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Effects of N₂ Binding Mode on Iron-Based Functionalization of Dinitrogen to Form an Iron(III) Hydrazido Complex

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Abstract

Distinguishing the reactivity differences between N₂ complexes having different binding modes is crucial for the design of effective N₂ functionalizing reactions. Here, we compare the reactions of a K-bridged, dinuclear FeNNFe complex with a monomeric Fe(N₂) complex where the bimetallic core is broken up by the addition of chelating agents. The new anionic iron(0) dinitrogen complex has enhanced electron density at the distal N atoms of coordinated N₂, and though the N₂ is not as weakened in this monomeric compound, it is much more reactive toward silylation by TMSI.

Double silylation of N₂ gives a three-coordinate iron(III) hydrazido(2-) complex, which is finely balanced between coexisting $S = 1/2$ and $S = 3/2$ states that are characterized by crystallography, spectroscopy, and computations. These results give insight into the interdependence between binding modes, alkali dependence, reactivity, and magnetic properties within an iron system that functionalizes N₂.

Abstract

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ASSOCIATED CONTENT

Supporting Information. Experimental details and crystallographic files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Introduction

Nitrogen is an essential element, but in its most abundant form as N₂ it is relatively unreactive, and thus it is challenging to find reactions that convert it into more useful compounds. In nature, the nitrogenase enzymes reduce N₂ to NH₃ at atmospheric pressure and room temperature using special iron-sulfur clusters, which have nearby positively charged residues that may participate in the reactions.¹ Alternatively, N₂ can be converted into NH₃ using H₂ through the Haber-Bosch (HB) process, which is done on a huge scale (140 million tons in 2017).² The Mittasch catalyst typically used in the HB process has a reduced iron/alkali metal surface that is competent for ammonia synthesis, but requires temperatures in excess of 300 °C to overcome the kinetic barrier and pressures greater than 100 bar to favor ammonia formation at such high temperatures.³ The activity is greatly enhanced by using alkali metal promoters in the catalyst, and they are localized at the surface.⁴ Recently, Chen *et al.* reported that first-row transition metal lithium hydride composite materials can lower the temperatures and pressures required for ammonia synthesis to 200 °C and 10 bar, supporting the notion that alkali cations play an important role in nitrogen fixation.⁵ Rigorous kinetic measurements on both the HB process⁶ and nitrogenase⁷ have led to the development of mechanistic scaffolds, but the structural details of N₂ cleaving steps in neither case are understood. Though positively-charged fragments are important in both processes, the roles of Lewis acids for activation of N₂ have been studied only recently in well-characterized synthetic complexes.^{4i,8}

Homogeneous transition metal complexes have been reported to catalytically reduce N₂ to ammonia using Ti, Mo, Fe, and Co catalysts.^{9,10,11} The efficacy of Fe complexes is of particular interest as all known nitrogenase enzymes utilize Fe-containing cofactors¹² and the most prevalent HB catalyst is Fe-based as noted above. Peters and coworkers have shown that iron complexes supported with EP₃ tetradentate supporting ligands (E = B, Si, C) can achieve up to 42 ± 4 turnovers (84 ± 8 equiv NH₃) using diphenylanilinium triflate as an acid and dcamethylcobaltocene (CoCp*₂) as a reductant.^{10d} Nishibayashi and coworkers described a PNP pincer supported system with up to 7 turnovers (14 equiv NH₃).^{10e} Ashley

and coworkers have shown that a phosphine-supported iron complex can catalytically reduce N_2 to hydrazine (N_2H_4) using $CoCp^*_2$ as the reductant and anilinium triflate as the proton source.¹³ Mechanistic and computational studies suggest that the catalytic systems proceed through an associative mechanism where the NN bond is reduced stepwise as reducing equivalents (H^+/e^-) are added.^{9–13}

In addition to the examples of catalytic N_xH_y formation, a growing number of catalytic N_2 silylation reactions have been reported.¹⁴ One major advantage of studying reactions between transition metal N_2 complexes and silyl halides is that the silylated N_2 products can be isolated more easily, giving insight into partially reduced dinitrogen species that are analogous to the intermediates in catalytic protonation.¹⁵ Being able to draw parallels between the silylation and protonation chemistries is particularly relevant for first row transition metals where the protonated intermediates are often thermally sensitive.^{10,11} Focusing on iron, Peters and coworkers have demonstrated the propensity of reduced iron- N_2 complexes in various oxidation states to undergo exclusively mono-silylation to form diazenido complexes upon addition of silyl halides (Figure 1, top).^{16a–d} The only examples with isolation of iron(II) hydrazido(2-) species, which come from multiple silylation of N_2 , were when 1,2-bis(chlorosilyl)ethane was used as the electrophile (Figure 1, bottom).^{16c} Lu and coworkers isolated analogous hydrazido(2-) complexes using cobalt and iron metallalumatrane, and calculations suggested that formation of a hydrazido(2-) complex is rate determining; this is consistent with the inability to observe this species during catalysis.^{14–16e}

A main determinant of N_2 reactivity in transition metal complexes is the coordination mode of N_2 .¹⁷ Interestingly, most of the Fe- N_2 complexes that are catalytically competent for trisilylamine or ammonia synthesis bind N_2 in a terminal κ^1 fashion. In some cases, the N_2 bridges to a κ^1 -bound alkali cation, which causes a small shift in the N-N stretching frequency but does not change the reactivity.^{4j} Another common binding mode for N_2 is end-on/end-on bridging ($\mu-\kappa^1:\kappa^1$) of N_2 between two iron centers. In iron chemistry, this has led to complexes with substantial weakening of the N-N bond, particularly when there is cooperation with alkali metals that bind side-on to the N_2 unit.^{16a,18,23a,b,f} Our group has reported numerous β -diketiminate supported iron(I) and iron(0) complexes with $\mu-\kappa^1:\kappa^1-N_2$ (Scheme 1), but these have not reacted with electrophiles or protons; when N_2 is involved in reactions, it is a leaving group that is displaced by donors.¹⁹ Thus, despite the substantial charge transfer into the N_2 unit of the bimetallic complexes, the partial reduction of N_2 has not led to functionalization. Reactivity associated with bridging N_2 has been observed only after dissociative cleavage of N_2 into nitrides, which subsequently react with Brønsted acids or methyl tosylate to form new N-H or N-C bonds.²⁰

The current work started from the hypothesis that reactivity could be modulated by changing or removing the alkali metal cation.²¹ Variation of the alkali metals M in $M_2[L^{Me}FeN_2FeL^{Me}]$ ($M = Na^+, K^+, Rb^+, Cs^+$), wherein the N_2 ligand is in a side-on interaction with the alkali cation, had little impact on the degree of N_2 activation. The strength of the N-N bond strength was insensitive to the alkali cation radius, with a variation of only $\sim 10\text{ cm}^{-1}$ in the ν_{N-N} frequencies.²²

Here, we report that alkali cation extraction using crown ethers has a much more dramatic effect, disrupting the FeNNFe core to give a mononuclear iron(0) complex with N₂ ligands in terminal binding modes. Importantly, this enables us to compare the reactivity of terminal and bridging N₂ complexes with the same supporting ligand and the same oxidation level, giving us fundamental information about the relationship of binding mode and reactivity. Terminally bound N₂ has much greater reactivity toward electrophiles, and we find that silylation of the N₂ unit leads to the first three-coordinate hydrazidoiron(III) complex, in which the unusual three-coordinate iron(III) is stabilized by iron-nitrogen multiple bonds.

RESULTS

Extracting Alkali Cations from Bridging N₂ Complexes.

Treatment of a diethyl ether solution of the known^{19b} K₂[L^{Me}FeNNFeL^{Me}] (**1**) with 2 equiv of 18-crown-6 in THF-*d*₈ under an atmosphere of N₂ or Ar leads to shifts of the resonances in the ¹H NMR spectrum at ambient temperature (Figure S-13), which suggests complexation of the alkali cations by the crown ether. We were unable to crystallize this thermally sensitive species under Ar. However, treatment of a diethyl ether solution of **1** with a combination of 2 equiv of 18-crown-6 and 2 equiv of 12-crown-4 under Ar and cooling to -40 °C yielded crystals of the [K(18-crown-6)(12-crown-4)] salt of dianionic **2** (Scheme 2). In this structure, the dinuclear FeNNFe core is maintained, but the potassium ions are held away from the core by the crown ethers (Figure 2). Comparison of the X-ray structure of **2** with those of **1** and the previously reported formally diiron(I) analogue, [L^{Me}FeNNFeL^{Me}],^{19b} reveals that the FeNNFe cores of all three species are very similar. The only statistically significant difference between the core of **2** and the previously reported structures is the N_L-Fe-N_L angle of 102.3°, which is the largest of reported Fe b-diketimate complexes (Table 1). In order to further support the N₂ binding mode, resonance Raman spectra of **2** were collected on THF solutions at -60 °C with 406.7 nm excitation. We observed a band at 1738 cm⁻¹, which shifted to 1680 cm⁻¹ when the complex was synthesized with ¹⁵N₂. Resonance Raman spectra recorded from solid state samples also showed a distinct band at 1683 cm⁻¹, which shifted to 1632 cm⁻¹ for the complex synthesized with ¹⁵N₂. The isotopic shifts are close to those predicted by the harmonic N-N oscillator model (1679 and 1626 cm⁻¹ for the solution and solid ¹⁵N isotopologues, respectively). The isotope shifts in all these complexes are well described by isolated, harmonic N-N oscillators indicating that their frequencies are indicative of the N-N bond strength. Thus, they convincingly show the effects of N₂ coordination on the strength of the N-N bond. These frequencies are substantially higher than the analogous compounds with Na⁺, K⁺, Rb⁺, or Cs⁺, where the frequencies lie in the range 1618 ± 7 cm⁻¹, indicating that the N-N bond is somewhat stronger without the alkali metals held within the bimetallic structure. (The bond distances are consistent with this trend, though they are within experimental uncertainty of one another and thus do not constitute independent evidence of bond weakening.) This conclusion is consistent with the alkali metals playing an electro-static role in heightening 3C0-backbonding from the formally iron(0) atoms into the N₂ unit, as we earlier proposed on the basis of computations with highly truncated model.^{19b}

Under an N₂ atmosphere, the addition of 2 equiv of 18-crown-6 to a diethyl ether solution of **1** at room temperature also led to formation of **2**, as judged by ¹H NMR spectroscopy. However, cooling the solution of **2** to –35 °C under N₂ led to a color change from green to red, and after 24 h dark red crystals of a very thermally sensitive monometallic bis(dinitrogen) complex **3** were isolated in 77% yield (Scheme 3). Formation of **3** occurs only in the presence of the crown ether, indicating that disruption of the cation- π interactions in **1** enables binding of additional N₂ to the core and cleavage of the bimetallic complex.

The diethyl ether solvate of **3** was characterized by X-ray crystallography (Figure 3). The structure features a distorted tetrahedral iron atom ($\tau_4 = 0.88$) with two bound N₂ units. One dinitrogen ligand (N-N = 1.144(3) Å) bridges to a potassium that is chelated by the 18-crown-6 cation, and the other dinitrogen ligand is in a terminal binding mode (N-N = 1.134(4) Å). The Fe-N₂ bond lengths are 1.809(3) Å for the bridging N₂ and 1.836(3) Å for the terminal N₂. The shorter Fe-N₂ distance and the longer N-N distance for the potassium-bound N₂ unit suggest that the coordination of the Lewis acid promotes backbonding into the π^* orbitals of the N₂ unit. However, the N-N distances are shorter and Fe-N₂ distances are longer than those in **1** and **2**, and thus there is less backbonding into N₂ activation in a FeNNK unit than in an FeNNFe unit. Two bands are present in the infrared (IR) spectrum of solid **3** at 1964 and 1844 cm⁻¹ (Figure 4, top) that shift to 1897 and 1781 cm⁻¹ in a sample that was crystallized under an ¹⁵N-enriched dinitrogen atmosphere (Figures S-26 & S-27). Surprisingly, the IR spectrum of a solid sample of the ¹⁵N₂ labeled **3** under an atmosphere of natural abundance N₂ showed only N-N stretching bands corresponding to the ¹⁴N₂ analogue, suggesting that there is fast exchange of bound dinitrogen in the solid state. DFT calculations (described below) indicate that these bands are not localized NN vibrations; rather they are the symmetric and asymmetric combinations of N-N stretching motions, respectively. These N-N stretching frequencies in **3** are higher in energy than in either **1** (1625 cm⁻¹) or **2** (1683 cm⁻¹), consistent with the shorter N-N bonds in **3** than those in **1** and **2**. This is reasonable, since only a single iron(0) center is backbonding into two N₂ units in **3** while in **1** and **2** there are two iron(0) centers backbonding into the same N₂ unit.

A solution of **2** formed *in situ* by mixing **1** and 18-crown-6 in diethyl ether showed no substantial changes in its electronic absorption spectrum between room temperature and –85 °C. However, cooling a stirred solution under an atmosphere of N₂ from 25 °C to –25 °C causes a shift in λ_{max} from 724 nm to 757 nm, and between –25 °C and –85 °C the peak at 757 nm disappears with concurrent appearance of new peaks at 540 and 995 nm, which are characteristic of **3** (Figure 5). The dependence of this behavior on the presence of N₂ is consistent with the stoichiometry of **3**, which requires additional N₂ relative to **1**. Since **2** does not form **3** under an Ar atmosphere, it indicates that **3** does not arise from the alternative mechanism of disproportionation of **2**. In order to probe further, a solution of **2** in diethyl ether was cooled to –80 °C and monitored by solution IR. This gave no changes under Ar, but under an N₂ atmosphere cooling gave a new peak at 1849 cm⁻¹ (Figure S-31 & S-32), which is close to that observed in solid **3** (1844 cm⁻¹). These data indicate that **2** and **3** are in a temperature-dependent equilibrium.

The lack of isosbestic points in the UV-vis spectra and trend of shifting peaks suggests that there is at least one other species in equilibrium with **2** and **3**. However, IR spectra displayed no bands between 1500–1900 cm^{-1} indicative of N_2 intermediates. (Unfortunately, noise above 1900 cm^{-1} from absorbance of the measurement system prevents monitoring of the higher energy peak *in situ*.) Identification of these intermediates was not successful.

Four-coordinate Fe- N_2 complexes are rare.^{16a,23} The spin state of **3** is not obvious from its geometry, and because of the low stability in the solid state, we did not pursue magnetic measurements of **3**. Instead, spectroscopically validated DFT calculations were used to resolve the spin state of **3**. Geometry optimizations were performed in the high-spin ($S = 1$) and the low-spin ($S = 0$) states starting from the X-ray structure (Figures S-33 & S-34). The high-spin optimization yielded a tetrahedral geometry ($t_4 = 0.84$) closely resembling the experimental geometry ($t_4 = 0.88$), while the low-spin computation optimized to a distorted square planar geometry ($\tau_4 = 0.49$). These geometries were used to calculate Mössbauer parameters for both possible spin states using the method we recently reported,²⁴ and compared to the experimental spectrum (Figure 4, **bottom**). The high-spin calculations predicted an isomer shift of 0.70 mm s^{-1} (exp. 0.53 mm s^{-1}) and quadrupole splitting of 0.83 mm s^{-1} (exp. 1.02 mm s^{-1}), while the low-spin structure gave much poorer agreement with an isomer shift of 0.35 mm s^{-1} and a quadrupole splitting of 1.89 mm s^{-1} . Thus, the accuracy of the geometry and the closer predicted Mössbauer parameters support the assignment of **3** as having a high spin iron(0) center. Broken symmetry calculations did not indicate redox activity of the ligands (less than $-0.11 e^-$ of spin density on the N atoms), and were consistent with the formal assignment of **3** as having a high-spin iron(0) center ligated by two neutral N_2 units. This contrasts with complexes **1** and **2**, for which calculations indicated a formal 2-electron reduction of the N_2 ligands, having $-0.27 e^-$ of spin density on N_2 .

Silylation of Terminally Bound N_2 .

The bridging dinitrogen complexes $[\text{L}^{\text{Me}}\text{FeNNFeL}^{\text{Me}}]$, $\text{M}_2[\text{L}^{\text{Me}}\text{FeNNFeL}^{\text{Me}}]$ ($\text{M} = \text{Na}^+$, κ^+ , Rb^+ , Cs^+), and $[\text{L}^{\text{Me}}\text{FeN}_2\text{MgN}_2\text{FeL}^{\text{Me}}]$ react with electrophiles such as silyl halides, but no N_2 containing products have been isolated. The lack of N_2 reactivity in these complexes indicates that even though there is substantial charge transfer from the formally iron(0) centers into the N_2 , the end-on/end-on bridging mode of N_2 is unreactive.¹⁷

In order to explore the influences of changing from the bridging to the terminal binding mode, we used DFT calculations to gauge the differences in charge and spin density on N_2 between **1** and **3**. Using the same level of theory that was successful above, we see that the N_2 unit in **1** has significantly more spin population on the N atoms (more than $0.5 e^-$) than in **3** (about $0.2 e^-$). However, in **1** the delocalized spin density is symmetric across both nitrogen atoms, while in **3** the delocalization is enhanced on the distal nitrogen atoms (green values in Figure 6). Similarly, the charges of $-0.70 e^-$ on each nitrogen atom in **1** are substantially larger than those on the distal nitrogen atoms in **3** ($-0.48 e^-$ and $-0.32 e^-$). Even though there is less charge on the N_2 units (consistent with the IR frequencies above), it is interesting that the N_2 ligands are polarized, with most charge on the distal nitrogen

atoms. We hypothesized that this polarization, and the exposure of the N₂ ligands, could lead to reactivity with electrophiles that was not observed for **1**.

Adding a diethyl ether solution of (CH₃)₃SiH (TMSI) to a diethyl ether solution of **3** at –116 °C and warming to ambient temperature while stirring led to formation of a brown product **4** in 59% spectroscopic yield based on Fe, as judged by comparison to a Cp₂Co capillary as an internal integration standard (Scheme 4). Cooling a concentrated hexanes solution to –35 °C overnight yielded crystals of **4** in 36% isolated yield based on Fe. Significantly, one of the bound N₂ units has been silylated twice at the distal nitrogen to form a disilylhydrazido(2-) ligand in **4**. Analysis of ¹H NMR spectra showed concurrent formation of an iron(II) iodide complex **5** that is formed in 39% spectroscopic yield based on Fe, using a Cp₂Co capillary as an internal integration standard. The ratio of approximately 2:1 of **4** and **5** (accounting for 98% spectroscopic yield of iron) suggests the stoichiometry shown in Scheme 4, where a portion of **3** acts as a reductant to provide the electrons necessary for the 4-electron reduction of N₂ that is evident in **4**.

We observed a significant increase in yield of the silylated product **4** when the reaction temperature was lowered from –60 °C to –116 °C (Table 2). The benefit of using low temperatures for N₂ functionalization by iron complexes has been described by Peters and coworkers.¹⁰ Addition of fewer than 1.5 equiv of TMSI led to a decrease in the observed yields of **4** and **5**, but a monosilylated diazenido species was not isolated (Table 3). No increase in the yield of silylation product was observed when excess TMSI was added. The less reactive (CH₃)₃SiCl (TMSCl) gave **4** and an iron chloride complex analogous to **5** albeit in lower spectroscopic yields of 46% and 38% respectively.

In order to clearly compare the bridging and terminal N₂ complexes, we performed control experiments with the silylation of the starting dinuclear N₂ complex **1**. Reaction of **1** with TMSI under analogous conditions to those for the silylation of **3** yields only 6% of **4**. If the reaction mixture is kept at –60 °C, the spectroscopic yield of **4** increases to 19% after 1 h, 28% after 2 h and 30% after 20 h with no further increase in yield up to 120 h. This is substantially slower than the formation of **4** from **3**, which is complete within 15 min, and confirms that the terminal binding mode is indeed more active toward N₂ silylation, with the same supporting ligand and oxidation state at iron.

In order to determine how **1** gives **4**, we repeated the reaction of **1** with TMSI under an atmosphere of Ar; under these conditions, we observed less than 5% of **4** by ¹H NMR spectroscopy (Scheme 5). Similarly, the reaction of **2** with TMSI under an Ar atmosphere gives 5% of **4** by ¹H NMR spectroscopy. The slow, low-yielding reactions indicate that the rate of silylation of the bridging N₂ unit is inferior to that of the terminal N₂ in **3**. We speculate that TMSI undergoes some reaction with **1** and **2** that yields a transient terminal N₂ species that can be silylated, however, we have been unable to observe it.

Properties of the Hydrazido Complex **4**.

The crystal structure of **4** shows two independent molecules in the asymmetric unit, and these two molecules have surprisingly different bond distances in the core (Figures 7 & 8). Each of the bonds to Fe2 is roughly 0.03 Å shorter than for the analogous bond to Fe1. The

N-N bond lengths are both 1.348(3) Å, a distance that lies between the values for an N-N single bond (1.45 Å) and an N-N double bond (1.25 Å) for the organic N₂H_x analogues, suggesting some p-bonding. The N-N distance, Fe-N distances of 1.638(2) and 1.671(2) Å, as well as N-Si distances of 1.773(3) Å and 1.774(3) Å are comparable to those in the analogous four and five-coordinate Fe-N₂(SiMe₂CH₂)₂ complexes reported by Peters and Lu.¹⁶ Bond angles are similar between the two molecules, with the sums of angles about Fe of >359° confirming the trigonal planar geometry. The angles between the N₃Fe and NSi₂ planes are somewhat different between the two molecules, at 54.9(7)° and 45.9(5)° respectively.

Consistent with the observation of two iron sites with different bond lengths, the zero-field Mössbauer spectrum of solid **4** displays a superposition of two quadrupole doublets in a 1:1 ratio. This ratio was unchanged in several different samples, and between spectra recorded at 80 and 173 K (Figure 9). The most reasonable fit has two nested quadrupole doublets, one with $\delta = 0.22 \text{ mm s}^{-1}$ and $E_Q = 1.99 \text{ mm s}^{-1}$, and the other with $\delta = 0.46 \text{ mm s}^{-1}$ and $E_Q = 1.16 \text{ mm s}^{-1}$ at 80 K. The significantly different isomer shifts found for components 1 and 2 can be rationalized from the significantly different average bond lengths of the two iron sites. According to the usual (positive) correlation of isomer shifts and iron–ligand bond lengths,²⁵ site 2 of compound **4** corresponds to component 1 with the lower isomer shift. The distinct difference of isomer shifts as well as bond length for sites 1 and 2, having identical ligands, moreover suggest different spin states. In order to further explore these features, we performed density-functional calculations on **4**. The geometry of full models of **4** were optimized in the three possible spin states for iron(III) ($S = 1/2, 3/2$, and $5/2$), using both BP86 and B3LYP functionals, and the parameters are compared in Table 4. In addition, we used our recently published correlation of Mössbauer isomer shifts and quadrupole splitting values with computationally derived electron densities and electric field gradients, in order to predict the zero-field Mössbauer parameters for each computational model.²⁴ The DFT results obtained with two functionals, BP86 and B3LYP, agree reasonably well with the different experimentally determined zero-field Mössbauer parameters for the two sites by adopting $S = 3/2$ and $S = 1/2$ respectively (Table 4). In addition to predicting comparable Mössbauer parameters, both functionals also reflect the expected response of the Fe-N₂ bond to the change in spin state. As spin increases from $S = 1/2$ to $S = 3/2$ the Fe-N distance elongates by ~0.06 Å in the DFT models while the experimental difference is smaller at 0.033(3) Å. Similarly, from $S = 1/2$ to $S = 3/2$ the N_{Ligand}-Fe distances elongate by ~0.04 Å in the DFT models while the experimental difference is smaller at 0.025(3) Å. These trends support the notion that the small change in the Fe-N distance within the solid-state structure between the two Fe sites is enough to cause the iron sites to have different spin states.

The energy difference between the low spin and intermediate spin states must be small in order for crystal packing effects to cause both to be populated. Both functionals show a small energy difference for the doublet and quartet states, with BP86 showing the quartet state 8.5 kcal mol⁻¹ higher in energy while B3LYP shows the doublet state to be higher in energy by 0.6 kcal mol⁻¹. Hybrid functionals like B3LYP have been shown to favor higher spin states due to underestimation of spin pairing energies.²⁶ BP86 and B3LYP both show

the $S = 5/2$ state to be substantially higher in energy by $+30.5 \text{ kcal mol}^{-1}$ and $+14.5 \text{ kcal mol}^{-1}$ respectively. While it is not surprising that there is some functional dependence, these results qualitatively support the idea that the doublet and quartet states are very close in energy and therefore crystal packing effects could exert enough force to push the molecule into different spin states at different crystallographic sites, while the sextet state is substantially higher in energy and not populated.

To further test the model in which there are both $S = 1/2$ and $S = 3/2$ sites in the crystal we computed the energies of the different spin states in the two crystallographic geometries (rather than the fully optimized geometries used above). In these cases, only the H-atom positions were optimized (to account for the systematic shortening that is always present in X-ray diffraction results).²⁷ Using BP86, Fe1 (longer Fe-N₂ distance) has a smaller energy gap between the doublet and quartet states of $3.3 \text{ kcal mol}^{-1}$ favoring the doublet, while for Fe2 (shorter Fe-N₂ distance) the doublet-quartet energy gap is $8.2 \text{ kcal mol}^{-1}$ (Table 5). These results suggest that Fe1 is best assigned as the $S = 3/2$ site with longer Fe-ligand distances, while Fe2 is best assigned as the $S = 1/2$ site with shorter Fe-ligand distances. Thus, the relative spin-state energetics in **4** are very sensitive to the geometry; a ligand-field explanation of this phenomenon (using the computed frontier orbitals) follows in the Discussion.

EPR spectra of frozen toluene solutions of **4** at 10 K showed exclusively an $S = 1/2$ species (Figure 10), which integrated to $110 \pm 15\%$ spin concentration using a copper(II) standard for double integration. Apparently, **4** has a low-spin ground state in solution, at least at the temperature accessible to EPR (10 K). A simulation provided principal g values of 1.79, 1.84, and 3.61. The large splitting of g values beyond $g = 2$ reflects orbital degeneracy and has precedent in ‘highly anisotropic’ low-spin Fe(III) heme complexes.²⁸ Unfortunately, there were no clear EPR signals corresponding to the $S = 3/2$ state of **4** either in the solid state or in frozen solution. We suspect that extreme magnetic anisotropy of the low-lying and energetically well isolated $m_s = \pm 3/2$ Kramers doublet of the $S = 3/2$ state leads to very low derivative signal intensity and prevents its detection. When E/D is small, such doublets can be EPR silent, in particular when ZFS is large as in axial Co(II) complexes with negative ZFS,²⁹ or a Fe(II) tetrazene complex with a $|S=3/2, m_s=\pm 3/2\rangle$ ground state.³⁰ More in-depth investigations of the magnetism of this complex will be reported separately.

We also measured the magnetic susceptibility of solid samples of **4** using a SQUID magnetometer from 2 to 270 K. The spin state is not uniquely specified by the data because the fits for two iron sites with anisotropic g values and large ZFS are severely underdetermined. However, we were able to fit the SQUID data to a model with the parameters from the Mössbauer/EPR model of $S = 3/2$ and $S = 1/2$ sites in a 1:1 ratio, when the $S = 1/2$ site undergoes a spin crossover transition with $T_c = 234 \pm 10 \text{ K}$ and an enthalpy difference of $442 \pm 100 \text{ cm}^{-1}$. These values are in the range found for other iron(III) spin-crossover complexes, and suggest that the size of cooperative domains is close to unity.³¹ A spin crossover is reasonable, given the nearness of the energies of the $S = 1/2$ and $S = 3/2$ states that results in the two crystallographic sites being able to coexist in one crystal. Details of this apparent spin crossover will be described in a future publication.

DISCUSSION

Binding Modes of N₂.

An important aspect of N₂ functionalization is the relationship between the binding mode of N₂ and its reactivity, a topic recently reviewed by Fryzuk.¹⁷ Despite the general trends in the literature, it is rare to find a situation in which the same oxidation state and supporting ligand can give multiple binding modes, enabling direct comparison. Here, we compare an end-on bridging N₂ complex **1**, which has a particularly great amount of ground-state N₂ weakening (N-N distance = 1.215(6) Å and $\nu_{\text{NN}} = 1625 \text{ cm}^{-1}$ which led to formal assignment of an N₂²⁻ ligand,³²), to the terminally bound monometallic analogue **3**. Both are in the Fe(0) oxidation state and supported by the same β -diketiminato ligand. Despite the substantial ground-state N₂ weakening in **1**, no functionalization of its N₂ unit has been observed, except a background reaction at higher concentrations that may result from its decomposition in the presence of TMSI. In fact, clear indications of N₂ functionalization have not been observed from any bridging Fe-N₂-Fe complex to our knowledge, regardless of the level of ground-state weakening of the N-N bond. Meanwhile, many terminal N₂ complexes of iron that exhibit significantly less ground-state activation of the N-N bond ($\nu_{\text{NN}} > 1900 \text{ cm}^{-1}$) have been shown to react with silyl electrophiles and acids both stoichiometrically and catalytically to give silylated and protonated N₂ reduction products.^{10,14–16} The observed lack of reactivity at N₂ of bridging **1** could be due to Hypothesis 1) the size of the ligands sterically encumbers approach of electrophiles to the N₂ unit causing N-X bond formation to be kinetically challenging, or Hypothesis 2) the symmetric binding mode of the N₂ leads to a less potent nucleophile since the negative charges on the N-atoms are directly bound to positively charged iron centers. Hypothesis 1 is supported by comparing the spacefilling models of **1** and **3** where the N₂ unit in the bridging complex **1** is almost completely hidden by the steric bulk of the supporting ligand and potassium cations, while in **3** the N₂ units are clearly visible and extend beyond the steric bulk of the supporting ligand (Figure 11). From these models, it is reasonable to assume the approach of ⁺Si(CH₃)₃ will have a higher activation barrier for **1** than **3** offering a possible explanation for the lack of reactivity of the prebound N₂ unit in **1**. Hypothesis 2 is supported by comparison of Mulliken charges on the N atoms in **1** and **3**, which correlates with the difference in reactivity. DFT calculations show that in **1** there is substantial reduction of the dinitrogen ligand to an N₂²⁻ ligand where the charge is equally distributed across the two N atoms. In **3**, the distal N atom of the terminal N₂ unit has about half of the charge of those in **1** while the proximal nitrogen shows little to no charge build up according to DFT demonstrating the polarizing nature of the terminal binding mode (Figure 6 above). The observed polarization could explain why the N₂ unit in **3** is more reactive than that in **1**, despite having significantly less ground state N-N bond activation.

Exposure of the N₂ unit was made possible through disruption of the cation- π interactions of **1** by sequestering the K⁺ ions with crown ethers. Previous work has shown that these interactions provide substantial stability to the complex as **1** does not react with aromatic solvents, while the diiron(I) analogue L^{Me}FeNNFeL^{Me} (which lacks stabilizing interactions from alkali metal cations) loses N₂ in the presence of potential donors such as benzene.^{19b} Upon extraction of the alkali cations in **1** with crown ethers, the resulting complexes **2** and **3**

react with benzene releasing N₂, yielding a formally iron(0) h⁴-benzene adduct **6** (Scheme 6). This process is not reversible. The identity of **6** was confirmed through an independent synthesis by reducing the previously reported iron(I) benzene complex^{19b} with KC₈ in the presence of 18-crown-6). The properties of **6** will be reported separately. These data demonstrate that the stabilization provided by the cation-p interactions in **1** prevents reactivity of the FeNNFe core supporting Hypothesis 1.

N₂ Silylation.

Addition of TMSI leads to **4**, which has double silylation of the iron-bound N₂. To our knowledge, it is the first isolated example of double silylation of N₂ by an iron complex without using 1,2-bis-(chlorodimethylsilyl)ethane. This is a four-electron reduction of N₂, but the iron is oxidized only from iron(0) to iron(III). Accordingly, formation of **4** relies on internal reducing equivalents from additional **3** in solution. Attempts to use an external reducing agent such as 1 equiv KC₈ with addition of 18-crown-6 led to complex mixtures. Protonation of **3** with anhydrous HCl led to the formation of 0.06(2) equiv of N₂H₄ and 0.03(2) equiv of NH₃ (average of two runs), while addition of HCl to **4** led to 0.75(5) equiv N₂H₄ and no detectable ammonia (Scheme 7).³³ Therefore, the silylation of the N₂ unit leads to selective formation of hydrazine from N₂. Addition of excess KC₈ and TMSI to **3** in the presence of excess crown ether followed by acidification gave no N₂H₄ and 1.8(1) equiv of NH₃ per iron (Scheme 8). Therefore, the system does not turn over, though the extra reducing agent does reduce the hydrazine.

Low-Spin and Intermediate-Spin Iron(III) in a Three-Coordinate System.

Three-coordinate iron compounds are rare, particularly in oxidation state +3 or higher.^{30,34} To date, a few examples of three-coordinate iron(III) complexes have been reported with weak field amide and alkoxide ligands leading to high-spin *d*⁵ electron configurations.³⁴ However, the presence of metal-ligand π -bonding can change the electronic structure. In relevant previous work, we reported a three-coordinate imido complex L^{Me}FeN(adamantyl), in which the iron(III) ion has an intermediate spin *S* = 3/2 configuration due to the presence of one *d* orbital that is strongly σ -antibonding to the diketiminate N atoms and also strongly π -antibonding to the imido group.³⁵

Given the similarity between L^{Me}FeN(adamantyl) and L^{Me}FeNNTMS₂, it is surprising that the latter achieves the low-spin *S* = 1/2 state, which is unprecedented for three-coordinate iron(III). However, a comprehensible ligand-field picture emerges from the Kohn-Sham orbital occupancies arising from the DFT computations described above. Using the axes shown, the plane of the ligands is the *xy* plane. The diketiminate constrains the bite angle to <100°, which breaks the three-fold axis of the *D*_{3h} point group and gives the *s*-only picture shown in Figure 12. It is similar to other three-coordinate diketiminate-supported iron(II) complexes, with the *d*_{*yz*} and *d*_{*z2*} orbitals very close in energy, which explains their magnetic and spectroscopic properties.³⁶

The presence of π -bonding influences the electronic structure. The *d*_{*z2*}, *d*_{*y2-z2*}, and *d*_{*yz*} orbitals do not have the correct symmetry to undergo p-interactions with a ligand along the *x* axis. Therefore, the *d*_{*z2*} and *d*_{*yz*} orbitals remain close in energy. In an *S* = 3/2 iron(III)

complex, these two d orbitals are differentially occupied, and their mixing may give a large orbital moment that explains the lack of an observable EPR signal for the $S = 3/2$ component as seen experimentally. Preliminary variable-field Mössbauer measurements support this model and will be discussed in more detail in a later publication.

π -Donation from the imido group in LFeNAd was previously shown to drive up the energies of the d_{xz} and d_{xy} orbitals; most importantly, a single d orbital (d_{xz}) is σ -antibonding to the supporting diketiminate and π -antibonding to the imido, driving it high in energy and enforcing the intermediate-spin ($S = 3/2$) configuration.³⁵ In the hydrazido(2-) complex, the additional N enhances the π -donor ability, driving these two orbitals even higher in energy. When both orbitals are high enough in energy, the $S = 1/2$ state becomes accessible, and is the ground state as observed. Nevertheless, an orbital excitation is low in energy, and the resulting orbital contribution to the magnetic moment of the $S = 1/2$ state leads to the large spread of g -values observed by EPR spectroscopy.

In the $S = 1/2$ state of $L^{\text{Me}}\text{FeNNTMS}_2$, there is a bond order of three between the iron and the N atom along the x axis, corresponding to the short Fe-N distance in the Fe2 site of the X-ray crystal structure. This bond is shorter than that in $L^{\text{Me}}\text{FeN}(\text{adamantyl})$ (1.67(1) Å), but similar to those in phosphine-supported C_{3v} imidoiron(III) complexes that are also low-spin (1.64(1) Å).^{16a,37}

Finally, it is interesting that this system is able to doubly silylate N_2 with TMSI. This may result from the electron-rich nature of the diketiminate ligand, which gives highly nucleophilic/basic nitrides in a $\text{Fe}^{2+}_2\text{Fe}^{3+}_2$ cluster that similarly can react with electrophiles.

20d

CONCLUSIONS

This work has demonstrated that cation- π interactions with Lewis-acidic alkali metals play an important role in modifying the energetics of low-valent bridging Fe- N_2 complexes. Disruption of these interactions through addition of crown ethers led to a new terminal dinitrogen complex at low temperature. These enabled comparison of reactivity between endon/end-on bridging N_2 and terminal N_2 using the same ligand scaffold, and terminally bound N_2 was substantially more active for N_2 functionalization. These results show that structural measures of activation are less important than kinetic factors such as access to the coordinated N_2 .

Functionalization of N_2 led to an three-coordinate hydrazido(2-) iron complex, which is the first example of double N_2 silylation at iron without use of a bis-silyl halide. Further silylation gives selective formation of hydrazine from N_2 , which could be of future utility. The hydrazido complex is interesting because it has stronger π -bonding between the iron and nitrogen than an alkylimido analogue. Its π -bonding puts it on the cusp between $S = 1/2$ and $S = 3/2$ electronic configurations, and it crystallizes with half of the molecules in each spin state as shown by spectroscopy, structure, and computations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Representative examples of stoichiometric silylation by Peters *et al.* demonstrating the propensity for formation of diazenido structures in the absence of 1,2-bis(chlorosilyl)ethane.
16c

Figure 2. ORTEP diagram of the X-ray crystal structure of $[L^{\text{Me}}\text{FeNNFe}L^{\text{Me}}]^{2-}$ (2) using 50% thermal ellipsoids. Hydrogen atoms and two $[K(18\text{-crown-6})(12\text{-crown-4})]$ cations were omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-N(1)*, 1.190(8); Fe(1)-N(1), 1.758(4); Fe(1)-N(11), 1.920(3); Fe(1)-N(1)-N(1)*, 175.9(6); N(1)-Fe(1)-N(11), 128.76(8); N(11)-Fe(1)-N(11)*, 102.26(17).

Figure 3.

ORTEP diagram of the X-ray crystal structure of **3** using 50% thermal ellipsoids. Only one of two molecules from the asymmetric unit is displayed. Hydrogen atoms and isopropyl groups have been omitted for clarity. Selected bond distances (Å) and angles (°): N(1)-N(2), 1.144(4); N(3)-N(4), 1.134(4); Fe(1)-N(1), 1.809(3); Fe(1)-N(3), 1.836(3); Fe(1)-N(11), 2.004(3); Fe(1)-N(21), 2.011(3); N(2)-K(1), 2.902(3); Fe(1)-N(1)-N(2), 178.7(3); Fe(1)-N(3)-N(4), 176.5(3); N(1)-Fe(1)-N(3), 101.05(13); N(11)-Fe(1)-N(21), 95.04(11); N(1)-N(2)-K(1), 159.9(3).

Figure 4.

Top: IR spectrum of a solid sample of **3** synthesized under natural abundance N₂ showing two N₂ bands at 1964 and 1844 cm⁻¹. These bands shift to lower frequencies with ¹⁵N₂ (Figures S-26 & S-27). Bottom: Zero-field Mössbauer spectrum of **3** recorded at 80 K. The black circles represent the data, the red line is a one-component simulation of the data ($\delta = 0.53$ mm s⁻¹, $|E_Q| = 1.02$ mm s⁻¹, $\Gamma = 0.26$), and the gray line is the residual.

Figure 5.

Variable temperature UV-visible spectra of **1** with 2 equiv of 18-crown-6 in diethyl ether under 1 atm N₂ (top) and 1 atm Ar (bottom). Absorbances were corrected for density change of the solvent with temperature.

Figure 6. Mulliken spin populations for the nitrogen atoms (green) and Mulliken charges (red) in **1** ($S = 2$, top) and **3** ($S = 1$, bottom).

Figure 7.

ORTEP diagrams of the X-ray crystal structure of $L^{\text{Me}}\text{FeNNTMS}_2$ (**4**) using 50% thermal ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond distances (Å), angles (°), and torsion angles(°): N(14)-N(24), 1.348(3); Fe(1)-N(14), 1.671(2); Fe(1)-N(11), 1.950(2); Fe(1)-N(21), 1.946(2); N(18)-N(28), 1.349(3); Fe(2)-N(18), 1.638(2); Fe(2)-N(15), 1.915(2); Fe(2)-N(25), 1.932(2); Fe(1)-N(14)-N(24), 176.3(2); N(11)-Fe(1)-N(14), 126.77(9); N(21)-Fe(1)-N(14), 137.62(9); N(11)-Fe(1)-N(21), 95.53(8); Fe(2)-N(18)-N(28),

176.41(18); N(15)-Fe(2)-N(18), 128.86(9); N(25)-Fe(2)-N(18), 136.70(9); N(15)-Fe(1)-N(25), 94.42(8); N(21)-Fe(1)-N(24)-Si(24), 53.8(2); N(15)-Fe(2)-N(28)-Si(18), 45.3(2).

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Figure 8.

Fe-N distances (Å) for the two independent molecules of **4** within the asymmetric unit of the X-ray structure. Bonds and distances are color coded.

Figure 9.

Zero-field Mössbauer spectra of solid **4**: **(top)** collected at 173 K. with parameters: Comp 1: $\delta = 0.23 \text{ mm s}^{-1}$, $E_Q = 1.52 \text{ mm s}^{-1}$ and rel. Area = 0.50; Comp 2: $\delta = 0.46 \text{ mm s}^{-1}$, $E_Q = 1.21 \text{ mm s}^{-1}$, and rel. Area = 0.50. **(bottom)** collected at 80 K with parameters: Comp 1: $\delta = 0.22 \text{ mm s}^{-1}$, $E_Q = 1.99 \text{ mm s}^{-1}$ and rel. Area = 0.53; Comp 2: $\delta = 0.46 \text{ mm s}^{-1}$, $E_Q = 1.16 \text{ mm s}^{-1}$, and rel. Area = 0.47.

Figure 10.

X- and Q-band EPR spectra of **4** in frozen toluene solution at 10 K (A), and as powder sample in fomblin oil (B; several derivative spectra were taken with step-wise rotation, summed up and numerically integrated to minimize the effects of crystallite texture). The blue lines are simulations for the $S = 1/2$ species with g values given in the text. The asterisk marks a minor (0.6%) impurity.

Figure 11. Spacefilling diagrams from the X-ray structures of **1** (top) and **3** (bottom) where iron atoms are orange, potassiums are purple, nitrogens are blue, oxygens are red, carbons are gray, and hydrogens are white.

Figure 12. Ligand-field energy diagram showing the influence of p-donation on the metal-centered orbitals.

Scheme 1.

Reported b-Diketiminato Complexes With Bridging N₂

Scheme 2.

Reaction of Compound 1 with Crown Ethers under Argon to Give Compound 2

Scheme 3.

Reaction of 1 with Crown Ethers under Dinitrogen at Low Temperature Yields Monometallic 3

Scheme 4. Slow reactions of **1** and **2** with TMSI under N_2 vs Ar atmospheres.

Scheme 5. Slow reactions of 1 and 2 with TMSI under N₂ vs Ar atmospheres.

Scheme 6.

Addition of Benzene to **2** and **3** Leading to Formally Iron(0) Benzene Complex **6**

Scheme 7. Addition of H^+ to 3 and 4

Scheme 8. Silylation of **3** to Give Ammonia

Table 1.Comparison of structural and spectroscopic parameters of β -diketiminate iron N₂ complexes.^{19b}

Complex	1	2	[L ^{Me} FeNNFeL ^{Me}]
Formal Fe Ox. State	0, 0	0, 0	+ 1, +1
Fe-N ₂ (Å)	1.750(4), 1.755(5)	1.758(4)	1.745(3)
N-N (Å)	1.215(6)	1.190(8)	1.186(7)
Fe-N _L (Å)	1.938(4), 1.918(4)	1.920(3)	1.949(2)
NL-Fe-N _L (°)	95.0(2), 96.2(2)	102.3 (2)	97.6(1)
ν_{14N14N} [ν_{15N15N}] (cm ⁻¹)	1625[1569]	1683/1738 [1632]/[1680]	1810[1745]
δ (mm s ⁻¹)	0.47	0.45	0.62
$ E_q $ (mm s ⁻¹)	2.48	1.74	1.41

Table 2.

Effect of temperature on the silylation of 3 by TMSI under standard conditions (see text).

Temp. (K)	Yield of 4 (%) ^a	Yield of 5 (%) ^a	Total Yield of Fe (%) ^a
298	0	95	95
213	44	38	82
195	48	49	97
156	59	39	98

^a Spectroscopic yields of iron based on ¹H NMR using a Cp₂Co capillary in toluene-*d*₈ as an internal standard. Estimated uncertainty ± 5%.

Table 3.

Effect of TMSI concentration on the silylation of 3 by TMSI under standard conditions (see text).

Equiv. TMSI	Yield of 4 (%) ^a	Yield of 5 (%) ^a	Total Yield of Fe (%) ^a
0.5	21	13	34
1.0	43	41	84
1.5	53	43	96
2.0	59	39	98
2.5	54	48	102
3.0	58	46	104

^a Spectroscopic yields of iron based on ¹H NMR using a Cp₂Co capillary in toluene-*d*₈ as an internal standard. Estimated uncertainty ± 5%.

^b The starting reaction temperature was −116 °C, then the reactions were allowed to warm to ambient temp.

Table 4.

Comparison of bond lengths between experimental X-ray structure and DFT fully optimized geometries using BP86 and B3LYP functionals.

Functional	Site or Spin State	Fe-N ₂ (Å) ^a	Fe-N _{ligand} (Å) ^b	N-N (Å) ^c	Rel. Energy (kcal mol ⁻¹) ^d	Calc. δ (mm s ⁻¹) ^e	Calc. E_Q (mm s ⁻¹) ^e
Exp.	Fe1 ^f	1.671(2)	1.950(2) 1.946(2)	1.348(3)		0.46 ^h	1.16 ^h
	Fe2 ^f	1.638(2)	1.915(2) 1.932(2)	1.349(3)		0.22 ^h	1.99 ^h
BP86	S = 1/2 ^g	1.628	1.882, 1.888	1.329	0.0	0.14	1.93
	S = 3/2 ^g	1.690	1.906, 1.932	1.325	8.5	0.51	1.72
	S = 5/2 ^g	1.774	1.960, 1.965	1.355	30.6	0.61	3.69
B3LYP	S = 1/2 ^g	1.660	1.924, 1.925	1.328	0.6		
	S = 3/2 ^g	1.725	1.968, 1.975	1.323	0.0		
	S = 5/2 ^g	1.850	1.993, 2.010	1.349	14.5		

^a Experimental and calculated Fe-N₂ distances for compound **4**.

^b Experimental and calculated Fe-N_{ligand} distances for compound **4**.

^c Experimental and calculated N-N distances for compound **4**.

^d Relative energies of computed spin states.

^e Experimental quadrupole splitting for solid state sample of **3**, and calculated quadrupole splittings using the method and correlation established in ref 24.

^f Distances from two unique molecules within the asymmetric unit of the crystal structure of **4**.

^g Computed geometries for the three possible spin-states of **4**.

^h Experimental zero-field Mössbauer parameters collected at 80 K and are assigned to the iron site based on the two site model proposed above.

Table 5.

Comparison of relative energies and predicted Mössbauer parameters for DFT H-atom only optimized geometries of **4** using BP86.

Iron Site ^a	Spin State ^b	Rel. Energy (kcal mol ⁻¹) ^c	Calc. δ (mm s ⁻¹) ^d	Calc. $ E_Q $ (mm s ⁻¹) ^e
Fe1	1/2	0.0	0.33	1.45
	3/2	3.3	0.55	1.38
	5/2	37.8	0.48	-5.08
Fe2	1/2	0	0.22	1.71
	3/2	8.2	0.47	1.32
	5/2	44.4	0.40	-5.37

^a Iron atom label in the X-ray structure of **4** representing the two molecules present in the asymmetric unit.

^b Possible spin states calculated for **4**.

^c Relative energies of the possible spin states for each of the two molecules within the asymmetric unit of the X-ray structure of **4**.

^d Calculated isomer shifts for the various spin states for each iron within the asymmetric unit of **4**.

^e Calculated quadrupole splittings for the various spin states for each iron within the asymmetric unit of **4**.