

A Multi-iron System Capable of Rapid N₂ Formation and N₂ Cleavage

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S Supporting Information

ABSTRACT: The six-electron oxidation of two nitrides to N₂ is a key step of ammonia synthesis and decomposition reactions on surfaces. In molecular complexes, nitride coupling has been observed with terminal nitrides, but not with bridging nitride complexes that more closely resemble catalytically important surface species. Further, nitride coupling has not been reported in systems where the nitrides are derived from N₂. Here, we show that a molecular diiron(II) diiron(III) bis(nitride) complex reacts with Lewis bases, leading to the rapid six-electron oxidation of two bridging nitrides to form N₂. Surprisingly, these mild reagents generate high yields of iron(I) products from the iron(II/III) starting material. This is the first molecular system that both breaks and forms the triple bond of N₂ at room temperature. These results highlight the ability of multi-iron species to decrease the energy barriers associated with the activation of strong bonds.

Reactive nitrido complexes of the late transition metals have aroused much interest, particularly in the past few years.¹ One exciting reaction of these complexes is nitride coupling to form N₂, a six-electron reaction that makes and breaks many bonds. In these reactions, N₂ formation is driven by the reduction of two metal nitrides, and thus it is seen with complexes of metals having high formal oxidation states. Nitride coupling is the microscopic reverse of N₂ cleavage, and thus it is mechanistically relevant to the industrial production of ammonia in the iron-catalyzed Haber–Bosch process. Dissociation of the N–N bond is the rate-limiting step in the Haber–Bosch process,² and likewise assembly of the N–N triple bond is the challenging step for NH₃ decomposition catalysts (which are of interest for NH₃ fuel cells).³

In molecular systems, nitride coupling has been seen with terminal M–N multiple bonds.¹ However, complexes with bridging nitrides would be more relevant to the bridging modes of the nitrides in heterogeneous catalysts, particularly the proposed nitride intermediates in catalytic ammonia synthesis and decomposition.² Additionally, reported examples of nitride coupling are limited to studies of terminal nitrides that are prepared from nitride/nitrene sources rather than N₂.¹ Studying nitride coupling in systems where the nitrides come from N₂ would be most relevant, given the reversible N₂ cleavage in the Haber–Bosch systems.

To our knowledge, there is only one reported iron system where a nitride complex is generated from N₂.⁴ Our group described a reaction sequence that started with reduction of LFeCl (L = bulky β-diketiminato ligand, shown in Figure 1) to

the iron(I) oxidation level. In the presence of 1 atm N₂, the N–N triple bond of N₂ was cleaved to give two bridging nitrides in a tetranuclear complex that has two iron(II) ions and two iron(III) ions (1 in Scheme 1). Herein, we report the

Scheme 1. Reactions of Compound 1 That Transfer Six Electrons from Nitrides to Iron

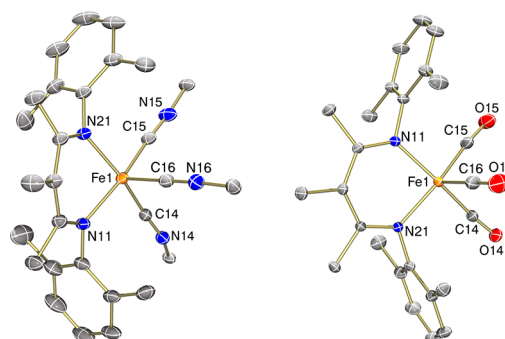
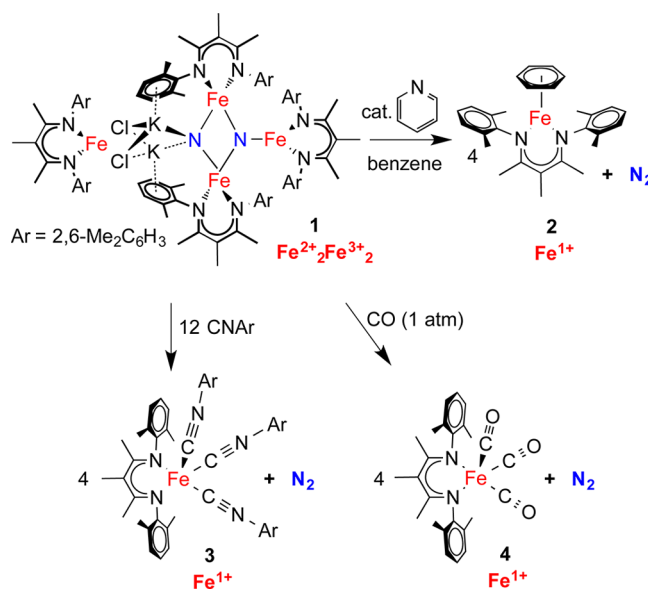


Figure 1. ORTEP diagrams of the X-ray crystal structures of LFe(CNXyl)₃ (3, left) and LFe(CO)₃ (4, right) using 50% thermal ellipsoids. The xylyl groups on the isocyanides in 3 are omitted for clarity.

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selective formation of N–N bonds in the bis(nitride) complex to release the two bridging nitride ligands as N₂ in high yield. This is the first demonstration of N–N triple bond cleavage and N–N triple bond formation by a single homogeneous system. Both reactions occur at or below room temperature, indicating that the multi-iron active site greatly lowers the kinetic barriers for N₂ formation and cleavage.

We previously reported a tetrairon–bis(nitride) complex (**1** in Scheme 1), in which the iron sites were shown to be two iron(II) and two iron(III).⁴ Crystalline samples of **1** are stable under N₂ or Ar for 1 month at –40 °C but decompose slowly in benzene solution at 25 °C with a half-life of 8 h. The major decomposition product under these conditions has now been identified as the iron(I) complex LFe(η^6 -benzene) (**2**) in 56% spectroscopic yield (Scheme 1).

Compound **2** was independently synthesized by reduction of [LFeCl]₂ with 2 molar equivalents of KC₈ in thf/benzene (4:1) under an argon atmosphere. The solid-state molecular structure of **2** (Figure S-20) showed the η^6 binding mode of the benzene ligand, with Fe–C distances ranging from 2.128(2) to 2.147(3) Å. The solution magnetic moment (1.7 μ_B) and rhombic EPR signal ($g = 2.182, 2.010, 1.979$) indicate that **2** has low-spin iron(I) with an $S = 1/2$ electronic configuration. The zero-field ⁵⁷Fe Mössbauer spectrum of solid **2** at 80 K has a single quadrupole doublet with $\delta = 0.68$ mm/s and $|\Delta E_Q| = 0.69$ mm/s (Figure S-1).

The rate of conversion of **1** to **2** increased in the presence of pyridine. Upon treatment of **1** in benzene with 4 equiv of pyridine, **1** was completely consumed within 10 min to produce **2** in 72% yield (determined by ¹H NMR and Mössbauer spectroscopies on the crude reaction mixtures; see Figures S-3 and S-11). Additionally, a sub-stoichiometric amount of pyridine (0.22 equiv compared to **1**) also produced **2** in 70% yield (determined by ¹H NMR spectroscopy), with the reaction requiring only 3 h to reach completion. The absence of pyridine in the reaction product, as well as the observed rate dependence on pyridine concentration, suggests that pyridine is a catalyst for decomposition of the bis(nitride) **1**. This indicates that Lewis bases may act to break up the tetrairon complex during formation of the iron(I) product, and thus subsequent research used slender Lewis bases that could access the metal sites more easily.

Treatment of a benzene solution of **1** with 12 equiv of CNXyl (2,6-dimethylphenyl isocyanide) caused a rapid color change from red-brown to green. Mössbauer analysis of a frozen solution (80 K) of the crude reaction mixture showed conversion to a single product (94%) with $\delta = 0.15$ mm/s and $|\Delta E_Q| = 0.79$ mm/s (Figure 2, top). On the basis of its Mössbauer parameters and ¹H NMR spectrum (Figure S-12), the predominant (94%) reaction product was identified as a tris(isocyanide) compound, LFe(CNXyl)₃ (**3**).

The independent synthesis of **3** was achieved by treating the iron(I) compound **2** with CNXyl. Crystallization from pentane provided a 5-coordinate tris(isocyanide) compound LFe(CNXyl)₃ (**3**) with a square pyramidal geometry at the iron center (Figure 1, left). The IR spectrum of **3** contained two bands at 2075 and 1977 cm⁻¹ (the latter of which is composed of two overlapping bands), which correspond to the isocyanide C–N stretching vibrations. Consistent with the solid-state structure, a frozen solution of **3** had an axial EPR signal with $g_{\perp} = 2.052$ and $g_{\parallel} = 2.002$, and a solution magnetic moment of 1.6 μ_B , indicating a low-spin ($S = 1/2$) iron(I) electronic configuration. The zero-field Mössbauer spectrum of solid **3**

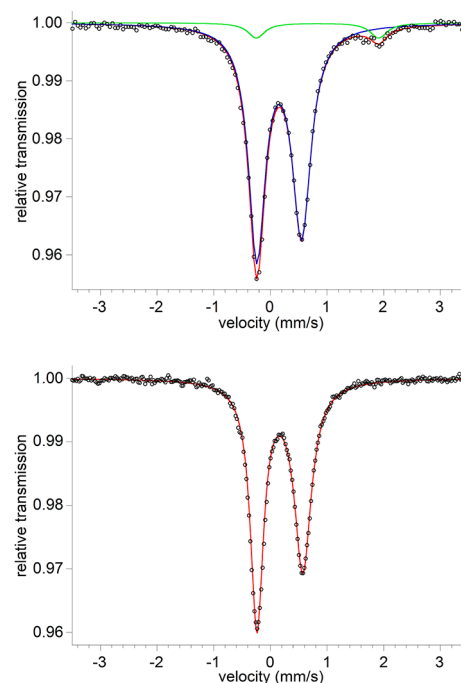
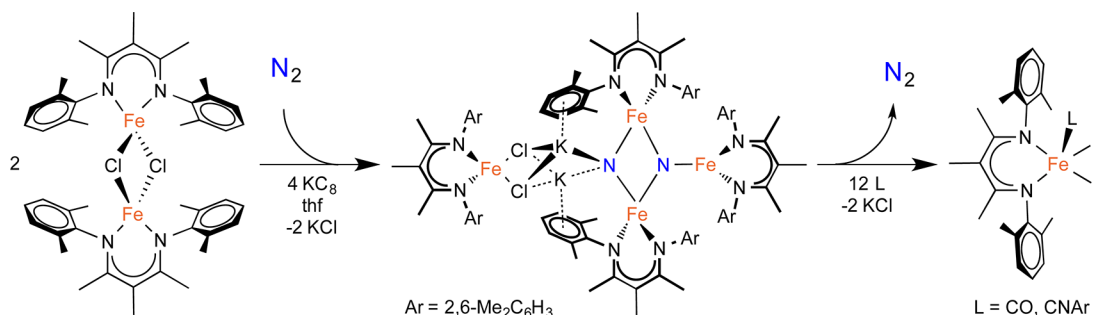


Figure 2. Zero-field Mössbauer spectra at 80 K. The black circles are the data, and the red lines are simulations. (Top) Mössbauer spectrum of a frozen benzene solution of the reaction mixture of **1** with CNXyl (12 equiv). The blue line represents the major product of the reaction (**3**) with $\delta = 0.15$ mm/s and $|\Delta E_Q| = 0.79$ mm/s accounting for 94% of the sample. The green line represents an unknown byproduct (6% of the sample) with $\delta = 0.83$ mm/s and $|\Delta E_Q| = 2.16$ mm/s. (Bottom) Mössbauer spectrum of independently synthesized LFe(CNXyl)₃ (**3**), with a fit having $\delta = 0.17$ mm/s and $|\Delta E_Q| = 0.81$ mm/s. Analogous spectra for the CO reaction are shown in the Supporting Information.

at 80 K showed a quadrupole doublet with $\delta = 0.17$ mm/s and $|\Delta E_Q| = 0.81$ mm/s (Figure 2, bottom), which are the same as the parameters observed for the product of the reaction of **1** with CNXyl. These results indicate that the reaction of the diiron(II)diiron(III) complex **1** with isocyanide yields 94% crude yield of the iron(I) product **3**.

The tricarbonyl analogue of compound **3** was also prepared independently by reaction of the iron(I) compound **2** with CO (1 atm), which resulted in a rapid color change to green. The solid-state molecular structure confirmed a five-coordinate square-pyramidal iron species of the formula LFe(CO)₃ (**4**, Figure 1, right). The IR spectrum of **4** contained three strong bands (2023, 1952, and 1938 cm⁻¹) in the C–O stretching region. Consistent with a square-pyramidal low-spin iron(I) electronic configuration, **4** had a solution magnetic moment of 1.8 μ_B , and a nearly axial EPR signal ($g = 2.043, 2.038, 2.000$). The zero-field Mössbauer spectrum of solid **4** at 80 K had $\delta = 0.12$ mm/s and $|\Delta E_Q| = 0.77$ mm/s accounting for 97% of the iron, and a second minor component (3%) with $\delta = 0.18$ mm/s and $|\Delta E_Q| = 2.04$ mm/s, which is assigned to a 4-coordinate dicarbonyl species LFe(CO)₂.^{5,6}

Treatment of a benzene solution of the bis(nitride) **1** with CO (1 atm) caused a rapid color change from red-brown to green. The zero-field Mössbauer spectrum of a frozen solution (80 K) of the crude reaction mixture contained signals corresponding to the tricarbonyl **4** and dicarbonyl analogue LFe(CO)₂ accounting for a combined 94% of the iron containing products (Figure S-4).^{1j} In summary, addition of either isocyanide or CO to the Fe²⁺₂Fe³⁺₂(N³⁻)₂ complex **1**

Scheme 2. Key N₂-Cleaving and N₂-Forming Reactions in the Multi-iron System

gives a high yield of an iron(I) product, suggesting that all four iron(II)/iron(III) sites are reduced by a total of six electrons. This, in turn, suggests the possible oxidation of the two N³⁻ ligands by a total of six electrons to give N₂.

Consistent with this hypothesis, compound **1** was observed to release a gas upon reaction with CNXyl or pyridine. Monitoring the pressure change upon addition of 13 equiv of CNXyl to a solution of **1** showed the production of 1.00 ± 0.04 mol of gas per mol of **1**. Analysis of the resulting gas by GC-MS under an Ar atmosphere confirmed that N₂ was formed in the reactions (Figure 3). A sample of **1** labeled with ¹⁵N gave ¹⁵N₂ that was observed in the mass spectrum at *m/z* = 30. These results demonstrate the quantitative release of N₂ from bis(nitride) **1** upon addition of CNXyl, which is accompanied

by formation of the reduced iron(I) compound LFe(CNXyl)₃ (**3**).

Though the mechanism of the N–N bond formation is not known in detail, mechanistic information was gathered using isotopically labeled **1**-¹⁵N₂. A benzene solution containing a 1:1 mixture of ¹⁵N-labeled **1** and unlabeled **1** was treated with 13 equiv of CNXyl. The headspace contained exclusively ¹⁴N₂ (*m/z* = 28) and ¹⁵N₂ (*m/z* = 30). The lack of mixed-label ¹⁴N¹⁵N at *m/z* = 29 indicates that N₂ formation proceeds by an intramolecular N–N bond formation process, and that the nitride ligands do not exchange between complexes. Additionally, the fact that ¹⁵N-labeled **1** can be handled and stored under N₂ atmosphere without loss of the ¹⁵N-labeled nitride ligands indicates that the nitride ligands do not exchange with atmospheric N₂ in either solution or the solid state prior to the addition of the π-acidic ligands.

In a previous report, we described the reduction of [LFeCl]₂ with 1 equiv of potassium per iron atom, which cleaves the N–N bond of dinitrogen at room temperature to form **1** (Scheme 2, left).⁴ We proposed that the iron(II) complex is first reduced by the potassium to form a transient intermediate with formally iron(I) ions, which react cooperatively with a single N₂ molecule.⁷ Notably, the ability of four iron centers to arrange around a single molecule of N₂ provided compound **1**, which has two iron(II) and two iron(III) metal centers. Therefore, the six-electron reduction of the N₂ unit was accomplished using four metal centers, thereby avoiding the need to access a high oxidation state of iron. In an equivalent manner, the N–N bond formation described herein is a six-electron oxidation of nitrides to N₂ with quantitative reduction of iron centers to iron(I) in compounds **2**, **3**, and **4** (Scheme 2, right).

A number of well-defined molecular systems are known to cleave the triple bond in dinitrogen.⁸ These systems use highly reducing metal centers, typically early transition metals in low oxidation states, and are driven by the oxidation of the metal and formation of a very strong metal–ligand multiple bond.⁹ Conversely, a number of reports have described the reverse reaction, N₂ formation as a result of metal–nitride coupling.¹ The N₂-forming systems use middle to late transition metals in unusually high oxidation states, and are driven by the reduction of the metal. Thus, the known reactions in each direction are brought about by a large thermodynamic driving force, which is unlike the reversible cleavage/formation of N₂ that is characteristic of the heterogeneous catalyst. To our knowledge, no homogeneous system has been reported to both cleave and form the N–N triple bond of dinitrogen, and it is distinctive that this multi-iron system is poised at the brink of N₂ activation. However, the N–N cleavage/formation here is not

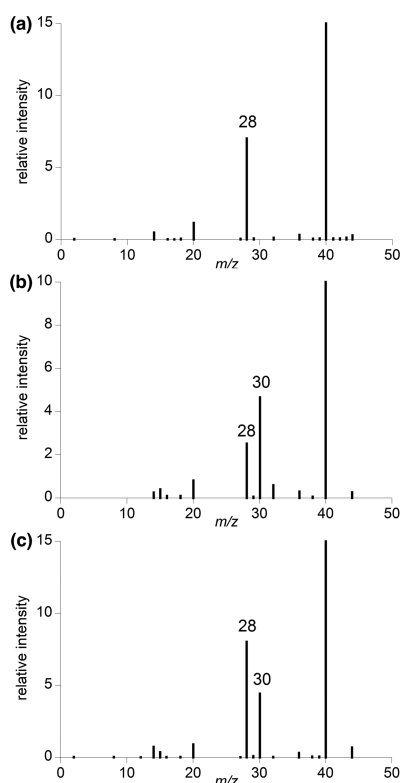


Figure 3. Mass spectra of the gas evolved during reactions with CNXyl under Ar (*m/z* = 40) with **1** (a), ¹⁵N-labeled **1** (b), and a mixture of ¹⁵N-labeled **1** and unlabeled **1** (c). The spectra indicate the formation of ¹⁴N₂ and ¹⁵N₂ with *m/z* = 28 and 30, respectively. The smaller peak at *m/z* = 28 in (b) resulted from unavoidable contamination by ¹⁴N₂ in air.

truly reversible, because the iron(I) species are not the same in both reactions. Driving forces for the new N₂-forming reaction likely include the stabilization of iron(I) by the π -accepting ligands in **2**, **3**, and **4**, and also the precipitation of KCl as a byproduct.

However, the kinetic aspects are most significant. This work suggests that the ability to place multiple iron centers (≥ 3) around a single molecule of N₂ gives fast rates for N–N bond cleavage/formation. As a testament to the low barriers for these reactions, both the N–N bond cleavage and formation reactions in this system occur rapidly at room temperature. This indicates that cooperation between several iron centers facilitates multi-electron reactions of difficult substrates like N₂, identifying this as a key strategy for accomplishing homogeneous reactions with this inexpensive metal. At the same time, it provides key insight into the bond cleaving and forming steps in the iron-catalyzed Haber–Bosch process, by showing that four iron atoms can cooperate to accomplish N–N bond transformations observed on heterogeneous iron catalysts.¹⁰

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and characterization data. 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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diketiminato iron(I) carbonyl compounds in the literature (Table S-1).⁶

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