Alkali Metal Control over N–N Cleavage in Iron Complexes

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ABSTRACT: Though N₂ cleavage on K-promoted Fe surfaces is important in the large-scale Haber–Bosch process, there is still ambiguity about the number of Fe atoms involved during the N–N cleaving step and the interactions responsible for the promoting ability of K. This work explores a molecular Fe system for N₂ reduction, particularly focusing on the differences in the results obtained using different alkali metals as reductants (Na, K, Rb, Cs). The products of these reactions feature new types of Fe–N₂ and Fe-nitride cores. Surprisingly, adding more equivalents of reductant to the system gives a product in which the N–N bond is not cleaved, indicating that the reducing power is not the most important factor that determines the extent of N₂ activation. On the other hand, the results suggest that the size of the alkali metal cation can control the number of Fe atoms that can approach N₂, which in turn controls the ability to achieve N₂ cleavage. The accumulated results indicate that cleaving the triple N–N bond to nitrides is facilitated by simultaneous approach of at least three low-valent Fe atoms to a single molecule of N₂.

Synthetic complexes offer a distinctive way of gaining insight into the steps involved in N–N bond cleavage, because it is possible to characterize their structures in detail and vary the Fe environment systematically. The trends and principles discovered during investigation of synthetic complexes lay the foundation for understanding the mechanism of N₂ cleavage on surfaces and in biological systems. In this Article, we address several important questions that relate particularly to the Fe surfaces that catalyze the Haber–Bosch process: (a) What is the smallest number of Fe atoms necessary to break the N–N bond into nitrides? (b) What oxidation level of Fe atoms is needed to bring about N–N bond scission? (c) Why is K the most effective alkali metal promoter?12

There have been numerous studies on iron-N₂ complexes.13,14 However, there are only a few compounds with Fe atoms positioned close to each other that are able to address the above questions.15 In previous work, we have shown that binding of N₂ can be assisted by K⁺, both by electrostatic forces that improve backbonding into the π* orbital of N₂ and by locking two Fe atoms in close proximity.16,17 We have also reported the only Fe system that is capable of completely cleaving the N–N bond of N₂ to nitrides.18,19 The product of this reaction (1-K, Scheme 1) contains four iron atoms and two K⁺ ions coordinated to two nitrides. However, it is not yet clear whether K is unique in facilitating the N₂-cleaving reaction, and the nature of the cooperation between the transition metal and the alkali metal needs to be elucidated.

In this contribution, we address the above questions by varying the choice and amount of alkali metal in the N₂−
cleaving system. Interestingly, supplying the system with more electrons yields less \( N^-N \) bond activation, and we offer an explanation for this counterintuitive trend. In addition, we describe a new type of triiron structure with three bridging \( N_2 \) units. Our results show the utility of alkali metals for influencing small-molecule reduction reactions, which complements a growing body of work in which alkali metal or Sc cations facilitate oxidation reactions.20

### RESULTS

**K and Rb Cleave \( N_2 \) to Give \( Fe_4^- \)Nitride Complexes.**

Our survey of reductants has shown that the most effective reductants for diketiminate-iron(II) complexes are MC8 (M = alkali metal), in which excess electrons lie on the graphite and the alkali metal cations are intercalated between the layers in a known stoichiometry.21 In previously reported experiments, we treated a THF solution of \([LFe(\mu-Cl)]_2\) (L = 2,4-bis(2,6-dimethylphenylimino)-3-methylpent-3-yl) with 2 equiv of KC8, which is the appropriate stoichiometry to reduce each iron(II) to the formally iron(I) oxidation level.18 Under an \( N_2 \) atmosphere, the presumed transient iron(I) intermediates 22 perform the six-electron reduction of \( N_2 \) to two \( N_3^- \), which is balanced by the six-electron oxidation of four \( Fe^{1+} \) to \( 2 \ Fe^{2+} \) and \( 2 \ Fe^{3+} \) in the fully characterized product \([LFe]_4 Cl_2 K_2 N_2\) (1-K, Scheme 1).

Since the oxidation product \( K^+ \) was a part of the final product structure, we anticipated that changing the reductant to RbC8 might have an influence on the structure. Thus, in a new reaction we used Rb on graphite (RbC8), which under analogous conditions gives 1-Rb (Scheme 1). Specifically, a concentrated solution of the \( Fe^{2+} \) compound \([LFe(\mu-Cl)]_2\) was treated with 2 equiv of RbC8 in thawing THF (ca. \(-100 \, ^\circ C\)) under an atmosphere of \( N_2 \). After removal of solvent and extraction with hexanes, the pure product 1-Rb crystallized from cold hexanes in 48% yield. The 1-Rb compound was characterized by X-ray crystallography (Figure 1), \(^1H\) NMR spectroscopy (Figure 2), and Mössbauer spectroscopy (Table 1, Figure S3). Its Mössbauer spectrum is analogous to the one reported for 1-K18 and consists of three doublets in a 2:1:1 ratio, which corresponds to two identical \( Fe^{3+} \) ions and two different \( Fe^{2+} \) ions. The isomer shifts for each iron environment in 1-K and 1-Rb are within 0.02 mm/s, and quadrupole splittings are within 0.13 mm/s (Table 1). Thus, the electronic structures of the iron sites are very similar between the two.

The crystal structure of 1-Rb (Figure 1) displays an \( Fe_4N_2 \) core with distances and angles that are indistinguishable from those in 1-K. The main difference is in the alkali-metal part of the molecule, where the Rb–N(1) distances are 1 Å shorter than the analogous K–N(1) distances (Table 1). We attribute the much shorter distance between Rb and N(1) to the longer bonds between Rb and the \( \pi \)-coordinated arene rings (average distance of M to centroids is 3.58 Å for 1-Rb vs 3.42 Å for 1-K), which push the Rb atoms closer to the nitride. In effect, the larger Rb+ cations more completely fill the alkali-metal pockets than K+, which may contribute to the higher stability of the Rb analogue (see below).
Further studies will be necessary to determine at what site in the molecule the benzene attacks 1-K and 1-Rb.

In attempt to better understand the strength of association of K⁺ and Rb⁺ in the bis-nitride structures in solution, we reacted solutions of 1-K and 1-Rb in THF with the trifluoromethanesulfonate salts KOTf and RbOTf. Addition of KOTf to 1-Rb or RbOTf to 1-K (either 2 or 20 equiv) gives product mixtures in which the alkali metal cations are partially or completely exchanged, though there was also substantial decomposition to unknown byproducts (Figures S9, S10). It was not possible to determine equilibrium constants, because of overlap of peaks in the ¹H NMR spectra, formation of byproducts, and the low solubility of the alkali metal triflates. With these caveats, we note that 1-K is completely consumed after reaction with 2 equiv of RbOTf (Figure S9), suggesting a favorable equilibrium constant. Conversely, when 1-Rb was treated with 2 equiv of KOTf, a significant amount of 1-Rb remained (Figure S10). Addition of 20 equiv of KOTf was necessary to deplete 1-Rb and form a significant amount of 1-K. This suggests that 1-Rb is more stable than 1-K, in agreement with the slower decomposition of 1-Rb.

**N₂ Cleavage Using Sodium Yields a New Fe₃N₂ Structure.** Because of the known difficulty of intercalating Na into graphite, we explored other methods to reduce [LFe(μ-Cl)]₂ with Na. Addition of sodium amalgam to a THF solution of [LFe(μ-Cl)]₂ did not reduce the iron(II) starting material (Figure S15). As an alternative, we sonicated a mixture of [LFe(μ-Cl)]₂ and metallic Na in THF at 0 °C for 1 h, which led to a triiron complex, 1-Na (Figure 3), in 48% yield. To compare this synthetic method to the one used for obtaining 1-K (reduction by KC₈), we also sonicated metallic K in THF at 0 °C for 1 h. ¹H NMR spectra of the crude reaction mixture (Figure S17) showed 1-K as the major species, and thus the product does not seem to be influenced by the use of powdered metal vs the graphite complex. This indicates that differences in the product structures can be attributed to the change in the alkali metal, rather than the preparation method.

**Figure 3.** Thermal-ellipsoid plots (50%) of 1-Na (top) and its core (bottom). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−N(1), 1.74(1); Fe(1)−N(2), 1.88(1); Fe(2)−N(1), 1.82(1); Fe(2)−N(2), 1.84(1); Fe(3)−N(2), 1.81(1); Na(1)−N(1), 2.85(2); N(1)−Fe(1)−N(2), 96.9(6); N(1)−Fe(2)−N(2), 95.7(6).

**Table 1.** Metrical and Spectroscopic Parameters for Compounds 1

|                | 1-Na       | 1-K         | 1-Rb         |
|----------------|------------|-------------|-------------|
| Fe(1)−N(1) (Å) | 1.74(1)    | 1.81(2)     | 1.81(2)     |
| Fe(2)−N(1) (Å) | 1.82(1)    | 1.80(2)     | 1.81(2)     |
| Fe(1)−N(2)−Fe(2) (deg) | 85.8(6) | 85.27(8) | 85.6(1) |
| M(1)−M(2) (Å) | N/A        | 3.8811(9)   | 4.1029(5)   |
| N(1)−M(1) (Å) | 2.28(1)    | 3.8212(6)   | 2.825(2)    |
| N(1)−M(2) (Å) | N/A        | 4.0017(6)   | 2.872(2)    |
| δ (mm/s)       | 0.33       | 0.29        | 0.31        |
| ΔEQu (mm/s)    | 1.56       | 1.79        | 1.87        |
| δ (mm/s)       | 0.74       | 0.68        | 0.66        |
| ΔEQu (mm/s)    | 1.20       | 1.54        | 1.86        |
| δ (mm/s)       | 0.90⁴⁻⁶        | 0.96       | 0.96        |
| ΔEQu (mm/s)    | 2.29⁴       | 1.80        | 1.91        |

⁴Ref 18. ⁵Based on similarity of shifts and quadrupole splitting, we assign the tetrahedral hs Fe²⁺ signals to the starting material [LFe(μ-Cl)]₂.

The number and integration of signals in the ¹H NMR spectrum of 1-Rb (Figure 2) suggest idealized C₄ᵥ symmetry in the four-iron cluster, which agrees with the solid state crystal structure. Since both 1-K and 1-Rb are soluble in hexane, and their ¹H NMR spectra in C₆D₁₂ and C₆D₆ solutions possess the number of peaks that are consistent with the crystal structures, it is likely that in hydrocarbon solvents the Fe₄(K/Rb)₂N₂Cl₂ cores remain intact. In addition, the chemical shifts of 1-Rb are similar to those in 1-K, which for paramagnetic molecules implies similar anisotropy in the magnetic moments of the Fe ions, and a similar electronic structure. Monitoring C₆D₆ solutions by ¹H NMR spectroscopy shows that 1-K (8.1 mM) and 1-Rb (either 12.1 mM or 6.3 mM) slowly degrade at room temperature, with 1-Rb (t₁/₂ = 21 h) decomposing more slowly than 1-K (t₁/₂ = 8 h). ¹H NMR spectroscopy shows that the primary iron-containing compounds after decomposition are the known iron(I) complex LFe(C₆D₆)₂ and the previously unreported iron(II) complex L₃Fe(2). Compound 2 is a pseudotetrahedral iron(II) complex, and its X-ray crystal structure and characterization are presented in the Supporting Information (Figure S1).

At first, formation of the iron(I) product LFe(C₆D₆) from reaction of benzene with the diiron(II) diiron(III) starting materials 1-Rb and 1-K might seem surprising. However, in a recent paper we described reactions of 1-K with CO, isocyanides, and benzene, which each gave iron(I) products LFe(CO)₅, LFe(CNXyl), and LFe(C₆H₆) where the reducing equivalents come from N₃⁻ oxidation. In the cited work, the rate of reaction decreased in order of increasing cone angle of the attacking reagent, with slim CO and isocyanides giving rapid reactions, and benzene a substantially slower reaction. No intermediates are observed during any of these reactions. Assuming that the degradation reactions have the same initial steps, this trend suggests that the decomposition in benzene involves association of the benzene molecule with 1 in the transition state. This model rationalizes the higher stability of 1-Rb, where the better fit of Rb⁺ into the pockets in the tetrairon structure holds the core together and slows benzene attack.
The X-ray crystal structure of 1-Na has a relatively high R value of 8.2%, mostly from explicit inclusion of a n-hexane solvent molecule and disorder in a xylol group; this gave relatively large esd values, but did not influence the assignment of the core structure of the molecule. 1-Na is different from 1-K and 1-Rb because it lacks the fourth, tetrahedral Fe atom and has only one alkali metal cation; the coordination at sodium is completed by two THF molecules. The Na−N(1) distance is 1.5 Å shorter than the K−N(1) distance in 1-K and 0.5 Å shorter than the Rb−N(1) distance in 1-Rb (Table 1). The Na-centroid distance is also shorter at 2.745(7) Å. The FeN3 core in 1-Na is more symmetric than that in 1-K and 1-Rb (Table 1, Figure S2), and the oxidation states of iron centers may be assigned as two equivalent Fe3+ sites (Fe1 and Fe2) and one Fe2+ site (Fe3) based on the overall charge count and the similarity of the Mössbauer parameters to the analogous positions in 1-K and 1-Rb (Table 1, Figure S4).

During formation of 1-Na, there is an apparent imbalance between the reduction (6e− reduction of N2) and oxidation (se− oxidation of 3 Fe) half-reactions. However, 1-Na is not the only species that exists in the reaction mixture. One of the most prominent byproducts is [LFe(μ-Cl)]2, which is difficult to separate and thus is present in amounts up to 0.89 mol per mol of 1-Na. This iron(II) chloride dimer was identified by comparison of its 1H NMR and Mössbauer parameters to the known compound.18 We propose that the sixth electron for N2 reduction comes from an unidentified Fe4+ species that (like the fourth Fe in 1-K and 1-Rb) is oxidized to an iron(II) chloride product; however, the Na+ cation fits so poorly into the K/Rb position of the tetranuclear structure that this iron(II) chloride does not bind in an analogous fashion. Rather, in the Na system the iron(II) chloride species dissociates and dimerizes to [1Fe(μ-Cl)]2. The heterogeneous nature of the reaction has prevented us from exploring this hypothesis in greater mechanistic detail.

Interestingly, the thermal stability of 1-Na in C6D6 solution (t1/2 = 35 h) is greater than its 1-K and 1-Rb analogues, which does not fit the trend of greater stability of heavier 1-Rb over 1-K. We propose that the reaction of 1-Na with benzene is slower because the mechanism is different; after all, there are not enough Fe sites to accept the six electrons from two N2 to reform N2 in the mechanism followed by 1-K and 1-Rb.24 The 1H NMR spectra after decomposition of 1-Na (Figure S16) similarly show significant formation of LFe(C6D6), which requires an external oxidant to accept the sixth electron. However, the decomposition mixture from 1-Na is complicated, and substantial amounts of 2 and [LFe(μ-Cl)]2 are also observed.

In order to test the ability to exchange the cations in the different bis-nitride structures, we treated 1-Na (which contained some [LFe(μ-Cl)]2, as noted above) with KOTf and RbOTf (20 equiv) in THF, and analyzed the products using 1H NMR spectroscopy (Figures S11−S14). As with the K/Rb exchange reactions described above, the product mixtures had substantial amounts of unidentified decomposition products, but the characteristic 1H NMR resonances of 1-K and 1-Rb were present. Interestingly, the addition of even this large excess of KOTf gave a mixture containing residual 1-Na, which supports the idea that 1-K is less stable than 1-Na. We also treated 1-K and 1-Rb with 20 equiv of NaOTf, which entirely consumed the starting materials and gave 1-Na as a major product. These support the idea that 1-Na has greater inherent stability, though the concurrent formation of [LFe(μ-Cl)]2 complicates any thermodynamic analysis.

We have also attempted to synthesize the Li analogue of complexes 1, using the sonication method described above for 1-Na. However, we have observed that even before the beginning of reaction, Li metal tarnished upon exposure to N2 atmosphere. This result is not surprising, as it is known that Li0 reacts with N2 to yield Li3N.29 Even though a brief formation of a new complex can be observed by 1H NMR spectroscopy, we were unable to isolate this new species, even by low-temperature crystallization. 1H NMR analysis of the post-crystallization mixture showed the presence of [LFe(μ-CI)]2, LFe(μ-Cl)(THF), and 2. Therefore, we surmise that the Li analogue of complexes 1 is very unstable.

**Triron Cores with N2 Bridges.** Reduction of [LFe(μ-Cl)]2 with 2 equiv of cesium graphite (CsC6) did not yield the Cs analogue of 1-K, but instead gave a trinuclear complex 3-Cs with two N2 units bound in an end-on/end-on mode (Figure 4). This compound has not been obtained in pure form. The presence of one Cl− bridge in the structure suggested incomplete reduction of the starting material.

![Figure 4. Thermal-ellipsoid plots (50%) of 3-Cs, from two views.](image-url)

Hydrogen atoms omitted for clarity. 3-Cs has crystallographic D3 symmetry imposed on each molecule, with disorder between two N2 and one Cl bridge. One chemically reasonable disorder component is shown. Selected bond distances (Å) and angles (deg): Fe−N(N2), 1.829(5); Fe−Cl(1), 2.505(3); N(N2)−N(N2), 1.234(11); Fe−N(diket), 1.979(3); N(N2)−Fe(1)−N(N2), 95.7(5), N(N2)−Fe(1)−Cl, 97.6(3); Fe−Cl−Fe, 140.5(4).

Addition of further equivalents of CsC6 to samples of 3-Cs did not give further N2 incorporation or reduction. This result, and the presence of chloride in 3-Cs, prompted us to add 4 equiv of CsC6 per [LFe(μ-Cl)]2 in a single step, which gave a new class of Fe−N2 complex. Interestingly, the use of 4 equiv of RbC6 or KC6 gave products with very similar 1H NMR spectra. The blue-green products were identified as M3[LFe(μ-N2)]3, (4-K, 4-Rb, 4-Cs) through X-ray crystallography of the Rb and Cs species (Figures 5 and S24).

The cesium compound 4-Cs was the most stable of these triangular complexes, and it was isolated in 86% yield, while 4-Rb was isolated in a lower yield of 69%. These molecules were not stable under a vacuum, as shown by cracking of crystals.
Further, the microanalytical results were systematically low in nitrogen, suggesting that N2 can be released from the structure; Mössbauer spectroscopy also showed presence of secondary doublets (see Figures S6 and S7). Despite these problems, the 1H NMR spectrum in C6D6 (Figure 6) indicated high purity, suggesting that the changes are reversible. The 133Cs NMR spectrum of 4-Cs in C6D6 showed a single broad peak with fwhm = 226 Hz (Figure S18). The broadness is attributed to rapid relaxation of the Cs nuclear spin by the nearby paramagnetic Fe centers. There are no other peaks in the spectrum corresponding to Cs-containing impurities.30

The isostructural triiron compounds 4-Rb (Figure 5) and 4-Cs (Figure S24) have interesting triangular Fe3(μ-N2)3 cores. Crystallographic C2 and C3 axes enforce D3 point group symmetry that makes all three Fe atoms and all six nitrogen atoms of the N2 bridges equivalent. The N–N distances in the N2 bridges are indistinguishable at 1.191(14) Å (4-Rb) and 1.200(9) Å (4-Cs). This extent of N–N lengthening is similar to that observed previously in linear Fe(μ-N2)Fe cores of larger diketiminate ligands, and suggests partial reduction of N2.16

Each of the triiron compounds 4 has a planar Fe3(μ-N2)3 core, with Fe–N distances of 1.839–1.841 Å, and N–N–Fe angles of 97–99°. The planar Fe3N6 core is capped on each face by an alkali metal, and the M–M distances between the alkali metals are similar (Rb–Rb = 5.017(3) Å; Cs–Cs = 5.172(2) Å). The distances between the alkali metals and the arene centroids are similar at 3.2980(8) and 3.3162(6) Å, respectively. Since the compounds are soluble in aromatic hydrocarbons, we infer that in solution the alkali metals remain coordinated, to give uncharged compounds in which cations are shielded from the external solvent by the surrounding xylyl arms. This assessment is also corroborated by 1H NMR studies on the electronic structure and magnetism of compounds 4 will be reported separately.

Detailed studies on the electronic structure and magnetism of compounds 4 will be reported separately.

Table 2. Mössbauer and Metrical Parameters of Complexes 4

|       | 4-K   | 4-Rb  | 4-Cs  |
|-------|-------|-------|-------|
| δ (mm/s) | 0.68  | 0.71  | 0.74  |
| |ΔE_Q (mm/s) | 0.67  | 0.58  | 0.47  |
| Fe–N(N2) (Å) | –     | 1.839(6) | 1.841(4) |
| N–N (Å)     | –     | 1.191(14) | 1.199(7) |

Figure 5. Thermal-ellipsoid plots (50%) of 4-Rb. The Cs analogue (4-Cs) is shown in Figure S24 (Supporting Information). Both molecules have crystallographic D3 symmetry. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)–N(N2), 1.839(7); N(N2)=N(N2), 1.191(14); Fe(1)–N(diket), 1.971(8); N(N2)=Fe(1)=N(N2), 99.3(5).

Figure 6. Comparison of the 1H NMR spectra of 4-Cs (top), 4-Rb (middle), and 4-K (bottom) in C6D6. The black circles represent the data, and the red line is the fit to parameters given in Table 2. Spectra of 4-K and 4-Rb are given in the Supporting Information (Figures S5, S6).

Figure 7. Zero-field Mössbauer spectrum of 4-Cs recorded at 80 K. The black circles represent the data, and the red line is the fit to parameters given in Table 2. Spectra of 4-K and 4-Rb are given in the Supporting Information (Figures S5, S6).
spectroscopy, where the number of peaks points to a $D_{3h}$ averaged structure in solution (Figure 6). However, the Mössbauer spectrum of a frozen THF solution of 4-Cs had a second, smaller doublet at $\delta = 0.37$ mm/s and $|\Delta E_{Q}| = 1.10$ mm/s that was not present in the solid sample. Considering the low N analysis, we attribute the second doublet to a solution species where THF has coordinated to one or more iron centers and/or replaced one or more N$_2$ units. Beer’s Law plots of 4-Cs in THF (Figure S23) was nonlinear, corroborating the idea that the behavior in THF is complicated.32

We were unable to obtain a single crystal of 4-K, which had lower thermal stability than its Rb and Cs analogues. Though it was not sufficiently pure for elemental analysis, it was isolated as a powder in 29% yield. The structure of 4-K is likely to be analogous to its Rb and Cs analogues based on the similarity of its solution $^1$H NMR (Figure 6) and solid-state Mössbauer (Figure S5) parameters to 4-Rb and 4-Cs. We propose that the lower stability of 4-K is a result of the smaller cation: only the Rb$^+$ and Cs$^+$ cations are large enough to form sufficiently stable cation-$\pi$ interactions with all three xylil appendages.

Reactions with Acid to Give Ammonia. We have previously reported that diketiminate-supported Fe complexes with bridging Fe-NN-Fe cores do not form any ammonia upon addition of acid, whether at the formal Fe$^{1+}$ or Fe$^0$ oxidation level.16 Consistent with this trend, treatment of the bridging N$_2$ complexes 4-Rb or 4-Cs with excess HCl gave no detectable ammonia, as measured using the indophenol test.33 In contrast, 1-Na released ammonia in a quantitative (99 ± 1%) yield. We propose that instead, the observed di

### DISCUSSION

Novel Fe–N$_2$ Compounds from Alkali-Metal Reduction of Iron(II) Chloride Complexes under N$_2$. The above results show that K is not unique in its ability to facilitate N$_2$ reduction by Fe in the iron(1) oxidation level. Na and Rb also promote complete six-electron reduction of N$_2$, and form compounds with analogous trinuclear Fe$^{3+}$Fe$^{2+}$ (N$_2$)$_2$ cores (1) where the two nitrides are derived from N–N bond scission. It is evident that the size of the alkali-metal cations influences the structure and stability of the N$_2$-cleaved complexes 1, with the larger cation Rb$^+$ resulting in higher stability than K$^+$. This trend is opposite of the one for the gas phase cation-$\pi$ interactions, which are strongest for the lighter alkali metals.34 M–N bond strengths are expected to follow a similar trend. Thus, it is likely that the stability is determined by the ability of the cation to fit into a cavity of the appropriate size, where the fit in the tetranuclear L$_4$Fe$_2$M$_2$Cl$_4$ structure is more ideal for Rb$^+$ than K$^+$.35

On the basis of these considerations, we propose that Na$^+$ fits so poorly into the tetranuclear structure that it forms the different trinuclear structure in 1-Na. Within this structure the “dangling” Fe–Cl is absent, and the Na$^+$ ion completes its coordination with THF molecules instead of bridging chlorides. Though the structure is different, addition of K$^+$ or Rb$^+$ salts to mixtures of 1-Na and [LFe($\mu$-Cl)$_2$] gives 1-K and 1-Rb, and vice versa. These metathesis reactions favor formation of 1-Na, which may be more thermally stable, but these reactions are accompanied by some decomposition that limits the ability to assess the thermodynamics of the system. Future studies will explore the reactivity of these cores and the possibility to remove the alkali metals completely.

This Article also reports a new kind of triangular metal-dinitrogen core (4) derived from three iron atoms and three end-on/end-on bridged N$_2$ units. This shape of metal-dinitrogen complex has not been reported in any literature metal-N$_2$ compounds, with the exception of a Re compound that was deposited in the CSD as a personal communication.35 Part of the stability of the Fe$_2$($\mu$-N$_2$)$_3$ core undoubtedly arises from cation-$\pi$ interactions between the alkali metal cation and the three nearby arene rings of the supporting ligands. The stability of the compounds in solution changes in the order Cs$^+$ > Rb$^+$ > K$^+$, which is consistent with the larger cation being able to more easily coordinate to three arene rings without steric destabilization.

More Reduction Gives Less N$_2$ Activation. Reduction of the Fe$^{2+}$ compound [LFe($\mu$-Cl)$_2$] by 1e$^-$ per Fe leads to N$_2$ cleavage to nitrides (1), which react with HCl to give high yields of ammonia. However, reduction by 2e$^-$ per Fe gives N$_2$ complexes (4) that neither cleave the N–N bond nor produce ammonia when treated with acid. Clearly, it is not the number of reducing equivalents present that determines the extent of N–N activation. Additionally, because we use graphite-supported alkali metals where the reducing electrons are on the graphite, the reducing power of the reductant is unlikely to vary significantly between the different alkali-metal reductants.

We propose that instead, the observed differences in the ability to reduce N$_2$ can be explained by considering the geometry of the multimetallic iron-alkali-N$_2$ species that are accessible at each reduction level.14 As shown in a recent computational paper, three neutral LFe$^{1+}$ fragments are sufficient to cooperatively weaken and cleave the N–N bond of N$_2$, with the participation of a K$^+$ ion.36 The key postulated intermediate derived from the computations is shown in Figure 8, and it can form when three iron atoms simultaneously approach N$_2$. We propose that this cooperative interaction is not possible when over-reduction gives species like 4, in which the cation-$\pi$ interactions enforce an expanded core size that prevents three Fe atoms from approaching one another closely. In the shape of the triangular clusters 4, no more than two iron atoms can reach a single molecule of N$_2$ at the same time, and N$_2$ cleavage is not observed. Thus, we propose that the key factor in the iron-mediated N–N bond scission is the number of Fe atoms that attack the N$_2$ unit simultaneously, and that the shape of the structure

Figure 8. Calculated structure for a potential N$_2$ reduction intermediate, indicating how three LFe units could interact with N$_2$.36
enforced by the cation-π interactions to the alkali metal cations is more important than the oxidation level of the iron atoms. This idea also explains the inability of iron complexes with larger diketiminate ligands to cleave the N=N bond,36 because they form protected FeNNe cores where the supporting ligand blocks approach of a third iron atom. Further support for these ideas will require isolation of intermediates, and/or computations that model more of the cluster environment.

It is interesting to compare these alkali cation linked diketiminate supporting ligands to the covalently linked cyclophane-diketiminate supporting ligands reported recently by Murray and co-workers, which can support three diketiminate supporting ligands to the covalently linked computations that model more of the cluster environment. Our results support the idea that alkali metals could bind to nitrides resulting from scission. We recommend that future studies test these ideas for the surface catalysts.

**CONCLUSIONS**

Diketiminate ligands can support a number of novel Fe–N2 complexes, including some containing a novel triangular N2-bridged trimetallic core, and others that are able to perform the six-electron reduction of N2 to nitrides. We have also addressed the influence of the identity of the alkali metal on N–N bond scission in multimetallic complexes. Our model, in which cooperation between three Fe atoms and N2 is necessary for N–N bond scission, explains the need for relatively small diketiminate supporting ligands to enable close Fe–Fe distances during the critical step.30 Overall, our results support the idea that alkali metals can steer three iron atoms to cooperatively cleave the N–N bond, whereas N–N cleavage does not take place when only two Fe atoms can approach N2. This observation has implications for the Haber–Bosch catalyst, where K-promoted triiron sites should be considered as key potential sites for N–N cleavage. Additionally, we propose that alkali metals could bind to nitrides resulting from N–N scission. We recommend that future studies test these ideas for the surface catalysts.

**EXPERIMENTAL SECTION**

General Methods. All manipulations were performed in an MBraun glovebox in an N2 atmosphere maintained at or below 1 ppm of O2. All glassware was oven-dried at 150 °C for at least 12 h before use. Pentane, hexanes, diethyl ether, and toluene were purified by passage through activated alumina and “deoxygenizer” columns (Glass Contour Co., Laguna Beach, CA). Tetrahydrofuran (THF) was dried by distilling from Na/benzophenone. All solvents were stored over activated 3 Å molecular sieves and passed through a plug of activated alumina before use. Deuterated benzene was dried over activated alumina and then filtered before use. THF-d8 was dried over CaH2 and then over Na/benzophenone, and vacuum transferred to a storage container before use. Graphite, Celite, and 3 Å molecular sieves were dried at 300 °C under a vacuum for >12 h.

1H NMR spectra were recorded on either an Avance 400, Avance 500, or Agilent 500 spectrometer, and are referenced to residual CD3OD at δ 7.16 ppm. UV–vis spectra were recorded on a Cary 50 spectrometer using Schlenk-adapted quartz cuvettes with a 1 mm path length. IR spectra were recorded as KBr pellets on a Shimadzu 8400S FTIR, or as solids in ATR mode on a Bruker Alpha FTIR. Elemental analysis data were obtained from the CENTTC Elemental Analysis Facility at the University of Rochester. The indophenol test for NH3 quantification was performed as previously described.33 Quantification of the amount of 1-Na for the indophenol procedures was performed using relative integration of the most downfield shifted peaks, which are assigned as 3 H in case of both [LFe(μ-Cl)]2 and 1-Na.

Benzyloctahydrasyn was synthesized using the published method.40 FeCl2(THF)1.5 and ligand HL16 were synthesized using previously published procedures. Rubidium trifluoromethanesulfonate was purchased from Sigma-Aldrich and dried under a vacuum (0.2 mTorr) for 24 h at 160 °C. Metals were obtained from the following vendors: lithium from ACROS (99%, granular, dry), sodium from TBJ Baker (Baker analyzed Na lump); potassium (98% pure) from Sigma-Aldrich; rubidium from Alfa Aesar (99.75% pure); cesium from Strem (99.9% pure). Potassium graphite (KC8) was prepared by heating stoichiometric amounts of potassium and graphite at 145 °C under an argon atmosphere. Rubidium graphite (RbC8) was prepared by heating stoichiometric amounts of rubidium and graphite at 130 °C under an argon atmosphere. Cesium graphite (CsC8) was prepared by mixing stoichiometric amounts of cesium and graphite at ambient temperature under argon atmosphere.45 **Warning:** Alkali metals and their graphite intercalates KC8, RbC8, and CsC8 are powerful reductants, which ignite on contact with air and moisture. Therefore, extreme care must be taken when synthesizing and handling these alkali graphite reductants!

[LFe(μ-Cl)]2, [LFe(μ-Cl)]2, was synthesized by a variant of the previously published procedure.18 In the glovebox, benzyloctahydrasyn (1.77 g, 14.0 mmol) was dissolved in 40 mL of THF and added to a rapidly stirring solution of HL (4.34 g, 14.0 mmol) in THF (10 mL) at ambient temperature. The reaction was stirred for 40 min until a uniform bright-yellow color was observed, indicating the formation of KL. At this point, the solution was cooled in the cold well below −78 °C. FeCl2(THF)1.5 (3.18 g, 14.0 mmol) was suspended in 100 mL of THF and cooled in the cold well below −78 °C. Next, the cold solution of KL was added very slowly to a rapidly stirring suspension of FeCl2 over 5 min and allowed to warm to ambient temperature while stirring for 2 h. The brown dark-green suspension was then filtered under vacuum (0.020 Torr) at 40 °C. The solid was then suspended in 60 mL of toluene, heated to reflux under N2 for 1 h, and filtered through Celite while still hot. The solvent was removed from the filtrate under vacuum, and the red-orange solid was washed with pentanes until the wash was colorless (3 × 15 mL). The yield of red-orange solid was 4.36 g (80%). The 1H NMR shifts match those reported previously.18 (500 MHz, C6D6): δ 53.7 (2H, 1H, Nδ), 12.2 ppm (4H, 1H, Nδ). The yield of red-orange solid was 4.36 g (80%). The 1H NMR shifts match those reported previously.18 (500 MHz, C6D6): δ 53.7 (2H, 1H, Nδ), 12.2 ppm (4H, 1H, Nδ).

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In an N$_2$-filled glovebox, [LFe(μ-Cl)]$_2$ (182.6 mg, 0.226 mmol) was dissolved in THF (2 mL), frozen, and then allowed to slowly thaw. The freshly thawed solution was added in one portion to cold (<−40 °C) solid RbC$_8$ (94.4 mg, 0.520 mmol) and the color immediately turned deep green. The mixture was stirred at ambient temperature for 40 min. The solvent was removed under reduced pressure, and resulting solid was extracted with 5 mL of hexanes and filtered through Celite to give a dark red solution. The filtrate was concentrated to 0.5 mL and cooled to −40 °C for 3 h to give dark red crystals (111 mg, 48%). This reaction failed when the concentration of the starting material [LFe(μ-Cl)]$_2$ was below about 0.15 mM. $^1$H NMR (500 MHz, C$_6$D$_6$): δ 175.3 (3H), 140 (3H), 50.6 (6H), 29.3/27.6 (1H), 22.0 (12H), 11.8/10.6 (12H), 6.00 (4H), 1.24/0.88 (hexane), −1.62 (18H), −8.14 (4H), −18.8 (8H), −37.2 (14H), −43.0 (12H), −68.5 (2H), −78.4 (6H) ppm. Anal. Calcd for Cs$_3$H$_8$Cl$_3$Fe$_3$Na$_2$Rb$_7$: C, 62.37, H, 7.11, N, 7.06. Found: C, 62.62, H, 6.94, N, 7.41. IR (significant bands; KBr, cm$^{-1}$): 2952 (s), 2917 (s), 2856 (s), 1530 (s), 1464 (s), 1346 (vs), 1290 (m), 1195 (vs), 1090 (m), 990 (s), 801 (m), 764 (vs). $\mu_{BB}$ = 7.50 ± 0.03 μB.

C$_8$L[Fe(μ-N$_2$)$_3$]$_3$ (3-Cs). In an N$_2$-filled glovebox, complex [LFe(μ-Cl)]$_2$ (33.6 mg, 0.042 mmol) was dissolved in THF (2 mL) and frozen. Upon thawing, this canary yellow solution was added to a cold (<−40 °C) solid CsC$_8$ (21.9 mg, 0.096 mmol), resulting in a dark green-blue suspension. This suspension was stirred for 30 min at ambient temperature. After this time solvent was removed under reduced pressure and obtained solid was suspended in hexanes (40 mL) and filtered through Celite. The solution was concentrated to ~1 mL under reduced pressure. The solution was cooled to −40 °C to give crystals. Crystals of this compound were obtained from a mixture and cocrySTALLized with complex 4-Cs, therefore $^1$H NMR shifts (ppm) and their assignments are somewhat ambiguous. The spectrum is shown in Figure S19.

K$_3$[LFe(μ-N$_2$)$_3$] (4-K). In an N$_2$-filled glovebox, [LFe(μ-Cl)]$_2$ (71.1 mg, 0.088 mmol) was dissolved in THF (2 mL) and frozen. Upon thawing, it was added to a cold (<−40 °C) flask containing solid KC$_8$ (50.0 mg; 0.370 mmol) and the mixture immediately turned dark green. The resulting suspension was stirred for 20 min at ambient temperature. The solvent was then removed under reduced pressure, and the resulting solid was suspended in 20 mL of pentane and filtered through Celite. The solvent was removed under reduced pressure and the resulting solid was washed once with cold (<−40 °C) hexanes (1 mL). After drying under a vacuum for 15 min, a dark blue-green solid was collected (22.0 mg, 29%). $^1$H NMR (500 MHz, C$_6$D$_6$): δ 178.5 (3H, β-Me), 34.3 (12H, α-Me), 15.2 (4H, m-Me), −5.6 (2H, p-Me), −107.4 (6H, β-Me) ppm. Drying led to apparent loss of N$_2$ as evidenced by results of elemental analysis, where low N numbers were dependent on the amount of time complex spent being dried under a vacuum (see Supporting Information).

Rb$_3$L[Fe(μ-N$_2$)$_3$]$_3$ (4-Rb). In an N$_2$-filled glovebox, [LFe(μ-Cl)]$_2$ (99.5 mg, 0.123 mmol) was dissolved in THF (2 mL) and frozen. Upon thawing, this canary yellow solution was added to a cold (<−40 °C) solid of RbC$_8$ (94.0 mg, 0.518 mmol). The mixture immediately turned dark green-blue. The suspension was stirred for 2 h at ambient temperature. After this time, THF (50 mL) was added and this diluted suspension was filtered through Celite to give a dark blue solution with a red tint. The solvent was then removed under reduced pressure and the solid was washed with cold hexanes until no red tint was observed in the wash (4 × 1 mL). The resulting solid was dried under a vacuum for 15 min (78.5 mg, 69%). Crystals for X-ray crystallography were obtained from hexanes solution at −40 °C. $^1$H NMR (500 MHz, C$_6$D$_6$): δ 179.4 (3H, α-Me), 37.4 (12H, α-Me), 14.8 (4H, m-Me), −5.6 (2H, p-Me), −117.0 (6H, β-Me) ppm. $^1$CsL[Fe(μ-N$_2$)$_3$] (4-Cs). In an N$_2$-filled glovebox, [LFe(μ-Cl)]$_2$ (42.8 mg, 0.052 mmol) was dissolved in THF (2 mL) and frozen. Upon thawing, this canary yellow solution was added to a cold (<−40 °C) solid of CsC$_8$ (51.0 mg, 0.223 mmol), resulting in a dark green-blue suspension, which was then stirred for 2 h at ambient temperature. After this time, THF (50 mL) was added and this diluted suspension was filtered through Celite to give a dark blue solution with a red tint. The solvent was removed under reduced pressure and the solid was washed with cold hexanes until no red tint was observed in the wash (4 × 1 mL). The resulting solid was dried under a vacuum for 15 min (44.8 mg, 86%). Crystals for X-ray crystallography were obtained from hexanes solution at −40 °C. $^1$H NMR (500 MHz, C$_6$D$_6$): δ 178.3 (3H, α-Me), 34.3 (12H, α-Me), 13.5 (4H, m-Me), −47.7 (2H, p-Me), −126.8 (6H, β-Me) ppm. UV–vis (toluene, mM$^{-1}$·cm$^{-1}$): 330 (=42), 390 (=20), 660 (=7.5) nm; assessment of extinction coefficients is approximate, as they do not obey the Beer–Lambert Law (Figures S22 and S23).

**Cation Exchange Experiments.** Complex 1 was dissolved in THF (1 mL) and added to a rapidly stirring suspension of the MOTf salt in THF. After 30 min of stirring, solvent was removed under reduced pressure. The resulting red solid was suspended in hexanes (15 mL) and filtered through a Celite plug. The filtrate was then brought to dryness under vacuum and analyzed by $^1$H NMR spectroscopy. Reactions with excess (20 equiv) of MOTf salts were performed and analyzed in the same manner. Reactions involving 1-Na started with mixture of 1-Na and [LFe(μ-Cl)]$_2$ in a 1:0.69 ratio (determined by $^1$H NMR spectroscopy) and the amounts of trimethanesulfonate salts were calculated assuming 100% 1-Na. The $^1$H NMR spectra are shown in Figures S9–S14.

$^{57}$Fe Mössbauer Spectroscopy. Solid Mössbauer samples were packed into Delrin sample cups and loaded into the spectrometer at 77 K. Mössbauer measurements were performed using a SEE Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N$_2$ cryostat for measurements at 80 K with a 0.07 T applied magnetic field. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fit using the program W Moss (SEE Co.), using Lorentzian doublets.

**X-ray Crystallography.** Single crystals (except of 1-Na) were placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K. A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using Mo Kα radiation (graphite monochromator) with appropriate frame times ranging from 45–90 seconds with a detector distance of 4.00 cm. Single crystal of 1-Na was placed onto the fiber loop and mounted on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) at 93(2) K. The structures were solved using SIR97 and refined using SHELXL-97 or SHELXL-2013. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Details are given in Table S2.

**ASSOCIATED CONTENT**

Supporting Information

Additional spectroscopic and crystallographic information. 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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