Studies of Low-Coordinate Iron Dinitrogen Complexes
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Abstract: Understanding the interaction of N2 with iron is relevant to the iron catalyst used in the Haber process and to possible roles of the FeMoco active site of nitrogenase. The work reported here uses synthetic compounds to evaluate the extent of NN weakening in low-coordinate iron complexes with an FeNNFe core. The steric effects, oxidation level, presence of alkali metals, and coordination number of the iron atoms are varied, to gain insight into the factors that weaken the NN bond. Diiron complexes with a bridging N2 ligand, L²FeNNFeL² (L² = β-diketiminate; R = Me, tBu), result from reduction of [L²FeCl]₂ under a dinitrogen atmosphere, and an iron(l) precursor of an N2 complex can be observed. X-ray crystallographic and resonance Raman data for L²FeNNFeL² show a reduction in the N–N bond order, and calculations (density functional and multireference) indicate that the bond weakening arises from cooperative back-bonding into the N₂ σ* orbitals. Increasing the coordination number of iron from three to four through binding of pyridines gives compounds with comparable N–N weakening, and both are substantially weakened relative to five-coordinate iron-N₂ complexes, even those with a lower oxidation state. Treatment of L²FeNNFeL² with K₂ gives K₅L⁴FeNNFeL⁴, and calculations indicate that reduction of the iron and alkali metal coordination cooperatively weaken the N–N bond. The complexes L⁵FeNNFeL⁵ react as iron(l) fragments, losing N₂ to yield iron(l) phosphate, CO, and benzene complexes. They also reduce ketones and aldehydes to give the products of pinacol coupling. The K₅L⁴FeNNFeL⁴ compounds can be alkylated at iron, with loss of N₂.

Introduction

Atmospheric N₂ is an abundant and cheap source of nitrogen for nitrogen-containing compounds. However, the N₂ molecule is difficult to manipulate due to both thermodynamic factors (N≡N bond strength of 944 kJ mol⁻¹; negative electron affinity; high ionization energy) and kinetic factors (poor electrophilicity and nucleophilicity; no permanent dipole). Catalysts are used in nature and industry to activate N₂, and the largest-scale processes use iron.

In nature, the nitrogenase enzymes catalyze the reduction of atmospheric dinitrogen to ammonium salts, which are in turn used in the biosynthesis of nitrogen-containing molecules. Iron is the only transition metal present in all nitrogenase enzymes, but iron−molybdenum nitrogenase is the best characterized. In iron−molybdenum nitrogenase, the site of substrate binding and reduction is the iron−molybdenum cofactor or “FeMoco” (Figure 1). The most recent X-ray crystallographic study of the enzyme (1.16 Å resolution) shows the FeMoco in the native state to be a MoFe₂S₆X cluster, and Mössbauer data indicate an (Fe³⁺)(Fe²⁺)(Mo⁴⁺) oxidation level. The six iron atoms in the center are bridged by a light atom X (C, N, or O).


Spectroscopic investigations with \(^{15}\text{N}_2\) and the spectroscopic similarity of active and inactive forms of the enzyme\(^2\) argue against the interstitial atom resulting from splitting of \(\text{N}_2\), suggesting that its role may be structural.

The picture in Figure 1 is not strictly relevant to \(\text{N}_2\) binding by the FeMoco, because the crystallographically characterized native state of the FeMoco does not bind substrates. Several reducing equivalents are required before \(\text{N}_2\) binds.\(^9\) ENDOR studies of mutant enzymes are most consistent with binding of the Fe intermediate, and this intermediate is subsequently protonated by a thiol, in a manner reminiscent of proposals by Sellmann.\(^13\) A very recent study shows a single \(\text{N}\) environment for an apparent adduct of \(\text{N}_2\) (or reduced form thereof) on the FeMoco, which is consistent with a symmetrical binding mode.\(^4\)

In addition to nitrogenase, there are heterogeneous iron systems that catalytically reduce dinitrogen. Some iron oxide\(^15\) and iron sulfide\(^16\) surfaces produce ammonia from \(\text{N}_2\). Most industrially relevant is the Haber–Bosch process, in which ammonia is synthesized from nitrogen and hydrogen over an iron catalyst.\(^17\) Single-crystal iron surfaces reduce \(\text{N}_2\), and the (111) face of iron is most active.\(^18\) LEED experiments suggest that \(\text{N}_2\) bound to Fe(111) is strongly inclined rather than perpendicular to the surface.\(^19\) Therefore, \(\text{N}_2\) bridged between iron atoms is again a potential binding mode.

Despite the importance of these iron catalysts, the current understanding of \(\text{N}_2\) reduction chemistry in synthetic iron compounds is rudimentary. Some solution Fe–\(\text{N}_2\) systems have been reported to give hydrazine or ammonia upon protonation,\(^20,21\) but these systems are not understood at a mechanistic level. For example, uncharacterized mixtures of iron(III) chloride and strong reducing agents are reported to give hydrazine upon protonation.\(^22\) Treatment of some iron–phosphine–\(\text{N}_2\) complexes with excess acid gives limited amounts of ammonia.\(^23\) In a well-characterized recent study, the reduced dinitrogen complex \(\text{Fe}[(\text{PhBPr})_3][(\text{N}_2)\text{MgCl}(\text{THF})_2] (\text{PhBPr})_3 = \text{PhB}(\text{CH}_2\text{P})_3\) reacts with electrophiles to give a diazenido ligand derived from dinitrogen.\(^24\)

One important difference between the catalytic iron sites and synthetic iron compounds is the coordination number at iron, which is typically 5 or 6 for synthetic compounds but possibly lower in the active forms of the catalysts. Because the bulky \(\beta\)-diketiminate ligands, \(\text{L}^{1\text{Me}}\) and \(\text{L}^{1\text{Bu}}\) (Figure 2) stabilize synthetic complexes with three-coordinate and four-coordinate iron centers,\(^12\) it is possible to evaluate the importance of iron coordination number. Here, we show that when \(\text{N}_2\) binds to low-coordinate iron, the \(\text{N}–\text{N}\) bond becomes much weaker than in other iron-\(\text{N}_2\) complexes. Further, we evaluate the structural
and spectroscopic evidence that large changes in oxidation level, coordination number, and steric bulk. The unusual N₂ complexes are characterized through structural, spectroscopic, and theoretical methods, as well as their characteristic reactivity patterns.

Results

Synthesis of L⁸FeNNFeL⁸. We previously reported that red-purple L⁸BuFeNNFeL⁸Bu could be prepared from L⁸BuFeCl by reduction with sodium naphthalenide.²⁵ Potassium/graphite (KC₈) has proven to be a more effective reducing agent for L⁸BuFeCl and [L⁸Fe(µ-Cl)]₂, leading to L⁸BuFeNNFeL⁸Bu and L⁸MeFeNNFeL⁸Me in about 70% yield (Scheme 1).²⁶ L⁸BuFeNNFeL⁸Bu is also produced by photolysis (4 d, RT, high-pressure mercury lamp) of [L⁸FeH]₂⁶ under an N₂ atmosphere.

We have reported the X-ray crystal structure of L⁸BuFeNNFeL⁸Bu.²⁵ Only seven resonances are observed in its ¹H NMR spectrum (C₆D₆), suggesting that the diketiminate ligand contains two mirror planes, and the molecule has averaged D₂h symmetry in solution. The ¹H NMR spectrum can be assigned on the basis of integration, chemical shift and relaxation time (T₁) from width of peaks. Although highly sensitive to air and moisture, solutions of L⁸BuFeNNFeL⁸Bu show no evidence of decomposition after several hours of heating in aromatic solvents at 100 °C. L⁸MeFeNNFeL⁸Me, on the other hand, reacts with aromatic solvents (see below).

We have obtained two different X-ray crystal structures of L⁸MeFeNNFeL⁸Me (Figure 3). In one crystal (Ia), a disordered pentane molecule lies in the unit cell, and the other crystal (Ib) is free of solvent. The two crystal structures give similar bond distances, which are similar to those in L⁸BuFeNNFeL⁸Bu (Table 1). The N=N bond lengths in L⁸MeFeNNFeL⁸Me are 1.18 ± 0.01 Å, indicative of substantial N=N bond weakening relative to free N₂ (1.098 Å). The iron-diketiminate ligand planes in L⁸MeFeNNFeL⁸Me are coplanar in each form of L⁸MeFeNNFeL⁸Me, in contrast to the nearly perpendicular ligand planes in the crystal structure of L⁸BuFeNNFeL⁸Bu (the angle between the diketiminate planes is 92.6°).²⁶ We ascribe this difference to steric interactions between the two diketiminate ligands, because molecular mechanics calculations²⁷ based on the crystallographic geometries of Ia and of L⁸BuFeNNFeL⁸Bu suggest that the parallel geometry is more stable by 2 kcal/mol in the L⁸Me complex, but less stable by 4 kcal/mol in the L⁸Bu complex. Interestingly, Ia and Ib differ by a surprising 20°−25° shift of the N₂ ligand off the line that bisects the diketiminate ligand. Apparently, the highly symmetric core found in Ia may be distorted by the small energy of crystal packing forces. The solution ¹H NMR spectrum of Ia in cyclohexane-d₁₂ is consistent with averaged D₂h symmetry. The complex has a large magnetic moment in solution, μₐeff = 7.9(3) μB, which compares well with its L⁸Bu analogue (8.4 μB).

The weakening of the N=N bond is also observed by resonance Raman spectroscopy. A band at 1810 cm⁻¹ in L⁸MeFeNNFeL⁸Me shifts to 1739 cm⁻¹ in L⁸MeFe¹⁵N¹⁵FeL⁸Me (Figure 4A and 4B). Similar N=N bond weakening is observed in L⁸BuFeNNFeL⁸Bu, for which νN=N occurs at 1778 cm⁻¹.²⁵ Both values are substantially decreased from free N₂ (2331 cm⁻¹).

Computations: Ground-State Multiplicities. Our computational models for evaluation of iron-dinitrogen complexes with multiconfiguration (MCSCF) and density functional theory

(²⁷) MM calculations were carried out with the MMFF94 force field (Halgren, T. A. J. Comput. Chem. 1998, 17, 616–641 and references therein) as implemented within the Spartan package (Spartan, Wavefunction, Inc., 18401 Von Karman Ave., Ste. 370, Irvine, CA 92612; http://www. wavefun.com).
For recent applications of this methodology to transition metal chemistry

\[ \text{Fe}^{2+} \text{N} \rightarrow \text{N} \rightarrow \text{N} \text{ Bond Stretching Frequencies for Crystallographically Characterized Iron Complexes with Bridging N}_2 \]

Table 1. Fe–N, N–N Bond Lengths, and N–N Bond Stretching Frequencies for Crystallographically Characterized Iron Complexes with Bridging N2

<table>
<thead>
<tr>
<th>complex</th>
<th>Fe CN ( ^{\text{a}} )</th>
<th>formal oxidation state of Fe</th>
<th>Fe–N (Å)</th>
<th>N–N (Å)</th>
<th>( \nu_{\text{vib}} ) (cm(^{-1}))</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>([{\text{PEt}_3}_2\text{FeN}_2]_2)</td>
<td>5</td>
<td>0</td>
<td>1.87(1); 1.89(2)</td>
<td>1.13(2)</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>([{\text{OPr}_{12}}_2\text{FeN}_2]_2)</td>
<td>5</td>
<td>0</td>
<td>1.876(9)</td>
<td>1.13(1)</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>(\text{L}^\text{Me}\text{Fe}^\text{Bu}^\text{Bu}^\text{NN}^\text{Bu}^\text{Bu}\text{Fe}^\text{L}^\text{Me})</td>
<td>4</td>
<td>1</td>
<td>1.816(2)</td>
<td>1.151(3)</td>
<td>1770</td>
<td>this work</td>
</tr>
<tr>
<td>(\text{L}^\text{Me}^\text{Fe}^\text{Bu}^\text{Bu}^\text{NN}^\text{Bu}^\text{Bu}\text{Fe}^\text{L}^\text{Me})</td>
<td>4</td>
<td>1</td>
<td>1.804(2); 1.794(2)</td>
<td>1.161(4)</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>({\text{PhBPy}_3}_2\text{Fe}^\text{NNFe}^\text{PhBPy}_3)</td>
<td>4</td>
<td>0.5</td>
<td>1.813(2)</td>
<td>1.171(4)</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>(\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me})</td>
<td>3</td>
<td>1</td>
<td>1.745(3)</td>
<td>1.186(7)</td>
<td>1810</td>
<td>this work</td>
</tr>
<tr>
<td>(\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me})</td>
<td>3</td>
<td>1</td>
<td>1.775(2)</td>
<td>1.172(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{K}^\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me})</td>
<td>3</td>
<td>0</td>
<td>1.741(5); 1.761(7)</td>
<td>1.215(6)</td>
<td>1625, 1437</td>
<td>this work</td>
</tr>
<tr>
<td>(\text{Na}_2\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me})</td>
<td>3</td>
<td>0</td>
<td>1.749(3); 1.746(3)</td>
<td>1.238(4)</td>
<td>1583, 1127</td>
<td>25</td>
</tr>
<tr>
<td>(\text{K}_2\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me})</td>
<td>3</td>
<td>0</td>
<td>1.773(7); 1.761(7)</td>
<td>1.241(7)</td>
<td>1589, 1123</td>
<td>25</td>
</tr>
</tbody>
</table>

\( ^{\text{a}} \) Coordination number at the iron atoms.

Figure 4. Resonance Raman spectra of FeNFe complexes showing \( ^\text{15} \text{N} \)-sensitive bands. Based on the isotope shifts, bands above 1500 cm\(^{-1}\) are attributed to modes with dominant N–N stretching character. A, \(\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\); B, \(\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\); C, \(\text{K}^\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\); D, \(\text{K}_2\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\); E, Difference spectrum \([\text{K}^\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\] - \([\text{L}^\text{Me}^\text{Fe}^\text{NNFe}^\text{L}^\text{Me}\] \) F, \(\text{L}^\text{Me}^\text{Fe}^\text{Bu}^\text{Py}^\text{NN}^\text{Bu}^\text{Py}^\text{Fe}^\text{L}^\text{Me}\); G, \(\text{L}^\text{Me}^\text{Fe}^\text{Bu}^\text{Py}^\text{NN}^\text{Bu}^\text{Py}^\text{Fe}^\text{L}^\text{Me}\). The spectra were obtained with 406.7 nm excitation. Samples A, B, F, and G were prepared in toluene. Samples C and D were prepared in pentane. Samples A, B, F, and G were prepared in toluene; toluene bands have been subtracted from the spectra.

(DFT) methods use a truncated diketiminate ligand \( \text{L}^\text{′} \) \((\text{C}_3\text{N}_2\text{H}_4)^{-}\). The starting geometry for calculations was derived from the experimental geometry of \(\text{L}^\text{H}^\text{Bu}^\text{Bu}^\text{Fe}^\text{NNFe}^\text{L}^\text{Bu}^\text{Bu}^\text{Fe} \). After replacement of 2,6-diisopropylphenyl and tert-butyl substituents with hydrogen, the geometry was slightly modified to yield an idealized \( D_{3h} \) geometry in L′FeNNFeL′. To evaluate the cooperativity between iron centers, L′FeNNFeL′ was further trimmed to yield L′FeNN and \( [\text{L}^\text{HN}^\text{NN}]^{-} \) (each with \( C_{2v} \) symmetry), as shown in Chart 1 on the next page.

We find a \( ^3 \text{B}_2 \) ground state for L′FeNN at the MRMP2/SBKJC(d) level of theory, whereas the lowest energy doublet states correspond to low spin states of \( ^5 \text{B}_2 \) and sextet \( ^6 \text{B}_2 \). There is evidence of \( ^7 \text{B}_2 \) state of Fe–Fe dinitrogen.

The computations indicate a synergistic iron center.

Computations: Synergism between Iron Centers. Geometry optimization (B3LYP/CZDZ**++) of the neutral, quartet L′FeNN yields Fe–N = 1.902 Å and N–N = 1.123 Å. This N–N bond length is significantly longer than that in free N\(_2\) (1.098 Å).

To determine the optimized parameters for L′FeNNFeL′ agree well with the experimental Fe–N and N–N distances given in Table 1. Coordination of L′Fe to the terminal N of L′FeNN results in formation of in-phase and out-of-phase combinations between Fe d\( \pi \) orbitals and the orbital depicted in Chart 1. This orbital overlap gives a greater influence of electron density into the \( \pi^* \) orbitals of N\(_2\).


(31) It was not possible to obtain SCF convergence for ROB3LYP/CSDZ**++ calculations on L′FeNNFeL′. Hence, unrestricted DFT calculations were employed. The literature suggests that spin contamination is less significant in UDFT in relation to comparable unrestricted Hartree–Fock (UHF) wave functions (e.g. ref 38). Geometry optimizations on quartet L′FeNNFeL′ show little difference in calculated metrics (ROB3LYP/UB3LYP), e.g., Fe–N = 1.902 Å/1.901 Å; NN = 1.123 Å/1.129 Å; FeN\(_2\) = 1.990 Å/1.980 Å; bite angle = 96°/96°; the total spin expectation value (S\(^2\)) is 3.934 versus the ideal value of 3.760.
Four-Coordinate Iron--N2 Complexes. Treatment of L4FeNNFeL4 with 2 molar equivalents of 4-tert-butylpyridine, 4-(dimethylamino)pyridine, or pyridine affords four-coordinate dinitrogen complexes of iron (Scheme 2). X-ray crystallographic analyses of the 4-tert-butylpyridine adducts, L4Fe(Bupy)NNNNFe(L4), are in the Supporting Information. The identification of the other pyridine adducts are based on the similarity of their 1H NMR spectra to the structurally characterized ones. Each iron atom is four-coordinate, with a trigonal pyramidal geometry (τ = 0.42±0.52) (32) that is reminiscent of the four coordinate pyridine adducts of L4BuFeH (46) L4BuFe (33) and L8Fe(NHR)6 (66).

The crystal structures of these complexes show that the N--N bonds are shortened by ~0.03 Å by the addition of a fourth ligand to iron (Table 1). However, this difference is only slightly larger than the 3σ threshold, and not much greater than the range seen in the two crystal structures of compound 1 above.34 Resonance Raman spectra of L4Fe(Bupy)NNNNFe(L4) and its 15N2 isotopomer (Figure 4F,G) show an isotopically sensitive band at 1770 cm\(^{-1}\) that is assigned to the N--N stretching vibration. Comparison to L4FeNNFeL4 shows that the frequencies for N2 bound to four-coordinate iron and three-coordinate iron are similar, indicating a similar force constant for the N--N bond (Table 1).

In the crystal structures of the L4Fe(Bupy)NNNNFe(Bupy)FeL4 complexes, there is a substantial angle between the two diketiminate planes (52.22(5)° in the LMe complex and 82.50-(7)° in the LBu complex). As a result of the twisting around the FeNNFe axis, there is no symmetry element in the diketiminate ligands: the two faces of the diketiminate differ in proximity to the nearby pyridine ligand, and the two sides of the diketiminate differ in proximity to the more distant pyridine ligand. However, the room temperature 1H NMR spectra of L4Fe(py-R)NNNNFe(py-R)LMe (py-R = 4-BuC6H4N and 4-NMe2C6H4N) in pentane-d12 show two sets of peaks for the meta aryl, isopropyl methyl, and isopropyl methine protons and one set of peaks for the α-methyl, para aryl, and the backbone C–H of the ligands. This suggests that at room temperature the two sides of the diketiminate are equivalent and the two faces are not. As the temperature was decreased to ~70 °C, the singlets of the α-methyl, para aryl, and one set of isopropyl methine and meta-aryl protons broadened and then split into two peaks. The observed exchange process is consistent with rotation around the FeNNFe unit with a barrier of 9.5 ± 0.2 kcal/mol for L4Fe(Bupy)NNNNFe(Bupy)LMe and 9.3 ± 0.2 kcal/mol for L4Fe(Me2Npy)NNNNFe(Me2Npy)LMe. Because the exchange process makes the two halves of the ligands equivalent but retains the inequivalence of the two faces, and because there is no measurable difference between the barriers for the different pyridine adducts, we conclude that neither pyridine nor N2 dissociates on the NMR time scale.

Reactions of the N2 Complexes. In evaluating the reactivity of L4FeNNFeL4, it is important to know whether the FeNNFe core is stable in solution. To test this possibility, resonance Raman spectra of a pentane solution of L4FeNNFeL4 have been monitored under an atmosphere of 15N2. Very little incorporation of 15N is observed over several days at room temperature, suggesting that no rapid cleavage/recombination events occur. L4FeNNFeLMe, on the other hand, incorporates added 15N2 gas in less than 2 d at ~78 °C in pentane, showing that the reduction of steric bulk makes the N2 ligand labile. Consistent with this idea, LMeFeNNFeLMe reacts with benzene to displace the N2 ligand irreversibly (Scheme 3). The rate of this reaction in mixtures of deuterated benzene and cyclohexane is strongly dependent on the concentration of benzene, suggesting an associative mechanism for the reaction (see Supporting Information for details). The X-ray crystal structure of the product reveals that it is LMeFe(η4-C6H4) (Figure 5). All benzene C–C and Fe–C bond distances are within 3σ of the mean indicating a η4-binding mode. At room temperature the 1H NMR spectrum (CD3) shows broad signals. The rhombic

(32) We define τ as a normalized measure of trigonal distortion of a tetrahedral structure, with τ = 0 representing tetrahedral geometry and τ = 1 representing a trigonal pyramid in which the metal lies in the plane formed by the three basal ligands. For details, see ref 26.


X-band EPR spectrum (g = 2.20, 2.01, 1.98; Figure 7c) and the solution magnetic moment (μ_eff = 2.5 μ_B) indicate an S = 1/2 ground state, so we formulate this compound as a low-spin iron(I) complex.

Reaction of L^{Me}FeNNFeL^{Me} with excess CO in diethyl ether affords a novel iron(I) complex, L^{Me}Fe(CO)_{3}, as dark green crystals (Scheme 2). The X-ray crystal structure of this compound is shown in Figure 6a. The geometry around the iron center is square pyramidal, where one of the carbonyl groups is in the axial position of the square pyramid. The bond length of the axial Fe–C bond (Fe–C(14) 1.871(2) Å) is slightly longer than the other two Fe–C bonds (Fe–C(13) 1.7957(16) Å). The IR spectrum of L^{Me}Fe(CO)_{3} in pentane shows three bands (2042, 1922, and 1971 cm^{-1}) in the carbonyl region. The magnetic moment is 2.0 μ_B, and an axial X-band EPR signal (Figure 7) is observed at 77 K in frozen toluene, with g_{||} = 1.99 and g_{\perp} = 2.04. Together, these measurements indicate that L^{Me}Fe(CO)_{3} has a low-spin (S = 1/2) electronic configuration at iron.

Reaction of L^{Bu}FeNNFeL^{Bu} with excess CO gives a product with more complicated characteristics. Its crystal structure consists of a superposition of two complexes (Scheme 2): L^{Bu}Fe(CO)_{3} and square-planar L^{Bu}Fe(CO)_{2}, which differ by the loss of the axial CO ligand. Consistent with a mixture of tricarbonyl and dicarbonyl species, the IR spectrum of this solid shows five bands at 2036, 2000, 1967, 1953, and 1922 cm^{-1}. The 77 K X-band EPR spectrum contains an axial signal closely resembling that of L^{Me}Fe(CO)_{3} as well as a rhombic signal (g = 2.35, 2.13, 1.98) tentatively assigned to L^{Bu}Fe(CO)_{2} (Figure 7). The EPR signature suggests that both carbonyl complexes have low-spin electronic configurations. Unfortunately, it has not yet been possible to separate these two complexes for more detailed characterization of the square-planar iron(I) complex.
β-diketiminate ligand, causing the β-diketiminate aryl rings to bend away from the phenyl ring so that the methine carbons of the isopropyl groups are 6.798(4) Å on one side but 4.166(4) Å on the other side. This asymmetry is evident in low-temperature 1H NMR spectra in pentane-Å on the other side. This asymmetry is evident in low-

The 1H NMR spectra exclude the presence of the meso diastereomer, which would show up to eight sets of isopropyl CH₃ groups.

**Reduction of L⁸⁸⁷⁸FeCl in the Absence of N₂.** Treatment of solutions of L⁸⁸⁷⁸FeCl with KC₈ in diethyl ether or THF, under an atmosphere of argon, results in the formation of forest green solutions of a metastable compound assigned as L⁸⁸⁷⁸Fe(KCl)-,(solv), (Scheme 4). When argon is removed from L⁸⁸⁷⁸Fe(KCl)-,(solv), under vacuum and nitrogen is introduced to the forest green solution, an instant color change from green to red-purple is observed and characteristic 1H NMR resonances for L⁸⁸⁷⁸FeNNFeL⁸⁸⁷⁸ appear. This confirms that transient iron(I) complexes are kinetically competent in the formation of the iron-dinitrogen complexes from L⁸⁸⁷⁸FeCl, KC₈, and N₂.

The green intermediate species decomposes to an intractable orange mixture within a few hours. However, performing the reduction in the presence of 18-crown-6 affords dark green crystals as part of a mixture of products. The X-ray crystal structure of one product, L⁸⁸⁷⁸FeNNFeL⁸⁸⁷⁸Bu(18-crown-6), is shown in Figure 9. The Fe−Cl−K angle is 134.17(11)°, and the Fe−Cl distance is 2.235(3) Å, compared with 2.172(1) Å in L⁸⁸⁷⁸FeCl. A solvent toluene molecule has a carbon roughly 3.6 Å from the potassium atom, opposite the bridging chloride. However, disorder of the toluene limits the precision of the structure. This is a rare example of a complex with an alkali halide as a ligand; to our knowledge the only related iron complex is [(Me₃Si)₂N]₂Fe[(μ-Cl)Li(THF)]₃.³⁷

**Two-Electron Reduction of L⁸⁸⁷⁸FeNNFeL⁸⁸⁷⁸.** Reduction of L⁸⁸⁷⁸FeNNFeL⁸⁸⁷⁸ or L⁸⁸⁷⁸Fe(Bupy)NNFe(Bupy)L⁸⁸⁷⁸ with additional KC₈ gives the dark blue-green complexes K₃L⁸⁸⁷⁸FeNNFeL⁸⁸⁷⁸, isolated in low yield (Scheme 5). They are soluble in pentane, suggesting that the alkali metal remains tightly bound in solution.

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Footnotes:


In solution, the K₃L⁶FeNNFeL⁶ complexes each adopt a D₂d or D₂h averaged structure, since again only seven signals are observed in ¹H NMR spectra.

The structure of K₃L⁶FeNNFeL⁶, as determined by X-ray crystallography (Figure 10), is analogous to that of M₄L⁶Bu₆FeNNFeL⁶Bu₆ (M = Na, K) twenty-five years ago when the potassium atom coordinates to the bridging N₂ and the aryl rings of the ligand. The K–N bond lengths in K₃L⁶FeNNFeL⁶ are (2.748(5)–2.800(6) Å) are slightly longer than those of K₃L⁶Bu₆FeNNFeL⁶Bu₆ (2.690(6)–2.796(5) Å), and K(2)–N(2) 2.778(6), K(1)–N(2) 2.748(5), K(2)–N(1) 2.800(6), K(2)–N(2) 2.796(5); N(11)–Fe(1)–N(21) 96.2(2), N(1)–Fe(1)–N(11) 131.3(2), N(1)–Fe(1)–N(21) 132.6(2), N(12)–Fe(2)–N(22) 95.0(2), N(2)–Fe(2)–N(12) 133.6(2), N(2)–Fe(2)–N(22) 131.0(2).

Scheme 5

![Scheme 5](image-url)

Resonance Raman spectra of the alkali metal complexes contain multiple bands with frequencies that are sensitive to isotopic substitution in the N₂ (Figure 4C,D; Figure 4E shows the difference spectrum). Using K₃L⁶Bu₆FeNNFeL⁶Bu₆ these bands appear at 1589 (1536/1565) and 1123 (1087) cm⁻¹, and using K₃L⁶Me₆FeNNFeL⁶Me they are at 1625 (1569) and 1427 (1389) cm⁻¹ (numbers in parentheses for the ¹⁵N isotope). The observation of multiple isotope-sensitive bands (with isotope shifts smaller than expected for a diatomic oscillator) indicates that there are multiple Raman active vibrational modes in which the bridging nitrogen atoms have significant kinetic energy. We attribute this effect to coupling between C≡N=C≡C bond stretches near 1500 cm⁻¹ and the N=N bond stretch. Although the absence of a localized N=N stretching vibration hinders the precise quantification of N=N bond weakening through vibrational spectroscopy, the N=N frequencies are clearly lower in the [L⁶FeNNFeL⁶]⁺⁻ complexes than in their less reduced L⁶FeNNFeL⁶ counterparts (Table 1).

Computations: Role of Alkali Metals. All experimental attempts to remove the alkali metals from these complexes have led to decomposition or intractable products. Therefore, we turned to calculations to distinguish the effects of reduction from the effects of alkali metal coordination. The theoretical model complex L⁶FeNN was first reduced by a single electron and then pairs of alkali metal ions were ligated to the dinitrogen ligand. Thus, B3LYP/CSDZ++ geometry optimizations of triplet [L⁶FeNN]+; [Na₃[L⁶FeNN]⁺]+ and {K₂[L⁶FeNN]+} were performed under C₂ᵥ symmetry using RODFT methods. The optimized geometry of [Na₃[L⁶FeNN]⁺]+ is shown in Figure 11, and the geometry of the potassium analogue is similar. The calculated bond lengths for these species are Fe–N = 1.755 Å ([L⁶FeNN]⁺), 1.690 Å ([Na₃[L⁶FeNN]⁺]+), and 1.709 Å ([K₂[L⁶FeNN]+]), while the calculated N=N bond lengths are 1.159, 1.191, and 1.176 Å, respectively, for these same complexes. These calculated values can be compared to Fe–N = 1.902 Å and N=N = 1.123 Å in L⁶FeNN (see above). Although the metrical parameters are not accurate due to the truncation of the model, two points are of particular interest in the context of N₂ activation. First, comparison of the results for L⁶FeNN and [L⁶FeNN]⁺ indicates that reduction of iron significantly weakens N₂ (Δ(N=N) = +0.037 Å). Second, coordination of alkali metal ions causes further dinitrogen stretching (Δ(N=N) ~ +0.02–0.03 Å). Both effects are comparable in terms of their impact on the N=N bonding.

Inspection of the Kohn–Sham orbitals suggests that reduction of L⁶FeNN places additional electron density in an orbital with Fe–N π-bonding character and N=N π antibonding character. Also, the anion shows greater mixing of NN with Fe-based dπ orbital than the corresponding (virtual) orbital in L⁶FeNN. We ascribe the greater orbital mixing to a better energy gap between the occupied (virtual) orbital and the Fe-based dπ orbital.

Reactivity of K₃L⁶FeNNFeL⁶. The complex of the larger ligand, K₃L⁶Bu₆FeNNFeL⁶Bu₆, is exceedingly sensitive, and upon standing it converts to L⁶Bu₆FeNNFeL⁶Bu₆. We believe the major source of decomposition to be trace water on the surface of reaction vessels, as using silylated glassware somewhat reduces the amount of decomposition. The fragile nature of this complex and Na₃L⁶Bu₆FeNNFeL⁶Bu₆ has precluded further studies of their...
reactivities. $K_d L_{Me}^{\beta} Fe NN Fe L_{Me}^{\beta}$ is slightly more robust. However, reactions with electrophiles give mixtures in which no product deriving from transformation of the $N_2$ group is evident. Reaction with CH$_3$OTf is cleaner, with quantitative formation of $L_{Me}^{\beta} Fe CH_3$ by $^1$H NMR spectroscopy.

**Discussion**

Given the presence of iron in large-scale natural and industrial $N_2$ fixation processes, it is surprising that until very recently all isolated complexes between iron and $N_2$ had very little ground-state weakening of the $N-N$ bond, with $N-N$ distances less than 1.14 Å and $N-N$ stretching frequencies greater than 1950 cm$^{-1}$.

As a result, synthetic iron-dinitrogen complexes were categorized as “unactivated.” However, the coordination number of iron in these complexes is five or greater. This contrasts with the iron atoms of the FeMoco, which are four-coordinate in the isolated Mn$^{III}$ form, and may reach an even lower coordination number in the reduced, activated form. On the surface of metallic iron, the (111) face of iron is thought to be most active, and it is perhaps significant that this surface has the greatest number of highly exposed iron atoms.

Our ability to make three- and four-coordinate complexes offers the opportunity to evaluate the effect of low coordination number of iron on coordinated $N_2$.

**Stretching of the $N-N$ Bond in Iron Dinitrogen Complexes.** The extent of $N_2$ reduction is much greater in $L_{Me}^{\beta} Fe NN Fe L_{Me}^{\beta}$ than in five-coordinate complexes with an Fe-N-Fe core (Table 1). The bond lengths (1.18 ± 0.01 Å) and stretching frequencies (1790 ± 20 cm$^{-1}$) for the NN bonds are characteristic of a bond order between two (MeN=NNMe 1.25 Å; 1575 cm$^{-1}$) and three (N=N 1.098 Å; 2331 cm$^{-1}$).

In other crystallographically characterized iron dinitrogen complexes, terminal $N-N$ bond lengths range from 1.07(1) Å – 1.14(1) Å,

and bridging $N-N$ have been observed at 1.13(2) Å.

Likewise, the $N-N$ stretching frequencies of most other terminal iron dinitrogen complexes are also consistent with minimal activation of the $N_2$ ligand ($v_{NN} = 1955$–2112 cm$^{-1}$). The exceptions are the heterobimetallic bridging complexes Fe(PhBP$_3$(N)(N))MgCl(ether)$_3$ (ether = THF, $x = 2$, $v(NN) = 1830$ cm$^{-1}$; ether = crown-6, $x = 0.5$, $v_{NN} = 1884$ cm$^{-1}$) and Fe(NN)Mo=N=N(3) (d(NN) = 1.20(3) Å – 1.27(2) Å, $v_{NN} = 1703$ cm$^{-1}$) complexes, where the iron atoms are also low coordinate.

The $N-N$ distances and $N-N$ stretching frequencies are similar between complexes of $L_{Me}^{\beta}$ and $L_{H_{30}}^{\beta}$, indicating that the size of the $\beta$-diketiminate ligand plays little role in weakening the $N-N$ bond. Additionally, the long $N-N$ bond is reproduced in density-functional and multireference calculations on the truncated $L_{Me}^{\beta} Fe NN Fe L'$, where all substituents are replaced by hydrogen. So, although the large ligands are essential for enforcing the low coordination number, they do not play a direct role in lengthening the $N-N$ bond.

Figure 12. Key frontier orbitals from the MCSCF calculations on $L' Fe NN Fe L'$. Orbital (a) has 48% Fe and 48% N character, (b) has 96% Fe and 2% N character, and (c) has 60% Fe and 35% N character. $NOON = natural orbital occupation number.

The effect of coordination number was evaluated through the use of 4-tert-butylpyridine, which coordinates to each iron atom to give trigonal pyramidal coordination. The frequencies of the $N-N$ stretching vibrations indicate similar extents of bond weakening between three- and four-coordinate complexes, and these are deemed more trustworthy than the minimal changes seen in $N-N$ distances (Table 1).

*Computations and Electronic Structure.** To tie these observations to specific orbital interactions, and to deconvolute the different contributions to $N-N$ bond weakening, MCSCF calculations were performed on $L' Fe NN Fe L'$, where $L'$ again represents a truncated $\beta$-diketiminate ligand. Multiconfiguration SCF computations of the type used here can offer a more accurate picture of electronic structure than DFT, but are often difficult to interpret as the natural orbitals derived from an MCSCF calculation are not limited to integral electron occupation numbers.

In this research, the natural orbitals (i.e., those orbitals obtained through diagonalization of the first-order density matrix) are analyzed, and from these are obtained the natural orbital occupation numbers (NOONs). The NOONs range from 0 to 2 $e^-$ and give a measure of the multireference character. Schmidt and Gordon describe NOONs between 0.1 and 1.9 as indicative of “considerable multireference character.”

The key frontier orbitals (Figure 12) of $L' Fe NN Fe L'$ have $\pi$-interactions between iron and nitrogen atoms, and are doubly degenerate because the diketiminate planes are perpendicular to one another. Figure 12c shows substantial population (NOON = 1.58 $e^-$ per member of the $E$ set) of a pair of natural MO’s that have bonding interactions between Fe and the N of the bridging $N_2$, and antibonding interactions between the two nitrogen atoms. This pair is strongly correlated with a pair of lower-occupation natural orbitals (NOON = 0.42 $e^-$ per member for this $E$ set) of higher energy (Figure 12a). Thus, the calculations indicate that in these $\beta$-diketiminate complexes,
The N–N π* orbital is a major contributor to the weakened N–N bond.

**Evaluation of Potential Pathways to the N₂ Complexes.**
Reduction of an iron chloride complex to the dinitrogen complexes requires (a) reduction of iron and (b) replacement of Cl⁻ with N₂ but the order of these steps was unknown. We find that reduction of L⁶⁰FeCl under Ar gives L⁶⁰FeCl(η²-Cl) (solvent), which in turn reacts with N₂ to give L⁶⁰FeN₂FeL⁶⁰Bu. The latter reaction occurs more rapidly than reaction of L⁶⁰FeCl with KC₅ under N₂. Therefore, the iron(II)-KCl complex is kinetically competent to be an intermediate during the reduction of L⁶⁰FeCl under N₂.⁴⁵

We have also observed that L⁶⁰FeN₂FeL⁶⁰Bu is formed by photolysis of the hydride complex [L⁶⁰BuFeH]⁶⁰ in benzene solution with a high-pressure mercury lamp, and during attempted resonance Raman experiments on the same hydride complex. As pointed out by Fryzuk, the accomplishment of homogeneous catalytic N₂ reduction is more feasible when strong reducing agents are not required to create the reduced metal center.⁴⁴ Therefore, there is much current interest in polyhydride complexes that lead to dinitrogen complexes. Tyler has recently reported formation of an iron-N₂ complex from dihydrogen reduction under N₂.²³b

**Two-Electron Reduction of the FeN₂Fe Core.** Three examples of the type (alkali)₂LNNFe⁶⁰L have been characterized. Two of the alkali metal cations are trapped within the complex, bound to the N₂ ligand and to the aren rings of the diketiminate. There is an increase in the N–N distance (0.03–0.05 Å). Resonance Raman spectra of these complexes give bands near 1600 cm⁻¹ that are sensitive to N₂ substitution in the bridging ligand. The N–N bond lengthening and stretching frequency reduction lead to a self-consistent picture in which the N–N bond is weakened by two-electron reduction.

According to the MCSCF description of L⁶⁰FeN₂FeL′ presented above, two-electron reduction of L⁶⁰FeN₂FeL′ unit places additional electron density (ca. 0.25 e⁻ according to the NOONs) in the MO that is bonding between Fe and the N of bridging N₂, and antibonding interactions between the two nitrogen atoms (Figure 12a). Therefore, reduction leads to greater population of the N₂ π* orbital. This model neatly accommodates the observation that reduction leads to greater N–N weakening and a reduction in the magnetic moment.

**DFT calculations on simplified L⁶⁰FeNN models also show that alkali metal coordination causes a similar amount of stretching as reduction (~0.03 Å). The stretching caused by side-on coordination of an alkali metal cation may seem unusual, because in the literature examples where N₂ is bound side-on to alkali metals, there is minimal disruption of N–N bonding.⁴⁸,⁴⁹ However, in combination with end-on binding to a transition metal (TM), alkali metal coordination increases polarization of the TM–N₂ unit, enhancing the effectiveness of TM back-bonding into the coordinated N₂.⁵⁰ It is perhaps relevant that small amounts of potassium are beneficial in the iron(0) catalyst in the Haber–Bosch process,³¹ and that LEED experiments suggest that N₂ bound to Fe(111) is not perpendicularly to the surface, but is strongly inclined,²⁵ suggesting a possible side-on binding mode.

The N–N bond lengths (and less dramatically, the Fe–N bond lengths) are dependent on the nature of the β-diketiminate ligand in the alkali metal containing complexes. In the less congested K₂L⁶⁰MeFeN₂Fe⁶⁰Me complex, the N–N bond length is only ~0.03 Å longer than in L⁶⁰MeFeN₂Fe⁶⁰Me, while in K₂L⁶⁰FeN₂FeL⁶⁰Bu the N–N bond length increases by about ~0.05 Å from L⁶⁰FeN₂FeL⁶⁰Bu. The Fe–N bond lengths in K₂L⁶⁰MeFeN₂Fe⁶⁰Me are also slightly shorter than in L⁶⁰FeN₂FeL⁶⁰Bu. The most likely reason is that the smaller binding pocket in K₂L⁶⁰FeN₂FeL⁶⁰Bu reduces the space for binding the alkali metals, and the only way to accommodate them is for the iron atoms to move away from each other. The greater apparent strain in K₂L⁶⁰FeN₂FeL⁶⁰Bu correlates with its lower stability (see below).

**Reactivity of Reduced Iron β-Diketiminate Dinitrogen Complexes.** In general, L⁶⁰FeN₂Fe⁶⁰L complexes react as low-coordinate Fe(I) sources by loss of N₂. Thus far, we have found L⁶⁰FeN₂FeL⁶⁰Bu to be less reactive than L⁶⁰MeFeN₂Fe⁶⁰Me, most likely due to greater protection of the N₂ ligand. Thus, dissolving L⁶⁰MeFeN₂Fe⁶⁰Me in benzene leads to quantitative formation of L⁶⁰Fe(p₆-C₆H₆)₆, but L⁶⁰FeN₂FeL⁶⁰Bu is stable in aromatic solvents at temperatures of up to 100 °C. While reaction of L⁶⁰FeN₂Fe⁶⁰Me with PPh₃ to quantitatively form L⁶⁰FePPh₃ is rapid at room temperature, L⁶⁰FeN₂FeL⁶⁰Bu reacts with PPh₃ only at elevated temperatures, giving an intractable mixture of products.

These displacement reactions likely take place through an associative mechanism, a conclusion that is supported by (a) the dependence of the rate constant for reaction with benzene, d₆ on [C₆D₆], (b) the isolation of pyridine adducts of L⁶⁰FeN₂Fe⁶⁰Me, and (c) the aforementioned steric dependence of the substitution reactions. It is notable that the high-spin N₂ complexes react with CO very rapidly to form the low-spin carbonyl complexes, indicating that the necessary spin flip accompanying ligand binding is very rapid.

**Attempts to Functionalize Coordinated N₂.** The classical mechanism of producing NH₃ from an N₂ complex is by adding


excess acid to release ammonia and/or hydrazine. Addition of HCl, thiols, alcohols, or H(OEt)$_2$+ to Et$_2$O solutions of L$^{60}$FeNNFeL$^{80}$ does not give detectable amounts (<5%) of ammonia or hydrazine. However, acid addition protocols are harsh, and it has been observed that the products of protonation may also depend on the acid used, casting some doubt on the generality of this method as a means of characterization.

Bridging N$_2$ complexes, particularly those of oxophilic early metal complexes, can react with aldehydes and ketones to give azines. However, treatment of L$^{80}$FeNNFeL$^{82}$ with acetophenone leads to the pinacolate complexes [L$^{80}$FeOC(Me)-Ph$_2$]. Transition metal mediated pinacol coupling is typically the province of early transition metal complexes, making this an unusual transformation for an iron complex. The observation of pinacol coupling suggests that the formally iron(I) metal center acts as a one-electron reducing agent, forming a carbon-based radical that undergoes coupling to give the pinacolate ligand of the product. In another example of L$^{80}$FeNNFeL$^{82}$ acting as a reducing agent, it reacts with elemental sulfur to give the diiron(II) complex L$^{80}$FeSFeL$^{82}$.26

Peters and co-workers have recently shown that iron-coordinated dinitrogen Fe(PhBP$_5$)$_2$(N$_2$)MgCl(THF)$_2$ reacts with CH$_3^+$ sources to give an iron complex of the methyldiazenido ligand. Theirs is the first well-characterized iron example of the electrophilic attack on coordinated nitrogen that has been long observed for dinitrogen complexes of early transition metals. Seeking to accomplish an analogous transformation, we treated the most reduced iron diketiminate dinitrogen complex, K$_2$ L$^{Me}$FeNNFeL$^{Me}$, with CH$_3$OTf. This reaction we treated the most reduced iron diketiminate dinitrogen complex, K$_2$ L$^{Me}$FeNNFeL$^{Me}$, with CH$_3$OTf. This reaction could be assigned. IR spectra were recorded on a Mattson Instruments 6020 Galaxy Series FTIR using solution cells with CsF windows. UV-vis spectra were measured on a Cary 50 spectrophotometer, using screw-cap cuvettes, and are listed as: $\lambda$ in nm (in m$^{-1}$ cm$^{-1}$). Solution magnetic susceptibilities were determined by the Evans method. Elemental analyses were determined by Desert Analytics, Tucson, AZ.

Pentane, diethyl ether (Et$_2$O), and tetrahydrofuran (THF) were purified by passage through activated alumina and "deoxygenizer" columns from Glass Contour Co. (Laguna Beach, CA). Benzene, benzene-d$_6$, cyclohexane-d$_{12}$, and THF-d$_6$ were first dried over CaH$_2$, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Diatomaceous earth was dried overnight at 200 °C under vacuum. Triphenylphosphine was recrystallized from pentane at −35 °C. The products were dried over molecular sieves, and acetonaphthone was crystallized from pentane and stored in the dark at −35 °C. The iron(II) β-diketiminate complexes L$^{80}$FeCl$_3$ and [L$^{80}$Fe(μ-Cl)$_3$]$_{60}$ were prepared by literature procedures. KC$_5$ was prepared by heating potassium and graphite at 150 °C under an argon atmosphere. $^{15}$N$_2$ (98% isotopic purity) was obtained from Cambridge Isotopes, and $^{15}$N-labeled compounds were handled under an atmosphere of argon. Photolysis experiments used a 200 W Hg/Xe lamp.

L$^{80}$FeNNFeL$^{82}$ (I). A yellow slurry of L$^{80}$Fe(μ-Cl)$_2$Li(THF)$_{60}$ (2.28 g, 3.27 mmol) in toluene (40 mL) was stirred at 80 °C overnight. The solution was decanted from the precipitated materials, and the filtrate was concentrated to 6 mL. The reaction mixture was stirred overnight at room temperature, and it slowly turned red with the formation of black graphite. After settling for 2 h, the supernatant was filtered through diatomaceous earth to give a dark red solution. The solution was concentrated to ca. 10 mL and stored at −35 °C. A very dark red solution was obtained in three crops (1.10 g, 69%). L$^{80}$Fe(μ-N)$_2$FeL$^{82}$ was synthesized in a similar fashion under an atmosphere of $^{15}$N$_2$ gas and handled under Ar. $^{15}$N NMR (CD$_2$Cl$_2$) $\delta$ 53 (12H, 0.6, CH$_2$), $\delta$ 19 (24H, 2, CH(CH$_2$)$_2$), $\delta$ 20 (8H, 2, CH(CH$_2$)$_2$), $\delta$ 98 (4H, 2, p-H), $\delta$ 112 (24H, 0.8, CH(CH$_2$)$_2$), $\delta$ 123 (8H, 2, CH(CH$_2$)$_2$); $\mu_{eff}$ (Evans, CD$_2$Cl$_2$) 7.93 (3) μ$_{B}$. Anal. Calcd for C$_{60}$H$_{10}$N$_2$Fe$_2$: C 72.26%, H 9.04%, N 8.03%. Found C 72.32%, H 9.04%, N 8.03%

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun glovebox maintained at or below 1 ppm of O$_2$ and H$_2$O. Glassware was dried at 150 °C overnight. $^{1}H$ NMR data were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 22 °C. All peaks in the $^{13}$C NMR spectra are referenced to residual protiated solvent. All peaks are singlets. In parentheses are listed: $T_2$ values in ms calculated as ($\pi_0$/$\nu_{1}^{2}$)$^{1/2}$, integrations and assignments. In some cases, overlapping peaks prevented $T_2$ determinations. For certain complexes, not all signals could be assigned. IR spectra were recorded on a Mattson Instruments 6020 Galaxy Series FTIR using solution cells with CsF windows. UV-vis spectra were measured on a Cary 50 spectrophotometer, using screw-cap cuvettes, and are listed as: $\lambda$ in nm (in m$^{-1}$ cm$^{-1}$). Solution magnetic susceptibilities were determined by the Evans method. Elemental analyses were determined by Desert Analytics, Tucson, AZ.

Pentane, diethyl ether (Et$_2$O), and tetrahydrofuran (THF) were purified by passage through activated alumina and "deoxygenizer" columns from Glass Contour Co. (Laguna Beach, CA). Benzene, benzene-d$_6$, cyclohexane-d$_{12}$, and THF-d$_6$ were first dried over CaH$_2$, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Diatomaceous earth was dried overnight at 200 °C under vacuum. Triphenylphosphine was recrystallized from pentane at −35 °C. The products were dried over molecular sieves, and acetonaphthone was crystallized from pentane and stored in the dark at −35 °C. The iron(II) β-diketiminate complexes L$^{80}$FeCl$_3$ and [L$^{80}$Fe(μ-Cl)$_3$]$_{60}$ were prepared by literature procedures. KC$_5$ was prepared by heating potassium and graphite at 150 °C under an argon atmosphere. $^{15}$N$_2$ (98% isotopic purity) was obtained from Cambridge Isotopes, and $^{15}$N-labeled compounds were handled under an atmosphere of argon. Photolysis experiments used a 200 W Hg/Xe lamp.
Iron Dinitrogen Complexes

L₄Fe[N(NO)₂] (1). The X-ray crystal structure revealed that the crystals used for the X-ray crystal structures were grown from pentane at -35 °C (1a) or ambient temperature (1b).

L₄Fe[N(NO)₂] (2). KC₆ (532 mg, 3.94 mmol) was added in portions to a red slurry of L₄FeCl₃ (2.0 g, 3.37 mmol) in Et₂O (40 mL). There was immediate formation of black graphite and a very dark red solution. Occasionally, the solution was observed to become deep green and change to dark red within a few minutes. The mixture was stirred overnight at room temperature, and the solvent was removed in vacuo.

The residue was extracted with pentane and filtered through diatomaceous earth to give a red-purple solution. The solution was concentrated (20 mL) and placed in the freezer to give a very dark red-purple solid in two crops (1.29 g, 70%).

L₄Fe[N(NO)₂] (3). A 20 mL scintillation vial was charged with L₄Fe[N(NO)₂] (100 mg, 103 μmol) and pentane (6 mL) to give a red-purple solution. 4-t-Bu-Butylpyridine (30 μL, 206 μmol) was added via syringe, immediately giving a dark blue solution. After stirring at room temperature for 30 min, the solution was concentrated to 2 mL and cooled to -35 °C using vapor diffusion with hexamethyldisiloxane. This gave dark blue crystals (100 mg, 78%). The complex is soluble in pentane and Et₂O. The ¹⁷N labeled analogue of 3 was synthesized using L₄Fe[N(NO)₂] and 4-t-butylpyridine. ¹H NMR (C₆D₁₂): δ 45 (4H, 0.7, o-CH₃NC(CH₃)₂), 25 (4H, 1, m-H), 22 (4H, m-CH₃NC(CH₃)₃), 7 (24H, 0.8, CH(CH₃)₂), 1 (24H, 0.7, CH(CH₃)₃), -1 (4H, 0.7, CH₂(CH₃)₂), -5 (18H, 0.4, CH(CH₃)₃), -8 (4H, 0.6, CH(CH₃)₃), -39 (4H, 1, p-H), -112 (2H, 0.2, backbone C-H), -162 (12H, 0.3, C₆H₄), Δμ₂ (Evans, C₆D₁₂) 5.9(3) μαₜ. Anal. Calc'd for C₆H₄N₂Fe₂C₂H₅: C 73.58, H 9.95, N 6.79. UV-vis (pentane): 914 (4.2), 720 (6.6), 583 (8.3).

L₄Fe(η⁶-C₄H₈) (4). A 20 mL scintillation vial was charged with L₄Fe[N(NO)₂] (100 mg, 103 μmol) and pentane (6 mL) to give a dark red solution. Benzene (0.5 mol) was added, and the solution was stirred at room temperature overnight. The solution was pumped down (2 mL), and the residue was dissolved in hexamethyldisiloxane (2 mL) and cooled to -35 °C to give dark red crystals (86 mg, 76%). ¹H NMR (C₆D₁₂): δ 118 (2H, 0.2, p-H), 11 (12H, 1, C(CH₃)₃), -2 (12H, 0.1, C(CH₃)₂), -42 (6H, 0.4, CH₃), -57 (4H, 0.6, m-H), -158 (1H, 0.5, backbone C-H), -205 (4H, 0.1, C(CH₃)₃), Δμ₂ (Evans, C₆D₁₂) 2.5 μαₜ. Anal. Calc'd for C₆H₄N₂Fe: C 76.29, H 8.01, N 5.28. UV-vis (pentane): 917 (0.4), 496 (1.3).

L₄Fe(PPh₃)(η⁶-C₄H₈) (5). A 20 mL scintillation vial was charged with L₄Fe[N(NO)₂] (100 mg, 103 μmol) and pentane (6 mL) to give a dark red solution. A solution of PPh₃ (54 mg, 206 μmol) in pentane (2 mL) was added to give a dark purple solution. The solution was stirred at room temperature for 30 min, and the solvent was pumped down (2 mL). The residue was redissolved in hexamethyldisiloxane (2 mL) and cooled to -35 °C to give two crops of dark purple crystals (110 mg, 72%). L₄Fe(PPh₃) is soluble in pentane and Et₂O, reacts with aromatic solvents, and is thermally unstable in solution. ¹H NMR (C₆D₁₂): δ 56 (1H, 0.7, backbone C-H), 37 (4H, 2, m-H), 8 (12H, 2, C₆H₄), 7 (6H, 3, p-Ph), 5 (3H, 3, p-Ph), 0.2 (6H, o-Ph) -14 (12H, 0.9, C(CH₃)₃), -24 (2H, 2, p-H), -29 (2H, 3, C(CH₃)₃), -100 (2H, 0.8, C(CH₃)₃), -122 (6H, 1, CH₃), Δμ₂ (Evans, C₆D₁₂) 3.6(3) μαₜ. Anal. Calc'd for C₆H₄N₂FeP: C 76.72, H 7.67, N 3.80. Found C 75.40, H 7.59, N 3.98. UV-vis (pentane): 583 (2.2).

L₄Fe(CO)₃ (6). A resealable flask was charged with L₄Fe[N(NO)₂] (100 mg, 103 μmol) and Et₂O (5 mL) to give a dark red solution. The flask was connected to a vacuum line, and the solution frozen at -196 °C. The headspace was evacuated, and the solution thawed. The flask was backfilled with CO to approximately 1 atm, leading to the immediate formation of a dark green solution. The solution was stirred for 30 min at room temperature and the volatile materials were removed in vacuo. The residue was extracted with pentane and filtered through diatomaceous earth. The solution was concentrated to 4 mL and cooled to -35 °C to give dark green crystals (67 mg, 58%). Δμ₂ (Evans, C₆D₁₂) 2.0 μαₜ. IR (C₆H₆): vCO 2042, 1971, 1960. Anal. Calc'd. for C₆H₄N₂FeC: C 68.94, H 7.41, N 5.02. Found C 68.94, H 7.41, N 5.08. UV-vis (pentane): 642 (0.94), 422 (1.7), 502 (1.1).

L₄Fe(CO)₄ (7). Similarly to the preparation of 6, L₄Fe[N(NO)₂] (100 mg, 87 μmol) in Et₂O (5 mL) was treated with CO. Brown-green crystals of the mixture were obtained from pentane at -35 °C. IR (C₆H₆): vCO 2036, 2000, 1967, 1953, 1922 cm⁻¹. L₄Fe(CO)₃(Ph)₄ (8). A 20 mL scintillation vial was charged with L₄Fe[N(NO)₂] (100 mg, 103 μmol) and pentane (8 mL) to give a dark red solution. The solution was concentrated at -35 °C for 30 min, and then acetophenone (25 mg, 205 μmol) in pentane (1 mL) was added to give a dark green solution. The reaction was warmed to room temperature and stirred overnight to give a dark yellow solution, with the precipitation of a yellow solid. The volatile materials were removed under reduced pressure, and the residue washed with hexamethyldisiloxane (1 mL) to remove dark colored impurities. The
remaining yellow solid was redissolved in Et₂O and filtered through diatomaceous earth. The solution was concentrated to 4 mL and pentane (2 mL) was added. A yellow powder precipitated from solution at −35 °C (70 mg, 57%). ¹H NMR (CD₂Cl₂) δ 193 (2H, backbone C–H), 145 (6H, 0.1, OCH₃), 71 (12H, 0.5, CH₃), 37 (4H, 1, m-O(C₆H₄)), 33 (2H, 2, p-O(C₆H₄)), 3 (4H, 5, o-O(C₆H₄)), −9 (12H, 1, CH(C₆H₃)), −11 (12H, 1, CH(C₆H₃)), −15 (4H, 2, m-H), −16 (4H, 2, m-H), −68 (4H, 2, p-H), −90 (12H, 0.4, CH(C₆H₃)), −95 (12H, 0.5, CH(C₆H₃)), −112 (4H, 0.1, CH(C₆H₃)), −158 (4H, 0.1, CH(C₆H₃)), μₑₛ (Evans, Cd₂) 6.7 μₑₛ. Anal. Calc’d. for Cs₅H₉N₃O₄Fe₂: C 76.84, H 8.32, N 4.13. Found C 76.86, H 8.35, N 4.18. UV (THF): 519 (1.1), 492 (4.13).

Reaction of K₂L₄MeFeNNFeL₄Me with CH₃OTf. K₂L₄MeFeNNFeL₄Me (10 mg, 9 μmol) and Cd₂ (ca. 0.5 mL) were added to a resealable NMR tube. Methyl triflate (2.0 μL, 18 μmol) was added via syringe to the dark blue solution. Gas evolution was observed, and the solution became yellow-orange in color with the formation of a white solid. ¹H NMR spectroscopy revealed the quantitative formation of L₄MeFeMe.²⁰³

X-ray Structural Determinations. Crystalline samples of all the complexes were grown in the glovebox from pentane solutions at −35 °C. All crystals were rapidly mounted under Paratone-8277 onto glass fibers, and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Bruker-axs SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame, using a detector-to-crystal distance of 5.09 cm. Frames were integrated to a maximum 20 angle of 56.5° with the Bruker-axs SAINT program. The final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centers of >3400 reflections for each crystal. Data were corrected for absorption with the SADABS program, except when noted otherwise. The space groups were assigned using XPREP, and the structures were solved by direct methods using SIR92.²⁰⁴ (WinGX v1.63.02) and refined employing full-matrix least-squares on F² (Bruker-axs, SHELXTL-NT, version 5.10). Nonhydrogen atoms were refined with anisotropic thermal parameters, except disordered solvent in some cases. Hydrogen atoms were included in idealized positions with riding thermal parameters. Details are provided in Table 2 and the Supporting Information.

Computational Methods. The calculations reported herein employed the GAMESS²⁰⁵ and Jaguar²⁰⁶ packages. GAMESS was used for multireference calculations and Jaguar for density functional theory (DFT) calculations. The Stevens effective core potentials and valence basis sets were employed, augmented with a d polarization function on main group elements. Hydrogen was described with the −31G basis set. For density functional calculations the B3LYP²⁰⁷ hybrid functional was used. This combination of theory level and basis sets was used in previous calculations on iron-β-diketiminate-dinitrogen complexes.²⁰⁸

Multireference calculations²⁰⁹ were used to cross-reference the ground state multiplicities obtained by experiment and density functional methods given the density of low energy states in these complexes. The active space was chosen to include all orbitals (and the electrons contained therein) needed to describe the Fe-dinitrogen moiety. All multireference calculations were performed using the FORS (fully optimized reaction space) paradigm, i.e., all possible configuration state functions, within the limits of spatial and spin symmetry, were generated for the active space of interest. For multireference Møller–Plesset 2nd

order perturbation theory (MRMP2) calculations, single and double excitations from the FORS active space to the remaining virtual orbitals were allowed.

Geometry optimization calculations utilized the B3LYP functional and density-functional methods given the much greater computational tractability of DFT in relation to MCSCF and MRMP2 methods. In all cases, the ground-state multiplicities predicted by B3LYP agree with those obtained from MCSCF and MRMP2 calculations. DFT calculations were performed within the restricted open-shell (RODFT) paradigm to obviate spin contamination issues.

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Supporting Information Available: Variable-temperature NMR spectra and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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