

## A Tetrahedrally Coordinated $L_3Fe-N_x$ Platform that Accommodates Terminal Nitride ( $Fe^{IV}\equiv N$ ) and Dinitrogen ( $Fe^I-N_2-Fe^I$ ) Ligands

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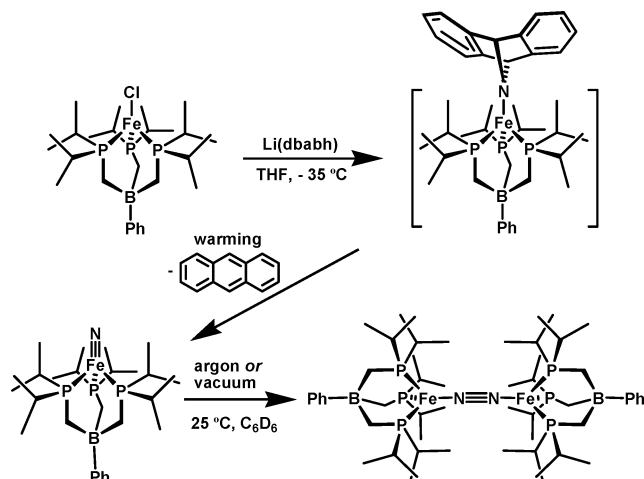
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High-oxidation state iron complexes featuring metal-to-ligand multiple bonds (e.g.,  $Fe=E/Fe\equiv E$ ) are proposed as key intermediates in numerous biocatalytic transformations.<sup>1</sup> Because such intermediates are typically too reactive to be directly observed,<sup>2a</sup> much effort has focused on developing low-molecular weight model complexes that enable the more systematic study of their physical characteristics and reactivity patterns.<sup>1,2b</sup> The vast majority of work in this field has been devoted to reactive ferryls ( $Fe^{IV}=O$ ) as these species are postulated as critical intermediates in a variety of enzymes that reduce dioxygen.<sup>3</sup> The reduction of dinitrogen constitutes an equally fascinating biocatalytic transformation.<sup>4</sup> A highly redox-active molybdenum center ( $Mo^{III}$  to  $Mo^{VI}$ ) has been suggested as the site of  $N_2$  binding and reduction in the well-studied  $FeMo$  cofactor.<sup>5</sup> Schrock's demonstration of catalytic ammonia production using a well-defined tris(amido)amine molybdenum complex elegantly establishes that such a scenario is chemically feasible.<sup>6</sup> One of the various alternative possibilities to consider is that a single low-valent iron site<sup>5a,7</sup> initiates the required redox transformations to convert  $N_2$  to  $NH_3$  by successive  $H^+/e^-$  transfer steps (e.g.,  $Fe^I-N_2 + 3 H^+ + 3 e^- \rightarrow Fe^{IV}\equiv N + NH_3$ ;  $Fe^{IV}\equiv N + 3 H^+ + 3 e^- \rightarrow Fe^I-NH_3$ ).

An intriguing intermediate to consider under the latter scenario is the iron nitride ( $Fe\equiv N$ ). At present, the only spectroscopic evidence for terminally bound nitrides of iron comes from frozen matrix experiments.<sup>8</sup> Nakamoto and co-workers reported the resonance Raman detection of an octaethylporphyrinato nitride ( $OEP$ ) $Fe^V(N)$  formed via photochemically induced  $N_2$  expulsion from a coordinated azide ligand.<sup>8a</sup> Wieghardt and co-workers used a similar photochemical strategy to generate a high-valent iron species assigned as an  $Fe^V(N)$  nitride based upon low-temperature EPR and Mössbauer data.<sup>8b</sup> The conditions under which these  $Fe^V(N)$  species were produced, in addition to their high degree of thermal instability, vitiated their more thorough spectroscopic and chemical interrogation. Herein we report the room-temperature observation of what is, to our knowledge, the first terminal iron-(IV) nitride,  $[PhBP^{iPr_3}]Fe^{IV}\equiv N$  ( $[PhBP^{iPr_3}] = [PhB(CH_2P^{iPr_2})_3]^-$ ).<sup>9</sup> The pseudotetrahedral  $L_3Fe-N_x$  platform described shuttles between the formal oxidation states  $Fe^{IV}$  and  $Fe^I$  as the terminal  $N_x$  ligand is transformed from the nitride functionality ( $Fe^{IV}\equiv N$ ) to dinitrogen ( $Fe^I-N_2-Fe^I$ ). In addition, the  $Fe^{IV}\equiv N$  subunit can serve as a source of  $NH_3$  in the presence of proton and electron equivalents.

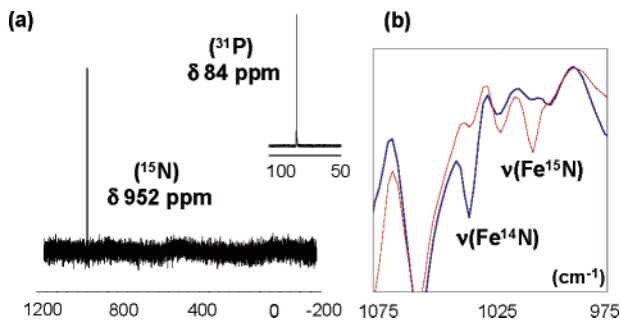
To explore the viability of a pseudotetrahedral iron nitride  $L_3Fe^{IV}\equiv N$ , we sought an anionic X-type ligand that would undergo clean oxidative N-atom transfer once coordinated to the "[ $PhBP^{iPr_3}$ ] $Fe$ " template. Choice of the "[ $PhBP^{iPr_3}$ ] $Fe$ " subunit as a suitable N-atom acceptor stemmed from prior work by our lab concerning the preparation of pseudotetrahedral, *low-spin*  $S = 1/2$   $Fe(III)$  imides of the type  $[PhB(CH_2PPh_2)_3]Fe\equiv NR$  and  $[PhBP^{iPr_3}]_3Fe\equiv NR$ .<sup>7c,10</sup> The lithium amide reagent  $Li(dbabh)$  ( $dbabh = 2,3,5,6$ -dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene),<sup>11</sup> which has been

Scheme 1

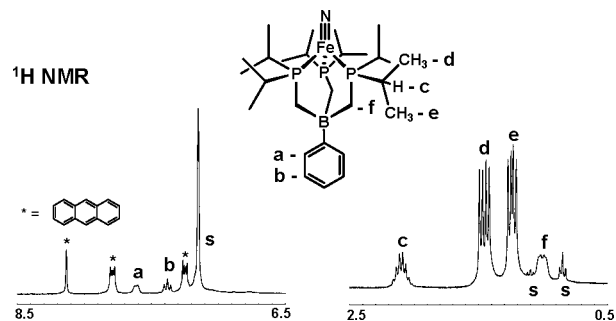


previously used by Cummins as an N-atom transfer agent,<sup>11b</sup> provided clean access to the desired reaction manifold (Scheme 1). Addition of  $Li(dbabh)$  to yellow  $[PhBP^{iPr_3}]FeCl$  in THF (or THF- $d_8$ ) at ca.  $-100$  °C formed a slurry which, upon warming to  $-35$  °C, generated a red species that is formulated as the high-spin amide complex  $[PhBP^{iPr_3}]Fe(dbabh)$ . For comparison, a structurally related and thermally stable red iron amide complex,  $[PhBP^{iPr_3}]Fe(NPh_2)$ , has been isolated and structurally characterized (see Supporting Information for details). The reaction between  $Li(dbabh)$  and  $[PhBP^{iPr_3}]FeCl$  to generate  $[PhBP^{iPr_3}]Fe(dbabh)$  can be monitored in situ by NMR spectroscopy in THF- $d_8$  and proceeds cleanly. A broad optical band associated with  $[PhBP^{iPr_3}]Fe(dbabh)$  is observed at 475 nm ( $\epsilon = 2300 M^{-1} cm^{-1}$ ), well-separated from yellow  $[PhBP^{iPr_3}]FeCl$  (420 nm) and  $Li(dbabh)$  (370 nm).

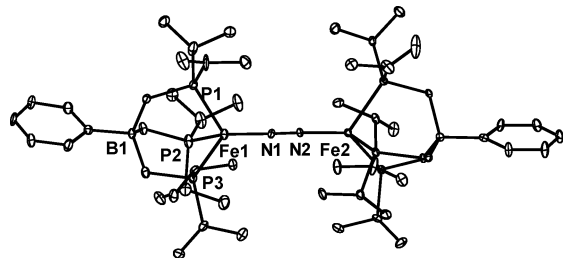
$[PhBP^{iPr_3}]Fe(dbabh)$  is thermally unstable and exhibits clean first-order decay when warmed to room temperature in solution ( $t_{1/2} \approx 11$  min at 22 °C)<sup>12</sup> to produce a stoichiometric equivalent of anthracene (NMR integration) and a new diamagnetic iron species assigned as the tan nitride complex  $[PhBP^{iPr_3}]Fe\equiv N$  on the basis of its NMR data. The  $^{31}P$  NMR spectrum of the reaction solution (in THF- $d_8$ ) shows a single sharp resonance at 84 ppm (Figure 1a inset) that is close in chemical shift to the structurally related complex  $[PhBP^{iPr_3}]Co\equiv N-p$ -tolyl (85 ppm).<sup>7c</sup> The  $^1H$  NMR resonances for the chelated  $[PhBP^{iPr_3}]$  ligand are also indicative of chemically equivalent phosphine donors (Figure 2), even at low temperature ( $-80$  °C). While these NMR data are consistent with a three-fold symmetric, pseudotetrahedral structure type, a  $^{15}N$ -labeling experiment was critical to more firmly establish the  $Fe\equiv N$  functionality. Terminally bound nitrides give rise to signature resonances by  $^{15}N$  NMR spectroscopy.<sup>13</sup> The diamagnetic nature of the  $d^4$   $[PhBP^{iPr_3}]Fe\equiv N$  complex therefore renders it particularly well-suited to direct NMR detection of the terminal nitride ligand



**Figure 1.** (a)  $^{15}\text{N}$  NMR and  $^{31}\text{P}$  NMR (inset) for  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{15}\text{N}]$ . (b) IR (pentane/KBr): (blue line)  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{14}\text{N}]$ , (red line)  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{15}\text{N}]$ .



**Figure 2.**  $^1\text{H}$  NMR of  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{15}\text{N}]$ . S = residual solvent.



**Figure 3.** Molecular representation of the solid-state structure of  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu^2\text{-N}_2)\}$ .  $\text{Fe1-N1} = 1.811(5)$  Å;  $\text{Fe2-N2} = 1.818(5)$  Å;  $\text{N1-N2} = 1.138(6)$  Å. See Supporting Information for details.

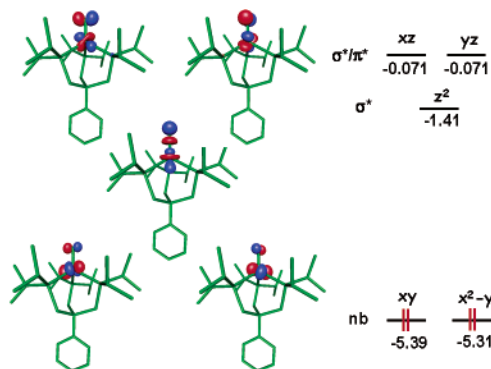
of interest. A  $^{15}\text{N}$ -labeled sample of  $\text{Li}(\text{dbabh})$  was prepared from commercially available  $^{15}\text{N}$ -labeled (ca. 98%  $^{15}\text{N}$ ) potassium phthalimide (see Supporting Information). Addition of  $^{15}\text{N}$ - $\text{Li}(\text{dbabh})$  to  $[\text{PhBP}^{\text{iPr}_3}\text{FeCl}]$  at low temperature in THF and subsequent warming of the sample to  $22$  °C for 25 min produced the expected  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{15}\text{N}]$  nitride product ( $^{31}\text{P}$  NMR). The sample was then cooled to  $-5$  °C, and a high-quality  $^{15}\text{N}$  NMR spectrum was obtained over a period of 8 h. The  $^{15}\text{N}$  NMR spectrum is shown in Figure 1a and exhibits a single sharp resonance at 952 ppm (referenced to nitromethane at 380 ppm), cementing our assignment of the complex as cylindrically symmetric with a terminally bound  $\text{Fe}\equiv\text{N}$  linkage.<sup>14</sup>

Akin to several high-valent osmium and ruthenium nitrides,<sup>15</sup>  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  exhibits a propensity to undergo bimolecular condensation via nitride coupling. This process generates the previously reported  $\text{N}_2$ -bridged complex  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu\text{-N}_2)\}$ .<sup>7c</sup> The coupling reaction takes place under an argon atmosphere or upon concentration under vacuum (Scheme 1). The solid-state molecular structure of  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu\text{-N}_2)\}$  has been obtained by XRD analysis, and its X-ray structural representation is shown in Figure 3. The  $\text{Fe}\equiv\text{N}$  coupling reaction is striking in that it constitutes what is, to our knowledge, the only example of a 6-electron redox process mediated by two iron centers. Each iron center formally shuttles from  $\text{Fe}^{\text{IV}}$  to  $\text{Fe}^{\text{I}}$  as the  $\text{N}_x$  ligand is

transformed from a  $\pi$ -basic nitride to  $\pi$ -acidic  $\text{N}_2$ . While the converse of this pathway (i.e.,  $\text{Fe}^{\text{I}}\text{-N}\equiv\text{N}\text{-Fe}^{\text{I}} \rightarrow 2 \text{Fe}^{\text{IV}}\equiv\text{N}$ ) is therefore kinetically competent by microscopic reversibility, it may not be thermally accessible in the present system. Heating a THF solution of  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu\text{-N}_2)\}$  at  $60$  °C brought about its gradual degradation; however, no  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  was detected, and the various reaction products produced were ill-defined. Evidence for a viable  $\text{Fe}^{\text{I}}$ -to- $\text{Fe}^{\text{IV}}$  redox couple was demonstrated by the addition of a high-valent  $\text{Mn}\equiv\text{N}$  source,<sup>16</sup> (*trans*-[1,2-cyclohexanediamino-*N,N'*-bis(4-diethylaminosalicylidene)] $\text{Mn}^{\text{V}}\equiv\text{N}$ ), to the  $\text{N}_2$ -bridged complex  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu\text{-N}_2)\}$ . Mixing a stoichiometric equivalent of these two complexes in THF solution generated  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  in minutes ( $\sim 40\%$  based on Fe). The reaction did not proceed to completion, and the reaction mixture likely contained equilibrating species.<sup>17</sup>

While the  $\text{Fe}^{\text{IV}}\equiv\text{N}$  coupling reaction to produce  $\text{Fe}^{\text{I}}\text{-N}\equiv\text{N}\text{-Fe}^{\text{I}}$  under argon further substantiates our assignment of the terminal nitride functionality, it has also frustrated our efforts to isolate  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  in crystalline form. To obtain satisfactory vibrational characterization of the  $\text{Fe}\equiv\text{N}$  functional unit it was necessary to reconstitute the nitride complex in a straight-chain hydrocarbon. To do this while circumventing its concentration-dependent degradation to  $\{[\text{PhBP}^{\text{iPr}_3}\text{Fe}]_2(\mu\text{-N}_2)\}$ , a  $\sim 0.02$  M solution of  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  was generated at  $-35$  °C in THF and then dried by removal of the reaction volatiles without warming the solution. The remaining residue was reconstituted in cold pentane and subsequently warmed to  $22$  °C to generate a solution containing  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  and the anthracene byproduct (see Supporting Information). Examination of the respective IR spectra of pentane solutions of  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  and  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv^{15}\text{N}]$  prepared in this fashion reveals an  $\nu(\text{Fe}\equiv\text{N})$  vibration at  $1034$   $\text{cm}^{-1}$  and an  $\nu(\text{Fe}\equiv^{15}\text{N})$  vibration at  $1007$   $\text{cm}^{-1}$  (Figure 1b). The isotopically labeled derivative thus shifts to lower frequency by  $27$   $\text{cm}^{-1}$ , the amount predicted from the reduced mass calculation for a simple harmonic oscillator model ( $28$   $\text{cm}^{-1}$ ). The energy of the  $\text{Fe}\equiv\text{N}$  vibration is reflective of the  $\text{Fe}\equiv\text{N}$  triple bond (vide infra) and is to be compared with related data for other bona fide  $\text{M}\equiv\text{N}$  triple bonds. For example, the  $\text{Mn}\equiv\text{N}$  vibration in  $(\text{TPP})\text{Mn}\equiv\text{N}$  is  $1036$   $\text{cm}^{-1}$  ( $^{15}\text{N}$ :  $1008$ ) and the  $\text{Mo}\equiv\text{N}$  vibration in Schrock's  $[\text{IPTN}_3\text{N}]\text{Mo}\equiv\text{N}$  is  $1013$   $\text{cm}^{-1}$  ( $^{15}\text{N}$ :  $986$ ).<sup>13b,18,19</sup> Nakamoto reported a much lower vibration ( $876$   $\text{cm}^{-1}$ ) for an  $(\text{TPP})\text{Fe}^{\text{V}}(\text{N})$  species detected in a frozen glass.<sup>8a</sup> The lower frequency for  $(\text{TPP})\text{Fe}^{\text{V}}(\text{N})$  likely results from attenuation of the  $\text{Fe-N}$  bond order ( $\text{Fe}\equiv\text{N}$ ) due to occupation of the  $\text{Fe-N}$   $\pi^*$  orbitals by two electrons.

Both five- and even six-coordinate iron complexes can be prepared using the  $[\text{PhBP}^{\text{iPr}_3}]$  ligand scaffold,<sup>9</sup> and we therefore suggest that there is an electronic stabilization of the  $\text{Fe}\equiv\text{N}$  linkage under three-fold symmetry that arises from the possibility to achieve one  $\sigma$ - and two  $\pi$ -bonding interactions. That this should be the case can be easily predicted from simple symmetry considerations and is also supported by DFT calculations. A DFT-minimized geometry for  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{N}]$  has been determined using the atomic coordinates reported previously for the  $S = 1/2$  imide complex  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{NAd}]$  as an initial HF guess.<sup>7c</sup> The calculation provides the geometric and electronic structure information provided in Figure 4. The  $\text{Fe-N}$  bond distance is calculated at  $1.49$  Å, appreciably shorter than the distance for its crystallographically characterized relative  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}\equiv\text{NAd}]$  ( $1.64$  Å).<sup>7c</sup> The  $\text{P-Fe-P}$  angles are appreciably expanded ( $99$ – $101^\circ$ ) in the calculated nitride structure by comparison to their more typical angles in a host of other  $[\text{PhBP}^{\text{iPr}_3}\text{Fe}]$  complexes ( $90$ – $95^\circ$ ),<sup>7c,9</sup> lending it a conformation that is somewhat more tetrahedral in nature. This fact, in



**Figure 4.** Theoretically predicted geometry and electronic structure (DFT, JAGUAR 5.0, B3LYP/LACVP\*\*) for  $S = 0$  [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡N. Lobe representations correspond to the frontier orbitals (energies in eV). Structural parameters: Fe–P = 2.28, 2.28, 2.29 Å; N–P–Fe = 117, 117, 119°; P–Fe–P = 99, 101, 101°; Fe–N = 1.490 Å.

addition to the distinct N-atom hybridization in the nitride complex by comparison to related imide structures,<sup>21</sup> dramatically destabilizes the iron-centered  $a_1$  orbital of  $d_2^2$  parentage. This situation gives rise to a large HOMO–LUMO gap for [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡N and a favorable ground-state  $(xy)^2(x^2 - y^2)^2(z^2)^0(xz)^0(yz)^0$  electronic configuration consistent with a  $d^4$ ,  $S = 0$  Fe<sup>IV</sup>≡N subunit. The diamagnetic  $d^4$  complex (mesityl)<sub>3</sub>Ir<sup>V</sup>≡O presumably owes its stability to similar electronic arguments.<sup>22</sup>

While we have yet to thoroughly survey the reactivity of [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡N, we note the following preliminary observations. The addition of PPh<sub>3</sub> or PEt<sub>3</sub> to THF solutions of [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡N appears to cleanly (<sup>1</sup>H NMR) generate the corresponding  $S = 2$  Fe(II) phosphiniminatos [PhBP<sup>Pr</sup><sub>3</sub>]Fe–N=PR<sub>3</sub> (R = PPh<sub>3</sub> or PEt<sub>3</sub>). The presence of the phosphiniminato functionality is in each case confirmed by the presence of intense IR vibrations (KBr/C<sub>6</sub>H<sub>6</sub>,  $\nu$ -(Ph<sub>3</sub>P=N) = 1223 cm<sup>-1</sup>,  $\nu$ (Et<sub>3</sub>P=N) = 1214 cm<sup>-1</sup>). Also, the corresponding R<sub>3</sub>P=NH<sub>2</sub><sup>+</sup> protonolysis products are liberated and detected by subjecting the reaction solutions to positive mode ES-MS (electrospray: Ph<sub>3</sub>PNH<sub>2</sub><sup>+</sup> =  $m/z$  278, Et<sub>3</sub>PNH<sub>2</sub><sup>+</sup> =  $m/z$  120). Perhaps most interesting to note is that the nitride ligand serves as a source of NH<sub>3</sub> upon the addition of proton and electron equivalents. For example, the addition of solid [LuH]<sub>3</sub>[BPh<sub>4</sub>] and CoCp<sub>2</sub> (3 equiv of each) to a room-temperature C<sub>6</sub>D<sub>6</sub> solution of [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡N produced after 2 h an appreciable quantity of NH<sub>3</sub>, easily identified by <sup>1</sup>H NMR in *d*<sub>6</sub>-DMSO as its NH<sub>4</sub>Cl salt after vacuum transfer of the reaction volatiles into an ethereal solution of HCl (ca. 1 M).<sup>13b</sup> Two independent runs using these nonoptimized conditions afforded 41 and 45% of NH<sub>3</sub> based upon NMR integration versus an internal standard. In a potentially related reaction, the release of *p*-toluidine by hydrogenation of the iron(III) imide [PhB(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>]Fe≡N-*p*-tolyl was observed.<sup>23</sup>

To conclude, the “[PhBP<sup>Pr</sup><sub>3</sub>]Fe–N<sub>*x*</sub>” chemistry discussed herein and that which we have reported previously<sup>7c</sup> collectively illustrate that the redox chemistry available to a pseudotetrahedral iron site can be remarkably rich. Examples of “[PhBP<sup>Pr</sup><sub>3</sub>]Fe–N<sub>*x*</sub>” complexes have now been characterized that feature five formal iron oxidation states based upon the magnetic data available:<sup>24</sup> [PhBP<sup>Pr</sup><sub>3</sub>]Fe<sup>0</sup>N<sub>2</sub><sup>-</sup> ( $S = 1$ ), [PhBP<sup>Pr</sup><sub>3</sub>]Fe<sup>I</sup>–N<sub>2</sub>–Fe<sup>I</sup>[PhBP<sup>Pr</sup><sub>3</sub>] ( $S = 3/2$  per iron center), [PhBP<sup>Pr</sup><sub>3</sub>]Fe<sup>II</sup>–N<sub>2</sub>Me ( $S = 2$ ), [PhBP<sup>Pr</sup><sub>3</sub>]Fe<sup>III</sup>≡NAd ( $S = 1/2$ ), and [PhBP<sup>Pr</sup><sub>3</sub>]Fe<sup>IV</sup>≡N ( $S = 0$ ). For each of these complexes, the dominant structural modification pertains to the nature of the fourth N<sub>*x*</sub> ligand:  $\pi$ -acidic N<sub>2</sub> favors the lower oxidation states, whereas  $\pi$ -basic nitride (or imide) favors the higher oxidation states.

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**Supporting Information Available:** Synthetic protocols and characterization data; crystallographic data including a CIF file; spectroscopic data; details for DFT study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) <sup>2</sup>J<sub>PN</sub> coupling is not observed in either the <sup>15</sup>N NMR spectrum or the <sup>31</sup>P NMR spectrum for [PhBP<sup>Pr</sup><sub>3</sub>]Fe≡<sup>15</sup>N. A number of phosphine-supported imides and nitrides that feature other metals (e.g., Mo, W) have been prepared for which <sup>15</sup>N and <sup>31</sup>P NMR data is available. <sup>2</sup>J<sub>PN</sub> coupling is not observed in these systems. See: (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077. (b) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. J. *Chem. Soc., Dalton Trans.* **1984**, 1329.
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- (16) (a) (*trans*-[1,2-Cyclohexanediamino-*N,N'*-bis(4-diethylaminosalicylidene)]-Mn<sup>V</sup>≡N) was synthesized from *trans*-[1,2-cyclohexanediamino-*N,N'*-bis(4-diethylaminosalicylidene)] according to: Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915. (b) Bendix, J. *J. Am. Chem. Soc.* **2003**, *125*, 13348. (c) Chang, C. J.; Low, D. W.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 270.
- (17) For instance, we suspect the reaction solution also contains a bridged nitride species (i.e., Fe=N=Mn). Studies are underway to resolve the complete product profile.
- (18) [TPP] = tetraphenylporphyrinato; [HIPTN<sub>3</sub>N] = tris(2-(2,4,6,2'',4'',6''-hexaisopropyl-1,1',3',1''-terphenyl-5'-amino)ethyl)amine.
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- (24) While their ground spin-state assignments (EPR, SQUID) are consistent with these formal oxidation states, studies are underway to further probe this family of [PhBP<sup>Pr</sup><sub>3</sub>]Fe–N<sub>*x*</sub> species by Mössbauer spectroscopy.

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