

Hydrazine Capture and N–N Bond Cleavage at Iron Enabled by Flexible Appended Lewis Acids

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S Supporting Information

ABSTRACT: Incorporation of two 9-borabicyclo[3.3.1]nonyl substituents within the secondary coordination sphere of a pincer-based Fe(II) complex provides Lewis acidic sites capable of binding 1 or 2 equiv of N₂H₄. Reduction of the 1:1 Fe:N₂H₄ species affords a rare Fe(NH₂)₂ complex in which the amido ligands are stabilized through interactions with the appended boranes. The NH₂ units can be released as NH₃ upon protonation and exchanged with exogenous N₂H₄.

The 6e[−]/6H⁺ reduction of N₂ to ammonia represents one of the largest-scale reactions on earth,¹ yet the discrete mechanistic steps in the biological reduction sequence are largely unknown.² To clarify these details and provide avenues that can ultimately be exploited in a synthetic catalyst, well-defined small-molecule systems can be used to study redox interconversions between nitrogenous substrates.³ A key redox transformation in the reduction sequence requires N–N bond scission to afford iron amido (–NH₂) intermediates.⁴ These species are common to both the alternating and distal mechanisms of N₂ fixation in the FeMo cofactor yet are exceedingly rare in synthetic systems⁵ because of the high Brønsted basicity of the –NH₂ moiety as well as their propensity to form aggregates. For a single ligand platform to accommodate multiple redox states of nitrogenous substrates, flexibility in geometric and/or electronic environments is required. Such flexibility is often achieved by supporting ligands that accommodate multiple ligand fields;^{5a} however, appending groups to the secondary sphere can also provide a strategy to capture and stabilize nitrogenous substrates.^{5b}

Secondary-sphere acidic groups serve a prominent role within enzyme active sites to promote cooperative binding/activation of small-molecule substrates.⁶ To replicate key functional design aspects, synthetic ligand architectures that contain appended Brønsted donor groups have been constructed. Although hydrogen-bonding interactions have been used to stabilize high-valent intermediates (i.e., metal-oxos),⁷ these types of secondary-sphere donors are generally incompatible with highly reducing conditions associated with N₂ fixation. Lewis acid-appended frameworks overcome this incompatibility,⁸ and ligand scaffolds containing two or more covalently appended Lewis acidic groups are ideally suited to facilitate binding/reduction of small-molecule substrates. Our group is working to evaluate how the precise structural, electronic, and cooperative modes in the secondary coordina-

tion sphere can be used to regulate reactivity.⁹ In an effort to highlight the compatibility of a pair of acidic units with multiple redox states of a substrate, we targeted a tridentate pincer-based ligand containing two flexible tethered boranes.

The pyridine(dipyrazole) (PDP) ligand platform presents a highly modular framework to introduce flexible boranes that capture substrates and occupy positions of varied distance from the metal (Figure 1).¹⁰ Fe(II) adducts within this ligand set

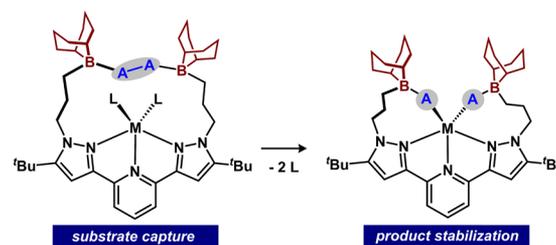


Figure 1. Design utility of flexible appended Lewis acids.

were recently shown to facilitate the disproportionation of hydrazine to ammonia and N₂.¹¹ We hypothesized that an appropriately modified ligand structure containing appended Lewis acidic sites could enable a reduction sequence involving nitrogenous substrates and also provide snapshots of a reduction sequence.

Control of Lewis acidity is a critical design aspect that is necessary to enable both capture and release of substrates/products. 9-Borabicyclo[3.3.1]nonyl (9-BBN) substituents were selected because they possess moderate Lewis acidity (acceptor number = 23.4) compared with B(O₂C₂(CH₃)₄) (10.0) or B(C₆F₅)₂ (71.8) (see the Supporting Information (SI)). The target ligand was prepared in 64% yield over two steps from 2,6-bis(5-*tert*-butyl-1H-pyrazol-3-yl)pyridine.¹² Hydroboration of the allylic ligand precursor, 2,6-bis(1-allyl-5-*tert*-butyl-1H-pyrazol-3-yl)pyridine, with 9-BBN quantitatively afforded the anti-Markovnikov product, ^{BBN}PDP^{tBu}. Metalation with FeX₂ (X = Br, Cl) in CH₂Cl₂ afforded light-orange (^{BBN}PDP^{tBu})FeX₂ (1-X). The ¹H NMR spectra (CDCl₃) contained 12 paramagnetically shifted resonances, consistent with C_{2v} symmetry. Solution magnetic susceptibility studies (25 °C, CDCl₃) were consistent with high-spin Fe(II) (μ_{eff} = 4.80(2)μ_B (1-Cl) and 4.88(2)μ_B (1-Br)). Finally, an X-ray diffraction experiment of 1-Cl revealed a distorted square

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pyramidal geometry at iron ($\tau_5 = 0.367$) with noninteracting boranes (Figure 2, middle) noted by their planarity ($\Sigma B_{1\alpha} = 358.9(5)^\circ$ and $\Sigma B_{2\alpha} = 360.1(6)^\circ$).

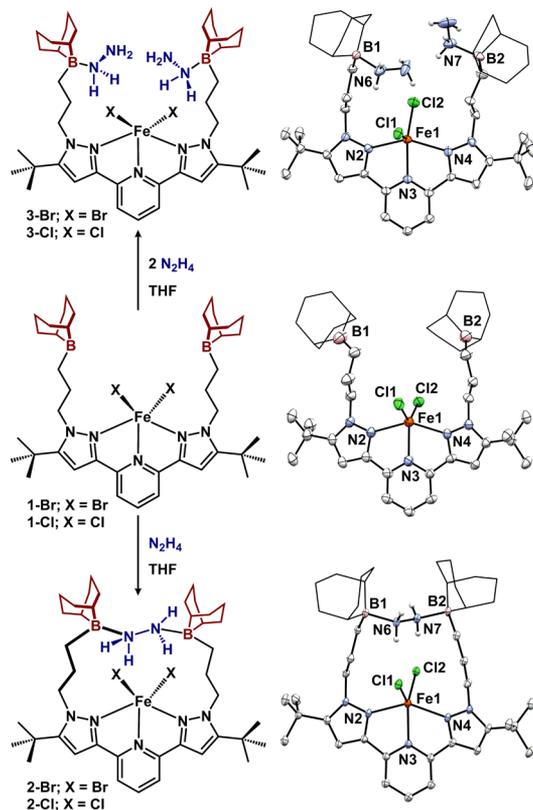


Figure 2. (left) Formation of 2-X and 3-X from 1-X. (right) Molecular structures of 1-Cl (middle), 2-Cl (bottom), and 3-Cl (top) (50% probability ellipsoids, selected H atoms omitted).

The ability of the tethered trialkylboranes to capture substrates within the metal's secondary coordination sphere was probed using hydrazine (N_2H_4). Addition either 1 or 2 equiv of N_2H_4 to 1-X afforded distinct products, as assessed by 1H NMR spectroscopy ($CDCl_3$). For the reaction with 1 equiv of N_2H_4 , we observed complete conversion to a new compound, ($^{BBN}PDP^{tBu}$) $FeX_2(N_2H_4)$ (2-X), which featured one resonance for the N_2H_4 moiety (X = Cl, -9.61 ; X = Br, -9.94 ppm). In contrast, addition of 2 equiv of N_2H_4 to 1-X afforded a pair of N_2H_4 resonances between -12 and -15 ppm, consistent with a 2:1 $N_2H_4:Fe$ species, ($^{BBN}PDP^{tBu}$) $FeX_2(N_2H_4)_2$ (3-X). The C_{2v} -symmetric spectra of either 2-Br or 3-Br remained unchanged upon heating to $50^\circ C$ with no evidence of interconversion.

We interrogated the structural metrics of 2-X and 3-X by X-ray diffraction (XRD) experiments. The solid-state structure of 2-Br revealed a five-coordinate iron ($\tau_5 = 0.423$) with a single molecule of N_2H_4 bridging between the two trialkylboranes (Figure 2). 2-Br is only the second crystallographically characterized example containing B–N interactions with both nitrogen lone pairs of N_2H_4 .¹³ Each borane is pyramidalized ($\Sigma B_{1\alpha} = 318.88(12)^\circ$ and $\Sigma B_{2\alpha} = 319.96(13)^\circ$) and features B–N distances (1.697(2) and 1.698(2) Å) that are longer than those in the related $BH_3N_2H_4BH_3$ (1.609 Å), likely as a result of both steric constraints of the 9-BBN within the ligand scaffold and the higher Lewis acidity of BH_3 . 2-Cl displayed

similar metrical parameters. 3-Cl possesses one N_2H_4 coordinated to each 9-BBN motif with shorter B–N distances (1.637(7) and 1.646(6) Å) than 2-X. The geometries at iron in complexes 3-X are best described as square-pyramidal ($\tau_5 = 0.210$ (3-Br) and 0.164 (3-Cl)). Notably, in 2-X and 3-X, the N_2H_4 moieties do not interact with the metal center (shortest Fe–N contact = 4.090 Å in 3-Cl). The solid-state structures of the 1:1 adducts, 2-X, display weak intramolecular hydrogen bonding between the hydrazine and adjacent Fe–X with N–X distances of 3.438 and 3.273 Å for 2-Br and 2-Cl, respectively.

The requirements of the appended borane groups to facilitate N_2H_4 binding were assessed using complementary control ligands and metals. A PDP ligand with a similar profile was synthesized with the $-(CH_2)_3BBN$ units replaced by *n*-butyl groups and metalated with $FeBr_2$ to afford ($^{Bu}PDP^{tBu}$) $FeBr_2$. The ($^{Bu}PDP^{tBu}$) ligand presents a similar ligand field as $^{BBN}PDP^{tBu}$, as noted by the similar electrochemical profiles of ($^{Bu}PDP^{tBu}$) $FeBr_2$ and 1-Br ($Fe^{II}/Fe^I \Delta E_{red} = 50$ mV). However, in contrast to 1-Br, the addition of 1 equiv of N_2H_4 to ($^{Bu}PDP^{tBu}$) $FeBr_2$ resulted in rapid demetalation without production of ammonia (Figure 3A).¹⁴

We prepared the analogous zinc complex, ($^{BBN}PDP^{tBu}$) $ZnCl_2$, to evaluate the generality of ligand-templated capture of N_2H_4 . The addition of 1 equiv of N_2H_4 afforded the 1:1 Zn: N_2H_4 adduct, ($^{BBN}PDP^{tBu}$) $ZnCl_2(N_2H_4)$. Similar to 2-Cl, the 1H NMR spectrum displays C_{2v} symmetry and a symmetric NH_2 resonance at 6.38 ppm. Capture of the hydrazine by the appended boranes was confirmed by ^{11}B NMR spectroscopy, which exhibits a resonance at -10.41 ppm, consistent with a tetrahedral boron. Single-crystal XRD confirmed that ($^{BBN}PDP^{tBu}$) $ZnCl_2(N_2H_4)$ is isostructural to 2-Cl with a single N_2H_4 moiety bridging the pendent trialkylboranes.

Although N_2H_4 adducts of $Fe(PDP)$ complexes have not been reported, a related variant bearing the proton-responsive ligand 2,6-bis(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine was recently shown to catalytically disproportionate N_2H_4 to NH_3 and N_2 .¹¹ In this case, ligand deprotonation was proposed to initiate the N–N bond cleavage. With Lewis acidic rather than Brønsted acidic groups appended on the $^{BBN}PDP^{tBu}$ framework, we sought to evaluate the extent to which appended acids could facilitate reductive cleavage of hydrazine.

Electrochemical investigation of 1-Cl using cyclic voltammetry (0.2 M [Bu_4N][PF_6], THF) revealed a reversible reductive event at -2.07 V vs Fc/Fc^+ —similar to the previously reported complex ($^{tBu}PDP^{tBu}$) $FeCl_2$ ($E_{pc} = -2.3$ V vs Fc/Fc^+).¹⁵ Upon N_2H_4 coordination, the reversible reductive wave for 2-Cl was modestly shifted to -1.98 V vs Fc/Fc^+ ($\Delta = +90$ mV), consistent with minimal perturbations of the overall geometry ($\Delta\tau_5 = 0.008$) and electronic environment at iron. To examine the reductive chemistry of 2-X using chemical reagents, 2 equiv of KC_8 was added to a thawing THF solution of 2-Br, which resulted in a rapid color change to dark green then light orange on warming to room temperature (Figure 3A). Analysis by 1H NMR ($CDCl_3$) and IR spectroscopies revealed a C_2 -symmetric complex, consistent with rigid $-CH_2CH_2CH_2BBN$ moieties, and retention of the N–H groups, providing an assignment of the complex as ($^{BBN}PDP^{tBu}$) $Fe(NH_2)_2$ (4) (80% isolated yield). Complex 4 is markedly less soluble than its precursors—consistent with higher rigidity—and gradually decomposes at room temperature in solution ($CDCl_3$, DCM, or THF) over 24 h.

Analysis of single crystals of 4 by XRD confirmed N–N bond scission to afford a rare bis(amido)iron complex in which the

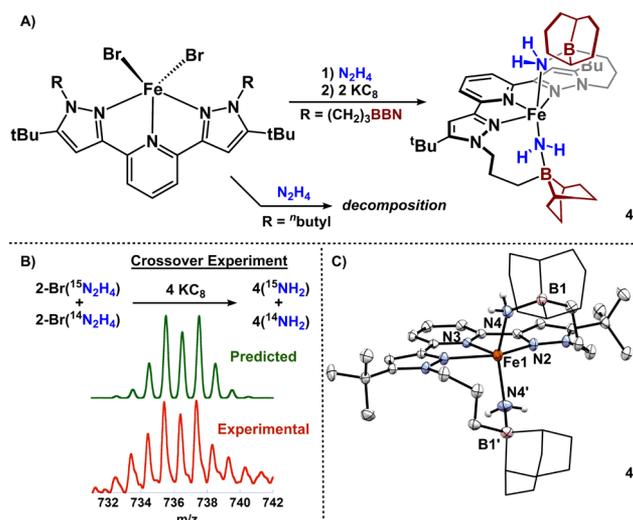


Figure 3. (A) Formation of **4** through reduction of **2-X** and control experiment using a complex without appended boranes. (B) Crossover experiment illustrating only formation of $4(^{14}\text{NH}_2)$ and $4(^{15}\text{NH}_2)$. The simulated spectrum (green) was modeled for no crossover occurring. (C) Molecular structure of **4** (50% probability ellipsoids, selected H atoms omitted).

amido substituents are capped by the trialkylboranes (Figure 3C). Following N–N cleavage, the resulting amido substituents are separated by 3.980 Å with nearly square-pyramidal geometry about iron ($\tau_5 = 0.017$). The molecular structures of **2-Br** and **4** demonstrate considerable flexibility of the appended boranes with respect to the iron center. The distance between iron and a centroid defined by B1–B2 decreases from 4.79 Å in **2-Br** to 1.85 Å in **4**. The Fe–NH₂ distance (2.075(2) Å) is markedly longer than in the Fe–NH₂ complexes reported by Peters and co-workers, likely because of quenching of the amido lone pair by the boranes (B–N = 1.633(3) Å),^{5a,b} and is most similar to that observed in LFe(NH₂)₂BEt₂ (L = 2,4-bis(2,6-diisopropylphenylimino)pent-3-yl) (Fe–NH_{2,av} = 2.064 Å).^{5g} Isolation of M(NH₂)₂ complexes often requires sterically encumbering ancillary ligands.¹⁶ Appended Lewis acidic groups provide an alternative strategy to stabilize these otherwise highly reactive units by attenuating the nucleophilicity of the amido nitrogen atoms.

Hydrazine can generate ammonia (or NH₂[−]) either by reductive scission of the N–N bond or by disproportionation, the latter of which affords N₂ or N₂/H₂ mixtures in addition to NH₃.¹⁷ Disproportionation pathways are chemically less efficient because the stoichiometry of NH₂[−] (or NH₃) to N₂H₄ will necessarily be unequal to 2:1. Experiments were performed to evaluate whether the reduction of hydrazine by **2-X** proceeds through a disproportionation pathway or, alternatively, through homolytic N–N bond scission mediated by iron. The stoichiometry of N₂H₄ to NH₂[−] for a series of control compounds was assessed by quenching the products of reduction with HCl and quantifying the amount of NH₄Cl produced by ¹H NMR spectroscopy.¹⁸ To confirm the NH₄⁺ quantification method, addition of 2 equiv of KC₈ to a freshly thawed THF solution of **2-Br** followed by HCl provided NH₄⁺ in high yield (1.74 equiv, 87% yield). In contrast, the analogous reaction with **2-Zn** afforded only 0.28 equiv of NH₄⁺. Similarly, control reactions with KC₈ and N₂H₄ produced only modest amounts of NH₄⁺ upon quenching (0.42 equiv; see the SI). Finally, addition of HCl to either **2-Cl** or **1-Cl** did not produce

any NH₄⁺. Collectively, these experiments confirm the requirements of a reductant and a redox-active metal to promote the stoichiometric cleavage of N₂H₄ into two NH₂[−] equivalents.

Although metal complexes have been used to promote hydrazine N–N bond scission, these reactions commonly proceed through disproportionation pathways.¹⁷ Within this context, and on the basis of the results of the stoichiometric studies noted above, we sought to investigate whether the reductive cleavage of N₂H₄ by **2-X** is inter- or intramolecular. Although oxidative addition of the N–N bond of N₂H₄ at a single metal center has not been reported, a recent report demonstrated homolysis of N₂H₄ to afford a Ni(II)–amido from a Ni(I) metalloradical.¹⁹ To probe the molecularity of hydrazine reduction, we performed a crossover experiment using ¹⁵N-labeled N₂H₄. Reducing an equimolar solution of **2-Br** and **2-Br**(¹⁵N) can result in two limiting scenarios: (1) formation of $4(^{14}\text{N}^{14}\text{N})$ and $4(^{15}\text{N}^{15}\text{N})$ if the reaction is unimolecular or (2) a statistical mixture of $4(^{14}\text{N}^{14}\text{N})$, $4(^{14}\text{N}^{15}\text{N})$, and $4(^{15}\text{N}^{15}\text{N})$ if an intermolecular pathway is operative. Analysis of the reduction products by mass spectrometry (MALDI-TOF, anthracene matrix) revealed data consistent with a unimolecular N–N bond scission pathway (Figures 3B and S46). These data highlight the utility of secondary coordination sphere interactions not only to capture a substrate and stabilize highly reactive fragments but also to enable new reaction pathways.

To complete a reduction cycle and release the captured NH₂[−] equivalents, **4** was treated with a Brønsted acid.²⁰ Addition of 2 equiv of [HNEt₃][Cl] afforded (BBN)²PDP^{ttBu}-FeCl₂(NH₃)₂ (**5-Cl**), wherein the NH₃ was released from iron and retained by the appended 9-BBN moieties. Single-crystal diffraction studies of **5-Cl** (Figure 4) confirmed the

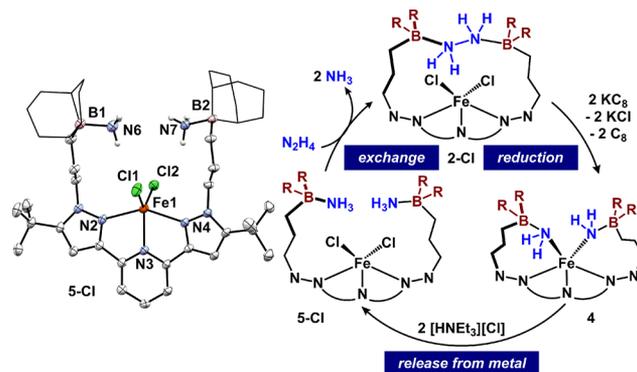


Figure 4. (right) Truncated model demonstrating N₂H₄ reduction, substrate release, and exchange. (left) Molecular structure of **5-Cl** (50% probability ellipsoids, selected H atoms omitted).

coordination of NH₃ to the 9-BBN units as well as coordination of the conjugate base (Cl[−]) to iron. In **5-Cl**, metrical parameters analogous to those of **3-Cl** were observed. Finally, the NH₃ units were exchanged by the addition of N₂H₄. Addition of 1 equiv of N₂H₄ to a freshly thawed CH₂Cl₂ solution of **5-Cl** regenerated **2-Cl** with only trace **3-Cl** observed (1.00:0.03 ratio by NMR spectroscopy). The exchange reaction clearly demonstrates that Lewis acids of appropriate strength can be used to capture, stabilize, and importantly release nitrogenous substrates.

In conclusion, we have described a new ligand framework wherein Lewis acidic 9-BBN fragments play key roles to

mediate the binding and reduction of nitrogenous substrates. The acidic groups serve to capture N_2H_4 , stabilize reactive Fe–NH₂ intermediates generated upon N–N scission, and finally release the reaction product, NH₃, upon addition of N_2H_4 . This rare example of hydrazine N–N homolytic addition was confirmed to occur at a single metal center by using ¹⁵N-labeled N_2H_4 . The tethered boranes are positionally flexible and adjust their distance by ca. 3 Å (borane centroid–Fe distance) to stabilize either the NH₂, NH₃, or N_2H_4 groups. The requirements of the Fe and Lewis acid groups were established by replacement of the appended boranes with inert *n*-butyl substituents and substitution of iron with redox-inactive zinc: these variants inhibited a homolytic reduction pathway of N_2H_4 .

Finally, appropriate electronic matching of acid/base pairs was exploited to enable a product/substrate exchange reaction (NH₃/ N_2H_4). The ability of acid/base pairs to equilibrate with small-molecule substrates and reduction products represents an important and underused design criterion that is required for turnover and underscores the value of selecting modestly acidic appended groups. Work is ongoing to interrogate the mechanism(s) of substrate redox transformations and also to capture more oxidized nitrogenous units.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11465.

Crystallographic data (ZIP)

Synthesis and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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