Published in final edited form as:

Eur J Inorg Chem. 2019 April 16; 2019(14): 1861–1869. doi:10.1002/ejic.201900133.

Dinitrogen Activation and Functionalization using β -Diketiminato Iron Complexes

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Abstract

Iron catalysts are adept at breaking the N–N bond of N₂, as exemplified by the iron-catalyzed Haber–Bosch process and the iron-containing clusters at the active sites of nitrogenase enzymes. This Minireview summarizes recent work that has identified a well-characterized set of multi-iron complexes that are capable of breaking and functionalizing N₂, and are amenable to detailed mechanistic studies. We discuss the redox balancing, the potential intermediates during N₂ activation, the variation of alkali metal reductant, the reversibility of N₂ cleavage, and the formation of N–H and N–C bonds from N₂.

Graphical Abstract

A series of low-valent iron complexes can break the N–N bond of N₂, followed by functionalization of the N fragments. The results of these studies give insight into the feasible pathways for N₂ activation on surfaces and in enzymes. We summarize recent work and highlight areas for future advances.

Keywords

nitrogen; nitrides; β -diketiminato complexes; alkali metals; iron

1. Introduction

Formation of ammonia (NH₃) by the reduction of N₂ has captivated the attention of researchers for decades. This vital chemical, which is used in a variety of applications including agriculture, plastics, explosives, and pharmaceuticals, is produced at a scale of

roughly 150 million tons per year.^[1] Currently the world relies on the Haber–Bosch process for the production of ammonia, which requires a metal catalyst at high temperature and pressure.^[2] Although the reduction of N_2 is thermodynamically favorable, the kinetic barrier associated with cleavage of the N–N triple bond necessitates harsh conditions in the industrial process, with temperatures ranging from 300–500 °C and pressures of 150–200 atmospheres.^[2–3] In addition, the Haber–Bosch process uses H_2 as the H source, presenting a separate challenge as the gas is currently formed via energy-intensive steam reformation of methane; however, this may be addressed in the future as cheaper, sustainable H_2 production from water becomes a viable alternative. Though the Haber–Bosch process suffers from these issues, the reaction benefits from a 97% conversion of starting materials to products^[2] as well as a perfect atom economy with N_2 and H_2 combining to generate NH_3 with no other byproducts, an ideal feature for industrial-scale processes.

The Haber–Bosch process requires the use of a metal catalyst to lower the activation energy for N_2 reduction. Various metals have been shown to catalyze the reaction, including ruthenium, osmium, uranium, and cobalt–molybdenum, however iron is used most widely in practice due to its high abundance and low cost.^[3] The mechanism of the iron-catalyzed Haber–Bosch process is commonly understood to employ iron surface sites that completely reduce N_2 into nitrides.^[3a,3c] The iron catalyst, with an average oxidation state between 0 and +1, provides the six electrons needed to fully reduce and cleave N_2 in a dissociative fashion (Figure 2, left), with H_2 providing the necessary H for the transformation into NH_3 . Potassium additives^[4] can increase the rate of N_2 adsorption on an iron surface as well as weaken the binding of ammonia to surface sites, thereby improving the catalytic activity of the surface and preventing product inhibition.^[5]

Nitrogenase enzymes are responsible for the reduction of N_2 in nature. Unlike the Haber–Bosch process, nitrogenases are able to catalyze N_2 reduction under ambient conditions, making use of the energy released from the hydrolysis of 16 ATP per molecule of N_2 .^[6] The mechanism is also quite different: in contrast to the H_2 used in the Haber–Bosch process, nitrogenases use proton and electron transfer to provide H. Nitrogenases feature sulfur-rich multimetallic clusters as active sites (FeMoco, FeVco, or FeFeco), which each have a carbide coordinated to six iron atoms in the center of the cluster,^[7] as illustrated for the Mo-containing cluster in Figure 1. In order to gain insights into its complex structure and unprecedented central carbide, synthetic chemists have attempted to independently synthesize these metalloclusters, but these efforts have so far been unsuccessful. Iron complexes with limited biomimetic features have been successfully synthesized,^[8] including various Fe–S clusters,^[9] Fe–carbide complexes,^[10] Fe– N_2 complexes with S- or C-supporting ligands,^[11] as well as Fe complexes with bridging hydrides to mimic catalytic intermediates in the nitrogenase cycle.^[12]

Ammonia formation in nitrogenase requires cooperation between the catalytic cofactor and nearby amino acid residues, which provide hydrogen bonding and/or proton relay functions.^[6a, 6b] The mechanism of enzymatic N_2 reduction is still debated, and two possible pathways have been put forth in the literature: alternating and distal (Figure 2, right).^[13] In the alternating pathway, N_2 initially binds to iron (or several iron atoms) and H atom equivalents are sequentially delivered to the nitrogen atoms in an alternating fashion to produce

ammonia in the last two steps. The distal pathway proposes that the distal nitrogen atom is reduced and protonated first after coordination to iron, ultimately resulting in N–N bond cleavage and formation of an iron nitride. Further reduction of this species leads to release of ammonia in the remaining steps of the mechanism. It is important to note that these pathways are two extremes and there could be crossover between the two.^[14]

Even though the mechanisms are different, both the Haber–Bosch process and nitrogenase make use of multiiron active sites for N₂ reduction. The mode of N₂ activation is not fully understood in either case, but extensive studies with small-molecule model systems have resulted in several plausible binding modes. These options include end-on binding of N₂, η^2 coordination, and end-on and/or side-on bridging modes.^[6b, 8, 15] In the case of nitrogenase, a diiron site for N₂ coordination and reduction recently has been supported in the vanadium-iron nitrogenase enzyme by a crystal structure where one of the belt sulfides is displaced from the cluster.^[16]

In the Haber–Bosch mechanism, the rate-determining step is N–N bond cleavage to form two nitrides.^[3c] With this in mind, many researchers have sought to synthesize complexes that can efficiently cleave the strong N–N triple bond. Several systems have been reported in the literature that use a dissociative mechanism to cleave the N–N triple bond into two nitrides before protonation or functionalization occurs (Figure 3, top).^[17] Cummins and coworkers reported a molybdenum(III) tris-anilide system which reacts with N₂ to form a terminal molybdenum(VI) nitride.^[17a, 17b] Pincer complexes have also been observed to promote N₂ cleavage, with Silantyev *et al.* reporting a system using a molybdenum(IV)-PNP pincer complex that forms a terminal molybdenum(V) nitride upon dinitrogen cleavage.^[17f] Bridging nitrides can also be formed from dinitrogen cleavage. For example, the Kawaguchi group reported a niobium system that cleaves N₂ to result in a diniobium complex with bridging nitrides,^[17c] as well as a vanadium system which also forms bridging nitrides.^[17d] Each of these systems react with dinitrogen at ambient room temperature but use expensive or relatively scarce metals.

Iron systems have also been reported to activate N₂ (Figure 3, bottom), and these are an ideal alternative due to iron's low cost and high natural abundance. Peters and coworkers have reported several iron systems that can bind and catalytically reduce N₂ to ammonia,^[14,18,19] including partially biomimetic systems that contain an Fe–C or an Fe–S bond.^[11g, 11h, 11k, 19] Similar to the molybdenum(IV)-PNP system mentioned earlier,^[17f] an Fe^I-PNP pincer complex was reported by Kuriyama *et al.* that can also bind N₂ and catalytically reduce it to NH₃.^[20] It is unclear if the transformation follows an alternating or distal pathway, although the authors suggest the possibility of an alternating/distal crossover pathway as demonstrated by the Peters group.^[14] These reported iron systems do not directly cleave the N–N triple bond to form a nitrido species, though the microscopic reverse reaction of the disproportionation of N₂H₄ to produce N₂ and NH₃ has been observed,^[11k] suggesting that N–N bond cleavage is possible. It is also worth pointing out that each of these systems bind N₂ in a monometallic fashion. There is evidence for both nitrogenase and the Haber–Bosch process that several iron atoms are involved in the reduction of N₂, motivating the desire to understand multiiron N₂ cleavage via a dissociative mechanism.

Herein, we overview our group's contributions to the area of N₂ activation and functionalization using a series of iron β -diketiminato complexes.

2. Isolation of an Iron Bis(nitride) Complex

2.1. Synthesis and Characterization

In 2011, we reported the first iron system to completely cleave N₂ into nitrides, in a system that makes use of a multinuclear iron core.^[21] Under an atmosphere of N₂, reduction of an iron β -diketiminato starting complex (**1**) with two molar equivalents of KC₈ in tetrahydrofuran (THF) yields the bis(nitride) product **2-K** (Scheme 1). Analogous formation of **2-K** under an atmosphere of ¹⁵N₂ yields the ¹⁵N isotopologue as demonstrated by protonation to ¹⁵NH₃ (see below), indicating that the nitrides are directly derived from dinitrogen.^[21] When an otherwise identical reaction is performed under an atmosphere of Ar, formation of **2-K** is not observed, further supporting that atmospheric N₂ is essential to form the nitride product. This system provided key experimental evidence that multiiron active sites can lower the barrier for complete scission of N₂.

Complex **2-K** was characterized using a variety of different spectroscopic and crystallographic techniques. X-ray crystallography gave the molecular structure of **2-K**, showing a triiron core surrounding two bridging nitrogen atoms with a long N–N distance of 2.799(2) Å that indicates the absence of a N–N bond. The structure also features a fourth “dangling” iron β -diketiminato fragment bound to the chlorides.^[21] The ¹H NMR spectrum of **2-K** is consistent with the solution-state structure of **2-K** having the tetrairon structure of its crystalline form, and the solubility of this complex in nonpolar solvents such as hexanes and diethyl ether indicates that the potassium cations are held within the structure in solution. Analysis of the zero-field Mössbauer spectrum indicates that **2-K** has two equivalent high-spin tetrahedral Fe^{III} sites and two distinct high-spin Fe^{II} sites (one planar and one quasi-tetrahedral). These Fe^{II} sites were assigned as the leftmost and rightmost Fe in the structure at the right of Scheme 1, while the Fe^{III} sites are in the top and bottom positions where they can bind to two nitrides.

During the synthesis of **2-K**, addition of KC₈ to the solution of the chloride dimer **1** in THF at –110 °C leads to an immediate color change of the reaction mixture from yellow to green, before eventually turning brown upon warming to room temperature. This initial color change possibly indicates the formation of an intermediate that progresses to the bis(nitride) product after the reaction mixture warms. Attempts to isolate and characterize this “green intermediate” have so far been unsuccessful; however, a reasonable working hypothesis is that the dominant species is a highly reactive Fe^I species. The “green intermediate” does not form under an Ar atmosphere, suggesting that N₂ is present in the intermediate.

2.2. Mechanistic Details of N₂ Cleavage

Though experimental characterization of the intermediates has not yet been possible, density functional theory (DFT) calculations can be used to provide a basis for an understanding of the roles of the K⁺ cations and added electrons, by suggesting feasible structures of the “green intermediate” during the mechanism of nitride formation.^[22] These computations

used a truncated model where ligand substituents were replaced with hydrogens. This severe limitation could give unreasonable structures because it ignores steric influences of the supporting ligands and electronic influences of cation- π interactions, but despite these caveats helps to understand what core structures are reasonable. Sequential addition of Fe^I fragments around a molecule of N₂ indicated that the most energetically favorable binding mode of dinitrogen has three Fe^I fragments bound in an end-on/end-on/side-on fashion (EES; Scheme 2, left). The binding of three Fe^I lengthens the N–N bond more than two Fe^I. Isomerization of the EES triiron species with a bridging N₂ ligand into the ESS (end-on/side-on/side-on) species with cleaved nitrides (Scheme 2, right) has a low barrier, suggesting that this is a reasonable mechanistic step. The ESS geometry has cleaved the N–N bond and resembles the core structure of the final bis(nitride) product **2-K**, but due to the presence of an apparent strained Fe–N double bond in the structure of the ESS-bis(nitride) isomer, the EES-dinitrogen species was still calculated to be more stable. Thus, three Fe^I alone are not enough to cleave the N–N bond.

Since the K⁺ cations interact with the nitrides,^[21] their role in the cleavage of N₂ was probed in this computational system. Addition of a K⁺ cation to the EES and ESS triiron species showed that K⁺ stabilizes the ESS-bis(nitride) product relative to the intact dinitrogen product (K⁺ binding is exergonic by 19 kcal/mol and 30 kcal/mol, respectively); however the EES-dinitrogen species is still more stable by 12 kcal/mol.^[22]

To simulate the reduction of the system by a fourth Fe^I (which leads to the “dangling” Fe^{II} in the final structure), an electron was added to the different triiron isomers. Once again, the largest effect was seen in the ESS-bis(nitride) product where the added electron occupies a bonding Fe-nitride orbital.^[22] Once a K⁺ ion was added to the reduced species, the DFT calculations showed that the ESS-bis(nitride) species was finally more stable than the EES-dinitrogen product by 3 kcal/mol, with the ESS-bis(nitride) species having a similar core structure to the experimentally-derived crystal structure of **2-K** (Scheme 2). These results indicate that for this iron β -diketiminate system, at least three Fe^I, a K⁺ cation, and an electron are sufficient for complete N–N cleavage.

3. Reactions with the Bis(nitride) Species

3.1. Reforming N₂ After Cleavage

Isolated **2-K** has a short half-life of eight hours in benzene solutions at 25 °C; however, purified crystalline samples are stable at –40 °C for roughly one month with no discernable decomposition.^[21] The decomposition product in benzene was discovered to be the Fe^I arene complex **3a** (Scheme 3). The formation of this product is the result of intramolecular nitride coupling to reform N₂.^[23] The spontaneous decomposition of an Fe^{II}Fe^{III} species to an Fe^I product was surprising since the N–N cleaving reaction requires only the number of electrons necessary to attain the Fe^I level,^[21] indicating that the active species in the reduction of N₂ is also an Fe^I species (at the oxidation level of the “green intermediate” discussed above). However, Mössbauer spectroscopy showed that the arene-bound decomposition product from **2-K** is low-spin Fe^I in contrast to the “green intermediate” which has no access to strong-field ligands and is presumably high-spin. This suggests that the stronger binding of the π -acceptor arene to the Fe^I fragment changes the

thermodynamics such that the product from N₂ cleavage is no longer more stable. Notably, the ability of the N₂ cleaving reaction to proceed in the opposite direction at room temperature suggests that both N–N cleavage and N–N formation have low barriers, though these barriers were not quantitatively measured.

The conversion of **2-K** to the decomposition product **3a** was catalyzed by pyridine, indicating that this more slender Lewis base is kinetically more facile for dismantling the triiron core. (A series of pyridine complexes, which are stable only in the absence of arenes, were later characterized.)^[24] When linear Lewis bases such as CO or CNXyl (2,6-dimethylphenyl isocyanide) were added to solutions of **2-K** in benzene, new Fe^I complexes were rapidly formed, bearing three equivalents of the Lewis base (**3b** and **3c**, respectively).^[23] The rate of conversion in these reactions was thus roughly dependent on the cone angle of the attacking reagent (CO > CNXyl >> pyridine > benzene). In the CO and CNXyl reactions, the Fe^I products accounted for 94–97% of the iron-containing products, indicating a complete six-electron reduction of all iron sites in **2-K** back to Fe^I. The stabilization of Fe^I by π -accepting ligands as well as the precipitation of KCl and release of N₂ helps drive the reaction, while the use of multiple iron centers helps to lower the barrier of N₂ formation (and cleavage in the reverse direction).

The production of 1.00 ± 0.04 mol of gas per mol of **2-K** was measured using manometry in reactions with isocyanides, and the identity of the gas was confirmed by GC-MS indicating quantitative reformation of N₂. Isotopic labelling studies with both ¹⁴N- and ¹⁵N-labeled **2-K** showed production of ¹⁴N₂ and ¹⁵N₂ with no mixed isotope ¹⁴N¹⁵N observed,^[23] indicating that the nitride coupling is an intramolecular process with no exchange of the nitride ligands between complexes. In addition, exchange of the nitride ligands with atmospheric N₂ was observed in neither solution nor solid state. Though this system of cleavage and reformation of N₂ is an interesting result, the main point of focus on the bis(nitride) **2-K** was how to move forward in forming new molecules from the atmospherically-derived nitrides.

3.2. Protonation and Ammonia Formation

An aspect of great importance for many N₂ activation systems is their ability to produce NH₃. Treatment of **2-K** with excess ethereal HCl yields NH₄⁺ in $82 \pm 4\%$ yield,^[21] demonstrating the reactivity of the nitrides and the ability of the β -diketiminato system to form ammonia. Ideally this reaction would be performed using H₂ as the hydrogen source to improve the atom economy of the reaction and mimic the Haber–Bosch process. The reaction between **2-K** and H₂ in benzene, however, yields no ammonia, instead producing a complex mixture with two dominant species: the hydride dimer **4** along with the known Fe^I arene complex **3a** (Scheme 4).^[25] It is likely that the complex releases N₂ and forms an Fe^I complex that could generate most of these byproducts. Treatment of the final reaction mixture with strong acids yields no ammonia or hydrazine, indicating that the nitride ligands are no longer present after the reaction with H₂.

Though treatment of **2-K** with anhydrous HCl does produce ammonia in good yields,^[21] one undesired result of this reaction is the ultimate loss of the β -diketiminato ligand, limiting the

prospect of making this reaction catalytic. Protonation reactions with various weaker acids were performed to find other proton sources that keep the ligand-iron core intact, and also to study the basicity of the nitride ligands. Though strong acids generally gave the highest yields of ammonia, no trend was noticed between pK_a and ammonia production, and the solubility of the acid did not have a systematic influence on ammonia yields either.^[25] In one exciting aspect to these studies, 2,4,6-tri-*tert*-butylphenol (TBP) was identified as an acid that yields substantial amounts of ammonia yet does not displace the β -diketiminate ligand. Using TBP, several partially protonated intermediates (NH, NH₂) were observed by ¹H NMR spectroscopy. These intermediates allowed for greater mechanistic insight into the individual steps towards ammonia production and the possibility of electrocatalytic N₂ reduction.

Four different intermediate species were observed in the transformation of the nitride ligands on **2-K** to free molecules of NH₃, shown in Scheme 5.^[25] First, proton transfer occurs to yield the nitride/imide species **5**, followed by a proton-coupled electron transfer (PCET) reaction to yield the nitride/amide species **6**. Protonation and reduction of **6** gives the bis(amide) species **7**, and final protonation of the amide ligands allows for the release of ammonia.

The protonation of one nitride to yield **5** could be carried out using a variety of different external proton sources. TBP protonated the nitride **2-K** in 78% yield, though terminal alkynes were shown to give the highest selectivity of **5** (Scheme 6).^[25] The observation of an acetylide product as well as the imido species **5** indicates a redox-neutral transformation of the two Fe^{II}- and two Fe^{III}-containing starting complex to the one Fe^{II}- and two Fe^{III}-containing imido species as well as the Fe^{II} alkynyl complex. The triiron core of **5** is very similar in both electronics and structure to **2-K**, as evidenced by very similar Mössbauer spectra and Fe–N bond lengths in crystal structures.^[21] Importantly, **5** is stable with respect to loss of N₂, in contrast to **2-K**. Thus, formation of the first N–H bond (and removal of the alkali metals) detracts from the inability to reductively eliminate N₂.

Mixing isolated samples of the imido species with TBP leads to the formation of the nitride/amide species **6** via proton-coupled electron transfer (PCET).^[25] A lengthening of the Fe–N bonds with the μ_2 -bridging N suggested the addition of a second proton. This was supported crystallographically by observation of the two hydrogen atoms in the difference map, and also spectroscopically by the observation of stretches at 3375 and 3299 cm^{–1} in the infrared spectrum of **6**, consistent with an amide ligand. The Mössbauer spectrum of **6** indicates that one of the Fe^{III} atoms in **5** is reduced by one electron to Fe^{II}, rendering the reaction a formal H atom transfer. The 2,4,6-tri-*tert*-butylphenoxyl radical that is expected from the H atom transfer was not observed, but this may be a result of its reaction with other species in the reaction mixture.

Attempts to discern if this PCET reaction occurs in a stepwise or a concerted fashion with TBP proved inconclusive. The one-electron reduced version of **6**, which would be the intermediate in the ET/PT stepwise pathway, was observed using KC₈ and indene via electrochemical processes.^[25] This suggests that the stepwise pathway is feasible, though it does not rule out a concerted pathway when the reaction is done with TBP.

The next observable “step” which transforms the nitride/amide **6** into the bis(amide) complex **7** using TBP requires two proton-transfer and one electron-transfer steps, and no intermediates are observed. This suggests that the first of these reaction steps is rate-limiting with the following steps occurring in rapid succession, although the sequence of these steps has yet to be determined. Analysis of the crystal structure of **7** shows that the Fe–NH₂ bond lengths for both amido groups to be similar to those of the amide Fe–NH₂ bond length in **6**.^[25]

Finally, the release of ammonia from **7** can be achieved with weaker acids while keeping the iron β -diketiminato ligand intact. The fate of the resulting iron-containing product then depends on the reagent used.^[25] For example, treating **7** with 2 equivalents of H₂O generates ammonia in 98% yield, along with the bridging hydroxide dimer of the iron β -diketiminato, [LFe(μ -OH)]₂ (L = 2,4-bis(2,6-dimethylphenylimino)-3-methylpent-3-yl). When 2 equivalents of TBP is used, the yield of ammonia is still high at 93% and the resulting iron-containing product is the iron aryloxide complex **8**. As noted above, TBP is able to carry out each step in the formation of ammonia, though the Fe^{II} compound **8** does not proceed to **2-K**, preventing catalysis with this system.

Comparison of the transformation of N₂ to NH₃ using the iron β -diketiminato system to the industrial-scale heterogeneous Fe catalyst shows the advantages and disadvantages for both. While the Haber–Bosch process requires high temperature and pressures in order to overcome the kinetic barrier of cleaving the N–N triple bond,^[2] each step in the β -diketiminato system is run at or below room temperature, indicating the system’s ability to facilitate N₂ scission under milder conditions. However, this is accomplished by using a much stronger reductant (KC₈ vs. H₂), and this seems to be a major factor preventing turnover in a catalytic cycle. Both systems achieve ammonia formation by initial cleavage of N₂ to nitrides followed by subsequent protonation steps, but the use of H₂ as an H source in the Haber–Bosch process instead of external acids allows for a milder reductant.

3.3. N–C Bond Formation and C–H Activation

The bis(nitride) complex **2-K** also participates in other noteworthy reactions. The reactivity of the nitrides in **2-K** can be greatly increased by removing the K⁺ cations with two equivalents of 18-crown-6 to remove the dangling iron (observed as **10**), and exposing a “naked” bridging nitride (Scheme 7).^[26] Without the cations to stabilize the negative charge on the nitride, the site becomes much more adept at nucleophilic attack. For example, 1 equivalent of methyl tosylate (MeOTs) reacts very slowly with **2-K**, but when 18-crown-6 is introduced to a mixture of **2-K** and MeOTs, the bridging methylimido complex **11** is rapidly formed, yielding a new N–C bond.

Without any additives, this exposed nitride deprotonates a benzylic proton on one of the aryl substituents of a β -diketiminato ligand in an intramolecular reaction; a new Fe–C bond is also formed to give the final product **12**.^[26] The Mössbauer spectrum of **12** shows three quadrupole doublets with analogous isomer shifts to the initial complex **2-K**, consistent with two high spin Fe^{III} ions and one high spin Fe^{II} ion. Thus, the reaction is redox neutral, consistent with a deprotonation rather than hydrogen atom abstraction. Similar

intramolecular deprotonation reactions can be performed starting from complexes **5** and **6** as well, though in each case the cluster must be reduced to a potassium salt of an anionic complex in order to perform the ligand activation; it is possible that the anionic charge on the complex adds to the basicity of the N atoms which allows them to deprotonate the benzylic carbon ($pK_a \sim 42$). This reactivity is not seen with 1,4-cyclohexadiene, showing the inability of the nitride to abstract an H atom from the weak C–H bonds of the diene, providing evidence against an H atom transfer pathway.

4. Alkali Metal Cation Variation

Though the majority of the experiments with the iron β -diketiminate system have used K^+ cations, N_2 reduction/cleavage can also be achieved using Na and Rb reductants, namely RbC_8 and Na^0 powder (Scheme 8).^[27] Attempts to synthesize and isolate the Li analogue of the bis(nitride) complex have proven unsuccessful; a new species was briefly observed in the 1H NMR spectrum when using Li metal but could not be isolated, suggesting that the Li analogue of complex **2-K** is highly unstable. Reaction with CsC_8 yielded a completely different core structure with three partially-reduced bridging N_2 units; a fully cleaved bis(nitride) structure consistent with **2-K** using Cs^+ cations was hypothesized to be unfavorable due to geometric constraints from the cation- π interactions which limits only two Fe fragments to be able to approach N_2 , less than the required three Fe fragments needed as discussed above.^[22]

The Mössbauer spectra of the three different fully cleaved nitride complexes show a similar electron structure in the triiron cores.^[21, 27] The spectrum of **2-Rb** is nearly identical to that of **2-K**, similarly indicating two equivalent high spin Fe^{III} sites and two different high spin Fe^{II} sites. The spectrum of **2-Na** contains features indicating two equivalent high spin Fe^{III} sites, but only one feature indicating a single high spin Fe^{II} site. The X-ray crystal structure explained this because there is no “dangling” iron β -diketiminate fragment, and only one alkali metal cation; two molecules of THF complete the coordination around sodium.^[27] This lack of a fourth iron fragment in the structure leads to an apparent imbalance of electrons between the six e^- reduction of N_2 and the five e^- oxidation of three Fe^I ions. However, a significant amount of **1** is observed in the final reaction mixture with sodium, suggesting that a fourth Fe^I fragment acts as a reducing agent and is oxidized to an Fe^{II} chloride, similarly to the K and Rb analogues. However, in the case of Na, this Fe^{II} chloride fragment dissociates from the nitride structure to give the iron-chloride complex as a byproduct. This trend was explained by noting that Na^+ is smaller than K^+ and Rb^+ , and it does not hold the “dangling” Fe^{II} as well as the K and Rb analogues.

With the exception of the missing fourth iron fragment in **2-Na**, the core geometries of the three alkali metal cation analogues are similar. However, there are slight variations in the bond distances between the alkali metal cations and their bound nitrides. Notably, the Rb–N bond distance in **2-Rb** is significantly shorter (1 Å) than the analogous K–N bond distance in **2-K**.^[27] This is likely due to the longer M- π coordination between the Rb^+ cation and the arene substituents on the β -diketiminate ligand, which pushes the Rb atoms closer to the nitride and suggests that the Rb^+ cation fills the alkali metal pocket better than K. Though

the Na–N bonds in **2-Na** are shorter than both the K and Rb analogues, the Na is held asymmetrically, and presumably contributes less to the stability of the complex.

Stability tests on the three analogous complexes showed that the rate of decomposition of **2-Rb** is slower than **2-K**.^[27] The extra stability of the Rb analogue can be explained by the reasoning (see above) that the Rb⁺ cation fills the alkali metal cation pocket better than a K⁺ cation, which holds the core of the structure together better and may slow benzene attack/N₂ reformation in the decomposition. The decomposition rate of **2-Na** is faster than the K and Rb analogues, which might be due to a different decomposition mechanism without the fourth iron fragment which is needed to re-form N₂ with formation of four Fe^I.

When anhydrous HCl is introduced to a solution of the bis(nitride) complexes, the nitrides can be protonated to release ammonia, as explained previously. The yields of ammonia from **2-K** and **2-Rb** are comparable ($82 \pm 4\%$ and $73 \pm 1\%$, respectively), though in the case of **2-Na**, ammonia yields are quantitative ($99 \pm 2\%$).^[21, 27] This difference in yields can be attributed to the limited ability of **2-Na** to unproductively reform the N–N triple bond.

5. Conclusions

In conclusion, this iron β -diketiminate system has led to a series of new discoveries in the area of Fe–N₂ chemistry. Not only can it cleave the N–N triple bond, but it also enables functionalization of the resulting nitrides, forming new N–C bonds and breaking sp^3 C–H bonds, and can even reform the N–N triple bond. The ability to isolate intermediate protonated species, and the detailed mechanistic studies following dinitrogen reduction, have given insight into the ways in which Fe interacts with N₂ and demonstrates the importance of alkali metal cations and multimetallic cooperativity for facilitating N₂ reduction. Since this system was first reported, Murray and coworkers have reported another multimetallic β -diketiminate system which achieves N₂ activation using tricopper and triiron complexes (Scheme 9).^[28] Notably, Murray's triiron complex is able to completely cleave the N–N triple bond in dinitrogen, yielding NH and NH₂ ligands derived from N₂.^[28b] Mechanistic work has been performed on this N₂ cleaving system, including the synthesis of a μ_3 -N species that mimics a potential intermediate in N₂ activation.^[28d] Murray has also shown that the triiron system can catalyze the reduction of N₂ in the presence of excess KC₈ and trimethylsilyl chloride (TMS-Cl), forming N(TMS)₃ in yields up to 87 equivalents per complex.^[28e] In addition, Murray has delved into more biologically-relevant nitrogenase chemistry, reporting several FeS clusters using these β -diketiminate systems to learn more about the potential roles of bridging sulfides in nitrogenase enzymes.^[9c, 29] These reports display the ability of β -diketiminate ligand systems to push the boundaries of Fe–N₂ chemistry while also expanding the field into other first-row transition metals.

There are still avenues using this system that have yet to be travelled and could lead to more exciting discoveries. The susceptibility of the bis(nitride) **2-K** to electrophilic attack leads to new N–C bonds from N₂, and one could imagine using other electrophiles to form more complex organic compounds, with abundant atmospheric N₂ serving as the nitrogen source. The characterization of the reactive Fe^I “green intermediate” would not only be mechanistically insightful, but would additionally aid in the design of more stable and

efficient iron systems for N₂ activation. Attempts to make NH₃ production catalytic using **2-K** is another route to be explored, using different reductants that reduce the Fe^{II} product **8** back into the active Fe^I intermediate in order to cleave another molecule of N₂ and complete a catalytic cycle. Modification of the β -diketiminato ligand to reduce the degradation in the presence of proton sources is another potential future direction, and it might even be possible to design proton relays into the ligand to allow NH₃ production from a wider variety of acids.^[30] We anticipate that this iron β -diketiminato system will continue to be a standout model in the field of dinitrogen activation.

Acknowledgments

The authors thank Sean McWilliams and Kazimer Skubi for valuable feedback on the manuscript. We acknowledge financial support from the National Institutes of Health (GM065313).

Biography

Samuel Bhutto obtained his B. Sc. in Chemistry from Brandeis University in 2016, under the supervision of Prof. Casey Wade. He is currently a PhD student in inorganic chemistry at Yale University in the group of Patrick Holland, and his research focuses on dinitrogen functionalization using iron β -diketiminato complexes.

Patrick Holland trained under Robert Bergman, Richard Andersen, and William Tolman, and brought the resulting mechanistic skills to the study of N₂ activation in his independent academic career at the University of Rochester (2000–2013) and Yale University (2013–present). His research aims to demonstrate the abilities of iron complexes for activating and forming strong bonds in chemistry.

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Figure 1.
Active site of the iron–molybdenum nitrogenase enzyme.

Figure 2. Cleavage of N_2 in the Haber-Bosch process via a dissociative mechanism (left) and pathways for NH_3 production in nitrogenase (right).

Schneider, 2017

Kawaguchi, 2014

Nishibayashi, 2016

Peters, 2014

Figure 3.
Examples of metal complexes derived from fixation of N₂.

Scheme 1.
 N_2 activation by an iron β -diketiminato complex.

Scheme 2.

Equilibrium between triiron EES-dinitrogen (left) and ESS-bis(nitride) (right) suggested by DFT calculations with a truncated model.

Scheme 3.

Formation of N_2 through nitride reductive elimination yields reduced Fe^{I} species.

Scheme 4.
Non-productive hydrogenation of bis(nitride) **2-K**.

Scheme 5.
Mechanistic model for NH₃ production from **2-K**.

Scheme 6.

Protonation of **2-K** to form an alkynyl product and an imido complex **5**.

Scheme 7.

N-C bond formation and C-H bond cleavage via removal of alkali cations.

Scheme 8.

Variation of the alkali metal cation in the bis(nitride) structure ($\text{M} = \text{K}, \text{Rb}$).

Scheme 9.
Dinitrogen activation using a variation of an iron β -diketiminato system