Published in final edited form as:

Inorg Chem. 2019 January 22; 58(2): 1147–1154. doi:10.1021/acs.inorgchem.8b02433.

Requirements for Lewis Acid Mediated Capture and N-N Bond Cleavage of Hydrazine at Iron

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Abstract

An iron complex bearing a pyridine(dicarbene) pincer was designed to probe the requirements of Lewis acid enabled N₂H₄ capture and subsequent N-N bond cleavage. Appended boron Lewis acids were installed by two methods to circumvent the incompatibilities associated with Lewis acid/base quenching of free carbenes and boranes. N₂H₄ capture by borane Lewis acids is dependent on both Lewis acidity and the steric profile about boron. A substitutionally inert primary coordination sphere at iron prevents an Fe-N₂H₄ interaction as well as N-N bond homolysis upon reduction.

Graphical Abstract

INTRODUCTION

The reductive capabilities of nitrogenase enzymes are unparalleled, and exemplified by their ability to reduce dinitrogen to ammonia.^{1–3} The 6H⁺/6e⁻ reduction of N₂ to NH₃ represents one of the largest scale reactions on earth,⁴ yet key mechanistic steps regarding the biological reduction pathways remain largely unknown.^{5,6} Well-defined small molecule complexes can aid in the elucidation of complex substrate reduction sequences because they can be engineered to test hypotheses regarding key redox transformations between

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The authors declare no competing financial interest.

ASSOCIATED CONTENT

Experimental procedures and spectroscopic characterization of all species are presented in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

nitrogenous substrates. Although at least two mechanistic pathways have been proposed for the N-N bond rupture event in N₂ reduction,^{7,8} synthetic platforms capable of accommodating the multiple products derived from N₂ reduction (N_xH_y, x = 1,2; y = 0–4) are rare, and necessarily require geometric and/or electronic flexibility.^{9,10} Another design strategy reminiscent of the enzyme is to modify the metal's secondary sphere with acidic/basic sites in order to capture and stabilize the array of nitrogenous substrates.

Second sphere interactions within enzyme active sites serve a variety of roles to facilitate substrate reduction by: (a) orienting small molecule substrates,^{11–14} (b) stabilizing high energy intermediates,¹⁵ or (c) providing channels for catalytic turnover.¹⁶ Synthetic systems have been designed to replicate this overall design aspect, most commonly, by incorporating Brønsted (hydrogen bond) donors within a ligand framework.^{17–20} Although hydrogen-bonding interactions serve a prominent role to stabilize high-valent intermediates,^{21–26} the highly reducing conditions associated with N₂ fixation are incompatible with Brønsted acidic groups. In contrast, Lewis acidic groups are a viable secondary sphere alternative to address the reductive incompatibilities of Brønsted acidic residues and achieve substrate capture/activation²⁷ and/or stabilization of high energy intermediates.^{28,29}

Recently, we reported the synthesis of a pyridine(dipyrazole) iron complex with flexible appended boron Lewis acids capable of capturing a single equivalent of hydrazine outside of iron's primary coordination sphere.³⁰ Reduction resulted in hydrazine N-N homolytic cleavage, with stabilization of the parent amido ligands augmented by appended acids. Crossover experiments confirmed N-N bond cleavage occurred at a single metal center, and notably, the appended 9-BBN Lewis acids were required for this transformation. To extend the scope of Lewis acid-assisted activation of small molecules beyond this ligand system, structure/function relationships are required. Importantly, the interplay between the electronic/steric requirements of the metal as well as the Lewis acid(s) needs to be carefully optimized to facilitate a closed-loop synthetic cycle that proceeds through: (a) substrate capture (independent or cooperatively with metal), (b) stabilization of intermediates, and (c) release/exchange of products. Boron Lewis acids are ideally suited to probe both the acidity and steric requirements of these reactions/equilibria. Whereas examples of redox chemistry with the pyridine(dipyrazole) framework are rare,³¹ pyridine(dicarbene) ligands are capable of stabilizing metal centers in multiple oxidation states.^{32,33} Herein, we describe the development of a highly modular pyridine(dicarbene) ligand platform with appended boron Lewis acids, the requirements of N₂H₄ capture, and consequence of a substitutionally inert primary coordination sphere on N-N bond cleavage.

RESULTS AND DISCUSSION

Appended BR₂ Installment on CNC Framework

To probe the requirement of N₂H₄ capture by boron Lewis acids independent of the metal center, we sought to design a system that was coordinatively saturated at iron with substitutionally inert ligands. The 2,6-bis(carbene)pyridine system^{34–39} presents a robust ligand template with a similar bite-angle and steric profile to the previously studied pyridine(dipyrazole) species. Installment of 9-borabicyclo[3.3.1]nonyl (9-BBN) and 4,4,5,5-tetramethyl-1,2,2-dioxoboryl (BPin) Lewis acids on the 2,6-bis(imidazol-1-yl)pyridine

(CNC) framework was achieved by two methods: 1) hydroboration of the previously reported 2,6-bis(*N*-allyl-imidazolium)pyridine,⁴⁰ [^{allyl}H₂CNC][BPh₄]₂, with 9-BBN in DCM to afford the anti-Markovnikov product, [^{BBN}H₂CNC][BPh₄]₂, and 2) nucleophilic addition of 2,6-bis(imidazol-1-yl)pyridine to Br(CH₂)₃BPin⁴¹ to afford [^{BPin}H₂CNC][BPh₄]₂ after anion metathesis.

Metalation of both [^{BPin}H₂CNC][BPh₄]₂ and [^{BBN}H₂CNC][BPh₄]₂ with Fe(N(SiMe₃)₂)₂ was attempted (Figure 2). Treating an acetonitrile solution of Fe(N(SiMe₃)₂)₂ with [^{BPin}H₂CNC][BPh₄]₂ affords low-spin [(^{BPin}CNC)Fe(MeCN)₃][BPh₄]₂ (**1-BPin**) as an orange powder. Under analogous reaction conditions, metalation of [^{BBN}H₂CNC][BPh₄]₂ did not afford a tractable iron containing species; instead, an inert Lewis acid/base pair formed between the free carbene and acidic 9-BBN (Figure 2).⁴² The identity of the quenched adduct was confirmed by independent deprotonation of [^{BBN}H₂CNC][BPh₄]₂ with ⁿBuLi, which afforded a tetrahedral ¹¹B NMR resonance at -15.44 ppm (C₆D₆), similar to the MeNHC^{Mes}.BEt₃ adduct (-13.1 ppm, C₆D₆),⁴³ as well as the absence of any imidazolium-CH resonances in the ¹H NMR spectrum.

To circumvent the acid/base quenching, we targeted a strategy of metalating the carbene ligand prior to installing the appended borane. Metalation of [^{allyl}H₂CNC][BPh₄]₂ with Fe(N(SiMe₃)₂)₂ in acetonitrile affords orange [(^{allyl}CNC)Fe(MeCN)₃][BPh₄]₂ (**1-allyl**), analogous to **1-BPin**. For each **1-allyl** and **1-BPin**, NMR spectroscopy (CD₃CN) confirmed metalation by disappearance of the diagnostic imidazolium CH¹H-resonance (9.80 and 9.15 ppm, respectively) concomitant with a new carbene resonance in the ¹³C spectrum (201.90 and 200.29 ppm, respectively). Structural confirmation of **1-allyl** was achieved by X-ray diffraction of single crystals, which revealed the expected *mer*-octahedral dicationic iron pincer species with pendent allylic moieties (Figure 2). Complex **1-allyl** is structurally analogous to previously reported [(^{DIPP}CNC)Fe(MeCN)₃][BPh₄]₂ (DIPP = 2,6-diisopropylphenyl)³⁹ but contains slightly longer Fe-C distances (1.975(2) and 1.970(2) Å).⁴⁴

Carbonyls are strong field ligands that often impart substitutional inertness and also provide a spectroscopic handle to assess electronic changes to the primary coordination sphere.⁴⁵ Carbonyl complexes were prepared by reduction of THF slurries of **1-allyl** and **1-BPin** with excess 0.4% Na(Hg) under a carbon monoxide atmosphere, affording (^{allyl}CNC)Fe(CO)₂ (**2-allyl**) and (^{BPin}CNC)Fe(CO)₂ (**2-BPin**) as red powders (Figure 2). Upon reduction, the ¹³C NMR resonances assigned to the carbene for **2-allyl** and **2-BPin** shift downfield to 211.58 and 211.06 ppm, respectively, and infrared spectroscopy (KBr) confirmed the presence of carbonyl ligands (**2-allyl**: 1896, 1832 cm⁻¹; **2-BPin**: 1900, 1841 cm⁻¹). The carbonyl ligands of complexes **2** are more activated than those in other dicarbonyl Fe(0) pincer compounds including (^{iPr}PDI)Fe(CO)₂ (1974, 1914 cm⁻¹) (^{iPr}PDI = 2,6-((DIPP)N=CMe)₂-C₅H₃N; DIPP = 2,6-diisopropylphenyl),⁴⁶ (PhPDPOSiMe₃)Fe(CO)₂ (1935, 1868 cm⁻¹),³¹ and, notably, (^{DIPP}CNC)Fe(CO)₂ (1928, 1865 cm⁻¹).³⁸ Single crystal X-ray diffraction studies on **2-allyl** confirmed a five-coordinate (τ₅ = 0.52) iron dicarbonyl complex with the allylic substituents intact (Figure 2). Following reduction, the Fe-C_{carbene} distances contract to 1.9194(15) Å and the Fe-C_{carbonyl} distances (1.7457(15) Å) are identical to (^{DIPP}CNC)Fe(CO)₂ (1.746(3) and 1.767(4) Å).³⁸ **2-allyl** is thermally stable in C₆D₆ in the

presence of small molecule substrates such as N_2H_4 or H_2 at 85 °C. Attempts to liberate the carbonyl ligands were unsuccessful: **2-allyl** was unreactive toward both stoichiometric NaOH ⁴⁷ and N-methylmorpholine N-oxide⁴⁸ at elevated temperature or under UV radiation and does not undergo ligand substitution reactions with trimethylphosphine or phenylisocyanide after 24 hr in C_6D_6 . These experiments clearly demonstrate a highly inert primary coordination environment about iron in **2-allyl**.

After establishing an inert primary coordination sphere, we targeted installment of the appended trialkylboranes. Anti-Markovnikov selective Lewis acid addition was achieved by treating THF solutions of **2-allyl** with dicyclohexylborane, disiamylborane, and 9-BBN at room temperature for 16 hr to afford $(^{\text{BCy}_2}\text{CNC})\text{Fe}(\text{CO})_2$ (**2-BCy₂**), $(^{\text{sia}_2\text{B}}\text{CNC})\text{Fe}(\text{CO})_2$ (**2-sia₂B**), and $(^{\text{BBN}}\text{CNC})\text{Fe}(\text{CO})_2$ (**2-BBN**), respectively, as red powders (Figure 3). In each case, ^1H NMR spectroscopy (C_6D_6) was employed to confirm consumption of the allylic resonances of **2-allyl** and the ^{11}B NMR spectra confirmed formation of the trialkylborane (**2-BCy₂** = 84.18; **2-sia₂B** = 81.10; **2-BBN** = 87.73 ppm). Infrared (KBr) and NMR spectroscopy established that hydroboration has a minimal effect on the electronic environment at the iron: ^{13}C -carbene resonances and $\nu(\text{CO})$ vibrations (**2-BCy₂** = 210.77 ppm, 1902/1839 cm^{-1} ; **2-sia₂B** = 211.23 ppm, 1901/1839 cm^{-1} ; **2-BBN** = 211.58 ppm, 1895/1835 cm^{-1}) are comparable to **2-allyl**.

Structural analysis of single X-ray quality crystals of **2-BR₂** revealed similar bonding metrics across the series (Figure 3, Table S14).⁴⁹ For each, the appended boranes are non-interacting as noted by their planarity ($\Sigma\text{B}_\alpha = 360^\circ$). The CNC ligands possess a bite angle ($\text{C}_{\text{carbene}}\text{-Fe-C}_{\text{carbene}} = 157^\circ$ for each) and geometry at iron ($\tau_5 = 0.47\text{--}0.52$) similar to $(^{\text{BBN}}\text{PDP}^{\text{Bu}})\text{FeCl}_2$ ($\text{N}_{\text{pyrazole}}\text{-Fe-N}_{\text{pyrazole}} = 148.83^\circ$; $\tau_5 = 0.37$) confirming that compounds **2-BR₂** are appropriate isostructural models to probe requirements of N_2H_4 capture and reduction.

Hydrazine Capture in Secondary Coordination Sphere

Given that the four appended Lewis acids within iron's secondary coordination sphere do not perturb the electronic and steric environment at iron (vide supra), we assessed their relative Lewis acidity by determining their acceptor numbers (AN) using the Gutmann-Beckett method (Table S16).⁵⁰ Model acids derived from styrene ($\text{PhCH}_2\text{CH}_2\text{BR}_2$ ($\text{BR}_2 = \text{BPin}$, sia_2B , BCy_2 , BBN)), were investigated as proxies to simplify experimental determination by eliminating any competitive inter/intramolecular acid/base equilibria. The acid derived from 9-BBN affords the largest AN (24.9) and is similar to that reported for BEt_3 ,⁵¹ while heteroatom stabilized $\text{PhCH}_2\text{CH}_2\text{BPin}$ is the poorest acceptor (AN = 10.0). Surprisingly, the other two trialkylboranes, $\text{PhCH}_2\text{CH}_2\text{B}(\text{sia})_2$ and $\text{PhCH}_2\text{CH}_2\text{BCy}_2$, also are best described as poor acceptors (AN = 10.2 and 13.0, respectively) by this method. The challenges of quantifying Lewis acidity is well documented^{51,52} and we propose the low acceptor numbers for $\text{PhCH}_2\text{CH}_2\text{B}(\text{sia})_2$ and $\text{PhCH}_2\text{CH}_2\text{BCy}_2$ are derived from their larger steric encumbrance, compared to $\text{PhCH}_2\text{CH}_2\text{BBN}$. This steric congestion weakens the Lewis acid/base interaction for triethylphosphine oxide, a base with a larger cone angle than N_2H_4 . Similar to a cone angle analysis, the steric contribution of the substituents on each acid was estimated by solid angle analysis, providing a relative ranking of steric accessibility

at boron: BPin < BBN < BCy₂ < B(sia)₂ (Table S17).⁵³ These data reinforce that Lewis acidity measurements are *substrate-dependent* and incorporate both steric accessibility and electrophilicity.

We interrogated the ability of the set of **2-BR₂** compounds, containing boranes of varied acidity to sequester a single equivalent of N₂H₄. **2-BPin** was unreactive toward N₂H₄, as determined by ¹H NMR and IR spectroscopies, consistent with its low AN. Conversely, **2-sia₂B** and **2-BCy₂** both react with a single equivalent of N₂H₄, despite their low AN, to afford 1:1 N₂H₄:Fe adducts (**3-sia₂B** and **3-Bcy₂**; Figure 4). The captured N₂H₄ was confirmed in each case by NMR spectroscopy by a broad N₂H₄ resonance in the ¹H-spectrum at 3.19 (**3-sia₂B**, C₆D₆) and 4.42 ppm (**3-Bcy₂**, THF-*d*₈) as well as an upfield ¹¹B resonance, consistent with a tetrahedral boron (**3-sia₂B** = -6.04; **3-BCy₂** = -8.41 ppm). IR spectroscopy (KBr) confirmed minimal perturbations to the iron center upon substrate capture by their similar ν(CO) vibrations (**3-sia₂B**: 1901, 1836 cm⁻¹; **3-BCy₂**: 1900, 1832 cm⁻¹). Single, X-ray quality crystals of **3-BCy₂** were investigated to probe the nature of the R₃B-N₂H₄ interaction. Data refinement revealed a polymeric species in which borane Lewis acids from opposing molecules cooperatively sequester the N₂H₄ molecule (Figure 4). This bonding arrangement directly contrasts our previous findings for (BBNPDP^{*t*Bu})MX₂ (MX₂ = FeCl₂, FeBr₂, ZnCl₂) in which N₂H₄ capture occurred at a single ligand platform and was augmented by weak MX-H₄N₂ hydrogen bonding interactions. The similarity in bite-angle and geometry about iron between **2-BCy₂** and (BBNPDP^{*t*Bu})MX₂ suggests the divergent mode of N₂H₄ capture (oligomeric vs. monomeric) is derived from the steric congestion imparted by the cyclohexyl substituents of **2-BCy₂** (and *sec*-isoamyl substituents of **2-sia₂B**), which prevents monomeric N₂H₄ capture.⁵⁴

In contrast to the polymeric structure for **2-BCy₂**, addition of a single equivalent of N₂H₄ to a THF solution of **2-BBN** results in precipitation of an orange solid assigned as (BBNCNC)Fe(CO)₂(N₂H₄) (**3-BBN**) that displays a large shift in the ν(CO) (KBr, 1859, 1785 cm⁻¹) that are broadened and bathochromically shifted, compared to **2-BBN** (= 36, 50 cm⁻¹; Figure 5). The increased activation of the carbonyl ligands in **3-BBN** is consistent with hydrogen bonding interactions^{55–57} between the captured hydrazine and carbonyl ligands in analogy to (BBNPDP^{*t*Bu})FeCl₂(N₂H₄). The insolubility of **3-BBN** in common organic solvents precluded solution NMR characterization; however, **3-BBN** gradually dissolved in DMSO concomitant with release of hydrazine (Figure S47). We propose the poor solubility is due to fewer degrees of freedom, compared to **2-BBN**, as a result of increased rigidity upon capturing the N₂H₄. The assignment of **3-BBN** is supported by the following data: 1) MALDITOF spectrometry is consistent with the (BBNCNC)Fe(CO)₂ fragment (m/z = 647.370), 2) elemental analysis establishes the molecular formulation as (BBNCNC)Fe(CO)₂(N₂H₄), 3) IR spectroscopy indicates the presence of N-H absorptions and CO bands (1859 and 1785 cm⁻¹; shifted to lower energy to due hydrogen-bonding with the captured N₂H₄),^{56,57} 4) release of N₂H₄ upon dissolution in DMSO to reform **2-BBN**,⁵⁸ 5) synthesis of a more soluble variant, (BBNCNC)Fe(CO)₂(1,4-diaminobutane) (vida infra), and 6) addition of a second equivalent of N₂H₄ affords the 2:1 N₂H₄:Fe complex (vida infra).

Due to the insolubility of **3-BBN**, we sought to develop a more soluble analogue to establish the entropic favorability of 1:1 Fe:substrate capture. We selected 1,4-diaminobutane as an extended diamine to impart higher solubility. Treating **2-BBN** with a single equivalent of 1,4-diaminobutane afforded the 1:1 Fe:1,4-diaminobutane adduct, $(^{BBN}CNC)Fe(CO)_2(1,4\text{-diaminobutane})$ (Figure 5). Crystallographic characterization confirmed capture of the diamine between the two appended trialkylboranes forming a 19-atom macrocyclic structure ($B-N = 1.657(3)$ and $1.654(3)$ Å). The flexibility of the attached trialkylboranes is highlighted by their ability to accommodate substrates of varied size: the B1-B2 distance in $(^{BBN}CNC)Fe(CO)_2(1,4\text{-diaminobutane})$ is 8.512 Å whereas the distance in $(^{BBN}PDP^{tBu})FeCl_2(N_2H_4)$ is 4.191 Å. These studies demonstrate that, when the steric environment surrounding the boron is able to accommodate a substrate, *intramolecular* capture is favored over oligomeric capture (i.e. **3-BCy₂**).

The chemical composition of **3-BBN** was further confirmed by addition of a second equivalent of hydrazine. Addition of N_2H_4 to an orange THF slurry of **3-BBN** gradually affords a homogenous red solution from which a red powder was isolated and assigned as $(^{BBN}CNC)Fe(CO)_2(N_2H_4)_2$ (**4**) (Figure 5). The IR spectrum (KBr) revealed $\nu_{(CO)}$ absorptions ($1896, 1826\text{ cm}^{-1}$) that are similar to complexes **2-BR₂** and suggest diminished hydrogen bonding interactions between the hydrazine and carbonyl ligands. NMR spectroscopy (THF-*d*₈) confirmed a tetrahedral boron ($^{11}B = -4.04$ ppm) in **4** as well as two distinct NH_2 resonances (1H : 3.38 ($B-NH_2$), 5.70 (BNH_2NH_2)). The molecular structure of **4** by an XRD experiment confirmed its identity (Figure 5). The metrical parameters of the primary coordination sphere remain unchanged with respect to **2-BR₂**. The tetrahedral trialkylborane units ($\Sigma B_a = 337.6(8)^\circ$) each engage a separate molecule of N_2H_4 ($B-N = 1.665(11)$ Å). The B-N distances in **4** are significantly shorter than those in **3-BCy₂**, consistent with smaller steric profile. In the solid state, each carbonyl ligand engages a separate N_2H_4 in moderate intramolecular hydrogen bonding interactions ($N_{proximal}-O = 3.089$, $N_{distal}-O = 3.016$ Å)^{59–61} that were not manifest in the IR spectra of the bulk samples.

The disparate modes of N_2H_4 capture between the four complexes, **2-BR₂**, suggests multiple factors, including Lewis acidity and steric profile, contribute to the ability to properly orient a small molecule substrate within the secondary coordination sphere. While **2-BPin** is sterically accessible for acid/base interactions, it lacks the acidity to capture N_2H_4 . Each trialkylborane variant, however, is sufficiently acidic. The large steric profile of **2-BCy₂** and **2-sia₂B**, evident by their low AN's, capably engage both N_2H_4 lone pairs, although this interaction requires an oligomeric conformation. Of the appended acids studied, only **2-BBN** offers both adequate acidity and steric accessibility to allow monomeric N_2H_4 capture. Notably, **2-BBN** is less reducing ($Fe(0)/Fe(I) = -1.19$ V vs. Fc/Fc^+) than complexes of the $^{BBN}PDP^{tBu}$ ligand class and may not be reducing enough on their own to reduce N_2H_4 .

Reduction of 1:1 Hydrazine Adduct

The isolation of **3-BBN** provided a platform to probe whether N_2H_4 coordination to the iron center was a requirement for N-N bond scission. The hypothetical product of hydrazine N-N bond scission, an amido-borane ($R_3B-NH_2^-$), are typically synthesized by ammonia-borane

deprotonation.^{62–64} We set out to assess whether isolation of these types of species was viable with this ligand platform. Addition of a THF solution of NH_3 to **2-BBN** affords the red ammonia-borane complex, $(^{\text{BBN}}\text{CNC})\text{Fe}(\text{CO})_2(\text{NH}_3)_2$ (**5**). Spectroscopic analysis revealed **5** is analogous to **4** with diagnostic NMR resonances (C_6D_6 : ^{11}B : -5.04 ; ^1H : 0.58 ppm (B-NH_3)) and infrared (KBr) $\nu(\text{CO})$ absorptions ($1889, 1821\text{ cm}^{-1}$). Addition of two equivalents of $\text{KN}(\text{SiMe}_3)_2$ to a freshly thawed THF solution of **5** affords the red amido-borane complex, $[\text{K}(\text{THF})]_2[(^{\text{BBN}}\text{CNC})\text{Fe}(\text{CO})_2(\text{NH}_2)_2]$ (**6**). Investigation of **6** by ^1H NMR spectroscopy (C_6D_6) revealed a C_{2v} symmetric species—consistent with the amido-borane motif *not* interacting with iron—with the $-\text{NH}_2$ resonance at -0.85 ppm. The ^{11}B NMR resonance in **4** is shifted upfield, relative to **5**, to -11.24 ppm. The infrared spectrum (KBr) reveals carbonyl ligands that are more activated ($\nu(\text{CO}) = 1871, 1801\text{ cm}^{-1}$) in comparison to **5**. The additional carbonyl activation in **6** is cation dependent: $\nu(\text{CO})$ absorptions shift to 1860 and 1794 cm^{-1} for the sodium analogue and upon half encapsulation of the potassium cations with 18-crown-6 to 1900 and 1839 cm^{-1} .

Single X-ray quality crystals of both **5** and **6** (18-crown-6 encapsulated variant) were analyzed for comparison (Figure 6B). The metrical parameters for the primary sphere environment for both complexes are analogous ($\tau_5 = 0.47$ and 0.46 for **5** and **6**, respectively). Each contain pyramidalized trialkylborane pendants (**5**: $\Sigma\text{B}_{1\alpha} = 335.4(6)$, $\Sigma\text{B}_{2\alpha} = 336.1(6)$; **6**: $\Sigma\text{B}_{\alpha} = 332.7(8)^\circ$) that interact with an ammonia (**5**: $\text{B-NH}_3 = 1.671(9)$ and $1.654(10)\text{ \AA}$) or an amido (**6**: $\text{B-NH}_2 = 1.615(11)\text{ \AA}$). The captured ammonia molecules in **5** engage in intermolecular hydrogen bonding interactions with THF solvate molecules while the amido substituent in **6** coordinates to the crown ether encapsulated potassium ($\text{N-K} = 2.792(10)\text{ \AA}$).

We attempted to prepare the amido-borane complex, **6**, through chemical reduction of captured hydrazine in **3-BBN**. Addition of two equivalents of KC_8 to a freshly thawed THF slurry of **3-BBN** gradually afforded a homogenous red solution. ^1H NMR spectroscopy revealed a mixture that does not contain either **5** or **6** (Figure 6A).⁶⁵ To probe whether NH_2^- (or NH_3) equivalents were formed, the reaction was quenched with HCl and the amount of NH_4Cl produced was quantified by ^1H NMR spectroscopy.⁶⁶ Each molecule of **3-BBN** can produce a maximum of two equivalents of NH_2^- if homolytic N-N cleavage occurs^{30,67} or between $4/3$ and $2/3$ equivalents for either limiting disproportionation pathways.^{68,69} Following reduction, quenching with HCl produced minimal NH_4^+ (0.08 equivalents, average of three runs, see SI). The digestion method was verified by quenching samples of **6**. Treating samples of **6** with HCl followed by ^1H NMR analysis confirmed each equivalent of **6** produces 1.83 equivalents of NH_4^+ (91.5% yield; average of 4 samples, see SI). These studies show that Lewis acid captured hydrazine cannot be reduced to NH_2^- equivalents if coordination to the metal center is inhibited.

CONCLUSION

Lewis acidic boranes were appended to a pyridine(dicarbene) ligand framework through late-stage hydroboration to circumvent the Lewis acid/base pair incompatibilities between the carbene and boron Lewis acid. The nature of the Lewis acid has consequences on the ability of the molecule to capture hydrazine: weakly acidic $-\text{BPin}$ is incapable of

sequestering N₂H₄, while sterically encumbered –BCy₂ and –B(sia)₂ Lewis acids favor oligomeric N₂H₄ capture. Only the moderately acidic and sterically accessible –BBN fragments enable hydrazine capture within a single ligand platform.

By incorporating substitutionally inert carbonyl ligand on the pincer dicarbene iron complex, insight into the reduction of the captured hydrazine was probed. Hydrazine reduction to NH₃ equivalents was completely suppressed by eliminating the possibility for N₂H₄ coordination to the metal (Figure 7). These findings demonstrate that hydrazine coordination to the metal center is a requirement for productive bond scission. The lack of N-N homolysis in this system augments our prior study of the reductive N-N cleavage in (BBN^tPDP^t)FeBr₂(N₂H₄). In that case, upon reduction, the captured hydrazine molecule must migrate to the metal center to effect N-N cleavage. This reduction sequence requires dissociation of hydrazine from the appended borane concomitant with coordination to iron, and is only possible when employing moderately Lewis acidic fragments (9-BBN). Control of Lewis acidity is a critical design aspect necessary to enable both substrate capture and subsequent substrate/product release.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

This work was supported by the NIGMS of the NIH under award numbers 1R01GM111486–01A1 (N.K.S.) and F32GM126635 (J.J.K.). N.K.S. is a Camille Dreyfus Teacher–Scholar. X-ray diffractometers were funded by the NSF under award number CHE 1625543 (M.Z.).

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SYNOPSIS

Coordinatively saturated Fe(0) complexes bearing flexibly appended boron moieties synthesized by two methods. N₂H₄ capture by the Lewis acids is depended on both the acidity and steric profile about boron. A substitutionally inert primary coordination sphere hydrazine N-N bond cleavage upon reductions by preventing a Fe-N₂H₄ interaction.

Figure 1.
Methods used to install boron Lewis acids in this work.

Figure 2.

Metalation of CNC ligand to afford compounds **1** and subsequent reduction to form **2-allyl** and **2-BPin**. Right: Molecular structures of **1-allyl** and **2-allyl** displayed with 50% probability ellipsoids. Hydrogen atoms not attached to allylic moiety are omitted for clarity.

Figure 3.

Top: hydroboration of **2-allyl** to afford **2-BR₂**. Bottom: molecular structures of **2-BPin**, **2-BBN**, **2-sia₂B**, and **2-BCy₂**. **2-BPin** and **2-sia₂B** are displayed with 30% probability ellipsoids while **2-BBN** and **2-BCy₂** are displayed with 50%. Hydrogen atoms have been removed for clarity and select carbon atoms are displayed in wireframe.

Figure 4.

Capture of N_2H_4 with sterically encumbered borane Lewis acids, **2-sia₂B** and **2-BCy₂**.

Bottom: molecular structure of **3-BCy₂** displayed with 50% probability ellipsoids. Hydrogen atoms not attached to nitrogen are omitted and cyclohexyl groups are displayed in wireframe for clarity.

Figure 5.

Top: capture of one and two equivalents of N_2H_4 . Bottom: synthesis of

$(\text{BBN}^-\text{CNC})\text{Fe}(\text{CO})_2(1,4\text{-diaminobutane})$ and molecular structures of **4** and

$(\text{BBN}^-\text{CNC})\text{Fe}(\text{CO})_2(1,4\text{-diaminobutane})$ displayed with 50% probability ellipsoids.

Hydrogen atoms not attached to nitrogen are omitted for clarity and BBN substituents are displayed in wireframe.

Figure 6.

A) Reduction of **3-BBN** does not afford NH_x equivalents. Synthesis of model amido-borane complex, **6**. B) Molecular structures of **5** and **6** displayed with 50% and 30% probability ellipsoids, respectively.

Figure 7. Requirements of the primary coordination sphere to accommodate N-N homolysis of captured hydrazine.