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H–H and Si–H Bond Addition to $Fe{\equiv}NNR_2$ Intermediates Derived from N_2

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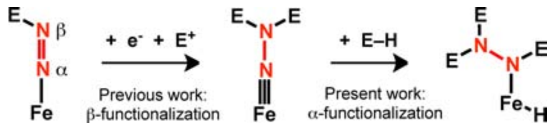
Ⓢ *Supporting Information*

ABSTRACT: The synthesis and characterization of Fe–diphosphineborane complexes are described in the context of N_2 functionalization chemistry. Iron aminoimides can be generated at room temperature under 1 atm N_2 and are shown to react with E–H bonds from $PhSiH_3$ and H_2. The resulting products derive from delivery of the E fragment to Nα and the H atom to B. The flexibility and lability of the Fe–BPh interactions in these complexes engender this reactivity.

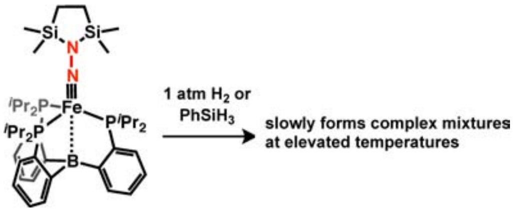
Dinitrogen functionalization reactions using synthetic Fe complexes typically employ reductants in conjunction with electrophilic reagents;[1] this strategy has allowed for the reliable functionalization of Nβ in terminal Fe–N_2 complexes (Scheme 1). Whereas early transition metal N_2 complexes display rich reactivity with nonpolar E–H (E = H, Si) bonds,[2] such reactivity using Fe has little precedent. The addition of H_2 to diiron-bridged nitrides has been demonstrated,[3] and in a recent report, N_2-derived bridging iron nitrides were shown to undergo hydrogenolysis to NH_3.[4] Hydrogenolysis of the terminal Fe–imide functional group has likewise been established,[5] though these imides were not prepared from N_2. As such, we sought to generate Fe–aminoimides from N_2 that could undergo subsequent E–H bond addition across the $Fe{\equiv}NNR_2$ linkage as a method for Nα functionalization (Scheme 1).

Scheme 1



In this context, we and others have studied Fe platforms that can accommodate both N_2 and terminal imide ligands,[1a,c,5a,6] and we recently reported that Fe–aminoimide complex **1** (Scheme 2) can be derived from N_2.[1c] Given previous studies demonstrating H_2 addition across the M–B bonds in related Ni complexes,[7] we expected that the Fe–B bond in **1** would facilitate an E–H activation step. However, **1** does not react with either H_2 (1 atm) or $PhSiH_3$ at room temperature (RT). At higher temperatures [see the Supporting Information (SI)], **1** decomposes, and no tractable products were identified in the presence of H_2 or $PhSiH_3$. We therefore explored the development of an Fe–diphosphineborane [(DPB)Fe] system that might be more reactive than the Fe–triphosphineborane [(TPB)Fe] system in **1**. We now describe new $(DPB)Fe{\equiv}NNR_2$ complexes that react with nonpolar E–H bonds at RT, thereby enabling the one-pot transformation of free N_2 to an Fe–hydrazido(–) species, the first such complex to be derived from N_2.

Scheme 2



As an entry to useful (DPB)Fe synthons, we found that reductive metalation of the isopropyl- and phenyl-substituted DPB ligands[8] $PhB(o\text{-}{}^iPr_2PC_6H_4)_2$ (**2a**, ^{iPr}DPB) and $PhB(o\text{-}Ph_2PC_6H_4)_2$ (**2b**, ^{Ph}DPB) with $FeBr_2$ and 1.0 equiv of Na/Hg in C_6H_6 affords (DPB)FeBr complexes **3a** and **3b** in yields of 84 and 64%, respectively (Scheme 3). Brown **3a** and **3b** are pseudotetrahedral $S = {}^3/_2$ complexes ($\mu_{eff} = 3.8\mu_B$ and $3.6\mu_B$ in C_6D_6 at RT, respectively) featuring η^2-BC interactions that have previously been observed in Cu and Ni complexes of this ligand class.[7,9] The structures determined by X-ray diffraction (XRD) analysis (Figure 1 and Table 1 for **3a**; for **3b**, see the SI) show close Fe–B [2.3243(11) and 2.330(4) Å, respectively] and Fe–C_{ipso} [2.2605(9) and 2.193(3) Å, respectively] contacts, supporting the formulation of the η^2-BC ligand as both a donor via a filled arene π orbital and an acceptor via an empty p orbital on B. In solution, **3a** and **3b** are C_s-symmetric as indicated by their ^{1}H NMR spectra.

Further reduction of **3a** with 1.0 equiv of Na/Hg under 1 atm N_2 results in the formation of the dinuclear N_2-bridged complex (^{iPr}DPB)Fe(μ-1,2-N_2)Fe(^{iPr}DPB) (**4**). The ^{1}H NMR spectrum of **4** in C_6D_6 indicates that the two Fe centers are equivalent and have local C_s symmetry. The solution and solid-state IR spectra of **4** lack an N–N stretch, suggesting that the complex maintains its pseudocentrosymmetric dinuclear structure in solution. The solution magnetic moment at RT is $4.6\mu_B$, which is somewhat higher than the spin-only value of $4.0\mu_B$ expected for two uncoupled $S = 1$ Fe centers.[10] The two pseudotetrahedral Fe centers in **4** have different local geometries in the solid state. The geometry about Fe_A (Figure

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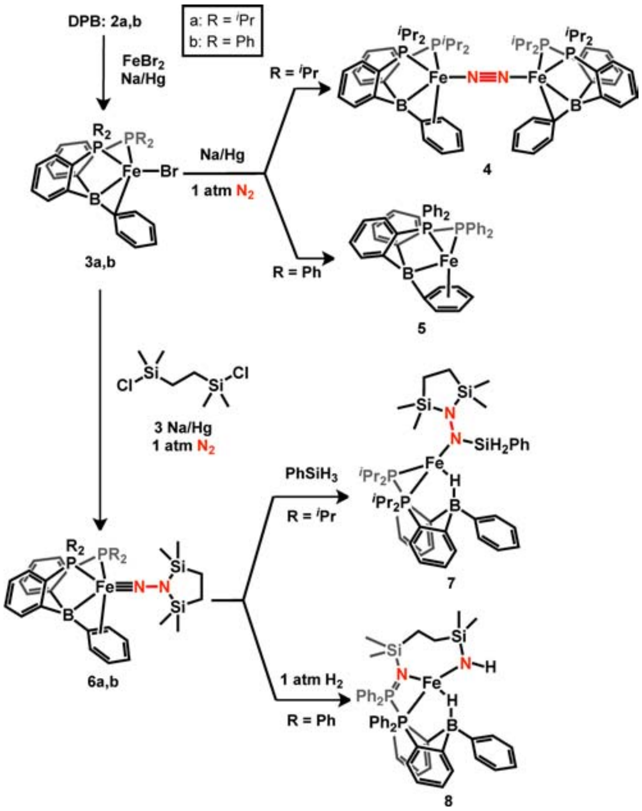
Scheme 3



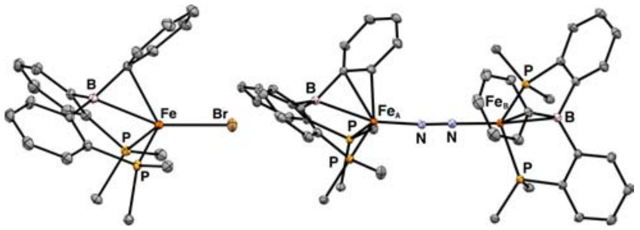


Figure 1. Displacement ellipsoid (50%) representations of (left) **3a** and (right) **4**. For clarity, the P^{i}Pr$_2$ groups have been truncated and the H atoms have been omitted.

Table 1. Selected Bond Lengths (Å)

	Fe−B	Fe−C$_{ipso}$	Fe−C$_{ortho}$
3a	2.3242(11)	2.2605(9)	2.5483(11)
4: Fe$_A$^{a}	2.3739(7)	2.2516(6)	2.2714(7)
4: Fe$_B$^{a}	2.3136(7)	2.2133(6)	2.6642(7)
6a^b	2.3768(6)	2.1492(5)	2.3403(6)
	2.4288(7)	2.1440(6)	2.2266(6)
7	2.859(5)	–	–

^{a}Fe$_A$ and Fe$_B$ are the two unique Fe atoms per molecule. ^{b}**6a** contains two molecules per asymmetric unit.

1) is distinguished by a short Fe−C$_{ortho}$ contact and relatively long Fe−B and Fe−C$_{ipso}$ distances (Table 1), while Fe$_B$ displays somewhat shorter Fe−B and Fe−C$_{ipso}$ distances and a negligible Fe−C$_{ortho}$ interaction. The phenyl ring bound to Fe$_A$ exhibits alternating C−C bond lengths between 1.4303(10) and 1.3711(12) Å (see the SI), whereas this asymmetry is negligible for the phenyl ring bound to Fe$_B$. These metrics indicate that back-donation to the arene ring is more significant for Fe$_A$ and back-donation to the B atom is more significant for Fe$_B$. Since the two (DPB)Fe fragments are equivalent in solution, the Fe−BCC interaction must be highly flexible, and the solid-state bond metrics reflect the large range of local geometries available to the Fe centers.

Performing an identical reduction of the phenyl derivative **3b** using 1.0 equiv of Na/Hg does not trigger N$_2$ binding but instead generates the brown diamagnetic complex **5** that contains an η^7-BPh interaction; to our knowledge, this coordination mode is unprecedented in the metal−borane literature. The XRD structure of **5** (Figure 2) shows tight Fe−η^7-BPh distances. The bound C$_{ipso}$ atom is significantly pyramidalized, as indicated by the sum of the C−C−C and two B−C−C angles (342°). Further showing the significant geometrical distortion of the bound arene is the contracted B−C$_{ipso}$−C$_{para}$ angle of 127.71(8)°. The η^7-BPh binding mode is maintained in solution, as evidenced by the upfield-shifted aryl resonances in the ^{1}H NMR spectrum (H$_{ortho}$, 3.63 ppm; H$_{meta}$, 3.24 ppm; H$_{para}$, 6.25 ppm) and the ^{13}C NMR spectrum (C$_{ipso}$, 106.77 ppm; C$_{ortho}$, 99.41 ppm; C$_{meta}$, 86.36 ppm; C$_{para}$, 78.73 ppm).

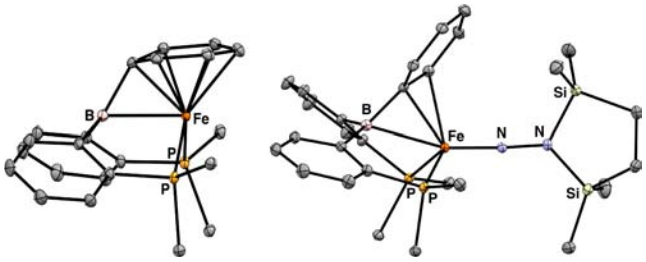
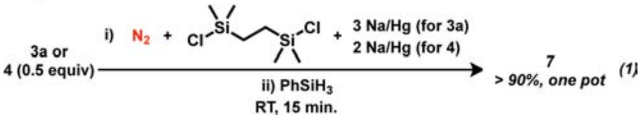


Figure 2. Displacement ellipsoid (50%) representations of (left) **5** and (right) **6a**. For clarity, PR$_2$ groups have been truncated and H atoms and solvent molecules have been omitted. For **6a**, only one of the two molecules per asymmetric unit is shown. Selected distances (Å) for **5**: Fe−B, 2.2667(13); Fe−C$_{ipso}$, 1.9669(11); Fe−C$_{ortho}$, 2.090 (av); Fe−C$_{meta}$, 2.169 (av); Fe−C$_{para}$, 2.1933(11).

Each of the complexes **3a**, **3b**, **4**, and **5** serves as a precursor to an Fe−aminoimide complex derived from N$_2$. In a procedure nearly identical to that for generating **1**,[1c] diamagnetic **6a** and **6b** can be accessed by stirring **3a** and **3b**, respectively, with 1.1 equiv of 1,2-bis(chlorodimethylsilyl)ethane and 3.1 equiv of Na/Hg in THF under 1 atm N$_2$. Alternatively, **4** or **5** may be employed as starting materials in conjunction with 2.1 equiv of Na/Hg. Both **6a** and **6b** are green in solution and dichroic green/brown when crystalline. The ^{1}H NMR spectrum of **6a** reveals its C_s symmetry in solution. In addition, the ^{1}H resonances of **6a** attributed to the bound aryl ring are upfield-shifted (H$_{ortho}$, 5.10 ppm; H$_{meta}$, 6.49 ppm; H$_{para}$, 4.72 ppm). This effect is not observed for **6b**, perhaps because of attenuated back-bonding in **6b** due to the less electron-rich metal center.

The solid-state structures of **6a** (Figure 2) and **6b** (see the SI) are similar. For **6a**, there are two molecules in the asymmetric unit. The short Fe−N distances [1.6607(5) and 1.6657(5) Å for **6a**; 1.6592(7) Å for **6b**] are consistent with those of other trigonal Fe(NR) linkages and imply an Fe≡NNR triple bond.[11] The bound arenes display alternating bond lengths that vary between ca. 1.36 and 1.44 Å (see the SI). Density functional theory (DFT) calculations (see SI) support the formulation of **6a** and **6b** as typical pseudotetrahedral d^6 Fe−imides[11] that are similar to **1** except that one phosphine donor in **1** has been replaced by the η^3-BCC interaction in **6a** and **6b**. Although the presence of an Fe–B bond is not required for the stability of pseudotetrahedral d^6 Fe–imides,[11,12] DFT calculations on **6a**, **1**,[1c] and related Fe–imides[6] show some degree of Fe–B σ bonding. Quantifying the extent of Fe–B bonding in these complexes thermodynamically is difficult because the boranes are contained within the cage structures of the ligands.

The reactions of E–H bonds with aminoimides **6a** and **6b** were next examined. We were satisfied to observe that in contrast to **1**, the addition of 1.1 equiv of $PhSiH_3$ to **6a** at RT readily generates a new orange species identified as the trisilylhydrazido(−) product **7** resulting from hydrosilylation of the Fe–N bond with delivery of SiH_2Ph to Nα and H to B. To our knowledge, this is the first Fe–hydrazido(−) complex to be derived from N_2, thereby adding to the body of previously reported mononuclear Fe–hydrazido(−) model complexes.[13] Having established this elementary step, we sought to combine the formation of **6a** and its subsequent hydrosilylation into a single procedure. Accordingly, **7** can be generated in one pot from **3a** or **4** (eq 1).



(1)

The IR spectrum of **7** exhibits an intense IR signal at 2090 cm^{-1} corresponding to the Si–H stretch and a broad, intense IR stretch at ca. 2000 cm^{-1} corresponding to the Fe–H–B functional group. The solution magnetic moment ($\mu_{eff} = 5.0\mu_B$, C_6D_6, RT) indicates an $S = 2$ spin state. The N–N bond is elongated from 1.326 Å (av) in **6a** to 1.492(4) Å in **7** (Figure 3). Although both distances are consistent with N–N single bonds, the comparatively short bond in **6a** is due to the sp hybridization of Nα and some degree of N–N multiple-bond character. The very long N–N bond in **7** (longer than that in free N_2H_4) is likely due to a high degree of steric pressure exerted by its bulky Si and Fe substituents. The sum of the C–B–C angles is 334°, reflecting the tetrahedral geometry of the borohydride ligand.

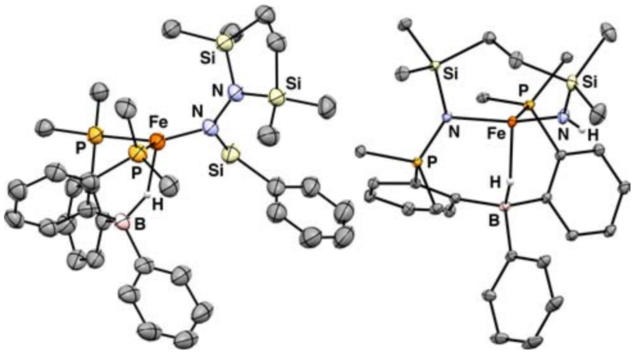
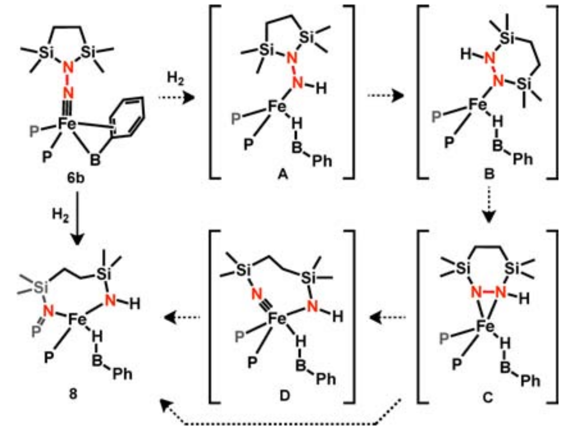


Figure 3. Displacement ellipsoid (50%) representations of (left) **7** and (right) **8**. For clarity, PR_2 groups have been truncated and H atoms not located in the difference map and solvent molecules have been omitted.

Addition of 1 atm H_2 at 50 °C to a C_6H_6 solution of **6b** affords a pale-brown solution from which colorless solids identified as the $S = 2$ product **8** ($\mu_{eff} = 4.8\mu_B$, C_6D_6, RT) can be isolated. Its IR spectrum contains a peak assigned to an N–H stretch at 3343 cm^{-1}; the corresponding D_2 addition product shows ν_{N-D} at 2476 cm^{-1} (2441 cm^{-1} calcd). The broad, intense ν_{Fe-H-B} stretch at ca. 2100 cm^{-1} is also sensitive to isotopic labeling ($\nu_{Fe-D-B} \approx 1550$ cm^{-1}). The connectivity of **8** was established by XRD analysis (Figure 3). In addition to the formation of new N–H and Fe–H–B bonds, the structure of **8** reflects cleavage of the N–N bond, rearrangement of the azadisilacyclopentane ring, and formal oxidation of one of the phosphines. This overall transformation is sufficiently complex that we felt it worthwhile to suggest a tentative mechanism (Scheme 4). Hydrogenation of **6b** to form **A** is analogous to the formation of **7** from **6a**. The hydrazine rearrangement step to form **B** has precedent for closely related disilylhydrazines.[14] Intermediate **B** may be sufficiently unencumbered to allow for η^2-NN binding to give **C**, which could lead to direct N–N cleavage and group transfer to a phosphine. Alternatively, the N–N bond in **C** may be cleaved to form Fe(IV)–imide[15] **D**, which could then undergo group transfer to give **8**. Cleavage of the N–N bond of N_2-derived ligands is rare for Fe,[1c,4] and has been observed for bimetallic early-transition-metal complexes.[2h,16] In addition, the transformation of **6b** to **8** is, to our knowledge, only the second example of N_2 functionalization with H_2 at a well-defined Fe complex.[4]

Scheme 4



In conclusion, we have reported the generation of Fe–aminoimides from N_2 that undergo subsequent addition of nonpolar E–H bonds. The significant flexibility of the Fe–BPh interactions facilitates both the initial formation of the Fe–aminoimide as well as the E–H activation step. Whereas previous functionalization reactions of terminal Fe–N_2 fragments allow for derivatization of Nβ, this report demonstrates that E–H addition to an unsaturated Fe–N bond is a viable strategy for Nα functionalization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectra, DFT calculations, and XRD tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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