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**RESEARCH ARTICLE**

**Characterization of a Proposed Terminal Iron(III) Nitride Intermediate of Nitrogen Fixation Stabilized by a Trisphosphine-Borane Ligand**

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Abstract: Terminal iron nitrides (Fe≡N) have been proposed as intermediates of Fe-mediated nitrogen fixation, and well-defined synthetic iron nitrides have been characterized in high oxidation states, including Fe(IV), Fe(V), and Fe(VI). This study reports the generation and low temperature characterization of a terminally bound iron(III) nitride, $P_3^3Fe(III)$-N (P$_3^3$ = tris( diisoproplyphosphinophenyl)borane), which is a proposed intermediate of iron-mediated nitrogen fixation by the P$_3^3$Fe-catalyst system. CW- and pulse EPR spectroscopy (HYSCORE and ENDOR), supported by DFT calculations, help to define a $\sigma$A ground state electronic structure of this C$_3$-symmetric nitride species, placing the unpaired spin in a sigma orbital along the B-Fe-N vector; this electronic structure is distinct for an iron nitride. The unusual d$^5$-configuration is stabilized by significant delocalization (~50%) of the unpaired electron onto the axial boron and nitrogen ligands, with a majority of the spin residing on boron.

Introduction

Iron complexes featuring metal-to-ligand multiple bonds have fascinated (bio)inorganic chemists for decades, particularly with respect to heme and non-heme iron oxo species. ¹⁻³,⁴ High oxidation state (³>4) iron oxo species play essential roles in oxidation catalysis in enzymes and synthetic systems. Related high oxidation state iron nitrides (³>4) have received significant interest in the past two decades, motivated by interest in their intermediacy in N-atom or group transfer catalysis and also their possible role/s as intermediates of catalytic Fe-mediated nitrogen fixation.¹⁵⁻⁷,⁸ To the latter point, our group reported a terminally bound pseudotetrahedral iron(IV) nitride (L:Fe(IV)(N)) in 2004,⁹ attributing its relative solution stability to a closed-shell 16-electron configuration with four valence electrons (d$^4$ system) that occupy a degenerate nonbonding set of orbitals (Figure 1). Its ligand field, manifested in a diagnostically large quadrupole splitting (~ 6 mm s$^{-1}$) that is observed in the Mossbauer spectra of L:Fe(IV)(N)$^*$ species.¹⁰ sharply contrasts the electronic structure of 6-coordinate iron nitrides that have been detected at very low temperature.¹¹⁻¹⁴ The electronic structures of these terminal low-coordinate iron nitrides (Figure 1) are reinforced by numerous examples of L:Fe(II)(N)$^*$ (and also L:Fe(III)(N)$^*$) species.¹¹⁻¹²,¹⁷⁻¹⁸,¹⁹,²⁰,²¹,²² some of which are sufficiently stable to be isolated and characterized in the solid-state.

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**Figure 1.** Simplified molecular orbital diagram of nitrido iron compounds with approximate $C_{nv}$ (A) and $C_{3v}$ (B) symmetry.

**Figure 2.** (A) Outline of an Fe-mediated distal catalytic cycle for P$_3^3$Fe$^{III}$-$\sigma^*$ highlighting nitride intermediates.

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**Figure 3.** Proposed nitride and oxo complexes nominally isoelectronic with P$_3^3$Fe$^{III}$-$\sigma^*$(N).

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**Figure 4.** Characterized at low T by EPR spectroscopy.

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**Figure 5.** Isolated and characterized in the solid-state by X-ray crystallography.
that have electronic structures isoelectronic with the \( P_3^{\text{Fe}}(\text{N}) \) species studied herein.

While the electronic structures and reactivity profiles of \( L_3\text{Fe}^{\text{ii}}(\text{N}) \) \( \text{N} \) species are fascinating in their own right, a central question has been whether they can participate as intermediates in a so-called Chatt-type (or distal) pathway for iron-mediated nitrogen fixation (Figure 2A).\(^6,9,10,16,17,23\) In this context, our lab reported in 2017 that an \( L_3\text{Fe}^{\text{ii}}(\text{N}) \) \( \text{N} \) species, supported by a tris(phosphine)borane ligand (i.e., \( P_3^{\text{Fe}}(\text{N}) \)), could be generated via the reductive protonation of \( \text{N}_2 \) with the key step being protonation of a hydrazido \( P_3^{\text{Fe}}(\text{N})\text{NNH}_2 \) intermediate to release \( \text{NH}_3 \) and \( P_3^{\text{Fe}}(\text{N}) \).\(^24\) Importantly, this \( P_3^{\text{Fe}} \) system is competent for catalytic \( \text{N}_2 \)–to-\( \text{NH}_3 \) conversion,\(^25,26,27,28\) implicating the viability of \( P_3^{\text{Fe}}(\text{N}) \) as an intermediate of the catalytic cycle.

With a pathway to liberation of the first \( \text{NH}_3 \) equivalent seemingly established, we have sought to consider the downstream steps of the fixation cycle that generate the second \( \text{NH}_3 \) equivalent, wound into whether a bond (iii) nitride, \( L\text{Fe}(\text{N}) \), might play an intermediary role via generation from 1-electron reduction of its \( P_3^{\text{Fe}}(\text{N}) \) precursor.\(^29\) Species of this geometry and d-count, formal or otherwise, are expectedly very rare for cases where a strong metal-to-nitride (or oxo) multiple bond is present; such cases place an unpaved spin in a destabilized antibonding orbital (vide infra). For iron, the only example for which a species with this electronic structure has been characterized is Smith’s very recently reported iron oxo complex, \( \text{PhB(Adim)}_3\text{Fe}^{\text{ii}}(\text{O}) \).\(^30\) While highly reactive, this species could be structurally characterized in the solid-state. Meyer and coworkers had earlier reported an isoelectronic \( L_2\text{Co}^{\text{ii}}(\text{N}) \) nitride species that was far too reactive to isolate (Figure 2B) but whose EPR signatures supported its assignment;\(^31\) at higher temperatures, insertion of the nitride ligand into the M–O bond was observed. Geometrically and electronically distinct but also worth mentioning is Borovik’s trigonal bipyramidal iron(III) oxo complex.\(^32\) This species does not feature iron-to-oxygen multiple bonding; H-bonds from the ligand framework instead stabilize its Fe-O linkage.

Herein we describe our efforts to generate and characterize a distinct example of a terminally bound iron(III) nitride, \( L\text{Fe}(\text{N}) \), using the \( P_3^{\text{Fe}} \) system that is catalytically active for nitrogen fixation. Low temperature photolysis combined with spectroscopy and theory enables the assignment of this species and a description of its electronic structure.

Results and Discussion

Anticipating iron(III) \( P_3^{\text{Fe}}(\text{N}) \) to be highly unstable we explored its generation at low temperature via photolysis of an azide precursor.\(^11,12\) The latter, \( P_3^{\text{Fe}}(\text{N}) \) \( \text{N} \) (2), was synthesized by reaction of \( \text{Na}_3\text{N} \) with \( P_3^{\text{Fe}}(\text{FeCl}) \) \( \text{Cl} \) \( \text{Cl} \) (Scheme 1). Synthesis of the \( ^1\text{H} \) labeled analogs \( (2-\text{L}) \) \( \text{N} \) was achieved using \( \text{Na}_{\text{13}}\text{N}_\text{NNN} \), yielding a 1:1 mixture of the \( \alpha \)- and \( \gamma \)-\( ^{13}\text{N} \) labeled compounds. Compound 2 exhibits an intense azide absorption at 2069 cm\(^{-1} \), which shifts to 2058 cm\(^{-1} \) for its \( ^{13}\text{N} \) labeled analog. Its solid-state structure (SI) exhibits crystallographic 3-fold symmetry and a geometry intermediate between trigonal-bipyramidal and pseudotetrahedral (\( \Sigma = \Sigma(P_3\text{-Fe}-P) = 348^\circ \)).

Photolysis of 2 in \( \text{CDCl}_3 \) solution at room temperature resulted in darkening of the brown solution accompanied by the appearance of new paramagnetic \( ^1\text{H} \) \( \text{NMR} \) resonances, corresponding to \( P_3^{\text{Fe}}(\text{N})(\text{N} \text{N} \text{N}) \) \( \text{N} \) (SI, Figure S3). Upon standing, such a solution deposited crystals of the mixed-valent diron bridged azide (3). X-ray crystallography of 3 reveals a symmetrical linear \( \text{Fe}–\text{NNN}–\text{Fe} \) linkage (SI). We presume its formation proceeds from the photoreduction of 2 to release \( P_3^{\text{Fe}}(\text{L}) \) and one equivalent of \( \text{N}_2 \); the latter then reacts with a second equivalent of 2 to form 3 (Scheme 1). Accordingly, 3 can be prepared by mixing a solution of 2 and the terminal \( \text{N}_2 \) complex \( P_3^{\text{Fe}}(\text{N}) \) \( \text{N} \) \( \text{N} \) (Scheme 2).

Changing the photolysis medium (and temperature) from solution phase to a frozen solvent has previously been shown to drastically affect product distributions in related reactions.\(^13\) Indeed, irradiation at 77 K of a frozen 1 mM solution of 2 in an EPR tube with a 40 W 390 nm LED produced a strong axial doublet signal rich in structure and centered at \( g = 2.02 \) (Figure 3, top). This signal corresponds to the desired \( S = \frac{1}{2} \) nitrido(iron(III)) complex \( P_3^{\text{Fe}}(\text{N}) \) \( \text{N} \) \( \text{N} \) \( \text{N} \) (Scheme 2).

An identical EPR spectrum was obtained upon irradiation of 1 mM solutions of 2 in various glassing solvents, including \( \text{d}-\text{toluene}, \text{cyclohexane}, \text{and methylcyclohexane} \) (See SI). A very similar signal, albeit one that is broader with more poorly resolved hyperfine structure, is obtained upon photolysis of frozen pentane solutions or thin films of 2 (See SI, Figure S8).

Irradiation of samples for 3 minutes afforded yields for 4 of ca. 40%, deduced from spin integration against an external standard (TEMPO). A decrease in signal intensity was observed upon prolonged photolysis, with a complete loss of signals corresponding to 4 in 30 minutes (Figure 3, bottom).\(^34\) CW-EPR spectroscopy at 5 K (See SI, Figures. S9, S10) revealed that besides the formation of \( P_3^{\text{Fe}}(\text{N}) \) \( \text{N} \) \( \text{N} \) \( \text{N} \) (4), two distinct high spin (\( S = 3/2 \)) species are also formed concomitantly, likely accounting for the remaining Fe speciation aside from the desired nitride and starting azide. These two species are unstable at higher temperatures, rendering their identification difficult (see SI). However, further experiments demonstrate that these high spin species cannot be attributed to complex 3 and are not due to ligand decomposition on their own (see SI, Figure 11). In addition, they do not correlate with any other high-spin species previously reported using this ligand platform.\(^35\)
Figure 3 (Top) X-band Continuous wave (CW) EPR spectrum of 4, after irradiating a 1 mM solution of 2 with a 40 W 390 nm LED for 3 minutes. (Bottom) X-band CW-EPR-monitored photolysis of 2 in a frozen 1 mM 2-MeTHF solution at 77 K.

The low g-anisotropy of 4 ($\Delta g = 0.032$, Table 1) and small deviation from the free electron g value (2.0023) sharply contrast with g-values observed for threefold-symmetric Fe(V) nitrides ($\Delta g > 0.175$). The anisotropy of the g-tensor arises from the combination of spin angular momentum ($S$) and orbital angular momentum ($L$). In general, $L$ is suppressed or quenched in systems with non-degenerate energy levels. Spin-orbit coupling can mix ground states with excited states, causing a small amount of orbital angular momentum in the ground state, creating a local magnetic field. This local magnetic field adds to the external field to produce shifts in the g-values. In threefold-symmetric Fe(V) nitrides, the unpaired electron resides in nearly degenerate $d_{xy}$ and $d_{x^2-y^2}$ orbitals (Figure 1) resulting in significant spin orbit coupling and a considerable increase in $\Delta g$.

The observed g-anisotropy of 4 is instead comparable to that of the very recently characterized exo complex PhB(AdIm)$_2$Fe(O) ($\Delta g = 0.050$; Figure 2b). Owing to its d$^5$ configuration, PhB(AdIm)$_2$Fe(O) contains an electron in an a-symmetry orbital (Figure 1). Likewise, the low g-anisotropy of 4 is consistent with a $^2A$ ground state for a $C_s$-symmetric iron nitride, where the unpaired electron resides in an orbital of d$^2$ parentage along the B-Fe-N vector. Indeed, the remarkably low g-anisotropy of the signal for 4 is diagnostic of its identity relative to other possible products.

Table 1 Experimental g-values, and experimental and theoretical hyperfine couplings (in MHz) for 4, $g_\perp > g_\parallel$, where $g_\parallel$ corresponds to the xy-plane ($g_z$ and $g_\parallel$) and $g_\perp$ to the B-Fe-N axis ($g_\perp$).

<table>
<thead>
<tr>
<th>g</th>
<th>$A(^{11}N)$</th>
<th>$A(^{13}B)$</th>
<th>$A(^{31}P)$</th>
<th>$A(^{55}Fe)$</th>
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<td>EPR</td>
<td>DFT</td>
<td>EPR</td>
<td>DFT</td>
</tr>
<tr>
<td>$g_\parallel$</td>
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<td>20.3</td>
<td>21.2</td>
<td>81.0</td>
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<td>$g_\perp$</td>
<td>2.029</td>
<td>-4.3</td>
<td>-7.7</td>
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</tr>
<tr>
<td>$\Delta g$</td>
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<td></td>
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</tr>
</tbody>
</table>

We also attempted to characterize 4 using Mössbauer spectroscopy. For similar nitrides in three-fold symmetry, a large quadrupole splitting ($\Delta E_Q$) and negative isomer shift (5) have been observed as distinct features of this electronic structure. However, only relatively broad quadrupole doublets were observed which decrease in intensity after 15 minutes of photolysis, only to be replaced with very similar, broader doublets with similar isomer shifts upon prolonged photolysis (see SI, Figure S19). Furthermore, (4) exhibits remarkably slow electronic relaxation ($T_m = 262$ ns at 85 K), as determined through $T_m$ measurements by Hahn-echo decay (see SI, Figure S17). This relaxation time is on the same order of magnitude as the lifetime of the excited vibrational state of the $^{57}$Fe nucleus ($T_m = 140$ ns) probed by Mössbauer spectroscopy, resulting in broad features instead of the usually observed sextets or quadrupole doublets. Relatively, an asymmetric signal is observed for Smith’s PhB(AdIm)$_2$Fe(O) at 80 K. The slow electronic relaxation, low conversion, and presence of two additional high spin species complicate a reliable determination of the isomer shift and quadrupole splitting for 4. As such, we instead relied fully on a suite of EPR spectroscopic methods to characterize the putative P$^{5+}$Fe(N) species.

Although low g-anisotropy is characteristic of organic molecules, the marked difference in the hyperfine patterns in the X- and Q-Band EPR spectra after photolysis of 2-$^{57}$Fe (Figure 4) demonstrates that the photolysis product contains iron and does not derive from an organic radical. At $g_\parallel$, the unresolved $^{57}$Fe hyperfine coupling results in broadening of the spectrum, while at $g_\perp$ a resolved change in the hyperfine splitting pattern is observed. Similarly, irradiation of 2-$^{11}$N results in a dramatic change in the X- and Q-Band EPR spectra at $g_\parallel$ (Figure 4). In contrast, no change is observed in the signal corresponding to liberated isopropyl radical in the presence of these same isotopic substitutions (See SI, Figure S9).

Overlap of the hyperfine coupling in the CW-EPR spectra complicates the accurate determination of the hyperfine coupling constants. To measure the hyperfine coupling constants more reliably, and thereby reveal details of the electronic structure of 4, Field-dependent Davies electron-nuclear double resonance (ENDOR) spectra were collected at Q-band (ca. 34.1 GHz, Figure 5) at 20 K, a temperature at which the aforementioned $S = 3/2$ byproducts of photolysis of 2 relax too fast to contribute to these pulse EPR spectra (see SI, Figure S17).
Figure 4 (left panel) X-band CW-EPR spectra (black) of isotopologues of P_3Fe(N)(4) with spectral simulations overlaid (red) using parameters in Table 1. MW frequency = 9.371-9.375 GHz; temperature = 77 K; MW power = 140 µW; modulation amplitude = 0.1 mT; conversion time = 10.24 ms. (middle and right panels) Pseudomodulated ESE-EPR spectra and corresponding simulations (red) of 4. MW frequency = 34.100 GHz; temperature = 20 K; τ pulse length = 160 ns; τ = 300 ns; shot rep time (srt) = 2 ms. The dashed dotted lines in the right panel serve as a guide for viewing, highlighting the change in hyperfine coupling with different isotopic compositions.

The ENDOR spectra exhibit clear signals arising from 31P and 11B hyperfine couplings, simulations of which aid in constraining the global fit between ENDOR and X- and Q-band field swept spectra. These data, in combination with hyperfine sublevel correlation (HYSCORE) spectroscopy (see SI, Figures S13 - S15) and the CW-EPR spectra, enabled reliable determination of distinct 14N, 31P, 32P, and 57Fe hyperfine tensors (Table 1). DFT (TPSS; CP(PPP) on iron; IGLO-III on all other atoms) recapitulates these observed hyperfine coupling constants remarkably well (Table 1 and SI).

Satisfactory simulation of the EPR data requires the presence of three identical phosphine nuclei (A(4P) = ±[45, 49, 35] MHz) (Table 1), underpinning the C2-symmetry of 4. The large axial anisotropy for 13B, 15N, and 57Fe, with the strongest hyperfine coupling for all nuclei observed at g<sub>P</sub>, as well as the relative order of the g values (g<sub>P</sub> > g<sub>Q</sub>) indicates that the unpaired electron resides in an orbitals oriented along the z-axis, in line with the expected electronic structure of 4.

Hyperfine anisotropy can arise from a through-space dipolar magnetic interaction or direct delocalization of spin density into, for example, the N 2p orbitals. The magnitude of hyperfine coupling constants is directly related to the electronic structure, and not just the nature of the ligand, complicating any direct comparison of 15N hyperfine coupling constants between 3-fold symmetric nitrides in different oxidation states. The nitrogen hyperfine coupling ±[-4.3, -4.3, 20.3] MHz of 4 is significantly larger than that observed for [PhB(BuIm):Fe(14N)(+) (9.11, 6.48, 0.71)] MHz. This significant difference is due to the intrinsic mechanism by which the spin on nitrogen arises. In [PhB(BuIm):Fe(14N)(+)], the spin on nitrogen arises through spin-polarization, whereas direct delocalization is the origin of unpaired spin on nitrogen in 4 (vide infra).

For [BIMP(NBu mes,Ac,Me)Co(14N)(N)], the only other example of a d<sub>5</sub> nitride, experimental 14N hyperfine coupling constants have not been reported. The hyperfine coupling parameters of the Co(IV) nitride predicted by DFT (A(14N) = [-18, -21, 46] MHz, a<sub>iso</sub> = 2 MHz, a<sub>iso</sub> have a similar axial nature with high anisotropy and a small anisotropic hyperfine coupling constant (a<sub>iso</sub> = 3.9 MHz for 4). The axial nature of the hyperfine coupling in 4 is indicative that the nitrogen ligand lies along the same axis as the spin and hence its insertion into the Fe-P bond has not occurred; the large anisotropy is characteristic of Fe-to-N multiple bonding. 38

Additional information about the electronic structure of the nitride moiety can be gleaned through examination of nuclear quadrupole interaction, parametrized by the nuclear quadrupole coupling constant (e<sup>2</sup>Qq/n) and electric field gradient asymmetry parameters (η). The 14N nuclear quadrupole interaction arises from the interaction between the 14N quadrupole moment with the inhomogeneous electric field produced by electrons in p-orbitals at the nucleus, further splitting the nuclear spin sublevels. To determine the nuclear quadrupole parameters e<sup>2</sup>Qq/n and η, HYSCORE spectra of 14N and 15N samples were compared, with

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simulations of the \(^{15}\text{N}\) signals providing constraints on the \(^{15}\text{N}\) hyperfine at \(g_z\), where this coupling is too small to be resolved within the field-swept spectra. Simulation of the \(^{15}\text{N}\) HYSCORE using hyperfine coupling values scaled by \(^{15}\text{N} / \text{N} \gamma\) gyromagnetic ratios (\(\gamma / \gamma\) \(^{15}\text{N}) = 0.713\) allowed the nuclear quadrupole parameters to be evaluated independently of the hyperfine, providing a nuclear quadrupole coupling constant of \(\varepsilon\text{Q}f/\hbar = \pm 3.1\) MHz for nitride 4 and an asymmetric parameter \(\eta\) of approximately 0. These values are almost identical to those predicted by DFT (Table 2) and are similar to those previously determined for (HITPNM)Mo\(^{2+}\)N\(^3\) 38 These quadrupole parameters can be discussed in terms of the Townes-Dalley model,\(^39\) in which the quadrupole coupling constant is directly proportional to the difference between the charge density in the nitride 2\(p_z\) and 2\(p_y\) orbitals. Based on the magnitude of its quadrupole parameter, the \(^{11}\text{B}\) ligand in 4 does not bind as a spherically symmetric nitride trianion, in contrast to the situation in [PhB(Bulm)Fe\(^{2+}\)N\(^3\)]\(^0\).\(^40\) This distinction is likely because donation of electrons from the filled 2\(p_z\) orbital of the nitride in 4 and its Fe 3\(d_z\) orbital is much smaller than the interaction between its filled 2\(p_y\) with empty 3\(dx_d\)/3\(dy_d\) orbitals, creating a charge density difference in the N 2\(p_y\) orbitals.

<table>
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<th>Compound</th>
<th>(\varepsilon\text{Q}f/\hbar) (MHz)</th>
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<tr>
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</tr>
<tr>
<td>(<a href="%5Ctext%7BN%7D">\text{PhB}(\text{Bulm})\text{Fe}</a>)</td>
<td>±0.03</td>
<td>n.d.</td>
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</tbody>
</table>

Importantly, the observed spectroscopic properties for 4 reliably rule-out other candidate structures that might be considered instead of the terminal nitride assignment. The structure that perhaps warrants most consideration is the terminal nitride cation, \(\text{P}^3\text{Fe}(\text{N})^+\), which could, for example, result from formal protonation of an incipient iron(III) nitride (which is likely basic in nature); a hypothetical \(\text{P}^3\text{Fe}(\text{N})^+\) species is also expected to have a doublet ground state. However, the electronic structure of \([\text{P}^3\text{Fe}(\text{N})^+]\) should be similar to that of its substituted imide congener, \([\text{P}^3\text{Fe}(\text{NH})\text{Ad}]\), which has been thoroughly characterized and shown to populate a \(^3\text{E}\) ground state.\(^41\) A characteristic feature of its \(^3\text{E}\) ground state is a relatively large g-anisotropy, which is in sharp contrast to the EPR signature of \(\text{Fe}^3\text{N}\). For a similar terminal \(\text{NH}\) imido, as in \([\text{HITPNM}](\text{Mo})\), strong rhombic hyperfine coupling to the proton is observed.\(^42\) For 4, no such hyperfine coupling to a proton can be detected, and no change in the CW-EPR spectrum is observed upon using deuterated toluene (see SI for discussion ruling out several other candidates based on the observed data).

The large boron and nitrogen hyperfine coupling constants provided by the EPR data indicate significant contribution of boron and nitrogen-based orbitals to the SOMO of nitride 4. Decomposition of the \(^{11}\text{B}\) hyperfine tensors into isotropic (\(a_{iso} = 1/3 (A_x + A_y + A_z) = \pm 41.6\)) and anisotropic components (\(T = (A_x - A_y + A_z)/2\) \((A_x - A_y - A_z)/2\)) can be used to determine the spin in boron-based orbitals.\(^43\) This analysis reveals an axial anisotropic boron hyperfine interaction with \(T = [-19.7 - 19.7 39.3]\) MHz. Defining the anisotropic tensor for an electron fully localized in a B 2\(p_z\) orbital as \(T_{0z} = -63.6 - 63.6 - 127.2\), yields a spin density in the B 2\(p_z\) orbital of \(\rho = 0.30\) (or ca. 30% of an electron). Using \(\omega_0^2 = 2547\) MHz, the 2s character in the SOMO is found to be 1.7%.

Performing a similar analysis for nitrogen yields a spin density in the N 2\(p_z\) orbital of \(\rho = 0.16\). Spin densities for \(^{11}\text{B}\) and \(^{15}\text{N}\) determined through this method are summarized in Table 3 and are close to Löwdin spin populations calculated by DFT, further supporting the assignment of 4. Most importantly, the experimental and Löwdin spin populations show that the spin density in 4 is significantly delocalized onto its nitrogen and boron atom, with the B \(p_z\) orbital accommodating a large degree of the spin.

### Table 3 Calculated experimental spin density estimation and Löwdin spin populations.\(^46\)

<table>
<thead>
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<th>(s)</th>
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[a] Spin densities are given as percentages. [b] Total spin density estimated from experimental EPR hyperfine coupling is calculated assuming that all spin is located in the orbitals included in the table.

The DFT-computed SOMO of 4 (Figure 6A) has \(\alpha\) symmetry and nicely illustrates its \(^3\text{A}\) ground state based on EPR spectroscopy. With strongly donating ligands such as nitrides it might be reasonably anticipated that the \(\alpha\) symmetry \(\sigma^*\) orbital would be too high in energy to be populated. However, the bonding interaction with the boron 2\(p_z\) orbital significantly reduces the energy level of the SOMO (Figure 6B). The electronic picture predicted features an unpaired electron in a polarized sigma orbital spread across three centers, interesting to compare with the case for a 1-electron polar sigma bond spread over two centers in \(S = 1/2\) \(\text{P}^3\text{Bu},^2\)Cu.\(^42\)

The boron contribution to the SOMO is large (~30%), and this fact, in combination with the appreciable nitrogen contribution (>15%), suggests that the electronic structure of 4 is better described on the continuum between an Fe(III) nitride, \(\text{P}^3\text{Fe}(\text{N})\), and an Fe(IV) nitride cation with a ligand-based radical anion, as in \(\text{P}^3\text{Fe}(\text{N})\), with a lesser contribution from \(\text{P}^3\text{Fe}(\text{N})^+\) (nitridyl radical) (Figure 6C). The significant delocalization onto boron differentiates this nitride from other open shell nitrides with significant nitridyl character such as those characterized with rhodium, ruthenium, iridium, and platinum.\(^43, 44, 45\)

The spin population analysis indicates that a low-spin Fe(IV) cation (\(S = 0\)) with a ligand-centered radical anion (e.g. \(\text{P}^3\text{Fe}(\text{N})\)) carries substantial weight in the electronic structure of 4 (Figure 6C). Given this, it is reasonable to constrain an estimate of a lower bound for the reduction potential of the previously reported iron(IV) nitride, \(\text{P}^3\text{Fe}(\text{N})\) (see cycle in Figure 2) with that of, for example, the reduction potential for Ph3B to its radical anion (~2.2 V vs. Fc\(^{0-}\)) in THF.\(^46\) This is a crude estimate as the potential for reduction of \(\text{P}^3\text{Fe}(\text{N})\) should be shifted anodically given its positive charge. We therefore expect the potential for the reduction of \(\text{P}^3\text{Fe}(\text{N})\) to be similar to, or more likely positive of, the \(\text{P}^3\text{Fe}(\text{N})\) couple known to dictate overall catalysis (~2.1 V vs. Fc\(^{0-}\) in THF). Therefore, the reduction of \(\text{P}^3\text{Fe}(\text{N})\) (as depicted in Figure 2), should be chemically viable under the reported conditions for catalytic N3RR.
very low temperature. A series of X- and Q-band spectra, in combination with ENDOR and HYSCORE spectroscopy, further supported by DFT calculations, provides conclusive evidence for the assignment of this highly unstable nitride species. In particular, the presence of nitrogen and iron is confirmed by dramatic changes in the field swept X- and Q-band spectra upon isotopic labeling with $^{15}$Fe and $^{15}$N, with a large anisotropic $^{15}$N hyperfine coupling being characteristic of the multiply-bonded nitride ligand. Additionally, the Cs symmetry and low g-anisotropy of this nitride reflect its unusual $^2$A ground state electronic structure. The $^{13}$B and $^{15}$N hyperfine coupling constants, recapitulated by DFT, reveal significant sigma orbital delocalization of the unpaired spin (~50%) onto the axial ligands, with the majority localizing on boron, highlighting the importance of the axial nitride and borane ligands in affording access to such a high d-count terminal iron nitride.

**Experimental Section**

$^1$H NMR spectra for complexes, $^{13}$C and $^{15}$N Mossbauer, UV-Vis, IR, and EPR spectroscopy as well as crystallographic data are given in the supporting information. CCDC 2182748, 2182749, and 2182750. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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**Keywords:** iron nitride • metal-to-ligand multiple bond • nitrogen fixation • nitriyl radical

![Figure 6](image_url)

**Figure 6** (A) Image of the calculated SOMO for $^{15}$Fe(N). (B) A qualitative MO diagram showing the 3-centered $\pi$-bonding of $^{15}$Fe(N). (C) Representative resonance structures for $^{15}$Fe(N) that emphasize different extremes in Fe-to-N and Fe-to-B bonding, and also different associated oxidation state assignments for Fe.

**Conclusion**

In summary, we have pursued the characterization of a terminal iron(II) nitride. Its unusual electronic structure is of fundamental interest in comparison to higher-valent nitrides (and oxos) that have been targeted previously, as is its possible role as an intermediate of catalytic Fe-mediated nitrogen fixation by a tris(phosphine)borane-iron catalyst system. The terminal nitride $^{15}$Fe(N) has been generated in moderate yield via photolysis at
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[39] \( \text{P}_{2n}^3 \text{Fe}^n \text{(II)} \) is not protonated at low temperature even with acids as strong as HOTf in ether, suggesting that the next step in the catalytic cycle is either reduction to \( \text{P}_{2n}^3 \text{Fe}^n \text{(II)} \), or N–H bond formation via a PCET reaction to instead generate the terminal imide \( \text{P}_{2n}^3 \text{Fe}^n \text{NH}^+ \). The latter species has not been experimentally identified but has been studied theoretically and features an estimated BDFE of 45 kcal mol\(^{-1}\) (see SI).


[37] For relaxation times \( \tau \gg \tau_B \), a Mössbauer spectrum consists of sextets with narrow lines, while a quadrupole doublet is observed for \( \tau \ll \tau_B \). In intermediate scenarios a broad feature is observed. See Marup, S. Magnetic Relaxation Phenomena. In Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications; P. Güttlich, Bill, E., A. X. Trautwein, Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; pp 201–234.


The generation and low-temperature characterization of a terminally bound iron(III) nitride, $P_3BFe(N)$ ($P_3B = \text{tris(o-diisopropylphosphinophenyl) borane}$), a plausible intermediate of iron-mediated nitrogen fixation, is reported. EPR spectroscopy supported by DFT calculations define a $^2\Sigma$ ground state electronic structure for this $C_3$-symmetric nitride, placing an unpaired spin in a sigma orbital along the B-Fe-N vector.

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