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Alkali-Controlled C-H Cleavage or N-C Bond Formation by N₂-Derived Iron Nitrides and Imides

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Abstract

Formation of N-H and N-C bonds from functionalization of N₂ is a potential route to utilization of this abundant resource. One of the key challenges is to make the products of N₂ activation reactive enough to undergo further reactions under mild conditions. This paper explores the strategy of "alkali control," where the presence of an alkali metal cation enables the reduction of N₂ under mild conditions, and then chelation of the alkali metal cation uncovers a highly reactive species that can break benzylic C-H bonds to give new N-H and Fe-C bonds. The ability to "turn on" this C-H activation pathway with 18-crown-6 is demonstrated with three different N₂ reduction products of N₂ cleavage in an iron-potassium system. The alkali control strategy can also turn on an intermolecular reaction of an N₂-derived nitride with methyl tosylate that gives a new N-C bond. Since the transient K⁺-free intermediate reacts with this electrophile but not with the weak C-H bonds in 1,4-cyclohexadiene, it is proposed that the C-H cleavage occurs by a deprotonation mechanism. The combined results demonstrate that a K⁺ ion can mask the latent nucleophilicity of N₂-derived nitride and imide ligands within a trimetallic iron system, and points a way toward control over N₂ functionalization.

Introduction

When homogeneous transition metal complexes are capable of cleaving the triple bond of N₂, the reactions are typically driven by the formation of nitride complexes with strong metal-nitrogen bonds.^{1,2} For example, Cummins has measured the Mo-N triple bond strength in a Mo(NR₂)₃N product of N₂ cleavage to be 155 kcal/mol.³ Because of the strong metal-nitrogen bonds, the N₂-derived nitrides often are unreactive toward reagents except high-energy species like silyl halides,² acyl halides,⁴ and alkyl triflates.⁵ Only recently has it become possible to functionalize N₂ with milder reagents like CO and silanes.⁶ In other cases, the nucleophilicity of coordinated N₂ has been utilized in order to bring about reactions with electrophiles by Hidai, Fryzuk, Chirik, Sita, Schrock, Nishibayashi, and Peters.^{7,8}

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Supporting Information. Synthetic, spectroscopic, and crystallographic details (PDF, CIF).

In order to undergo further functionalization, an ideal N₂-derived nitride would be reactive enough to break other strong bonds. The only literature examples of N₂ cleavage products that break an *sp*³ C-H bond come from group 4 chemistry (Scheme 1); note that the H goes to the N, and the C to the metal.⁹ Fryzuk and Chirik have reported cleavage of C-H bonds in terminal alkynes by side-on coordinated N₂ as well.¹⁰ Here we describe intramolecular C-H activation by iron nitride, imide, and amide products of N₂ cleavage, showing that multinuclear iron systems can accomplish sequential N-N and C-H cleavage reactions.

The iron nitrides under study here arise from reduction of N₂ by a Fe-K system that is supported by a β -diketiminato (L = 2,4-bis(2,6-dimethylphenylimido)-3-methylpentyl). In this system, N₂ reduction gives a bis(nitride)tetrairon product (**1**) in which two K⁺ ions are coordinated to one of the nitride ligands (Scheme 2).¹¹ This reaction does not give any N-N cleavage when 18-crown-6 is included in the reaction mixture, demonstrating the importance of the potassium. Computational studies on truncated models suggest that potassium cations can play a key role in N₂ cleavage within a trimetallic intermediate, where their positive charge lowers the energy of the nitride product.¹² We reasoned that this nitride stabilization could be dispelled by removal of the alkali metal cations *after* the N-N cleavage was complete. In this contribution, we show that release of K⁺ from this bis(nitride)tetrairon product unmasks a very strong base that can deprotonate benzylic C-H bonds. In effect, the K⁺ is added to facilitate N-N cleavage and then removed to facilitate C-H cleavage. We refer to this strategy as "alkali control," and demonstrate that it can also be used to activate other related species that also come from N₂ reduction. This approach works with three different species, which suggests that the alkali control strategy may be applicable more broadly to N₂ functionalization.

Results and Discussion

Alkali Control over C-H Cleavage in a Bis(μ -nitrido)tetrairon Complex

Treating a THF solution of **1** with 2 equiv of 18-crown-6 produces two products as judged by ¹H NMR spectroscopy: the known LFe(Cl)₂K (18-crown-6) (**2**)¹¹ in 82% yield, and a new anionic triiron complex (**3**) in 77% yield (Scheme 3). Exchanging the crown ether for 2.2.2-cryptand yields single crystals of **3** suitable for X-ray crystallography, though the quality of the structure we obtained was not sufficient for detailed analysis of metrical parameters. It is evident that **2** accounts for the LFeCl₂[−] fragment from **1**, while **3** contains the L₃Fe₃N₂ cluster. In the anionic portion of **3**, which we call **3**[−] (Figure 1), an intramolecular C-H splitting reaction is evident: a methyl group on one of the β -diketiminato supporting ligands has lost an H to the nitrogen atom labeled N2, giving a bridging NH ligand with concomitant formation of a new Fe–C bond. Electrospray FT-ICR mass spectrometry of **3** in THF reveals an ion at 1153.459 *m/z* (sim. 1153.463 *m/z* most abundant mass,¹³ Figure 1) corresponding to **3**[−].

Mössbauer spectroscopy can be used to characterize the oxidation states and spin states of the iron sites (Table 1). The Mössbauer spectrum of solid **3** at 80 K shows three quadrupole doublets of equal intensity with isomer shifts (δ) of 0.31, 0.35, and 0.66 mm/s. The low isomer shifts indicate two high-spin iron(III) ions, while the high isomer shift of the third doublet indicates one high-spin iron(II) ion. This agrees with the valence of these three sites

previously established in **1**, where the triiron portion had $\delta = 0.29, 0.29$, and 0.68 mm/s. Therefore, C-H cleavage the ligand takes place without a net redox change at the metal centers. We assign the iron(II) valence to Fe1 (the iron site on the right of the picture), based on the shortening of the bonds to this iron atom upon oxidation of the cluster to a triiron(III) form (see below). Note that the two iron(III) sites in **3** are inequivalent, because one has a functionalized ligand. As a result of this loss of symmetry, the ^1H NMR spectrum of **3** in THF- d_8 has 40 signals, with integrations that are consistent with a C_1 -symmetric structure (see Supporting Information for spectra of all species reported here).

Treating a solution of **3** with 2.2.2-cryptand causes a shift in the ^1H NMR resonance of the 18-crown-6, indicating that the K^+ ion becomes encapsulated in the cryptand (see SI for crystallographic support). The ^1H NMR resonances of the triiron anion of **3** do not shift upon crown ether exchange, suggesting that the cation and anion of **3** are not associated in THF solution. 2.2.2-Cryptand reacts with **1** similarly, producing the cryptand-substituted version of **3** in 91% yield.

Cyclic voltammetry of **3** in THF shows a reversible oxidation wave at -1.91 V vs $\text{Cp}_2\text{Fe}^{0/+}$. Chemical oxidation of **3** with $[\text{Cp}_2\text{Co}]\text{PF}_6$ ($E_{1/2} = -1.33$ V versus $\text{Cp}_2\text{Fe}^{0/+}$ in CH_2Cl_2)¹⁴ gives a neutral complex **4** and 1 equiv of Cp_2Co (Scheme 4). The zero-field Mössbauer spectrum of solid **4** at 80 K shows three quadrupole doublets of equal intensity with isomer shifts of 0.37, 0.32, and 0.22 mm/s, with the low values indicating three high-spin iron(III) centers. Again, the three iron sites are inequivalent because of the ligand activation. Even though the structure of **3** is poor, there are some differences between **4** and **3** that exceed the uncertainty limits (Figure 2). First, the Fe–C bond in **4** ($2.033(4)$ Å) is 0.05 Å shorter than the Fe–C bond in **3** ($2.083(8)$ Å). Additionally, the C-bound Fe has an Fe–N bond to the μ_3 -nitride that is more than 0.15 Å shorter in the oxidized complex **4** ($1.788(3)$ Å) than the anionic precursor **3**[–] ($1.950(6)$ Å). The other Fe–N bonds to this Fe also contract by more than 0.05 Å upon oxidation. These data suggest that the oxidation occurs at the C-ligated Fe center.

Alkali Control over C-H Cleavage in a (μ -imido) (μ -nitrido)triiron Complex

Next, we tested alkali control using the previously reported triiron nitride/imide complex (**5**), which is neutral and has two iron(III) and one iron(II) like **1**.¹⁵ Compound **5** reacts with KC_8 to produce **6** (Scheme 5). Though **6** has not been crystallographically characterized, it has a simple ^1H NMR spectrum indicative of C_{2v} symmetry, indicating that the supporting ligand has not undergone C-H activation. The Mössbauer parameters of **6** indicate two inequivalent high-spin iron(II) centers ($\delta = 0.63, 0.73$ mm/s) and one high-spin iron(III) center ($\delta = 0.24$ mm/s).¹⁶ Thus, one of the two Fe^{3+} sites is reduced to make a mixed-valence pair on the left side of the picture: these spectroscopic data indicate that the two sites have slow electron exchange on the Mössbauer time scale but rapid exchange on the NMR time scale. The high symmetry also indicates that the K^+ ion is in a time-averaged position, though our data do not give more detail on the structure. Lowering the temperature of a sample of **6** to -80 °C gave no decoalescence (Supporting Information).

Treating a THF solution of *in situ* generated **6** with 1 equiv of 18-crown-6 leads to rapid formation of a new triiron complex **7** in 66% isolated yield. The X-ray crystal structure of **7** shows a μ_2 -amido (NH_2) ligand and a C-ligated Fe center that is formed as a result of intramolecular C-H cleavage. The FT-ICR-MS of a solution of **7** (exp. 1154.560 m/z , sim. 1154.471 m/z) indicates the addition of one additional H atom in **7**⁻ relative to **3**⁻ (Figure 1). The Mössbauer spectrum of **7** suggests two high-spin iron(II) centers ($\delta = 0.69, 0.71$ mm/s) and one high-spin iron(III) center ($\delta = 0.36$ mm/s). Unfortunately, the crystal structure does not have sufficient quality to distinguish which of the iron atoms are iron(II) and iron(III).

Alkali Control over C-H Activation in a (μ -amido) (μ -nitrido)triiron Complex

A third example of alkali control involves the reduction of an N_2 -derived triiron nitride/amide complex (**8**) that has two iron(II) sites and one iron(III) site (Scheme 6).¹⁶ It reacts with 1 equiv of KC_8 at -78°C to give a color change from orange-brown to dark red-brown over a period of 10 min. The ^1H NMR spectrum of the crude reaction mixture shows a new set of resonances consistent with a C_{2v} -symmetric triiron framework (**9**). Again, the high symmetry indicates that the supporting ligands are intact. Though **9** has proven too unstable for isolation, Mössbauer analysis of the crude reaction mixture gives a spectrum with two Fe environments in a 2:1 ratio with $\delta = 0.71$ and 0.61 mm/s. These Mössbauer data are consistent with one-electron reduction to **9**, a triiron nitride/amide complex having three high-spin iron(II) centers, two of which are equivalent.

Reacting *in situ* generated **9** with 1 equiv of 18-crown-6 causes a rapid color change to red, and the product **10** can be isolated in 67% yield. The ^1H NMR spectrum of **10** indicates a C_1 -symmetric triiron complex (**10**). The X-ray crystal structure of **10** shows that one methyl group of a β -diketiminato supporting ligand is activated as in compounds **3**, **4**, and **7**. In the all-iron(II) compound **10**, the μ_3 -coordinated N atom is more pyramidalized (sum of Fe–N–Fe angles = $342.0(5)^\circ$), suggesting that the H resides on N1, consistent with a peak in the Fourier density map that refines to an N–H distance of $1.09(7)$ Å. The FT-ICR-MS of **10** in THF shows a peak at 1155.584 m/z (sim. 1155.479 m/z , Figure 1) consistent with the mass of **10**⁻. The Mössbauer spectrum of **10** shows three doublets with isomer shifts of 0.72 – 0.73 mm/s, confirming that all three iron sites are high-spin iron(II).

CIVP Spectroscopy

We used Cryogenic Ion Vibrational Predissociation (CIVP) spectroscopy with N_2 tagging at 25 K to measure the infrared spectrum of mass selected **3**⁻· N_2 by photoevaporation of the tag.¹⁶ CIVP of **3**⁻· N_2 (Figure 3) shows a number of CH stretching bands as well as a sharp band at 3352 cm^{-1} , a frequency that is characteristic of N–H stretching vibrations. Not only does this observation confirm the assignment of the weak feature in the FT-IR spectrum of the solid sample attributed to the NH stretching mode, it also confirms that this band is a property of the isolated **3**⁻ anion.

We collected the CIVP spectrum of **7**⁻· N_2 as described above, and observed a peak at 3360 cm^{-1} that was not evident in the FT-IR spectrum of the solid sample (Figure 3). This band is consistent with the asymmetric NH_2 stretching fundamental, which is calculated to be

significantly stronger than the symmetric stretch (see Supporting Information for calculations).

CIVP spectroscopy of $10^-\cdot\text{N}_2$ exhibits a peak at 3375 cm^{-1} (Figure 3) confirming that the anion is the carrier of the weak band in the FT-IR spectrum of solid **10** at 3371 cm^{-1} (see Supporting Information). We assign this feature to an asymmetric NH_2 stretching fundamental based on the fact that this mode carries most of the intensity arising from the NH manifold. The relatively small blue-shifts of the asymmetric NH_2 stretches of $7^-\cdot\text{N}_2$ and $10^-\cdot\text{N}_2$ (8 and 15 cm^{-1} , re-spectively) compared to the NH stretch of $3^-\cdot\text{N}_2$ are consistent with the expected splitting of the two modes in $-\text{NH}_2$ ($\nu = 68\text{ cm}^{-1}$) along with the $\sim 23\text{ cm}^{-1}$ red-shift of the centroid frequency of the NH_2 group upon stepwise reduction of the adjacent iron centers.¹⁷

Mechanistic Tests, and N-C Bond Formation from the Nitride Complex

The intramolecular C-H activation reactions shown here could in principle proceed through H^+ transfer or $\text{H}^\bullet$ transfer. In an experimental test for $\text{H}^\bullet$ transfer (Scheme 7), addition of 18-crown-6 to **1** in the presence of a high concentration of 1,4-cyclohexadiene (2.6 M) led only to **3**, just as seen in the absence of the additive. The inability to attack the very weak C-H bond in 1,4-cyclohexadiene argues against a C-H cleavage mechanism involving H atom abstraction by an unobserved intermediate. Though we cannot definitively rule out steric effects as an explanation for the inability to perform the intermolecular reaction, another trap was effective at lower concentration (see next paragraph), suggesting that the lack of reaction of the transient intermediate with 1,4-cyclohexadiene is an accurate reporter of its lack of H atom abstraction ability.

Contrasting results were seen when the electrophile methyl tosylate (MeOTs , where $\text{OTs} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$) was used to trap unobserved intermediates. MeOTs reacts very slowly with **1**, but treating a mixture of **1** and 1 equiv of MeOTs with 18-crown-6 (2 equiv) in C_6D_6 for 30 min gives complete conversion to a mixture of **2** in 74% spectroscopic yield and a new neutral methylimide complex (**11**) in 88% spectroscopic yield (Scheme 7). The X-ray crystal structure of **11** (Figure 4) shows that CH_3^+ has added to a N atom of **1** to give a new N-C bond. The ligands are intact and no **3** is observed, and thus CH_3OTs has effectively intercepted the intermediate. We know of only one other Fe nitride complex that reacts with a C-based electrophile, and this nitride was not derived from N_2 .¹⁸ There are few examples of N-C bond formation from any Fe- N_2 derived complexes.¹⁹ Nitride alkylation is more common with complexes of early transition metals.⁴⁻⁷

The Mössbauer spectrum of solid **11** at 80 K shows two quadrupole doublets in a 2:1 ratio, with $\delta = 0.35\text{ mm/s}$ indicating two equivalent high-spin iron(III) sites and $\delta = 0.65\text{ mm/s}$ indicating a high-spin iron(II) site.¹¹ These parameters are similar to those of **5** (0.29, 0.61 mm/s). The bond lengths within the core are also similar (Figure 2).

The ability of a simple CH_3^+ source to react with K^+ -free nitride, while 1,4-cyclohexadiene does not, supports the idea that the C-H bond activation to make **3** proceeds through H^+ transfer rather than $\text{H}^\bullet$ transfer. This conclusion is also consistent with the observation¹⁶ that

1 can be converted to its protonated analogue **5** by terminal alkynes, which have relatively low pK_a values but high homolytic bond dissociation energies.

Alkali Control over Basicity

The reactions with 18-crown-6 described above elucidate the requirements for attack on ligand C-H bonds in this system. Reduction is needed in each case, but the ^1H NMR spectra of reduced species **1**, **6** and **9** indicate intact supporting ligands. Thus the lowering of oxidation state alone is not sufficient to bring about C-H activation. However, starting from **1**, **6** and **9**, K^+ chelation by crown ethers leads to rapid deprotonation of the supporting ligand. These results indicate that removal of K^+ ions in reduced compounds uncovers a very basic bridging nitride or imide that can deprotonate the benzylic C-H bond of the supporting ligand. The pK_a of these benzylic C-H bonds is estimated as *ca.* 42 by analogy to the analogous protons in toluene.²⁰

It is somewhat surprising that the ligand deprotonation occurs equally well starting from nitrido, imido, and amido complexes. The examples used here not only have different nitrogen-based groups, but also have different formal oxidation states at the triiron site. Since only the anionic complexes engage in the ligand activation, the charge seems to be most influential. We suggest that the negative charge enhances the basicity of the bridging N atoms. The oxidation state of the iron sites is not as important, because the deprotonation is not a redox reaction. Future studies will aim to determine the scope of the reaction and to better bracket the pK_a of the reactive bases.

Unfortunately, our experiments are unable to distinguish the *initial* site of N-H bond formation. In Scheme 7, we propose that the two-coordinate nitride is the base, since potassium has been removed from this site and because the N-H bond is formed at this site. Deprotonation would then be followed by rotation around the $\text{C}_{\text{aryl}}\text{-N}$ bond to place the deprotonated carbon near the iron atom where it binds in the product. We cannot rule out intermolecular or relay mechanisms, but there is no compelling reason to invoke these more complicated explanations.

In **6** and **9**, it is less clear which nitrogen atom deprotonates the ligand. Deprotonation by the μ^2 nitrogen would be particularly surprising in the transformation of the amido/nitrido species **8**→**9**→**10**, because there is no lone pair on a bridging amido group. However, only **8** has been structurally characterized. It is possible that one of the Fe-N bonds of **9** breaks transiently to form a terminal amido group that acts as the base, or that there is a proton transfer to the μ -nitride prior to the left N acting as a base, and it is also possible that the μ^3 nitride is the active base. Future computational studies are planned, to resolve these possibilities.

In the literature, the use of a chelating agent is well established as a strategy to increase the basicity of an alkali metal salt: for example, addition of tetramethylethylenediamine (TMEDA) increases the basicity of alkyllithium reagents.²¹ However, we know of no other examples where alkali chelation has been used to enhance the reactivity of N_2 reduction products. We anticipate that future ligand designs could encourage alkali metal binding that can be turned on and off to modulate the reactivity.²² We also envision changing reactivity

by tuning the size and charge density of alkali metals, which we have utilized to vary the extent of N-N activation in relatives of **1**.²³

Perspectives

Another multiiron system that cleaves N₂ was recently reported by Murray.²⁴ They used a cyclophane-based trinucleating ligand in which β -diketiminates suspend three iron atoms at distances similar to those in **1-11** (Fe-Fe distances of ~3.5 Å are also found between the three-coordinate iron and the other two Fe sites in the cores of the compounds presented above). Cleavage of N₂ came from a synthetic strategy related to that used for **1**: the addition of KC₈ to an iron-halide complex. Interestingly, a nitride complex was not isolated, and instead the product had NH/NH₂ bridges. The source of the N-bound hydrogen atoms was unknown, but the results described here suggest that benzylic protons on the ligand may have provided them. One possibility is that the transient nitrides in their system may not have benefitted as much from stabilizing K⁺ ions in the appropriate geometry, and attacked the supporting ligand rapidly.

In previous work, Lewis acids have been used to stabilize species that are otherwise too reactive to be isolated: these include alkylidenes, alkylidynes, oxides, and terminal imides.^{25,26,27,28} There are a few examples of terminal nitride complexes with accessory K⁺ ions; for example, isolable uranium terminal nitride complexes often depend on alkali-metal cations for stabilization.²⁹ However, we are aware of no other examples where Lewis acids have been used to modulate the reactivity of N₂-derived fragments. We anticipate that "alkali control" could be a useful concept for the development of catalytic N₂ functionalization reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(Top) Crystal structures of **4** and the anions in **3**, **7**, and **10** using 50% thermal ellipsoids.

Hydrogen atoms (except N-H), 2,6-dimethylphenyl groups are omitted for clarity. (Bottom)

High-resolution electrospray mass spectra of **3**⁻, **7**⁻, and **10**⁻ confirm the number of protons.

The black lines are the spectra, and the red lines are simulations.

Figure 2.
Bond Distances within Triiron Cores and Reference Compounds, Organized by Oxidation Level

Figure 3.

CIVP spectra of 3⁻·N₂, 7⁻·N₂ and 10⁻·N₂. The black dotted line highlights the blue-shift of the NH stretch as a function of oxidation state of the iron centers. The blue dashed line indicates the DFT derived shift of the centroid of the NH₂ symmetric and asymmetric peaks upon addition of an additional H atom. Full DFT calculations are included in the SI.

Figure 4.
Crystal structure of **11** with 50% thermal ellipsoids. H atoms and 2,6-dimethylphenyl groups omitted for clarity.

Scheme 1.

Previous Example of C-H Activation by an N₂ Complex (Ref 9)

Scheme 2.
 N_2 Activation by an Fe-K System (Ref 11)

Scheme 3.

Reaction of 18-crown-6 with 1

Scheme 4.
Oxidation of the C-H Activation Product

Scheme 5.

Reduction of a Triiron Nitride/Imide (5) Followed by K^+ Abstraction Gives C–H Bond Cleavage

Scheme 6.

Reduction of a Triiron Nitride/Amide (**8**) Followed by K^+ Abstraction Gives C–H Bond Cleavage

Scheme 7.

Proposed Intermediates Before Formation of N-H or N-C Bonds

Table 1Mössbauer Parameters for Triiron Clusters^a

Compound	δ (mm/s)	$ E_Q $ (mm/s)	Assignment
3	0.31	2.15	h.s. Fe ³⁺
	0.35	1.74	h.s. Fe ³⁺
	0.66	1.70	h.s. Fe ²⁺
4 ^b	0.22 (0.22)	2.00 (2.00)	h.s. Fe ³⁺
	0.32 (0.32)	1.43 (1.34)	h.s. Fe ³⁺
	0.37 (0.38)	1.22 (1.23)	h.s. Fe ³⁺
7	0.36	3.35	h.s. Fe ³⁺
	0.69	1.00	h.s. Fe ²⁺
	0.71	0.72	h.s. Fe ²⁺
9	0.61	1.56	h.s. Fe ²⁺
	0.71	1.15	h.s. Fe ²⁺
10	0.72	0.98	h.s. Fe ²⁺
	0.72	1.33	h.s. Fe ²⁺
	0.73	1.71	h.s. Fe ²⁺
11	0.35	1.66	h.s. Fe ³⁺
	0.65	1.33	h.s. Fe ²⁺

^aThe fits (see SI) are constrained to 1:1:1 unless indicated otherwise.^bValues in parentheses are for an alternative fit.