The Reactivity Patterns of Low-Coordinate Iron–Hydride Complexes


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Abstract: We report a survey of the reactivity of the first isolable iron-hydride complexes with a coordination number less than 5. The high-spin iron(II) complexes [(µ-diketiminate)Fe(µ-H)]_2 react rapidly with representative cyanide, isocyanide, alkyne, N_2, alkene, diazene, azide, CO_2, carbodiimide, and Brensted acid containing substrates. The reaction outcomes fall into three categories: (1) addition of Fe–H across a multiple bond of the substrate, (2) reductive elimination of H_2 to form iron(I) products, and (3) protonation of the hydride to form iron(II) products. The products include imide, isocyanide, vinyl, alkyl, azide, triazenido, benzoiçinnoline, aminate, formate, and hydroxo complexes. These results expand the range of known bond transformations at iron complexes. Additionally, they give insight into the elementary transformations that may be possible at the iron–molybdenum cofactor of nitrogenases, which may have hydride ligands on high-spin, low-coordinate metal atoms.

Introduction

Organometallic chemists have long appreciated the many reactions of transition-metal hydride complexes, especially reductions.1 Recently, hydride chemistry has become established in bioinorganic systems.2 Nitrogenases are prodigious reductants reductions.1 Recently, hydride chemistry has become established in reactions of transition-metal hydride complexes, especially that cleave double and triple bonds in N_2, C=O, N_2O, N_3. Addition of protons, chemists have often speculated about the potential role of hydrides.4

Recently, the first direct evidence for hydride intermediates in nitrogenase emerged from electron–nuclear double resonance (ENDOR) studies of nitrogenase mutants freeze-trapped during substrate turnover. For example, a Val70Ile mutant of A. vinelandii molybdenum–iron nitrogenase freeze-trapped during proton reduction shows two hydrogen nuclei with very strong coupling to the S = 1/2 iron–sulfur cluster, strongly suggesting the presence of Fe–H bonds.5 This frozen species loses two molecules of H_2 upon annealing to −20 °C, raising the possibility that these two hydride ligands can combine with nearby protons to release H_2.6 This species is thought to be in the redox state that reacts directly with N_2 in the wild-type MoFe nitrogenase,7 underscoring the importance of hydride-containing intermediates in enabling the nitrogen reduction activity characteristic of this enzyme.

From the perspective of the coordination chemist, there are a number of ways that potential FeMoco-bound hydrides differ from the majority of known synthetic transition-metal hydride complexes. First, FeMoco hydride adducts could achieve a number of different oxidation levels. One-electron redox changes undoubtedly occur in the FeMoco because electrons are supplied to the FeMoco one at a time by the Fe protein, which dissociates and reassociates before each one-electron reduction of the FeMoco.3 However, most synthetic hydride complexes have diamagnetic metal centers, and little one-electron chemistry has


FeMoco (MN) does not have hydrides, as shown by ENDOR: or M8S9No rM8S9O) that is unknown in synthetic chemistry.15,16 (weak-field sulfide donor set, coordination number less than five) expected to be high-spin, based on ligand field considerations

iron ions in the FeMoco are expected to be high-spin, based on ligand field considerations (16) Nitrogenase enzymes without Mo probably have a similarly-shaped

Iron complexes, on the other hand, typically have strong-field organometallic or phosphine coligands, which enforce a low-spin electronic configuration.12,13 These fundamental differences motivate synthetic research aimed at the creation of iron−hydride complexes with weak-field ligands and low coordination number, to determine their characteristic reactivity patterns and reaction mechanisms, which can in turn be correlated with nitrogenase reactions.

Our studies on low-coordinate iron are complemented by those of Peters and co-workers, who use tridentate, strong-field tris(phosphino)borate (BP3) supporting ligands that contain “soft” phosphate donors, and more often give low-spin electronic configurations.22 In the BP3 systems, it has not yet been possible to isolate a low-coordinate iron hydride, but the presence of a terminal hydride in four-coordinate complexes is strongly implicated by theoretical calculations.20,21

For these reasons, we have created one- and two-iron compounds that focus on two key features of the nitrogenase-hydride intermediates: the weak-field ligands and the coordination number less than five.18,23 Extremely bulky bidentate H-diketiminate ligands (Figure 2) have μ-donating nitrogen atoms that lead to a weak ligand field.19 The bulky disopropylphenyl groups maintain a low coordination number that mimics the ligand-poor environment of the iron atoms in the FeMoco. Using these ligands, we have isolated the only examples of iron-hydride complexes with a coordination number less than five (Figure 2).20,21

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Peters and Holland have independently proposed that dissociation of X is important in enabling substrate binding to iron, based on the binding of N2 to synthetic iron complexes.18 Computational studies come to a variety of conclusions regarding the structural flexibility of the FeMoco during catalysis.11 In short, there are many questions about the structure of the iron−hydride nitrogenase intermediates, and the available data are not sufficient to provide guesses about their structure(s).


Figure 1. The iron−molybdenum cofactor (“FeMoco”) of iron−molybdenum nitrogenase in the isolated M8 form.8 This form is reduced (with incorporation of hydrides in an undisclosed location) to give the intermediate that reacts with N2 and other nitrogenase substrates. X is C2−, N3−, or O2−.
implied by the isolation of products that result from activation of solvent or the supporting ligand.\textsuperscript{23} Bridging hydrides have recently been observed in a few electronically unsaturated dinuclear complexes,\textsuperscript{24,25} and borohydrides have been studied on iron–sulfur clusters.\textsuperscript{26}

Recent contributions from our group have described the reaction of [L\textsuperscript{18}FeH\textsubscript{2}] with azobenzene to cleave the N-N bond.\textsuperscript{20,27} The reaction of [L\textsuperscript{14}FeH\textsubscript{2}] with boranes to cleave B-C bonds.\textsuperscript{28} This manuscript reports a wider variety of reactions with unsaturated small molecules that are nitrogenase substrates or organic-soluble mimics of these substrates. By examining the reactions with representative compounds, one may begin to understand some of the unusual reaction patterns available to hydride complexes with a high-spin electronic configuration. In addition, a number of the products have novel structural and/or electronic features that are interesting from a fundamental perspective.

Results

Iron-Hydride Starting Materials. The synthesis and characterization of [L\textsuperscript{14}FeH\textsubscript{2}] (1a) and [L\textsuperscript{18}FeH\textsubscript{2}] (1b) have been presented previously.\textsuperscript{20,21,27,28} They are each synthesized from iron(II) chloride complexes ([L\textsuperscript{14}MeFeCl\textsubscript{2}] or [LtBuFeCl]) by reaction with potassium triethylborohydride for 0.5 h in toluene, followed by the prompt removal of solvent and BEt\textsubscript{3}, then extraction with pentane and crystallization to give brown powders or crystals. Crude reaction mixtures are contaminated with the chloride starting material and the dihydridoborate complex L\textsuperscript{14}Fe(\mu-H)\textsubscript{2}BEt\textsubscript{3}.\textsuperscript{28} Multiple crystallizations are typically necessary to remove these impurities, and \textsuperscript{1}H NMR spectroscopy is used to judge purity of the hydride complexes. The good yields of many of the products derived therefrom support the purity of 1a and 1b.

The \textsuperscript{1}H NMR spectrum of 1a consists of seven resonances; the number of signals and their integrations are characteristic of the diketiminate ligand in a local C\textsubscript{2v} symmetry environment. It has no unusual temperature- or concentration-dependent changes in its \textsuperscript{1}H NMR or UV–vis spectra, suggesting that the dimeric structure in the solid state is always maintained. To learn more about the electronic structure of 1a, we examined a solid sample using Mössbauer spectroscopy. The zero-field Mössbauer spectrum at 80 K (Supporting Information, Figure S-6) exhibits a superposition of two quadrupole doublets with 72% and 28% relative intensities. The major component has \(\delta = 0.70(2)\ mm/s\) and \(\Delta E_Q = 0.86(2)\ mm/s\), whereas the minor component shows \(\delta = 0.49(2)\ mm/s\) and \(\Delta E_Q = 2.06(2)\ mm/s\). The values for the minor component are relatively similar to those of a high-spin Fe(I) diketiminate complex (\(\Delta E_Q = 2.02\ mm/s\), \(\delta = 0.41\ mm/s\ at 180 K\)).\textsuperscript{19c} Therefore, we assign the component to contamination from an unidentified Fe(I) impurity.

In contrast, the Mössbauer parameters of the major component, particularly the isomer shift, are in the range of high-spin iron(II) diketiminate complexes (\(\delta = 0.62–0.86\ mm/s\), and so it is assigned to 1a.\textsuperscript{19,20} Magnetic Mössbauer spectra measured at 4.2 K with applied fields up to 7 T show that the major component is diamagnetic, suggesting antiferromagnetic coupling between the two iron(II) ions. In sum, the spectroscopic data support the formulation of 1a as an exchange-coupled pair of high-spin iron(II) ions with a ground state of \(S = 0\).

The \textsuperscript{1}H NMR spectrum of 1b has at least 17 overlapping peaks, because of extreme steric crowding in the dimer that presumably renders some ligand bond rotations slow on the NMR time scale.\textsuperscript{27} Upon heating a solution of 1b in CD\textsubscript{6}, there is growth of a simple seven-line \textsuperscript{1}H NMR spectrum with chemical shifts much like trigonal-planar alkyl complexes L\textsuperscript{18}HuFe\textsubscript{2} \textsuperscript{20} This behavior is ascribable to equilibration between dimeric [L\textsuperscript{18}HuFe\textsubscript{2}]; and monomeric L\textsuperscript{18}HuFe\textsubscript{2} that is slow on the NMR time scale (ms) but rapid on the time scale of the equilibration (min). Therefore, in the discussion below it should be understood that 1b does not refer specifically to the monomer or dimer, but the equilibrating mixture of the two.\textsuperscript{30}

Reactions with C=\textsuperscript{14}N Triple Bonds, and with N\textsubscript{2} and CO. Carbon monoxide (CO) is an inhibitor of \(N\textsubscript{2}\) reduction by nitrogenase.\textsuperscript{3} Methyl isocyanide (CH\textsubscript{3}NC) and cyanide (CN\textsuperscript{-}) are also inhibitors but are substrates as well: CN\textsuperscript{-} is reduced to CH\textsubscript{2}NH\textsubscript{2}, NH\textsubscript{3}, and CH\textsubscript{4}, while CH\textsubscript{3}NC is reduced to CH\textsubscript{2}NH\textsubscript{2}, (CH\textsubscript{3})\textsubscript{2}NH, and CH\textsubscript{4}.\textsuperscript{31} Therefore, it is of interest to examine the reactivity of small molecules containing CO and CN triple bonds with synthetic hydride complexes that mimic potential activated forms of the FeMoco. We use alkyl cyanides as surrogates for CN\textsuperscript{-} and tert-butyl isocyanide in place of CH\textsubscript{2}NC\textsubscript{3}.

The addition of CO or isocyanide to 1a results in the rapid release of H\textsubscript{2}. Adding an excess of CO to 1a gives L\textsuperscript{14}MeFe(CO)\textsubscript{3} through formal reduction of the iron. Because L\textsuperscript{14}MeFe(CO)\textsubscript{3} has been characterized previously, the reader is referred to the earlier paper for its properties.\textsuperscript{27}

Addition of a large excess of tert-butyl isocyanide gives an intractable mixture, but treatment of a solution of 1a in pentane or toluene with 4 equiv (per dimer) of tert-butyl isocyanide results in the formation of a mononuclear iron(I) complex, L\textsuperscript{14}MeFe(CN)(Bu\textsubscript{3})\textsubscript{2} (2a). Integration of the \textsuperscript{1}H NMR spectrum against an internal standard (L\textsuperscript{18}FeCl in a capillary) indicated 62% conversion to 2a, among other unidentified products. The production of H\textsubscript{2} was quantified by GC to be ca. 0.2 equiv per mole of 1a. The low yield of dihydrogen may be due to hydrogen incorporation into some of the unidentified products. Because of the low conversion, samples of 2a for further spectroscopic study were generated through an alternative method, by adding 4 equiv of BuNC to L\textsuperscript{14}MeFe(NMe\textsubscript{3})\textsubscript{2}.


The ambiguous spectroscopic and crystallographic data left unanswered questions about \( \text{2a} \). Therefore, hybrid quantum mechanics/molecular mechanics (QM/MM) computations were performed to study complete models of \( \text{2a} \). The optimized geometry of the doublet state \( (E_{\text{relative}} = 0) \) is square planar about iron, but the higher energy quartet state \( (E_{\text{relative}} = 3.9 \text{ kcal/mol}) \) has a tetrahedral coordination geometry upon QM/MM geometry optimization. The calculated metrical parameters for doublet \( \text{L}^\text{MeFe(CNtBu)}_2 \) (compared to experimental ones in parentheses) are \( \text{Fe}^\text{−C} = 1.83 \text{ Å} (1.82 \text{ Å}); \text{CN} = 1.18 \text{ Å} (1.15, 1.17, 1.22 \text{ Å}) \). Both the lower calculated energy and the geometrical similarity to the experimental structure support the contention that \( \text{2a} \) has an \( S = \frac{1}{2} \) ground state.

The computations also address the unusual difference between the CNC angles of the two isocyanide ligands (we denote the difference between these CNC angles as \( \theta \)). The optimized geometry had CNC angles of 171° (close to the crystallographic angle of 170°) and 162° (between the observed 164° and 148° disorder components). A search of the Cambridge Structural Database for neutral, monometallic complexes with at least two ‘BuNC ligands indicated that the average \( \theta \) is 6.9 ± 1.0° (170 examples) with a median value of 2.9°. Hence, our computed value of \( \theta = 9° \), while somewhat large, is not outside experimental norms. Computations indicate that bending the CNC angle from 180° to 150° requires 4 kcal/mol in free ‘BuNC and only 0.4 kcal/mol in the QM/MM model of \( \text{2a} \). Considering the softness of this bending distortion, it is not surprising that the isocyanide is unusually flexible and can exist in multiple geometries in the solid state.

In the next section, we turn to reactions with nitriles, mimics of cyanide with substituents on the carbon. Scheme 1 shows the reduction products obtained from \( \text{CH}_3\text{CN} \) and ‘BuCN. Heating \( \text{1a} \) with 2 equiv of \( \text{CH}_3\text{CN} \) in toluene at 45 °C for 18 h affords \( \text{3a} \). Heating \( \text{1a} \) or \( \text{1b} \) with 1 equiv of ‘BuCN at room temperature in pentane 2 h affords \( \text{4a} \). Heating \( \text{1a} \) or \( \text{1b} \) with 2 equiv of ‘BuCN at room temperature in \( \text{Et}_2\text{O} \) for 1 h affords \( \text{5b} \).
18 h gives an orange-yellow precipitate in 88% yield. The X-ray crystal structure shows that the product is LMeFe(μ-N=C=CHCH3)2FeLMe (3a) (Figure 4, top), with a crystallographic inversion center relating the two halves of the molecule. Each nitrile molecule has been reduced to a bridging N=C=CH molecule with an N=C distance of 1.258(2) Å. The iron centers in 3a have roughly tetrahedral geometries. The 1H NMR spectrum of 3a in toluene-d8 has peaks from 50 to −40 ppm, and the number and integrations are consistent with the C2h symmetry in the crystal structure.

When 1a is treated with the bulkier nitrile 'BuCN, brown LMeFe(μ-N=C=CH('Bu))FeLMe (4a) is obtained in 85% yield. The diiron complex incorporates only one equivalent of the nitrile, even in the presence of excess 'BuCN. Addition across an N=C bond has formed a bridging N=C=CH('Bu) ligand, while the other bridging hydride remains untouched. The crystal structure of 4a (Figure 4, bottom) indicates that the large 'Bu group pushes the two β-diketiminate ligands toward the bridging hydride, which significantly reduces the dihedral angle between the two β-diketiminate planes to around 81° in each of the two independent molecules in the crystal structure. This structural distortion makes the 1H NMR spectrum more complicated than in 3a. At ambient temperature, approximately 16 peaks are observed. Severe overlap between peaks has made attempts to assign peaks and measure the solution magnetic moment unsuccessful. At −20 °C, these ~16 peaks split into ~25 peaks, consistent with a reduction of symmetry from C3v (in a conformation like that in the crystal structure, but with the two β-diketiminate ligand planes coplanar on average) to C1 (the symmetry in the solid state).

Another kind of insertion product is observed when 1b is treated with 'BuCN. In this case, the orange product is monomeric LMeFe(μ-N=C=CH('Bu)) (5b) in 67% yield. The geometry around the iron atom is trigonal planar (Figure 5). A C≡N double bond is indicated by the 1H NMR spectrum of 5b (Figure 4, bottom) as shown by 1H NMR spectroscopy. These diiron complexes have a formal oxidation state of +3 for each iron atom, and therefore result from reduction.36 Therefore, it is possible to induce these hydride complexes to reductively eliminate H2 and bind N2, but this transformation requires photolysis.

Table 1. Comparisons among C≡N Insertion Products

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<thead>
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<th>property</th>
<th>3a</th>
<th>4a</th>
<th>5b</th>
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<tbody>
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<td>Symmetry from 1H NMR at RT</td>
<td>C2h</td>
<td>C1</td>
<td>C2h</td>
</tr>
<tr>
<td>Fe−Fe distance (Å)</td>
<td>3.0790(5)</td>
<td>2.7816(8)</td>
<td>N/A</td>
</tr>
<tr>
<td>N=C distance (Å)</td>
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<td>1.258(4)</td>
<td>1.256(3)</td>
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<tr>
<td>Dihedral angle between β-diketiminate ligand planes (deg)</td>
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<td>N/A</td>
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<tr>
<td>N=C stretching frequency (cm⁻¹)</td>
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<td>1629</td>
<td>1687</td>
</tr>
<tr>
<td>N−C−C angle in imide (deg)</td>
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<td>129.3(3)</td>
<td>127.2(3)</td>
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<tr>
<td>Fe−N(imide) distance (Å)</td>
<td>2.041(2)</td>
<td>2.000(3)</td>
<td>1.857(2)</td>
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</table>

*The two β-diketiminate ligand planes are related by a crystallographic inversion center.

Endnotes:

36) Loss of H2 to give the dinitrogen complex is formally a reductive elimination, but the iron atoms in LMeFeNNFeLMe36 are best described as Fe3+−N2−−Fe3+ because of charge transfer to the N2 ligand. See ref 19d.
Reactions with C≡C Triple Bonds. Acetylene is the most commonly studied unnatural substrate of nitrogenases, and it is reduced to ethylene.\(^{37}\) Mutant nitrogenase enzymes can also reduce longer-chain alkynes.\(^{38,39}\) Here, we examine the reactivity of the low-coordinate iron hydride complexes with alkynes diphenylacetylene and 3-hexyne.

Complex \(1a\) inserts into the C–C triple bond in PhCCPh to form \(\text{L}^\text{MeFeC(Ph)}\equiv\text{C(H)Ph}\) (6a) in 75% yield. This vinyl product is analogous to \(\text{L}^\text{MeFeC(Ph)}\equiv\text{C(H)Et}\) (6b), which was previously reported from the reaction of \(1b\) with 3-hexyne.\(^{20}\) Figure 6 presents the crystal structure of 6a. The C–C distance (1.347(2) Å) and C–C–C angles (129.0(2)°, 121.6(2)°) in the vinyl ligand confirm that both carbons of the C≡C double bond have sp\(^2\) hybridization. The \(^1\)H NMR spectrum of 6a shows seven peaks for the \(\beta\)-diketiminate protons, indicating averaged C\(_2\) symmetry from rapid rotation around the Fe–C14 bond on the NMR time scale.

Monitoring the reaction of \(1a\) with PhC≡CPh, or the reaction of \(1b\) with EtC≡CEt, shows no dependence of the reaction rate on [PhC≡CPh] (Table 2). Therefore, the rate laws are rate = \(k[1]\) with first-order rate constants 1.7(2) × 10\(^{-3}\) s\(^{-1}\) (\(1a/\text{PhCCPh}\) at 31 °C) and 5.0(5) × 10\(^{-3}\) s\(^{-1}\) (\(1b/\text{EtCCET}\) at 15 °C). The first-order rate law is consistent with the interaction of alkylene with \(1a\) or \(1b\) during or prior to the rate-limiting step of the reaction. Two mechanistic possibilities consistent with the rate law are shown in Scheme 2. In pathway A, the opening of a single Fe–H bond is the rate determining step. We consider this Fe–H bond opening pathway to be more likely for the reaction of alkylene with \(1a\) because (1) there is no other evidence for any monomer form of \(1a\) by NMR or UV–vis spectroscopy; (2) in the reaction of \(1a\) with boranes, the rate law was first-order in \([1a]\) and first-order in [BEt\(_3\)] but independent of the steric demands of the borane or iron complex.\(^{28}\) These data were consistent with dissociation of \(1a\) into monomers (which predicts a half-order dependence on [\(1a\)]) and most consistent with single Fe–H opening, as in the bottom reaction pathway here. In pathway B, dimer cleavage is the rate determining step, as proposed for the reaction of \(1b\) with 3-hexyne.\(^{20}\) This pathway is reasonable for \(1b\), because the monomer is rapidly accessed at room temperature (see earlier). The rate of the reaction is consistent with the rapid equilibrium of monomer and dimer observed previously.\(^{28}\) So, although the evidence is not definitive, the kinetic data here and elsewhere are most indicative of the pathway A in the reactions of alkylene with \(1a\), but pathway B for alkylene reactions with \(1b\). This difference is consistent with the greater steric demands of the diketiminate ligands in \(1b\) than \(1a\).

Reactions with C≡C Bonds. We previously reported that \(\text{L}^\text{MeFe(alkyl)}\) complexes with \(\beta\)-hydrogen can act as sources of transient hydride species \(\text{L}^\text{MeFeH(alkene)}\). These react with alkynes to give insertion products, and complexes \(\text{L}^\text{MeFeR'}\) (\(R' = \text{ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, cyclohexyl, 2-phenethyl}\) were fully characterized.\(^{30}\) We have also characterized numerous alkyl complexes of iron with the larger \(\text{L}^\text{Bu}\) ligand.\(^{40}\) With isolated iron hydride complexes in hand, we verified that the addition of alkylene to isolated \(1a\) or \(1b\) gives alkylene complexes of the same type through [1,2] addition across the double bond. For example, reaction of \(1a\) with 1-hexene quantitatively gives a 1-hexyliron complex, as judged by \(^1\)H NMR spectroscopy. It is worth noting that the transient iron hydride \(\text{L}^\text{MeFeH(alkene)}\) also adds across the C≡N bonds of imines (forming \(\text{L}^\text{MeFeN(R)C=O}\)) from \(R_2C=NR'\) and the C≡O bonds of ketones (forming \(\text{L}^\text{MeFcOCHR}(_2\) from \(R_2C=O)\).\(^{30}\) Because these reactions have already been characterized starting from the alkyl complexes,\(^{30}\) the reactions with isolated hydride complexes were not investigated further.

Reactions with Azides. The azide ion (\(\text{N}_3^–\)) is transformed by nitrogenase into \(\text{N}_2, \text{NH}_3,\) and \(\text{N}_2\text{H}_4\).\(^{40}\) Here, substituted azides \(\text{AdN}_3, \text{Ad} = 1\text{-adamantyl}\) and \(\text{Me}_3\text{SiN}_3\) are used as

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Scheme 3

\begin{align*}
\text{L} & \rightarrow \text{Fe} \text{Bu} \text{Bu} \text{Bu} \text{N}3 \text{Fe} \text{Bu} \text{Bu} \text{Bu} \text{N3} \\
\text{L} & \rightarrow \text{Fe} \text{Bu} \text{Bu} \text{Bu} \text{N}3 \text{Fe} \text{Bu} \text{Bu} \text{Bu} \text{N3}
\end{align*}

models. The reactions of organic azides with transition-metal complexes have been reviewed recently.42

Reactions of complex 1a with Me3SiN3 give mixtures, as judged from 1H NMR spectra. However, complex 1b, when treated with 2 equiv of trimethylsilyl azide in diethyl ether, gives a dimeric azide complex, L\text{Bu}Fe(µ-N3)2Fe\text{Bu}N3 (7b) in 79% yield (Scheme 3). Compound 7b can be prepared independently by reacting L\text{Bu}FeCl43 with sodium azide.

The X-ray crystal structure of 7b (Figure 7) shows that the compound is dinuclear in the solid state with an Fe-Fe distance of 5.096(4) Å. Each iron atom is coordinated to two azide ions, which bridge the iron atoms in a µ,µ,µ-end-to-end fashion with inequivalent iron–nitrogen bond lengths of 2.061(1) and 2.025(1) Å. The eight atoms of the FeN3 core are coplanar, in contrast to the only other crystallographically characterized end-to-end bridged iron azide complex, [(PhBP3)2Fe(µ-1,3-N3)]2, which has a chair conformation.

The dihedral angle between the FeN6 plane and the FeN2 (diketiminate) plane is 87.41(4)°. The azide ligands are almost linear (N–N–N angle of 177.0(1)° and the N–N bond lengths within the azide groups (1.167(2), 1.176(2) Å) show double bond character similar to N–N distances in other bridging azide complexes.44 The solid-state IR spectrum of 7b shows characteristic azide bands at 2129 and 2081 cm\(^{-1}\).45

29Si\(^{1}H\) NMR analysis of the volatile products in the reaction mixture revealed a resonance at –22 ppm for Me3SiSiMe3, but none for Me3SiH. The production of Me3SiMe3 implies that two hydrogen atoms were lost. However, H2 was not detected in the headspace by gas chromatography, so the fate of the hydrogen atoms is unclear. The coupling of two trimethylsilyl units strongly implies the intermediacy of Me3Si• radicals. These in turn might derive from the attack of an iron radical on trimethylsilyl azide.46 To test this idea, the iron(I) sources L\text{Bu}FeN3Fe\text{Bu}N3 and L\text{Bu}FeClK(solvent)\text{Bu}47 were each treated separately with Me3SiN3. In each case, [L\text{Bu}FeN3]2 was formed. Therefore, iron(I) species of this type are reasonable intermediates that could be formed by homolysis of Fe–H bonds. Homolysis of Fe–H bonds does not occur spontaneously in 1b at room temperature, and therefore we infer that coordination of Me3SiN3 weakens the Fe–H bond and brings about Fe–H homolysis.

Compound 1b undergoes an insertion reaction with AdN3 to give 67% yield of a triazenido complex, L\text{Bu}Fe(η2-HNNNAd) (8b), which is shown in Scheme 4 and Figure 8. The bidentate triazenido and β-diketiminate ligands are perpendicular to each other, which gives a distorted tetrahedral geometry around the metal center. The presence of an N–H bond in 8b is confirmed by the observation of a weak bond at vN–H at 3371 cm\(^{-1}\) in the infrared spectrum. The \(^1\)H NMR spectrum of 8b is indicative of C\text{η}2, local symmetry at temperatures from room temperature to –75 °C, despite the C\text{η}2-idealized symmetry of the molecule in the solid state (each face of the diketiminate ligand should be inequivalent). This observation implies that there is rapid exchange between the two possible orientations of the triazenido ligand. Considering the stability of three-coordinate complexes L\text{Bu}FeX and the large size of the

\text{Scheme 4}

\begin{align*}
\text{tBu} & \rightarrow \text{Ar} \text{Ad} \text{N}3 \text{N}3 \text{Ar} \text{tBu} \\
\text{tBu} & \rightarrow \text{Ar} \text{tBu} \text{N}3 \text{N}3 \text{Ar} \text{tBu}
\end{align*}
adamentyl group, it seems most reasonable to attribute this behavior to a rapid, reversible isomerization of the triazenido ligand from $\eta^2$ to $\eta^1$, followed by rotation and recoordination.

Although disubstituted triazenido complexes are well-known in the literature, there are few examples of triazenido complexes bearing H as one substituent; they come from insertion of azide into a hydride complex, and from protonation of an azide complex. Free $\text{H}_2\text{NNNR}$ compounds are extremely unstable with respect to loss of N$_2$. Although compound 8b is thermally stable for hours in solution at room temperature, it eventually decomposes to the Fe(II) amido complex $\text{L}^{\text{Bu}}\text{FeNHaHb}$ with loss of N$_2$. For identification, $\text{L}^{\text{Bu}}\text{FeNHaHb}$ was synthesized independently from $\text{L}^{\text{Bu}}\text{FeCl}$ and $\text{LiNHbHd}$ by analogy to other known iron(II) amido complexes. Quantitative transformation from triazenido to amido was observed by $^1$H NMR spectroscopy after heating a sample of 8b in C$_6$D$_6$ at 80 °C for 5 h.

**Reactions with N=N Double Bonds.** Diazene (HN=NH) is a possible intermediate of N$_2$ fixation by nitrogenase. Consistent with this idea, both HNN=NH and CH$_2$N=NCH$_3$ are reduced by nitrogenase to give ammonia, methane, and methylamine. Very recently, hydrazine (N$_2$H$_2$), methyldiazene (HN=NCH$_3$) and N$_2$ derived nitrogenase intermediates have been freeze-trapped. Free diazenes bearing hydrogen substituents are extremely difficult to handle, because they decompose in seconds or minutes. As an alternative approach, we have used the stable diazenes PhN=NPhe and benz[c]cinoline.

We recently reported a detailed study of the reaction of 1b with PhN=NPhe, which leads first to the [1,2]-addition product $\text{L}^{\text{Bu}}\text{FeNPheHb}$, and subsequently to the amido complex $\text{L}^{\text{Bu}}\text{FeNPheHb}$. Mechanistic studies were most consistent with a radical chain mechanism, mediated by an iron(I) carrier.

Reaction of the smaller 1a with PhN=NPhe at ambient temperature gives a mixture of products as judged by the $^1$H NMR spectrum. It has not been possible to purify and isolate these compounds, but they may be tentatively assigned as $\text{L}^{\text{Me}}\text{FeNPhPHa}$ and $\text{L}^{\text{Me}}\text{FeNPheHb}$ on the basis of the similarity of their $^1$H NMR spectra with the $\text{L}^{\text{Bu}}$ analogues. Longer reaction time or heating does not drive the reaction mixture to benz[c]cinoline. Instead decomposition occurs, probably due to the instability of $\text{L}^{\text{Me}}\text{FeNPheHb}$.

We also investigated the reaction of 1a with 2 equiv of benz[c]cinoline, which gave 90% conversion to deep green 9a. The detection of 1.07(3) equiv of H$_2$ by GC is consistent with the reaction stoichiometry shown in Scheme 5. In this case, there is no addition across the N=N double bond; rather, H$_2$ is lost and the benz[c]cinoline coordinates to iron. Alternatively, 9a could be isolated in 91% yield from the reaction of $\text{L}^{\text{Me}}\text{FeNPheL}^{\text{Me}}$ and benz[c]cinoline.

The crystal structure of 9a (Figure 9) shows that benz[c]cinoline binds face-on to iron(I) through the N=N $\pi$-bond, and the N=N distance is 1.138(5) Å. The dihedral angle between the benz[c]cinoline and the $\beta$-diketiminate FeNCCNFe plane and the benz[c]cinoline plane is 55.35(5)$^\circ$. A side-on interaction between iron and an N=N double bond has been crystallographically confirmed in only two other compounds. In [Fe(NO)$_2$(PPh$_2$CH$_2$CH$_2$PPh$_2$NNAr)][PF$_6$], the diazenate (N=1.403(5) Å) is constrained to bind using a bidentate phosphine, and our recently reported $\text{L}^{\text{Bu}}\text{FePHNPHa}$ has an N=N distance of 1.398(2) Å.

The peaks in the $^1$H NMR spectra of C$_6$D$_6$ solutions of 9a are unusually broad. Mixing different ratios of 1a and benz[c]cinoline indicates that the broadness of the peaks increases with a greater concentration of benz[c]cinoline, and becomes substantially sharper at a 1:1 ratio of 1a to benz[c]cinoline (see Supporting Information for spectra). This behavior suggests that free and bound benz[c]cinoline exchange at a rate near the NMR time scale (milliseconds). The spectra are substantially sharper in C$_6$D$_{12}$, indicating that exchange of the aromatic with C$_6$D$_6$ is part of this process. We have previously characterized $\text{L}^{\text{Me}}\text{Fe}(\eta^5$-C$_5$H$_5$), in which the benzene ligand is bound relatively weakly (it is displaced rapidly by phosphines, alkynes, and alkenes). Since benzene competes effectively with benz[c]cinoline as a ligand, it shows that the heteroaromatic $\pi$-ligand is bound weakly as well.

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Reactions with Carbon Dioxide and Carbodiimide. After azide, CO$_2$ is another heterocumulene that is a substrate of nitrogenase. Seefeldt and co-workers have shown that CO$_2$ is reasonably attributed to the steric hindrance of the isopropyl group on the ary1 rings or are omitted for clarity. The structure of 10b is similar and is shown in the Supporting Information. Selected bond distances ($\text{Å}$) and angles (deg) for 10a: Fe$\cdots$O, 1.978(2), 2.006(2); C$\cdots$O, 1.245(3), 1.246(3); O$\cdots$Fe$\cdots$O, 115.57(7); O$\cdots$C$\cdots$O, 127.9(2). For 10b: Fe$\cdots$O, 1.967(1), 1.994(1); C$\cdots$O 1.248(2), 1.245(2); O$\cdots$Fe$\cdots$O, 106.98(6); O$\cdots$C$\cdots$O, 128.2(2).

The formate-bridged diiron complexes are insoluble in pentane, and only somewhat soluble in aromatic solvents, a problem that was especially severe for 10b. The solution magnetic moment of 10a is 8.8(2) $\mu_B$, consistent with two nearly uncoupled high-spin iron(II) ions, and 10b was too insoluble to derive a reliable value. The $^1$H NMR spectrum of 10a at room temperature has six peaks with chemical shifts that range from 18 ppm to 60 ppm, suggesting idealized D$_{2h}$ symmetry. Although this observation is consistent with either monomer or dimer in solution, no decoalescence is seen in the $^1$H NMR spectrum of 10a in toluene from $-35$ to $120$ $\degree$C, indicating that the crystallographically observed dimer is the most likely solution species. In 10b, the $^1$H NMR spectrum at $85$ $\degree$C has only seven peaks that integrate as expected for a fully symmetric diketiminate ligand, and the chemical shifts are similar to those in 10a. Interestingly, new peaks appear at lower temperatures.

These peaks are consistent with splitting of an isopropyl methine and one isopropyl methyl resonance, which correspond to the protons closest to one another in the dimer. Unfortunately, the poor solubility of 10b, especially at low temperature, prevents us from fully characterizing this phenomenon. The available data are consistent with either a monomer–dimer equilibrium, or a change from slow to rapid flipping of the diketiminate planes to each side of a dimer (change from C$_{2h}$ to effective D$_{2h}$ point group symmetry).

To overcome the issues caused by the low solubility of these products, we investigated the analogous reaction of disopropyl carbodiimide (PrN$\equiv$C=NPPr) with 1b. This reaction proceeded rapidly and quantitatively at room temperature to give the formamidinate complex L$^{\text{form}}$Fe(PrNCHNPr) (11b) in 89% yield. This compound is monomeric, in contrast to the dimeric formate complexes derived from CO$_2$, a result that is most reasonably attributed to the steric hindrance of the isopropyl groups on the carbodiimide. In the solid state structure of 11b (Figure 11) both the diketiminate ligand and the formamidinate ligand are coordinated in an $\eta^5$ fashion to the Fe atom, giving a distorted tetrahedral geometry around the metal center. The N$\cdots$Fe$\cdots$N bite angle of each ligand is typical.

Reactions with Bronsted Acids. As described above, EPR investigations suggest that an FeMoco species with two hydrides can lose two equivalents of H$_2$ to return to the hydride-free resting state. This suggests that some low-coordinate iron hydride complexes could be protonated by nearby Bronsted acids to give H$_2$. To investigate the susceptibility of synthetic Fe$\cdots$H compounds to protonation of the hydride, we explored the reactions of 1a and 1b with weak acids.

In the presence of excess water, the low-coordinate iron hydride complexes decompose to intractable mixtures that contain free $\beta$-diketimine, suggesting that the acid protonates the $\alpha$ position of the $\beta$-diketiminate ligand. Reaction with smaller amounts of water often gives mixtures as well. In a few cases, using solutions of H$_2$O in tetrahydrofuran gives mixtures in which one compound predominates, enabling isolation. For example, we reported that addition of 1 equiv of H$_2$O to 1b (0.5 equiv per iron) gives the unique oxodiron(II) complex L$^{\text{form}}$FeOFeL$^{\text{form}}$ in 71% yield. In another reaction, the addition of 2 equiv of water to 1a gives a green iron complex, L$^{\text{form}}$Fe($\mu$-OH)$_2$FeL$^{\text{form}}$ (12a) in 67% yield (Scheme 6).

The solid state structure of 12a (Figure 12) has pseudo-D$_{2h}$ symmetry, and half of the molecule is related to the other half.

Figure 10. Molecular structure of L$^{\text{form}}$Fe($\mu$-OCHO)$_2$FeL$^{\text{form}}$ (10a) showing 50% thermal ellipsoids. Isopropyl groups on the ary1 rings are omitted for clarity. The structure of 10b is similar and is shown in the Supporting Information. Selected bond distances ($\text{Å}$) and angles (deg) for 10a: Fe$\cdots$O, 1.978(2), 2.006(2); C$\cdots$O, 1.245(3), 1.246(3); O$\cdots$Fe$\cdots$O, 115.57(7); O$\cdots$C$\cdots$O, 127.9(2). For 10b: Fe$\cdots$O, 1.967(1), 1.994(1); C$\cdots$O 1.248(2), 1.245(2); O$\cdots$Fe$\cdots$O, 106.98(6); O$\cdots$C$\cdots$O, 128.2(2).

Figure 11. Molecular structure of 11b, showing 50% thermal ellipsoids. Selected bond distances ($\text{Å}$) and angles (deg): Fe$\cdots$N1, 2.1358(9); Fe$\cdots$N2, 2.0675(8); Fe$\cdots$N11, 2.0663(8); Fe$\cdots$N21, 1.9908(8); N1$\cdots$C1, 1.318 (1); N2$\cdots$C1, 1.323(1); N1$\cdots$Fe$\cdots$N2, 64.50(3); N11$\cdots$Fe$\cdots$N21, 97.44(3); N1$\cdots$C1$\cdots$N2, 116.27(8).

by a crystallographic inversion center. The metrical parameters compare well with other complexes containing a Fe(μ-OH)₂ core.⁵³,⁶³ Seven paramagnetically shifted peaks are observed in the ¹H NMR spectrum of 12a, consistent with D₂₅₈ symmetry in solution. No peak clearly corresponding to the bridging OH is observed in the ¹H NMR spectrum, but O−H stretching vibrations are seen at 3709 and 3668 cm⁻¹ in the IR spectrum. This binuclear complex has a solution magnetic moment of 7.5(1) μ₅ per dimer, suggesting two uncoupled high-spin Fe(II) centers. Dihydrogen is observed by GC as another product of the reaction. Unfortunately, the THF and H₂O peaks overlap with the peak from the internal standard CH₄, which prevented quantitative measurement of the H₂ produced.

Finally, we tested 2,6-diisopropylaniline (dippNH₂), which has a similar acidity as water in organic solvents (the pKa values in DMSO are 32 for H₂O and 30.6 for PhNH₂).⁶⁴ A mixture of 1a and dippNH₂ in C₆D₆ quantitatively gives the iron amido complex LMeFeNHdipp within a few hours (Scheme 6), as judged by ¹H NMR spectroscopy. Dihydrogen (1.6 equiv) is detected from the reaction, close to the 2 equiv expected. This iron amido complex was previously synthesized from [LMe-FeCl]₂.⁵²

Discussion

Addition of Fe−H across a Multiple Bond. The low coordination number at the iron atoms in these hydride complexes enables reactions with many unsaturated organic compounds. Rapid [1,2] additions are seen with alkenes, alkynes, imines, ketones, nitriles, carbodiimides, and carbon dioxide. These reactions generally place the iron fragment on the more electronegative atom. These are not uncommon reactions in the1H NMR spectrum of 12a, showing 50% thermal ellipsoids. Isopropyl groups removed for clarity. Selected bond distances (Å) and angles (deg): Fe–O1, 2.082(3), 2.059(6); Fe–O1–Fe’, 98.7(2); O1–Fe–O1’, 81.3(2).

Figure 12. Molecular structure of 12a, showing 50% thermal ellipsoids. Isopropyl groups removed for clarity. Selected bond distances (Å) and angles (deg): Fe–O1, 2.082(3), 2.059(6); Fe–O1–Fe’, 98.7(2); O1–Fe–O1’, 81.3(2).

mullen (CO₂, CS₂, carbodiimides) reacting with iron hydrides, these reactions appear to be facile in one case.⁶⁸ Cyanide compounds (nitriles) are not usually reactive toward insertion into the Fe−H bonds of iron−hydride complexes, aside from one example of insertion from a dinuclear iron−carbonyl complex.⁶⁹ Acetonitrile more typically coordinates to iron.⁷⁰ In the β-diketiminate complexes described here, the iron hydrides reduce RCN to a RC(H)=N⁻ ligand under mild conditions. Interestingly, the outcome of the insertion reactions is dependent on the steric demands of the β-diketiminate ligand and the nitrile. With the bulkiest β-diketiminate (L²Me) and nitrile (CH₃CN), the product is a dimer with two bridging imidoyl ligands. Finally, with BuCN and the less bulky hydride complex, a single insertion occurs and the steric bulk prevents access of the second nitrile to the remaining bridging hydride. The reaction of adamantyl azide with 1b gives a triazenido complex that results from formal [1,1]-addition. A few late-metal alkyl complexes have been observed to give [1,1]-addition to azides.⁷⁰ The lone example of a triazenido ligand on iron is in a dinuclear iron−carbonyl complex, where the triazenido derives from protonation of an anionic azide complex.⁷¹ To our knowledge, the only other reaction of an iron hydride complex with an azide involves the addition of sodium azide to L₂FeH₂.
Recent reports of other low-coordinate iron systems are also indicative of high reactivity, although hydride species were not isolable in these systems. For example, Chirik has used low-coordinate pyridinediimine—iron and α-dimine—iron complexes as precatalysts for catalytic alkene hydrogenations, though hydride complexes were not isolated.35 Peters has proposed a transient four-coordinate iron hydride complex that adds across an aromatic C=C bond of benzene,79 and Ohki and Tatsumi have proposed the intermediacy of CpFeH in the cleavage of N≡N bonds.77 These precedents imply that the high activity of the isolable low-coordinate iron-hydride complexes described here is likely to have broader generality to other supporting ligands.

Reductive Elimination of Dihydrogen. Numerous polyhydride complexes, both monometallic and multimetallic, are capable of formal reduction through loss of H2 when a ligand is added.78 Some synthetic hydride complexes have been observed to lose H2 with the addition of N2.79,80 Specifically with iron, a few polyhydride complexes reductively eliminate H2 with ligand binding.25,81 Iron-dihydrogen complexes have been studied in octahedral systems. The reactions typically involve reduction of iron(II) to iron(0), not to iron(I) as observed here. In a recent paper, Peters has presented evidence supporting reversible metalation of a ligand alkyl group in a low-coordinate iron(I) complex.23b

We see no evidence of stable H2 complexes in thermal or photochemical elimination reactions of the diketiminate-supported iron hydride complexes, because any putative transient “FeH” or “Fe(H2)” is trapped by N2 (in the photochemical reaction) or the added ligand (thermal reactions with CO or CNR). The thermal reactions must proceed through a mechanism in which substrate binding preceeds H2 loss, because 1a and 1b are stable at room temperature in solution and under vacuum. We infer that interaction with ligands activates the iron hydride species toward H2 loss. As described above in the context of alkene/alkyne insertion, the available evidence suggests that [LMeFeH2] reacts through a low-population isomer in which one iron—hydrogen bond has opened in the Fe2H2 core. The subsequent LMeFe(substrate)(μ-H)Fe(H)MC complex could be unstable with respect to breaking the remaining Fe—H bond to give an iron(I) product and an unstable iron(III) dihydride complex LMeFeH2, which could lose H2 leading to the remaining iron(I) product. Though other mechanisms are consistent with the data, this is a working model for further studies of these reactions; it also rationalizes why the stronger ligands and those more resistant to insertion reactions (isocyandiones, benzo[η]cinnolines, some azides) lead to iron(I) products. In the case of Me5SiN3, the product is not the iron(I) compound itself, but instead the result of reductive coupling of trimethylsilyl groups in Me5SiN3. Because the reductive coupling product also results from treatment of Me5SiN3 with the iron(I) source LFeNNFeL, iron(I) species are likely intermediates in this reaction.

The product of the reaction of 1a with benzo[η]cinnoline is especially interesting. Despite the presence of lone pairs on the two nitrogen atoms of this heterocycle, the iron coordinates instead to the π-system. There are only four previous crystal structures in which benzo[η]cinnoline is a ligand to a transition metal: Ti and Yb complexes with the metal in the plane of the aromatic rings,83 a complex with the diazene bridging the iron atoms in a Fe2(CO)8 fragment,84 and the cobalt(0) complex (PM(e)3)Co(benzo[η]cinnoline).85 The latter complex is the most similar to the one shown here, from its formal d-electronic configuration to the similar angle between the MN2 and aromatic planes (69° vs. 55° here).85 We have previously shown that benzo[η]cinnoline in a η6 binding mode in LMeFe(C6H5)47, but the η7 binding of benzo[η]cinnoline is clearly stronger, since the benzo[η]cinnoline complex is stable in benzene solution. Why, then, is the binding stronger for the more hindered benzo[η]cinnoline? Previous studies on the binding constants of alkynes, alkynes, and other ligands to the iron(I) LMeFe fragment showed that backbonding dominates the selectivity of binding.57 Because of the greater electronegativity of nitrogen than carbon, the stabilizing shift of electron density from the iron to the unsaturated ligand is more effective in the iron(I) complex of benzo[η]cinnoline.

We also note that strongly hydridic M—H bonds like those in 1a and 1b are characteristic of early transition metal hy-
drides,\textsuperscript{86} consistent with the Fe\textsuperscript{b+}–X\textsuperscript{b−} character of iron alkyl, amido, and alkoxo complexes demonstrated in our earlier studies.\textsuperscript{10,32,57} Further research will show whether the reactivity of other low-coordinate late-metal systems will also tend to mimic the behavior of transition metals with a lower \( d \) electron count.

Protonation To Give Dihydrogen. Many iron–hydride complexes are protonated by acids to release \( H_2 \). For example, in iron complexes of a PNP ligand, the necessary \( pK_a \) of the acid was determined to be less than 10.5 (a coordinated nitrogen inhibited by \( H_2 \) because the extra “boost” in reducing power nitrogenase during \( N_2 \) reduction as the result of ligand-assisted zinc.\textsuperscript{27} Using literature values in DMSO,\textsuperscript{64} one can conclude by weak acids such as diisopropylaniline and diphenylhydrazine.\textsuperscript{87} On the other hand, the diketiminate-bound iron hydrides are protonated with weak acids such as diisopropylaniline and diphenylhydrazine.\textsuperscript{87} Using literature values in DMSO,\textsuperscript{64} one can conclude that acids with \( pK_a \) value up to 32 (and perhaps higher) can protonate 1a and 1b.

Protonation of a hydride ligand may be a key step in nitrogen fixation by nitrogenases. In this hypothesis, one of the metal-bound hydride ligands is protonated and released as dihydrogen to open a coordination site for dinitrogen binding.\textsuperscript{89} This hypothesis is consistent with Hoffman’s ENDOR-based conclusion that the \( N_2 \) binding form of the iron–molybdenum cofactor is at the \( E_4H_2 \) state.\textsuperscript{6} There are a number of acidic Arg residues near the binding face of the iron–molybdenum cofactor.\textsuperscript{87} This hypothesis finds support here, in that weak acids are capable of protonating the hydride ligand to form \( H_2 \).

Insight into Potential Nitrogenase Mechanisms. Some nitrogenase researchers have explained the production of \( H_2 \) by nitrogenase during \( N_2 \) reduction as the result of ligand-assisted reductive elimination.\textsuperscript{3} In this model, creation of hydrides provides a way for the FeMoco to store electrons for \( N_2 \) reduction without reaching an unrealistically low charge and reduction potential. Release of \( H_2 \) from the FeMoco is thought to be concurrent with \( N_2 \) binding, explaining why \( H_2 \) is a competitive inhibitor of \( N_2 \) reduction.\textsuperscript{7} Other substrates are not inhibited by \( H_2 \) because the extra “boost” in reducing power from \( H_2 \) loss is not necessary. The reactivity of complexes 1a and 1b can be viewed using this model, in that they have sufficient reducing power to react thermally with all nitrogenase substrates except \( N_2 \). Thus, the reactivity of compounds 1 mimics not the \( E_4 \) state, but a less reduced FeMoco intermediate (\( E_2 \) or \( E_3 \)) that reduces alternative substrates like alkynes, \( CO_2 \), cyanide, and azide. Photolysis of the hydride complexes 1a and 1b provides the “boost” required to bind the weak ligand \( N_2 \).

Even though 1a and 1b do not reduce \( N_2 \), their reducing power is superior to octahedral Fe–H complexes, a difference that might arise from the low coordination number, the high-spin electronic configuration, the weak Fe–H bond strength, and (most likely) a combination of these effects. Considering that iron atoms in the FeMoco have a low-coordinate geometry and high-spin electronic configuration, these factors are clearly identified as reasonable targets for evaluation in the enzyme.

It is notable that nitrogenase inhibitors (or analogues thereof) like CO, RNC, and \( RN_3 \) typically cause the synthetic hydride complexes 1a and 1b to lose \( H_2 \) and bind the small molecule that was added. Therefore, one may hypothesize that these small molecules might inhibit enzymatic \( N_2 \) reduction by binding strongly to the FeMoco, causing premature loss of \( H_2 \). The addition of 1a and 1b to small molecules that are substrates of nitrogenase (or analogues thereof), like RNC, alkynes, \( RN_3 \), and \( RN=NR \), typically forms a new substrate–H bond, and \( N_2 \) is lost. An exception is benzo\{c\}cinnoline,\textsuperscript{90} although it mimics the nitrogenase substrate diazene, it displaces \( H_2 \) like an inhibitor. This may be attributed to the aromatic nature of benzo\{c\}cinnoline,\textsuperscript{90} which perhaps makes it more resistant to reduction than other diazenes. Azides and cyanides are inhibitors and substrates in the enzyme, and in the synthetic compounds they sometimes give \( H_2 \) and sometimes are reduced. Therefore, the reactions of the synthetic compounds 1a and 1b recall the bifurcated reactivities of these molecules with the enzyme.

It is also worth comparing the specific products of substrate reduction by nitrogenase and the products from the synthetic iron complexes. The synthetic compounds typically do not complete the reduction and release the appropriate product, but maintain a bond between the iron atom and the partially reduced substrate. For example, 1a and 1b reduce alkynes to iron–vinyl complexes, but do not release alkene. They reduce \( C=O \) bond of \( CO_2 \), but do not eliminate water to give \( CO \).\textsuperscript{91} They reduce \( C≡N \) bonds to \( C≡N \) bonds, but do not continue the reduction to methylamine or methane/ammonia. These outcomes may be attributable to the absence of protons in the synthetic system that would release the anionic ligand, either as a product or as an intermediate that is subsequently reduced to the final product. Future studies will examine the further transformations of these small molecules at iron.

Conclusions

In summary, we have shown that the first isolable low-coordinate iron hydride complexes are highly reactive toward various unsaturated small molecules. The reactions can be categorized into three types: (1) insertions of a multiple bond of the substrate into the Fe–H bond with two-electron reduction of the substrate; (2) reductive elimination of \( H_2 \) and coordination (or one-electron reduction) of the substrate; (3) loss of \( H^− \) to an acidic proton of the substrate, releasing \( H_2 \) and giving an iron complex of the conjugate base. Some of the products isolated have novel structural features, such as a square-planar iron(I) complex, a face-bound complex of benzo\{c\}cinnoline, and a monoalkylated triazenido complex. The reaction patterns are reminiscent of elementary steps in the proposed nitrogenase catalytic mechanism and support the idea that hydrides on the low-coordinate, high-spin iron atoms of the FeMoco would be capable of some of the characteristic reactions of the FeMoco. In addition, these studies identify some possible reasons why certain small molecules are substrates of nitrogenases and others are inhibitors.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere by Schlenk techniques or in an M. Braun
Pentane, tetrahydrofuran (THF), diethyl ether, and toluene were purified by passage through activated alumina and "deoxygenizer" columns from Glass Contour Co. (Laguna Beach, CA). Deuterated solvents were first dried over CaH₂, 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 benzenophenone ketyl in THF solution. Celite was dried overnight at 200 °C under vacuum. CO₂ was purchased from Air Products, NJ. Diketiminate backbone, µ-(N,C) were crystallized from pentane in the glovebox. Compounds Diphenylacetylene, benzo[5.8 (12H, -H or backbone CH₃)]cinnoline, and 1-azidoadamantane (AdN₃) were crystallized from pentane in the glovebox. Compounds 1a and 1b were prepared by published procedures.²⁰,²¹

**L₃Fe(CN)Bu₂ (2a).** Reaction of 1a and BuNC in Cd₂ gives complex 2a, in a crude yield of 62% based on H NMR integration with an internal integration standard. However, it can be more conveniently synthesized from L₄FeNNFeLMe and BuNC as follows. A solution of L₄FeNNFeLMe (205 mg, 0.21 mmol) in pentane (15 mL) was treated with BuNC (105 µL, 0.93 mmol) with stirring. Immediate bubbling was observed and the solution color changed from deep brown to bright orange. The reaction solution was stirred at ambient temperature for 5 h. Volatile materials were removed under vacuum and the residue was extracted with pentane (20 mL) and filtered through Celite. The solution was concentrated to 3 mL and cooled to −35 °C to give bright orange crystals of 2a (145 mg, 54%). H NMR (500 MHz, CD₂): δ 9.1 (2H, aryl -H), 5.8 (4H, 3.5(12H, -Pr-CH₃), 2.5 (18H, Bu), 1.3 (4H), −2.0 (6H, backbone CH₂), −5.8 (12H, Pr-CH₃) ppm. (Peaks integrated as 4H could be aryl -m-H or Pr methine CH2; the backbone CH not observed), UV–vis (pentane): 317 (25.3 m³/m⁴ cm⁻¹), 447 (3.9 m³/m⁴ cm⁻¹), 808 (0.2 m³/m⁴ cm⁻¹) nm. IR (KBr pellet): 2122 (vs), 2050 (m), 1969 (m), 1948 (m) cm⁻¹. The NMR spectrum, the broad peaks, and the low symmetry of the molecule led to severe overlap between peaks, which made assignment unsuccessful. The spectrum is shown in the Supporting Information. UV–vis (pentane): 332 (30 m³/m⁴ cm⁻¹), 1300 (1.6 m³/m⁴ cm⁻¹), 2345 (0.9 m³/m⁴ cm⁻¹).

**L₄Fe(N-C≡CHMe)FeL₄ (3a).** A stirring solution of [L₄Fe(N-C≡CHMe)FeL₄] (1a) (146 mg, 0.15 mmol) in toluene (30 mL) was treated with MeCN (18.0 µL, 0.34 mmol). The reaction solution was heated at 45 °C for 18 h and the color changed from deep brown to yellow. All volatile materials were removed under vacuum and the residue was extracted with toluene (30 mL), filtered, and concentrated to 5 mL. Cooling to −35 °C gave orange-yellow crystals of 3a (155 mg, 88%). H NMR (500 MHz, CD₂): δ 50 (6H, N=CHC≡CH), 20 (12H), 13 (4H), 12 (4H), −2 (12H), −7 (12H), −12 (4H), −16 (4H), −21 (12H), −22 (4H), −31 (2H, diketiminate backbone), −40 (12H) ppm. (No peak corresponding to the imine proton was identified. Peaks integrated as 4H could be Pr methine, aryl -H, or aryl -O; peaks integrated as 12H could be Pr-CH₂ or backbone CH₂). UV–vis (toluene): 337 (34.2 m³/m⁴ cm⁻¹), 392 (4.8 m³/m⁴ cm⁻¹) nm. IR (KBr pellet): 1637 cm⁻¹.
orange crystals (70 mg, 79%). 7b is insoluble in benzene, and slightly soluble in toluene, at room temperature. 1H NMR (500 MHz, C6D6, 75 °C): δ 15.1, 1.3, −24, −24, −46 ppm. The broadband of the peaks prevented accurate integration and assignment of the peaks. µeff (C6D6, 348 K): 4.1 μB. IR (KBr pellet): 2962 (s), 2929 (w), 2869 (m), 2129 (vs), 2081 (w), 1529 (w), 1490 (m), 1463 (w), 1346 (w), 1380 (m), 1357 (s), 1317 (s), 1259 (m), 1215 (w), 1190 (w), 1097 (m), 1054 (w), 1024 (m) cm⁻¹. UV–vis (toluene): 337 (15.5 mM cm⁻¹) nm. Anal. Calcld for C9H10NO4Fe2: C, 70.10; H, 8.91; N, 11.68. Found: C, 70.04; H, 8.71; N, 11.02.

L⁶⁺Fe(μ-OCHO)₂FeLMe (10a). A reasable flask was loaded with 1a (254 mg, 0.27 mmol) and pentane (15 mL). CO₂ (256 mbar, 61.7 mL, 0.64 mmol) was condensed in the reaction flask at 77 K over 30 min. The flask was warmed to room temperature and stirred for 22 h. Volatile materials were removed from the yellow mixture under vacuum and the residue was extracted with toluene (30 mL), filtered, and concentrated to 5 mL. Cooling to −35 °C gave yellow blocks of 10a (138 mg, 50%). 1H NMR (500 MHz, C6D6): δ 18 (4H), 5 (12H, Pr-CH3), −11 (12H + 4H, Pr-CH3 + another 4H; possible assignments for this 4H peak are listed below). −19 (1H, backbone CH), −42 (2H, aryl p-H), −60 (6H, backbone CH₃). (Peaks integrated as 4H could be m-CH or Pr-CH₃; the two bridging formate H were not observed in the NMR spectrum). UV–vis (pentane): 332 (ϵ = 29.9 mM cm⁻¹) nm IR: 1628 cm⁻¹ (C=O), µeff (C6D6, 25 °C): 8.8(1) μB per dimer. Anal. Calcld for C50H46FeO12: C, 71.52; H, 8.63; N, 5.40. Found: C, 71.32; H, 9.52; N, 5.62. Repeated attempts at elemental analysis did not give better agreement, indicating a possible small impurity not visible by NMR spectroscopy.

L⁶⁺Fe(μ-OCHO)₂FeLμ (10b). This was identical to the synthesis of 10a, but using 1b (17 mg, 0.15 mmol), diethyl ether (15 mL) and CO₂ (99 mbar, 7.73 mL, 30 μmol). The yield of 10b was 15 mg (82%). 1H NMR (500 MHz, C6D6, 85 °C) δ 30 (1, backbone C–H), 19 (18H, 'Bu), 16 (4H, Pr-CH₃), −8 (12H, Pr-CH₂), −42 (12H, Pr-CH₂), −50 (2H, p-H or O-CH₃), −70 (2H, p-H or O-CH₃) ppm. A 4H peak for the m-Pr αs was not observed, and is possibly obscured by the solvent. UV–vis (toluene): 339 (43 mM cm⁻¹), 393 (6.0 mM cm⁻¹), 516 (sh) nm. IR (KBr pellet): 3059 (w), 2962 (vs), 2929 (s), 2869 (m), 1622 (w), 1585 (w), 1526 (w), 1491 (s), 1464 (m), 1429 (w), 1380 (vs), 1356 (vs), 1311 (m), 1263 (w), 1215 (w), 1182 (w), 1153 (w), 1099 (m), 1022 (m) cm⁻¹. Elemental analysis could not be obtained for this compound as 8b is thermally unstable.

Thermal Conversion of 8b to L⁶⁺FeNHNAd. A sample of 8b (~5 mg) in C6D6 was heated to 80 °C for 5 h. The 1H NMR spectrum was identical to a sample prepared independently through the following method. A mixture of L⁶⁺FeCl (257 mg, 0.43 mmol), LiNHAd (68 mg, 0.43 mmol), and diethyl ether (10 mL) was stirred at room temperature for 2 h. The yellow-orange solution was filtered through Celite, and the volatile materials were removed by vacuum. The compound was dissolved in n-hexane (3 mL), and the solution was brought to −45 °C afforded L⁶⁺FeNHNAd as bright orange crystals in 2 crops (230 mg, 75%). 1H NMR (500 MHz, C6D6): δ 95 (6H, Ad-α), 67 (3H, Ad-β or γ), 42 (3H, Ad-β or γ), 37 (18H, 'Bu), 31 (3H, Ad-β or γ) −1 (4H, m-Ad), −24 (12H, Pr-CH₃), −93 (4H, Pr-CH₂), −102 (2H, p-Ad), −118 (12H, Pr-CH₂) ppm. The N-H and backbone C=H protons were not located. µeff (C6D6, 298 K): 4.6(3) μB. IR (KBr pellet): 1510 (w), 3052 (w), 3013 (w), 2959 (vs), 2925 (s), 2803 (vs), 1584 (m), 1534 (m), 1502 (s), 1459 (m), 1434 (m), 1385 (vs), 1364 (vs), 1319 (s), 1303 (m), 1253 (w), 1218 (m), 1197 (m), 1131 (m), 1093 (s), 1055 (m), 1029 (m), 946 (w), 933 (w), 890 (w) cm⁻¹.

N⁶⁺Fe(benzoc)Cinnoline (9a). Although reaction of 1a and benzoc]cinnoline gives complex 9a (yield 90% by 1H NMR spectroscopy), it is more easily synthesized from L⁶⁺FeNFeNFeLMe and benzoc]cinnoline. A vial was loaded with L⁶⁺FeNFeNFeLMe (94 mg, 96 μmol) and benzoc]cinnoline (35 mg, 190 μmol). Pentane (15 mL) was added, causing an immediate color change from brown to green. The reaction solution was stirred at room temperature for 5 h, filtered through Celite, concentrated to 3 mL, and cooled to −35 °C to give dark green plates of 9a (113 mg, 91%). 1H NMR (500 MHz, C6D6, 2°): δ 140 (4H), 111 (4H), 17 (12H, Pr-CH₃), −17 (6H, backbone CH), −21 (4H), −52 (12H, Pr-CH₂), −78 (2H, p-Ad) ppm (peaks integrated as 4H could be m-Ad, Pr-CH₃, or overlapped peaks for benzoc]cinnoline ligand). UV–vis: 305 (16.3 mM cm⁻¹), 325 (13.1 mM cm⁻¹), 388 (9.7 mM cm⁻¹), 419 (7.0 mM cm⁻¹), 585 (2.3 mM cm⁻¹) nm. µeff (C6D6, 25 °C): 3.1(1) μB. Anal. Calcld for C9H9NO4FeC: 75.33; H, 7.55; N, 8.57. Found: C, 73.31; H, 7.68; N, 7.98. Repeated attempts at elemental analysis did not give better agreement, indicating a possible small impurity not visible by NMR spectroscopy.

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Detection of H₂ Using Gas Chromatography. The reaction solution from a given reaction in 3 mL of toluene was performed in a 25 mL round-bottom flask. The flask was capped by an adapter with a stopcock leading to a rubber septum. Using a syringe, 8 mL of the gas inside was removed and 8 mL of CH₄ (1043 mbar) was injected into the flask as an internal standard. An aliquot (20 µL) of the gas was withdrawn and injected into a GC (Shimadzu GC-17A) with a 5 Å molecular sieve column (30 m x 0.25 mm) at 26 °C, carrier gas N₂, 600 kPa. The ratio of integrated H₂/CH₄ responses were compared to a calibration plot previously determined by injecting known amounts of H₂ into the same flask with 3 mL of toluene.

Mössbauer Spectroscopy. Mössbauer data were recorded on a spectrometer with alternating constant acceleration. The minimum experimental line width was 0.24 mm/s (full width at half-height). The sample temperature was maintained constant either in an Oxford Instruments Variox or an Oxford Instruments Mössbauer-Spectromag cryostat. The latter is a split-pair superconducting magnet system for applied fields up to 8 T where the temperature of the sample can be varied in the range 1.5–250 K. The field at the sample is perpendicular to the γ-beam. The ⁵⁷Co/Rh source (1.8 GBq) was positioned at room temperature inside the gap of the magnet system at a zero-field position. Isomer shifts are quoted relative to iron metal at 298 K. Magnetic Mössbauer spectra for the paramagnetic contamination of 1a were simulated by using a spin-Hamiltonian description of the electronic ground state:

\[
H_e = D[S_{1,z}^2 - S_z(S_z + 1)]/3 + (E/D)(S_{1,x}^2 - S_{1,y}^2)] + \mu_B \cdot B \cdot S_z
\]

(1)

where \(S_z\) is the total spin of the system, and \(D\) and \(E/D\) are the axial and rhombic zero-field parameters. The hyperfine interactions for ⁵⁷Fe were calculated by using the usual nuclear Hamiltonian. For 1a only the nuclear Hamiltonian was used.

Computational Methods. The Gaussian 03 package was used for all calculations described herein. Hybrid quantum mechanics/molecular mechanics (QM/MM) calculations were used to study full experimental models of L¹¹¹²Fe(CNᵗBu)₂. The QM/MM calculations utilized the ONIOM methodology. The MM region was modeled with the universal force field (UFF) and included the Ar and Me substituents of L¹¹¹²Fe(CNᵗBu)₂. The remainder of L¹¹¹²Fe(CNᵗBu)₂ was modeled at the B3LYP/6-31+G(d) level of theory. Geometries were fully optimized using gradient methods unless otherwise noted. The unrestricted Kohn–Sham formalism was used for the description of all open-shell species. The energy Hessian was calculated for all stationary points and thus confirmed the calculated stationary points as minima (no imaginary frequencies). All reported enthalpies are calculated at 1 atm and 298.15 K.

Acknowledgment. This work was supported by grants from the National Institutes of Health (Grant GM065313 to P.L.H.) and the National Science Foundation (Grant CHE-0701247 to T.R.C.), as well as a Sloan Research Fellowship (P.L.H.) and a Weissberger Fellowship (Y.Y.). We thank Bernd Mienert for collection of Mössbauer data. Calculations employed the UNT computational chemistry resource, whose purchase was supported by a NSF CRIF grant (CHE-0342824).

Supporting Information Available: Complete ref 94; spectra (PDF) and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA710669W