

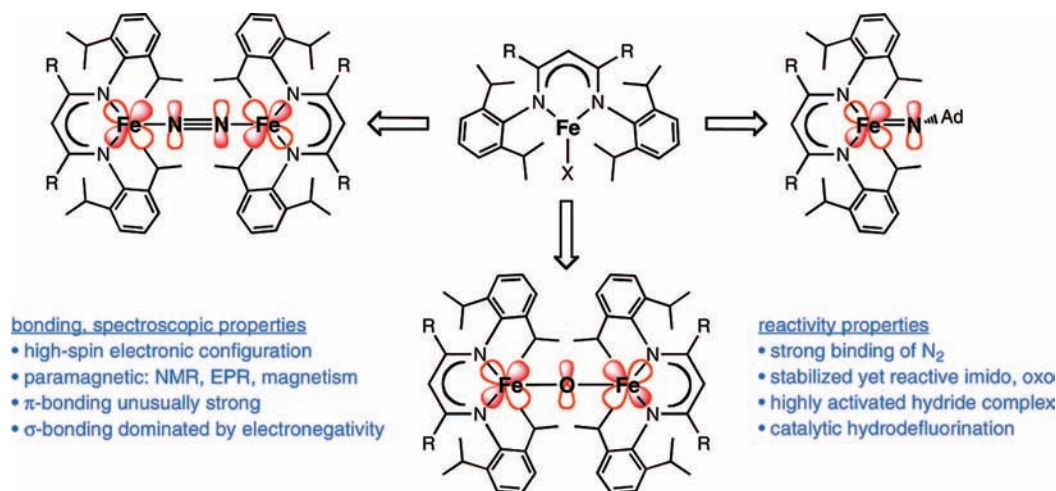
## Electronic Structure and Reactivity of Three-Coordinate Iron Complexes

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### CON SPECTUS



The identity and oxidation state of the metal in a coordination compound are typically thought to be the most important determinants of its reactivity. However, the coordination number (the number of bonds to the metal) can be equally influential. This Account describes iron complexes with a coordination number of only three, which differ greatly from iron complexes with octahedral (six-coordinate) geometries with respect to their magnetism, electronic structure, preference for ligands, and reactivity. Three-coordinate complexes with a trigonal-planar geometry are accessible using bulky, anionic, bidentate ligands ( $\beta$ -diketiminates) that steer a monodentate ligand into the plane of their two nitrogen donors. This strategy has led to a variety of three-coordinate iron complexes in which iron is in the +1, +2, and +3 oxidation states.

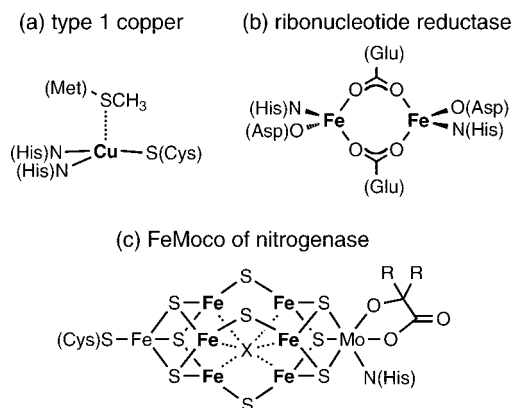
Systematic studies on the electronic structures of these complexes have been useful in interpreting their properties. The iron ions are generally high spin, with singly occupied orbitals available for  $\pi$  interactions with ligands. Trends in  $\sigma$ -bonding show that iron(II) complexes favor electronegative ligands (O, N donors) over electropositive ligands (hydride). The combination of electrostatic  $\sigma$ -bonding and the availability of  $\pi$ -interactions stabilizes iron(II) fluoride and oxo complexes. The same factors destabilize iron(II) hydride complexes, which are reactive enough to add the hydrogen atom to unsaturated organic molecules and to take part in radical reactions. Iron(I) complexes use strong  $\pi$ -backbonding to transfer charge from iron into coordinated alkynes and  $N_2$ , whereas iron(III) accepts charge from a  $\pi$ -donating imido ligand. Though the imidoiron(III) complex is stabilized by  $\pi$ -bonding in the trigonal-planar geometry, addition of pyridine as a fourth donor weakens the  $\pi$ -bonding, which enables abstraction of H atoms from hydrocarbons. The unusual bonding and reactivity patterns of three-coordinate iron compounds may lead to new catalysts for oxidation and reduction reactions and may be used by nature in transient intermediates of nitrogenase enzymes.

### Introduction

In a number of reactive metalloproteins, metal ions are in environments that are unusual in smaller coordination compounds. Chart 1 shows

protein-bound metal atoms that have unusually low coordination numbers (the “coordination number” indicates the number of atoms directly bound to the metal atom, and “low-coordinate” here

## CHART 1

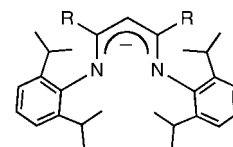
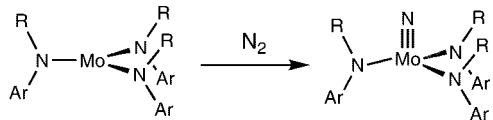


means a coordination number of 4 or less). Synthetic chemists use observations like this to launch “biomimetic” or “bio-inspired” coordination chemistry, where they build new molecules to discover (a) how to capture the enzyme’s reactivity characteristics in a synthetic molecule, (b) new strategies for making catalysts, and (c) detailed mechanisms that provide biochemists with precedents for enzymatic mechanisms. In the case of low-coordinate metals in metalloproteins, the metal is found in a pocket consisting primarily of noncoordinating amino acid residues and only a few potential donors.

The creation of an isolated pocket finds parallels in the early synthetic chemistry of low-coordinate transition metal complexes. Pioneers such as Bradley used bulky amide groups to generate some of the first isolable examples of three-coordinate transition metal complexes.<sup>1</sup> Later innovators include Power and Wolczanski, who in the 1980s used other ligands of prodigious size to access three-coordinate transition-metal complexes.<sup>2</sup> Interestingly, the synthetic strategy is reminiscent of the low-coordinate enzymes: the donors are attached to bulky, noncoordinating organic fragments that envelop the metal. In both synthetic complexes and metalloproteins, the ligand is viewed as a “scaffold” or “rack” that forces the metal to assume a high-energy, reactive geometry.

The high energy of low-coordinate complexes was exploited by Wolczanski and Cummins, who demonstrated the ability to break strong C≡O, C–H, and N≡N bonds (Scheme 1).<sup>3–5</sup> These reactions are each driven by the formation of strong metal–ligand bonds between the transition metal and

**SCHEME 1.** An Extreme Bond-Breaking Reaction of Three-Coordinate Molybdenum<sup>5</sup>



**FIGURE 1.** Bulky  $\beta$ -diketiminato ligands, which stabilize three-coordinate complexes of iron.  $L^{\text{Me}}$  has  $R = \text{Me}$ , and  $L^{\text{tBu}}$  has  $R = \text{tBu}$ .

a fragment of the substrate. In each case, the bond cleavage reaction was not catalytic, because the metal–ligand bonds formed are so strong that the low-coordinate starting material cannot be reformed *in situ* to complete the cycle. Thus, in addition to demonstrating amazing stoichiometric reactions, these researchers identified a pitfall in the design of reactive complexes: if the reactions lead to very stable bonds, it impedes catalytic turnover.

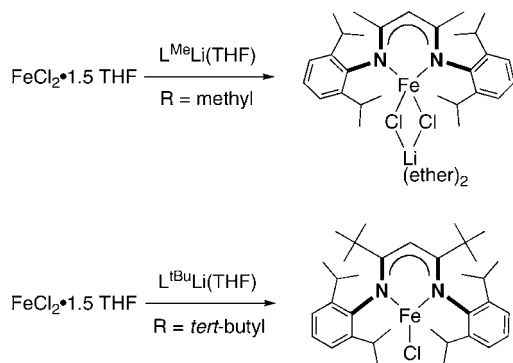
It might be possible to overcome these problems by targeting low-coordinate complexes that form weaker metal–ligand bonds, particularly with the biologically relevant 3d transition metals Mn, Fe, Co, Ni, and Cu. A number of chemists have contributed to this vibrant area of research, but this Account limits its detailed descriptions to the investigations of my research group. These studies have begun to elucidate the range of oxidation states, ligands, and reactions that are possible in three-coordinate iron complexes, the spectroscopic signatures and magnetic properties of these complexes, and the strength of  $\sigma$  and  $\pi$  bonding interactions between the metal and the three donors.

## Synthesis of Three-Coordinate Iron Complexes Using Bulky $\beta$ -Diketiminato Ligands

In order to explore the chemistry of three-coordinate iron, it was necessary to find a ligand with the following properties: (1) easy to synthesize and modify; (2) coordinates strongly to iron, preferably as a bidentate ligand; (3) includes extremely bulky, rigid groups that discourage the coordination of more than three lone pairs. A ligand that fits these criteria was the bulky  $\beta$ -diketiminato (Figure 1).  $\beta$ -Diketiminatos have played a role in inorganic chemistry back to the 1960s, but only in the late 1990s did chemists incorporate 2,6-diisopropylphenyl groups that surround the metal site, leaving a small pocket for additional ligands.<sup>6</sup> A growing number of studies have demonstrated that  $\beta$ -diketiminato complexes of small late metals and main-group metals can be isolated with a coordination number of only two or three.<sup>6</sup>

At the outset of our research, complexes of bulky  $\beta$ -diketiminatos had not been synthesized with iron, cobalt, or nickel. Treating tetrahydrofuran (THF) adducts of the metal

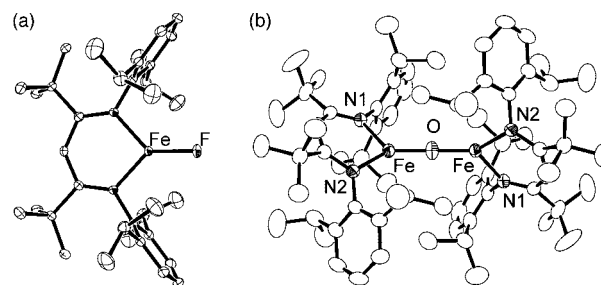
**SCHEME 2.** The Coordination Number in Iron(II) Chloride Complexes Depends on the Size of R, as Evidenced by Changes in the C–N–C Angle (Highlighted with Bold Bonds)



dihalides  $\text{FeCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{NiCl}_2$  with lithium  $\beta$ -diketiminates gave 1:1 complexes of the type  $\text{L}^{\text{R}}\text{MCl}$ .<sup>7,8</sup> The 2,6-diisopropylphenyl groups are essential for isolating 1:1 complexes; reactions with smaller 2,6-dimethylphenyl substituents on the diketiminate can generate  $\text{L}_2\text{M}$  complexes. The four symmetry-related isopropyl groups extend above and below the  $\text{N}_2\text{M}$  plane, protecting the faces of the diketiminate–metal unit. The result is a metal center with two donors and only a small pocket available for additional ligands. This pocket has enough space that reactions can take place at the metal; in this way, the  $\beta$ -diketiminate gives an excellent balance between adequate and overbearing steric protection.

In this Account,  $\text{L}^{\text{Me}}$  and  $\text{L}^{\text{tBu}}$  represent the  $\beta$ -diketiminate with methyl and with *tert*-butyl groups on the ligand backbone (Scheme 2), and  $\text{L}^{\text{R}}$  is used to generically indicate  $\text{L}^{\text{Me}}$  or  $\text{L}^{\text{tBu}}$ . The X-ray crystal structures of the products from reaction of iron(II) chloride with  $\beta$ -diketiminates showed that the size of the R group on the  $\beta$ -diketiminate backbone influences the size of the ligand-binding pocket. As shown in Scheme 2, treating the THF adduct of  $\text{FeCl}_2$  with a lithium  $\beta$ -diketiminate in THF yielded a tetrahedral complex  $\text{L}^{\text{Me}}\text{Fe}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  when the  $\beta$ -diketiminate ligand with R = methyl was used but gave a trigonal-planar complex  $\text{L}^{\text{tBu}}\text{FeCl}$  when the ligand with R = *tert*-butyl was used (Scheme 2).<sup>7</sup> The C–N–C angle of the  $\beta$ -diketiminate ligand (indicated with bold bonds in Scheme 2) in complexes of  $\text{L}^{\text{tBu}}$  is consistently about  $8^\circ$  larger than that in analogous complexes of  $\text{L}^{\text{Me}}$ .<sup>9</sup> This is attributed to a steric clash between the *tert*-butyl group and the 2,6-diisopropylphenyl group that pushes the aryl toward the binding pocket, limiting accessibility of additional ligands.

Numerous iron(II) complexes can be synthesized from the chloride complexes described in the previous paragraph. The ( $\beta$ -diketiminate)iron platform enables the isolation of  $\text{L}^{\text{R}}\text{FeX}$ , where X represents carbon ligands like alkyl, aryl, acetylide, and vinyl; nitrogen ligands like amido, amidinate, and imi-



**FIGURE 2.** The trigonal planar geometry allows the isolation of iron(II) complexes containing “hard” ligands: (a) thermal-ellipsoid plot of  $\text{L}^{\text{tBu}}\text{FeF}$ ; (b) thermal-ellipsoid plot of  $\text{L}^{\text{tBu}}\text{FeOFEL}^{\text{tBu}}$ .

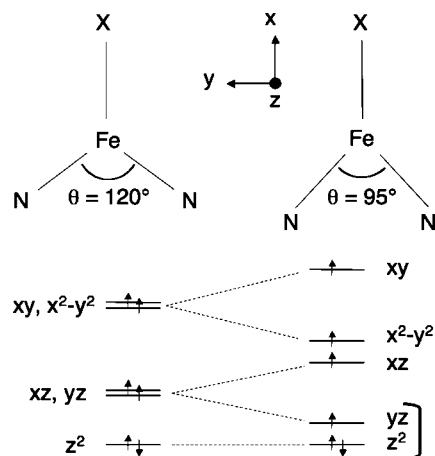
doyl; oxygen ligands like alkoxide, aryloxy, carboxylate, and oxo; all halides; hydride; and sulfur ligands like thiolate and sulfide.<sup>8–16</sup> Many of these iron(II) complexes come from double metathesis reactions of  $\text{L}^{\text{R}}\text{Fe}(\text{halide})$  and  $\text{LiX}$ . The  $\beta$ -diketiminate ligand imparts solubility in alkane solvents, and the halide byproduct of such reactions can be removed by filtration. Another benefit of the  $\beta$ -diketiminate group is that it packs well into crystal lattices, and most complexes can be identified and evaluated using X-ray crystallography.

Some of these iron(II) complexes have structural types that were unknown prior to our studies. For example,  $\beta$ -diketiminate ligands stabilize the first crystallographically characterized iron(II) fluoride<sup>14</sup> and iron(II) oxo<sup>13</sup> complexes (Figure 2). The stability of oxo, alkoxo, and fluoride complexes contradicts the conventional wisdom that “soft” late transition metals do not bind well to “hard” ligands with electronegative atoms, and the reasons for this observation will be explored in more depth below.

## Electronic Structure and Spectroscopy of Three-Coordinate Iron Complexes

The isolation of a large number of  $\beta$ -diketiminatoiron complexes has led to some useful generalizations about their electronic and spectroscopic properties. First, the three- and four-coordinate complexes almost always have a high-spin electronic configuration:  $S = 3/2$  for iron(I),  $S = 2$  for iron(II), and  $S = 5/2$  for iron(III). The only isolated low-spin  $\beta$ -diketiminatoiron complexes have higher coordination number and strong-field ligands like CO. For example, the carbonyl complex  $\text{L}^{\text{Me}}\text{Fe}(\text{CO})_3$  has low-spin iron(I) ( $S = 1/2$ ) as shown by electron paramagnetic resonance (EPR) and magnetic susceptibility,<sup>17</sup> and the acyl complex  $\text{L}^{\text{tBu}}\text{Fe}(\text{CO})_2(\text{COCH}_3)$  has diamagnetic, low-spin iron(II).<sup>10</sup>

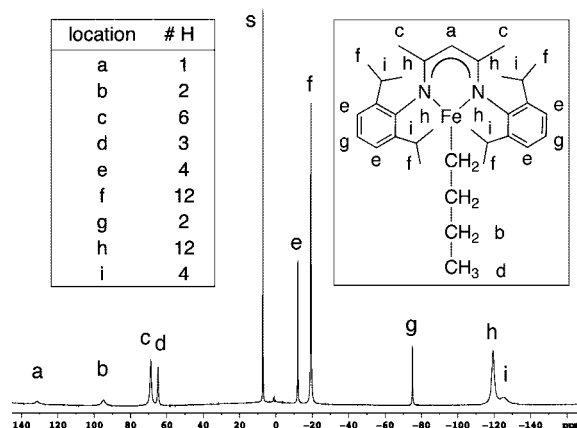
The  $S = 2$  ground state in the high-spin diketiminatoiron(II) complexes with a trigonal-planar geometry was evaluated in detail by Mössbauer and EPR spectroscopies and theoretical calculations, in collaboration with Profs. Eckard



**FIGURE 3.** Changes in d orbital energies that result from the  $95^\circ$  bite angle of the  $\beta$ -diketiminato ligand. The  $yz$  and  $z^2$  orbitals are very close in energy, giving unusual magnetic properties. The  $xy$  orbital, which points directly at the N atoms of the  $\beta$ -diketiminato ligand, becomes highest in energy. In this picture, the  $z$  axis is chosen to be out of the plane, rather than the standard  $y$  axis choice in the  $C_{2v}$  point group.

Münck and Emile Bominaar.<sup>18</sup> In order to understand the results of their studies, it is necessary to first consider the effect of distorting a perfect trigonal-planar geometry ( $D_{3h}$  symmetry) by constraining two of the donors as a bidentate  $\beta$ -diketiminato ligand to a bite angle ( $\theta$ ) of roughly  $95^\circ$ . A Walsh diagram is shown in Figure 3. The symmetry is lowered to  $C_{2v}$ , and therefore all degeneracies are removed. Interestingly, at  $\theta \approx 95^\circ$ , the  $z^2$  and  $yz$  orbitals (indicated with a bracket) have roughly the same energy. This d-orbital splitting was confirmed by computations using multiconfiguration self-consistent field (MCSCF) and restricted open-shell density functional theory (RODFT) methods.<sup>8,18</sup> In an iron(II) complex with a high-spin  $d^6$  configuration, this crystal-field splitting diagram predicts two nearly isoenergetic  $S = 2$  states that differ only by the placement of the sixth electron in one of these two orbitals.

However, the previous analysis uses one-electron orbitals and ignores spin-orbit coupling, which can mix orbitals of different symmetries if they lie close in energy. In three-coordinate diketiminatoiron(II) complexes, mixing of the  $z^2$  and  $yz$  orbitals is extensive. One effect of spin-orbit coupling between two orbitals is to increase the orbital angular momentum along the axis that rotates the orbitals into one another (the  $x$  axis in this case). The large, oriented orbital angular momentum has several profound influences on the properties of three-coordinate iron(II)  $\beta$ -diketiminato complexes. First, there is a directional paramagnetic response to the application of an external field. This "internal field" ( $\mathbf{B}_{int}$ ) in several  $L^{tBu}FeX$  complexes was

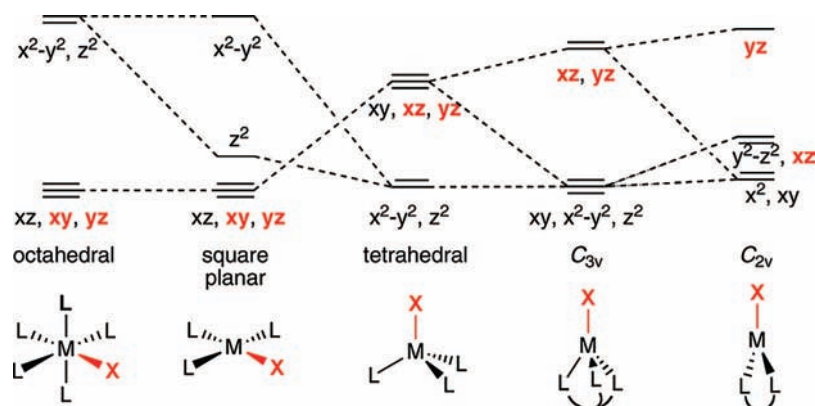


**FIGURE 4.**  $^1H$  NMR spectrum of  $L^{Me}Fe(n\text{-butyl})$  at room temperature, showing peak assignments and integrations.

measured as 62–82 T using variable-field Mössbauer spectroscopy, values that were at the time the largest ever measured for a mononuclear complex. (Larger values have since been measured for  $Fe(C(SiMe_3)_3)_2$ , a linear iron(II) complex with strict degeneracy of low-lying orbitals.)<sup>19</sup> Second, there is huge zero-field splitting that makes the  $m_s = \pm 2$  levels by far the lowest in energy ( $D$  values of ca.  $-50\text{ cm}^{-1}$ ). Third, the magnetic susceptibility, as evident from magnetic and NMR measurements, is large and axial. Solution magnetic moments for  $L^{tBu}FeX$  are typically near or above  $5.5\ \mu_B$ , substantially raised from the spin-only value of  $4.9\ \mu_B$ .<sup>18</sup>

The anisotropic magnetic susceptibility also affects the Larmor frequencies of nearby nuclei by means of the through-space "dipolar" or "pseudocontact" shift. Figure 4 shows the  $^1H$  NMR spectrum of  $L^{Me}Fe(n\text{-butyl})$  as an example.<sup>9</sup> Protons along the  $x$  axis (the Fe–C bond vector) are shifted downfield (the addition of the internal field to the applied field causes them to resonate at an unusually low applied field), and those along the  $yz$  plane (perpendicular to the Fe–C bond vector) are shifted upfield. (An analogy to this phenomenon is the diamagnetic "ring current" in aromatic organic compounds, which gives downfield shifts of protons in the plane of the electron circulation and upfield shifts of protons normal to the plane of the electron circulation. The paramagnetic current in the iron compounds shifts protons in the  $yz$  plane upfield and those normal to the  $yz$  plane downfield.) The dominance of the pseudocontact shift is anomalous for paramagnetic complexes, for which the chemical shifts typically are dominated by the through-bond "contact" shift.

Despite the paramagnetism of the complexes, proton NMR spectroscopy is an extremely useful technique for characterizing high-spin iron(I) and iron(II)  $\beta$ -diketiminato species. (The tetrahedral iron(III) complexes of  $\beta$ -diketiminato ligands, on the

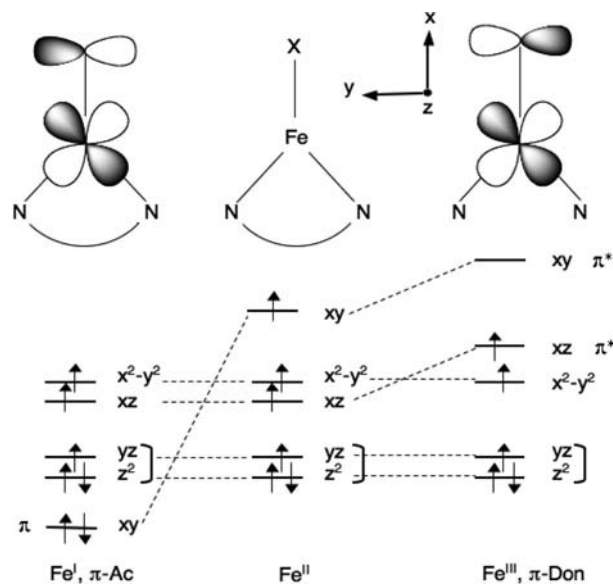


**FIGURE 5.** Ligand-field splitting in some common geometries, compared with the  $C_{3v}$  symmetry of pseudotetrahedral complexes of tripodal ligands<sup>25</sup> and the  $C_{2v}$  symmetry of trigonal-planar  $\beta$ -diketiminato complexes. In each complex, the z axis is vertical on the page; note that the change in orientation causes the orbital labels for  $\beta$ -diketiminato complexes to be different than those in Figures 3 and 6. The bold red labels highlight the two d orbitals that have the correct symmetry for  $\pi$ -interactions with the ligand labeled X.

other hand, generally have broad, uninterpretable, or absent NMR spectra.)<sup>11</sup> The peaks for protons more than three bonds away from iron(II) are easily discernible (Figure 4), probably because electronic relaxation is fast from the presence of low-lying excited states. Because the resonances are spread over a wide chemical shift range, overlap is not a serious problem. In addition, the chemically distinct protons on  $\beta$ -diketiminato ligands fall into groups with different numbers of symmetry-related protons, and therefore integration can be used to assign peaks. (Because of peak broadness and baseline deviations over the wide chemical shift range, it is important to use wide integration regions and carefully adjust the phasing on each integral.) Mononuclear iron(II) complexes generally have a wider range of chemical shifts (+150 to -200 ppm), while dinuclear iron(II) complexes are generally in a smaller range (+60 to -80 ppm) from antiferromagnetic coupling between the metals.

### $\pi$ -Interactions are Strong in Three-Coordinate Iron Complexes

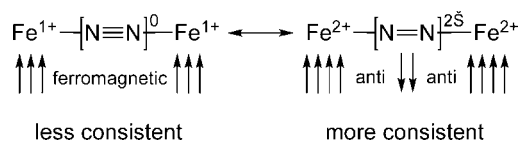
In addition to the near-degeneracy of the lowest orbitals, the ligand-field splitting diagram for three-coordinate diketiminatoiron complexes has other interesting aspects. The right side of Figure 5 shows the energies of d orbitals in the  $C_{2v}$  symmetry of the diketiminatoiron complexes.<sup>8</sup> The relative ordering of these orbitals contrasts with the relative ordering in more common coordination geometries. Figure 5 especially highlights the orbitals that have the correct symmetry to engage in  $\sigma$  or  $\pi$  bonding with the ligand labeled X. Thus, in contrast to octahedral and square-planar complexes, three-coordinate complexes have high-lying orbitals that can overlap with p orbitals on the coordinated atom. In a high-spin iron species with a  $d^5$ ,  $d^6$ , or  $d^7$  configuration, these  $\pi$ -bonding



**FIGURE 6.** Effect of  $\pi$ -acceptor and  $\pi$ -donor ligands on the energies of the ligand-field orbitals of three-coordinate iron compounds, as shown by computational studies.<sup>8,18,21,30</sup> Interestingly, iron(I), iron(II), and iron(III) complexes can each have three electrons in the nearly degenerate  $yz/z^2$  orbitals. As in Figure 3, a nonstandard choice of axes is used.

orbitals are singly occupied, so overlap with them could be favorable for filled ligand orbitals (leading to formal metal–ligand multiple bonding) or for empty ligand orbitals (leading to back-bonding interactions). Both of these kinds of  $\pi$ -interactions are evident in the three-coordinate iron compounds, as shown below.

In reduced compounds with a formal oxidation state of iron(I), the primary  $\pi$ -interaction is back-bonding from iron into unsaturated ligands. In one example, iron(I) complexes of  $\eta^2$ -alkyne ligands exhibit several characteristics attributable to  $\pi$ -back-bonding.<sup>20</sup> (1) The C–C bonds are lengthened by about 0.1 Å. (2) DFT computations show that the alkyne  $\pi^*$



**FIGURE 7.** Resonance structures for  $L^R\text{FeNNFe}L^R$ . The coupling model on the right is more consistent with Mössbauer data and computations.

orbital interacts strongly with the  $d_{xy}$  orbital, making it drop precipitously in energy (Figure 6).<sup>21</sup> (3) The C–C stretching frequency in arylacetylene complexes is lowered by binding, and this effect is greater with electron-withdrawing groups on the aryl ring. (4) Alkynes with electron-withdrawing substituents bind in preference to those with electron-donating substituents. (5) Computations indicate a transfer of 0.8 electrons from iron to the alkyne.<sup>21</sup>

Extensive  $\pi$ -back-bonding is also evident in the dinitrogen complexes  $L^R\text{FeNNFe}L^R$ .<sup>17,22</sup> Although formal electron counting describes the complex as  $L^R\text{Fe}^{1+}(\text{N}_2)\text{Fe}^{1+}L^R$ , several pieces of data are more consistent with the formulation  $L^R\text{Fe}^{2+}(\text{N}_2)^{2-}\text{Fe}^{2+}L^R$ .<sup>23</sup> (1) The N–N bond is lengthened from 1.10 Å (free  $\text{N}_2$ ) to 1.18–1.19 Å, and the N–N stretching frequency is lowered from 2331  $\text{cm}^{-1}$  (free  $\text{N}_2$ ) to 1772  $\text{cm}^{-1}$ , more consistent with an N–N double bond as in  $\text{N}_2^{2-}$ . (2) The unpaired spins on the two iron ions are *parallel* with one another in the  $S = 3$  ground state, giving a large magnetic moment and internal magnetic field (Mössbauer). If  $L^R\text{FeNNFe}L^R$  were to have two high-spin ( $d^7$ ) iron(I) ions and neutral  $\text{N}_2$  (Figure 7, left), it would imply strong ferromagnetic coupling that would be extremely unusual in a linear bridge. A more reasonable alternative is triplet  $\text{N}_2^{2-}$  (isoelectronic with  $\text{O}_2$ ) antiferromagnetically coupled to two equivalent high-spin iron(II) ions (Figure 7, right). Not only does this charge redistribution explain the magnetic coupling, it is confirmed by two independent computational studies that suggest occupancy of molecular orbitals with contributions from the  $\pi^*$  orbital of  $\text{N}_2$ .<sup>17,23</sup> It is worth noting that five- and six-coordinate iron–dinitrogen complexes show much less weakening of the N–N bond.<sup>24</sup> In tetrahedral iron(I)– $\text{N}_2$  complexes synthesized by Peters and co-workers, the amount of electron delocalization from Fe to  $\text{N}_2$  is somewhat less, giving a shorter N–N bond and different magnetic coupling.<sup>25</sup>

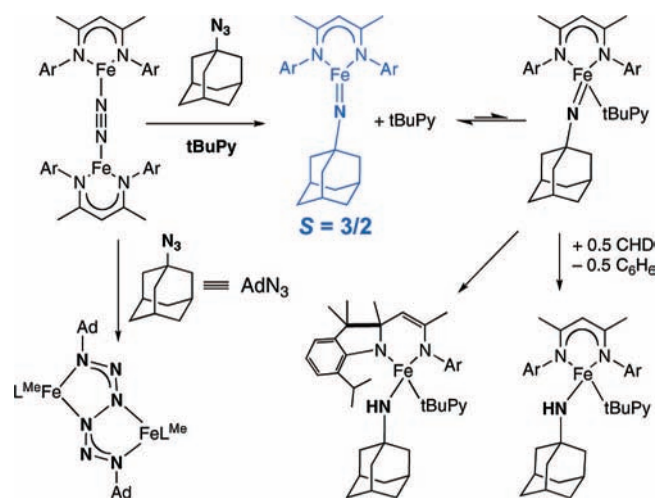
In more oxidized iron(II) and iron(III) compounds, the primary  $\pi$ -interaction is donation of lone pairs into singly occupied d orbitals on the metal. One of our original goals in pursuing the chemistry of low-coordinate metals was to take advantage of this  $\pi$ -interaction for stabilizing previously unobserved terminal oxo and imido complexes of these metals. Others simultaneously saw this opportunity, and the research

groups of Hillhouse and Warren reported stable trigonal-planar nickel(II), nickel(III), and cobalt(III) imido complexes.<sup>26,27</sup> Based on the same principle, Peters and co-workers synthesized tetrahedral iron(II), iron(III), and iron(IV) imido complexes, and even a metastable iron(IV) nitrido species.<sup>25b,28</sup>

Our own studies initially and unsuccessfully aimed at a terminal oxoiron(III) species  $L^R\text{Fe}=\text{O}$ , starting from  $L^R\text{FeNNFe}L^R$  (which is synthetically equivalent to the iron(I) fragment  $L^R\text{Fe}$  by loss of  $\text{N}_2$ ). All attempts to generate  $L^R\text{Fe}=\text{O}$  from the addition of “O” sources to iron(I) species led to oxodiiron(II) compounds, which are conceptually derived by reaction of “O” with *two* iron(I) ions. Clearly the steric hindrance is not sufficient to avoid the binding of two iron atoms to the oxo group. The oxodiiron(II) species with  $L^{\text{tBu}}$  has been fully characterized, and this characterization again benefitted from the contributions of Münck and co-workers, who showed that there are two high-spin iron(II) ions coupled antiferromagnetically.<sup>13</sup> The Fe–O–Fe angle is 167.6(1)°, and the nearly linear core geometry is suggestive of  $\pi$ -bonding between the oxygen atom and each metal.  $L^{\text{tBu}}\text{FeOFe}L^{\text{tBu}}$  is the only literature example of a crystallographically characterized oxo complex of iron(II), and its isolability is most likely from a combination of stabilizing  $\pi$ -interactions and steric protection.

Frustrated by the tendency of oxo to bridge between iron atoms, we sought to create an imidoiron(III) complex  $L^{\text{Me}}\text{Fe}=\text{NR}$  through the use of adamantyl azide, a convenient source of the “AdN” fragment with loss of  $\text{N}_2$ . Again we were stymied by a bimolecular reaction: addition of  $\text{AdN}_3$  to  $L^{\text{Me}}\text{FeNNFe}L^{\text{Me}}$  or addition of  $\text{AdN}_3$  to  $L^{\text{tBu}}\text{FeNNFe}L^{\text{tBu}}$  at high concentration or low temperature gives reductive coupling of the azide fragments to yield diiron(II) species with an unprecedented  $\text{AdNNNNNNAd}$  (“hexazene”) bridge (Scheme 3).<sup>29</sup> However, this bimolecular reaction can be avoided in the  $L^{\text{Me}}$  case by adding pyridine before treatment with  $\text{AdN}_3$ . The product is a mixture of  $L^{\text{Me}}\text{Fe}=\text{NAd}$  and  $L^{\text{Me}}\text{Fe}(\text{=NAd})(\text{py})$ , which are in rapid equilibrium on the NMR time scale.<sup>30</sup> EPR and Mössbauer spectra show an  $S = 3/2$  species with large negative zero-field splitting. This has been assigned as  $L^{\text{Me}}\text{Fe}=\text{NAd}$  based on the results of computations by Prof. Thomas Cundari, which predict a quartet ground state for the three-coordinate imido species. The ligand-field orbitals for  $L^{\text{Me}}\text{Fe}=\text{NAd}$  are shown at the right of Figure 6. The  $\pi$ -interaction with the nitrogen p orbital has driven the  $xy$  orbital so high in energy that it is not occupied. In effect, there is a full  $\pi$ -bond in the plane of the  $\beta$ -diketiminate (no antibonding electrons), and a half  $\pi$ -bond perpendicular to the plane (one antibonding electron). This is less  $\pi$ -bonding than in tetrahedral iron(III) imido complexes of tris(phosphino)borate ligands

**SCHEME 3.** Products from Reaction of an Iron(II) Complex with 1-Azidoadamantane<sup>a</sup>



<sup>a</sup> *tert*-Butyl pyridine catalyzes N<sub>2</sub> loss to give an imidoiron(III) complex that abstracts hydrogen atoms from the ligand or added substrates.

(which have no electrons in  $\pi$ -antibonding orbitals)<sup>28</sup> but more than in octahedral iron(IV) oxo species (which have two half-filled  $\pi$ -antibonding orbitals).<sup>31</sup>

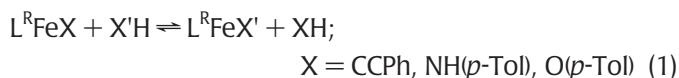
Consistent with relatively weak  $\pi$ -bonding, the Fe–N double bond in L<sup>Me</sup>Fe=NAd is very reactive. Scheme 3 highlights hydrogen atom abstraction reactions of the imido species. For example, solutions generated as described above react rapidly with 1,4-cyclohexadiene (CHD) at low temperature, giving the iron(II) product L<sup>Me</sup>Fe–NHAd and benzene.<sup>30</sup> The rate of this reaction has a first-order dependence on Fe, py, and CHD concentrations, implying that the predominant iron species is pyridine-free but gains a pyridine ligand before or during the rate-limiting transition state. The rate law therefore implies that the *four-coordinate* pyridine adduct of the imidoiron(III) compound reacts much more quickly than the *three-coordinate* imido species! While this result conflicts with the commonly held assumption that more coordinatively unsaturated compounds should be more reactive, it can be rationalized by the computational results. These show that the four-coordinate imido complex has a low-lying  $S = 5/2$  state, has much more radical character on the imido nitrogen, has less Fe–N  $\pi$ -bonding, and has much more bending at the nitrogen atom.<sup>30</sup> Each of these effects may contribute to the increased reactivity of the pyridine adduct of L<sup>Me</sup>Fe=NAd.

The take-home messages with regard to  $\pi$ -bonding in three-coordinate species are illustrated in Figure 6. First, the C<sub>2v</sub> ligand field of the diketiminatoiron complexes leaves some d orbitals available for  $\pi$ -interactions, whether the formal source of the electrons is the metal (in iron(I) alkyne

and N<sub>2</sub> complexes) or ligand (in iron(III) imido complexes). These stabilizing  $\pi$ -interactions between the metal and ligand can be used to activate (weaken the bonds in) substrates like alkynes and N<sub>2</sub> through back-bonding (occupation of a M–L  $\pi$ -bonding orbital) or to stabilize inherently reactive fragments like the imido (NR) or oxo (O) group (emptying of a M–L  $\pi$ -antibonding orbital). In the former case, the ligand becomes more electron-rich, with the results of calculations showing roughly one electron per iron atom transferred into the ligand.<sup>21</sup> In the latter case, the imido and oxo ligands (which are usually highly nucleophilic on late transition metals) become electrophilic enough to activate C–H bonds (in the imido complex) or at least non-nucleophilic enough to be stable (in the oxo complex). Similar trends may emerge for electrophilic cobalt(III) and nickel(III) imido complexes of  $\beta$ -diketiminates synthesized by Warren and co-workers.<sup>27</sup>

### Three-Coordinate Iron Prefers Electronegative Ligands

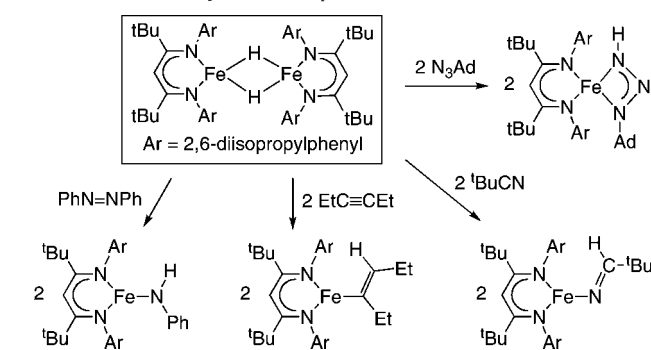
When exploring the chemistry of iron(II) complexes L<sup>R</sup>FeX with carbon, nitrogen, and oxygen donors as X, we noticed that in exchanges with X'H (eq 1), the equilibrium favored the side of the equation having the more electronegative atom bound to iron.<sup>11</sup> In other words, the preference for iron over a proton increased in the order C < N < O.



Interestingly, this trend cannot be explained by Fe–X  $\pi$ -bonding, because amido (NHR) donors are the strongest  $\pi$ -donors of the three ligands. To confirm the idea that  $\pi$ -effects were not dominant, we found a way to evaluate the preferences for alkyl ligands through the reversible intramolecular isomerization of substituted phenethyl complexes (eq 2).<sup>9</sup> In alkyl complexes,  $\pi$ -effects are minimized, so the preferences should be exclusively from the metal–ligand  $\sigma$ -interaction.



The equilibrium constant lies further to the right with more electron-withdrawing groups on the aryl ring. The preferences in both eqs 1 and 2 fit a model in which the metal prefers a ligand that can most easily stabilize negative charge at the metal-bound atom. Consistent with the stability of complexes with electronegative ligands, fluoride complexes are unusually stable in the three-coordinate iron(II) system.<sup>14</sup> The preference for electronegative ligands is not evident in series of platinum and ruthenium complexes<sup>32</sup> and is less pronounced

**SCHEME 4.** Insertion and Bond Cleavage Reactions of a Low-Coordinate Iron(II) Hydride Complex<sup>a</sup>

<sup>a</sup> The hydride dimer is in equilibrium with a three-coordinate monomer.<sup>35</sup>

in a series of nickel complexes.<sup>33</sup> However, these trends based on electronegativity are very important in early metal complexes.<sup>34</sup> Although there are not yet enough systematic data to definitively tease apart the differences between the effect of metal, coordination number, metal oxidation state, and ancillary ligands, one can tentatively suggest that the low coordination number makes iron "behave more like an early transition metal". This analogy extends to the stability of oxo and imido complexes and to the distinct weakening of coordinated  $N_2$ , phenomena that are common with transition metals in groups 5–7 but rare for iron. Although this oversimplified model ignores important details of the bonding, it is a rough guide for thinking about the effect of coordination number changes and serves as a hypothesis for further studies.

Conversely, the ligand with the lowest stability on low-coordinate iron is the electropositive ligand hydride. We first gained evidence for a hydridoiron(II) complex in studies of alkyl isomerization.<sup>9</sup> In these reactions, alkyliron(II) complexes undergo reversible  $\beta$ -hydride elimination to form transient (alkene)(hydride) isomers, which exchange alkene to give a new alkyl complex. The  $\beta$ -hydride elimination mechanism was supported by activation parameters and a H/D kinetic isotope effect. However, it is difficult to generate the free hydridoiron(II) species in this way because the transient hydride reacts instantly with alkenes to form a [1,2]-addition product.

Fortunately, hydride complexes  $[L^RFeH]_2$  can be isolated from the reaction of  $[L^{Me}FeCl]_2$  or  $L^{tBu}FeCl$  with  $KBET_3H$ .<sup>35</sup> These are the only examples of hydridoiron complexes with a coordination number less than five. The high-spin iron ions have a pseudotetrahedral geometry and are bridged by two hydrides. These species react with many unsaturated organic compounds to give [1,2]-addition products (Scheme 4).<sup>16</sup> An especially interesting example is the complete cleavage of  $N=N$  bonds in azobenzene by the hydride complex, which

uses a combination of two-electron steps ([1,2]-addition across a double bond) and one-electron steps (hydrogen atom abstraction and reductive N–N bond cleavage).<sup>36</sup>

The facility of insertions into the Fe–H bond can again be viewed through the lens of thermodynamic preferences: the entropic penalty of the insertion reaction is more than compensated by the enthalpic preference for a Fe–C, Fe–N, or Fe–O bond over the Fe–H bond. Additional evidence for a weak homolytic Fe–H bond energy comes from the reaction of  $[L^RFeH]_2$  with strong donor ligands like CO and  $CN^tBu$ , which gives iron(I) products and  $H_2$  through ligand-assisted reductive elimination of  $H_2$ .<sup>16</sup>

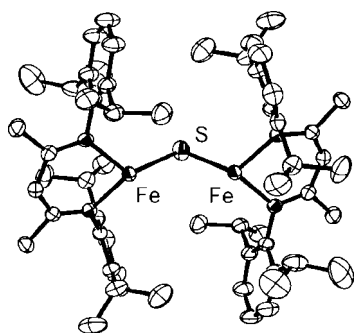
## Inspirations from Nitrogenase Intermediates

Azotrophic microorganisms cleave the N–N bond of  $N_2$  to form  $NH_3$ , and this amazing transformation is brought about by nitrogenase enzymes.<sup>37</sup> The FeMoco of iron–molybdenum nitrogenase (Chart 1c) has iron atoms with only three strong bonds and a weaker ionic interaction with X (a light atom in the center of the cluster). The results of directed evolution and computational studies both support the idea that iron is the site of  $N_2$  binding and activation,<sup>38</sup> and we and others have hypothesized that bonds to X are disrupted in or before the  $N_2$  binding step.<sup>39</sup> If bonds between Fe and X break, it would leave one or more coordinatively unsaturated, high-spin iron atoms, which might be capable of reducing N–N or other bonds.

These ideas about nitrogenase motivated us to focus on low-coordinate iron complexes containing  $N_xH_y$  fragments ( $x = 0–2$ ;  $y = 0–5$ ), which would occur in intermediates along an iron-based  $N_2$  reduction pathway. The exceptional N–N bond weakening in the low-coordinate iron– $N_2$  complexes and the high reactivity of the low-coordinate iron–hydride complexes support the idea that nitrogenase reductions at iron are reasonable.<sup>16,17</sup> Further, the discovery of radical intermediates in N–N bond cleavage reactions suggests that radical mechanisms should be considered in nitrogenase.<sup>36</sup>

Speculation about nitrogenase also encouraged us to synthesize the diiron(II) complex  $L^{Me}FeSFeL^{Me}$ , which has two three-coordinate iron(II) ions surrounding a space that lies in the fourth coordination position of both metals (Figure 8).<sup>12</sup> We hypothesized that cooperative reactivity by the two iron atoms might lead to interesting reductions. A survey of nitrogen-containing compounds showed that some (alkylhydrazines) bind without reduction, while others (phenylhydrazine) give partial reduction to ammonia. The ability of *pairs* of three-coordinate iron(II) ions to break N–N bonds suggests that one





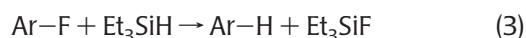
**FIGURE 8.** Thermal-ellipsoid plot of  $L^{\text{Me}}\text{FeSFeL}^{\text{Me}}$ , which features two low-coordinate iron(II) ions bridged by sulfide.

of the important features of the FeMoco may be the coordinative flexibility of the iron–sulfur cage, which enables iron atoms to work together to break strong bonds. Clearly more research is needed, and current work aims at the binding and functionalization of  $\text{N}_2$  at unsaturated iron complexes of one and two iron atoms.

## Perspectives on Catalysis and Future Prospects

The most widely used metal catalysts for organic chemistry contain ruthenium, rhodium, and palladium. However, these metals suffer from the disadvantages of high cost and toxicity. If comparably active catalysts could be designed using iron, these limitations could be avoided. Therefore, it is important to examine the catalytic capabilities of iron compounds.<sup>40</sup> Given the substantial modulation of iron's behavior upon lowering the coordination number, it seems possible that new roles for iron in catalysis will emerge, and the cheapness and lack of toxicity of iron may be a great advantage in creating "green" catalysts.

Our initial investigations along these lines have focused on systems in which we could take advantage of the thermodynamic preferences of three-coordinate iron, especially toward electronegative ligands. These efforts paid off when we discovered that three-coordinate iron compounds catalyze the transfer of F from fluoroaromatics to a silyl group (Equation 3).<sup>14</sup>



Most compounds that react with C–F bonds use early transition metals, but the M–F bonds formed are very stable (as a result, the reactions are stoichiometric but not catalytic). In contrast, the strong Fe–F interaction provides sufficient driving force to break the C–F bond, but a silane is able to remove the fluoride and regenerate the hydride complex. In the future, we envision low-coordinate iron enabling cleav-

age of other strong bonds (especially N–N bonds and C–X bonds) by cycling between three coordination (driving the binding of electronegative ligands) and four coordination (releasing products because of the weaker metal–ligand bonds).

The rapid equilibrium between three-coordinate and four-coordinate forms is also likely to be useful for controlling the reactions of the imido species  $L^R\text{Fe}=\text{NR}$  (discussed above).<sup>30</sup> Recall that coordination of a fourth donor is necessary to enable abstraction of hydrogen atoms from hydrocarbons. This implies that the fourth donor can be used to tune the imido reactivity or to control the selectivity of hydrogen atom abstraction. Most importantly, we have learned that one can add ligands to destabilize a complex, rather than removing them, as usually done to make a reactive catalytic intermediate. In these ways, we anticipate that low-coordinate metals, both synthetic and biological, will continue to challenge the limits of coordination chemistry.

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## BIOGRAPHICAL INFORMATION

**Patrick L. Holland** was born in Pennsylvania in 1971 and was raised in Ohio and in Jacksonville, Florida. After earning an A.B. in chemistry with high honors from Princeton University in 1993, he pursued graduate work with Robert Bergman and Richard Andersen at the University of California at Berkeley and received his Ph.D. in 1997. An NIH postdoctoral fellowship enabled his study of copper chemistry at the University of Minnesota with William Tolman. In 2000, he began his independent career at the University of Rochester, where he is currently Associate Professor of Chemistry. He has been the recipient of an NSF CAREER award and a Sloan Research Fellowship. His research interests include the synthesis, reactions, and mechanisms of low-coordinate iron, cobalt, and nickel compounds and synthetic analogues of iron-containing enzymes.

## FOOTNOTES

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