1.8	-3.4

* See figures 9, 10. Approximate error estimates for A values determined from simulations are: ^{11}B ($A \pm 2\%$); ^{31}P ($A \pm 5\%$); $^{14}\text{N}_\alpha$ ($A \pm 10\%$); $^{14}\text{N}_\beta$ ($A \pm 10\%$).

Table 4:

g-Values and Nuclear Hyperfine Couplings (in MHz) derived from CW-EPR, ENDOR and HYSCORE for $[\text{ArP}_3\text{BFe}(\text{NNH}_2)][\text{BArF}_{24}]$.^{*}

g	2.004	2.087	2.176	
Nucleus	A_1	A_2	A_3	a_{iso}
$^1\text{H}_a$	16	21	27	21.3
$^1\text{H}_b$	10	13.5	15	12.8
^{11}B	9.5	7.5	6.1	7.7
$^{31}\text{P}_{(1)}$	40	16	23	26.3
$^{31}\text{P}_{(2)}$	46	47	47	46.7
$^{31}\text{P}_{(3)}$	64	78	65	69
$^{14}\text{N}_a$	-0.9	-7.1	0.1	-2.6

Note: $^1\text{H}_a$ includes an Euler rotation of the hyperfine tensor relative to the molecular frame of $(\alpha, \beta, \gamma) = [0, 35, 0]^\circ$.

^{*} See figures 11, 12. Approximate error estimates for A values determined from simulations are: ^1H ($A \pm 5\%$); ^{11}B ($A \pm 2\%$); ^{31}P ($A \pm 5\%$); $^{14/15}\text{N}_a$ ($A \pm 10\%$).

Table 5:

^{14}N Hyperfine Coupling Parameters (in MHz) for N_α in the $(^{\text{Ar}}\text{P}_3\text{B})\text{Fe}(\text{N}_\alpha\text{N}_\beta\text{H}_x)$ series.

Compound	$A(^{14}\text{N})$	a_{iso}	A_{aniso}
$[^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{N}_2)]^-$	$[-1.4, -2.3, 0.7]$	-1.0	$[-0.4, -1.3, 1.7]$
$^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH})$	$[-2.5, -7.1, -1.8]$	-3.8	$[1.3, -3.3, 2]$
$^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNSiMe}_3)$	$[-5.5, -7.6, -1.6]$	-4.9	$[-0.6, -2.7, 3.3]$
$[^{\text{Ar}}\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)]^+$	$[-0.9, -7.1, 0.1]$	-2.6	$[1.7, -4.5, 2.7]$
$[\text{P}_3^{\text{B}}\text{Fe}(\text{NNH}_2)]^+{}^\ddagger$	$[-6.2, -7.2, -4.3]$	-5.9	$[-0.3, -1.3, 1.6]$

‡ See ref 23

Table 6:¹⁴N Nuclear Quadrupole Parameters derived from ENDOR and HYSCORE for N_a.

Compound	e^2Qq/h (MHz)	η
[^{Ar} P ₃ ^B Fe(N ₂)] ⁻	3.4	0.1
(^{Ar} P ₃ B)Fe(NNH)	2.0	0.6
^{Ar} P ₃ ^B Fe(NNSiMe ₃)	2.0	0.6
[^{Ar} P ₃ ^B Fe(NNH ₂)] ⁺	1.7	0.7
[P ₃ ^B Fe(NNH ₂)] ⁺ [†]	1.74	0.64

[†] See ref 23. Approximate error estimates for e^2Qq/h and η are ± 0.2 and ± 0.1 MHz, respectively.