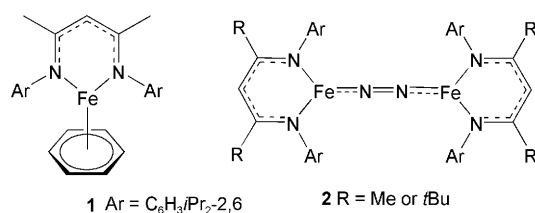


Synthesis and Characterization of Amidinate–Iron(I) Complexes: Analogies with β -Diketiminato Chemistry

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Over the past five years sterically hindered examples of β -diketiminates (e.g., Nacnac^- , that is, $[\{\text{ArNC}(\text{Me})_2\text{CH}\}]^-$ Ar = 2,6-diisopropylphenyl) have been enlisted for the preparation of a variety of stable Group 5–12 first-row transition-metal(I) complexes, for example, **1**.^[1] These are gener-



ally synthesized by the reduction of β -diketiminato metal halide precursors with *s*-block metals. The high reactivity of such metallacycles is lending them to an increasing array of synthetic applications, which include uses as reagents for small-molecule activation, reductive coupling, metal–imide formation, and so forth.^[1] Of most relevance to this study is the work of Holland et al., who have shown that β -diketiminato–iron(I) fragments can activate dinitrogen to give complexes (**2**) with partially reduced N–N bonds that are significantly elongated with respect to that in gaseous N₂.^[1d,2] Accordingly, complexes such as **2** have been suggested as

models for the likely FeNNFe intermediates in the binding of N₂ to iron sites (e.g., the iron–molybdenum cofactor) of nitrogenase enzymes.^[3] Such enzymes are of immense biological importance as they catalyze the reduction of dinitrogen to ammonium salts, which are used as building blocks in numerous biosynthetic processes.

Recently we have utilized bulky amidinate and guanidinate ligands ($[(\text{ArN})_2\text{CR}]^-$ R = *t*Bu (Piso⁻), N(C₆H₁₁)₂ (Giso⁻) or NiPr₂ (Priso⁻)) for the stabilization of a variety of Group 2,^[4] 13,^[5] 14,^[6] and 15^[7] metal(I) complexes, and planar four-coordinate lanthanide(II) complexes.^[8] Throughout these investigations, the stabilizing and ligating properties of the bulky amidinates and guanidinates have been shown to be strikingly similar to those of β -diketiminates. As a result, we saw the potential to extend their coordination chemistry to the formation of first-row transition-metal(I) complexes. This is of interest for a number of reasons. Firstly, such compounds should show enhanced and/or differing patterns of reactivity relative to their β -diketiminato counterparts, as the greater angular extent of the cavity between their N-aryl substituents should provide less steric protection to the coordinated transition-metal center. Also, despite the plethora of less bulky amidinate and guanidinate first-row d-block complexes in the literature,^[9] there are no known examples of carbonyl-free metal(I) species incorporating *N,N'*-chelating ligands. Indeed, the only metal(I) complexes are di- or polynuclear species with the amidinate or guanidinate acting as a bridging ligand between copper^[9,10] or, in one case, nickel^[11] centers. Here, we report the first amidinate–iron(I) complex and discuss its reactivity towards dinitrogen and carbon monoxide.

The amidinato–iron(II) bromide precursor complex **3** was readily prepared in good yield by treating FeBr₂ with one equivalent of K[Piso] in THF.^[12] An X-ray crystallographic analysis (see Supporting Information) of the complex revealed it to be a bromide-bridged dimer with iron centers coordinated by delocalized Piso⁻ ligands. The metal centers have differing geometries that both lie between square planar and tetrahedral. It is of note that the complex is ther-

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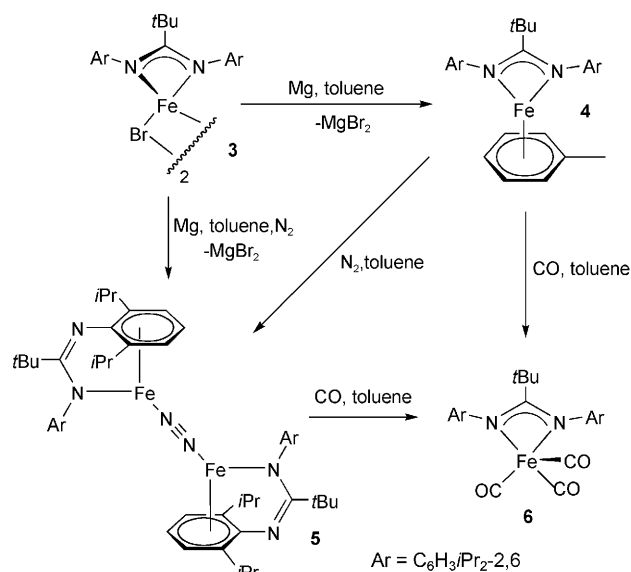
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mally stable in the solid state and in solutions of non-coordinating solvents. This differs from the closely related, but less hindered, heteroleptic amidinate-iron(II) complex, $[\text{Fe}\{(\text{ArN})_2\text{CPh}\}(\text{Cl})(\mu\text{-Cl})\text{Li}(\text{THF})_3]$,^[13] which readily redistributes in toluene at room temperature to give homoleptic $[\text{Fe}\{(\text{ArN})_2\text{CPh}\}_2]$.

The solution-state thermal stability of **3** allowed us to investigate its reduction with magnesium metal in toluene/THF under an argon atmosphere. This afforded the monomeric iron(I) complex **4** in moderate yield after recrystallization from hexane (Scheme 1). Alternatively, when the re-



Scheme 1. Synthesis of compounds **4-6**.

duction was carried out in toluene/THF or THF under an atmosphere of dinitrogen, the N₂-bridged dimeric complex **5** was formed in good yield. Although the similarities between **1** and **4** are evident, it is interesting to note that **1** is formed by the irreversible displacement of neutral N₂ from **2** (R = Me) upon its treatment with benzene.^[14] This occurs despite the significant Fe–N multiple bond character implied by marked reduction of the bridging N₂ ligand of **2**. Conversely, treatment of solutions of **4** in toluene with N₂ slowly led to the displacement of its toluene ligand and the formation of **5**, despite the fact that the degree of N₂ reduction (and concomitant Fe–N multiple bond character) is much less pronounced than for the β-diketiminato analogues (vide infra). This displacement is irreversible, as evidenced by the fact that **5** can be recrystallized intact from toluene under an argon atmosphere. The differences in the reactivity of **2** and **5** towards arene solvents most likely result from the ability of the Piso[−] ligand to vary its coordination mode between N,N' and N,arene chelating. In the case of **5**, this presumably leads to its Fe^I centers being more electronically satisfied than those of **2**. There are, however, parallels between the reactivities of **2** and **5**, in that their treatment with CO leads to the structurally similar square-based pyramidal com-

plexes, $[\text{Fe}^{\text{I}}(\text{Nacnac})(\text{CO})_3]$ ^[14] and $[\text{Fe}^{\text{I}}(\text{Piso})(\text{CO})_3]$ (**6**), respectively, through displacement of the N₂ ligand. In addition, the toluene ligand of **4** is readily displaced by CO to give **6**.

It is of note that the bulky guanidinate ligands Giso[−] and Priso[−] have comparable, if not enhanced, abilities to stabilize low-oxidation metal systems, relative to the amidinate (Piso[−]).^[5-7] Accordingly, the guanidinato-iron(II) halides, $[\text{Fe}(\text{Giso})\text{I}]_2$ and $[\text{Fe}(\text{Priso})\text{Cl}]_2$, were prepared and structurally characterized (see Supporting Information). Their reductions with either magnesium or potassium in toluene/THF under atmospheres of either argon or dinitrogen, were attempted. In all cases, however, only intractable mixtures of products were obtained.

The X-ray crystal structures of **4-6** were determined and the molecular structures of **4** and **5** are depicted in Figures 1 and 2.^[14] That for **6** is included in the Supporting Information. The structure of **4** is closely related to that of **1** in that

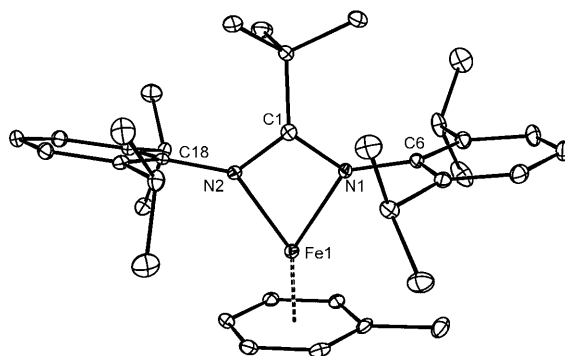


Figure 1. Molecular structure of **4** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Fe1–N2 1.969(2), Fe1–N1 1.9724(18), N1–C1 1.339(3), N2–C1 1.344(3), Fe1–centroid 1.564(3), N2–Fe1–N1 66.57(8), N1–C1–N2 107.4(2).

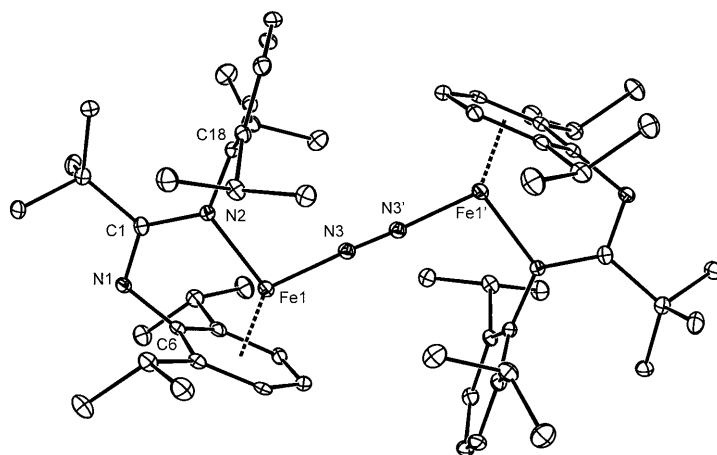


Figure 2. Molecular structure of **5** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Fe1–N3 1.834(3), Fe1–N2 1.945(3), N3–N3' 1.124(6), N1–C1 1.307(5), N2–C1 1.373(5), N1–C6 1.407(5), Fe1–centroid 1.560(3), N3–Fe1–N2 100.30(14), N3'–N3–Fe1 176.9(4), C1–N2–Fe1 114.4(2), N1–C1–N2 120.0(3), C1–N1–C6 111.4(3). Symmetry operation: $-x, -y+1, -z+2$.

its delocalized amidinate ligand coordinates an iron(I) center in an *N,N'*-chelating fashion. The distance from the iron center to the centroid of the η^6 -coordinated toluene ligand of **4** (1.564(3) Å) is markedly shorter than the equivalent distance in **1** (1.63 Å).^[1d,15] A reasonable explanation for this observation derives from the smaller cone angle of the Piso^- ligand (vs. Nacnac^-), which leads to a less steric interaction with the η^6 -arene ligand. In addition, toluene might be expected to be a better donor towards Fe^I than the less electron-rich benzene ligand in **1**.

There are significant differences between the structures of **4** and **5**. Most notably, the Piso^- ligands in the latter act as localized iminoamides that chelate the iron(I) centers in an *N*-arene fashion. A similar coordination mode has been seen for this ligand in its monomeric indium(I) and thallium(I) complexes.^[16] Despite the differences in the structures, the $\text{Fe}-\eta^6$ -arene centroid and $\text{Fe}-\text{N}(\text{amido})$ distances are similar in both complexes. The coordinative flexibility of Piso^- leads to the iron centers of **5** having a higher coordination number (CN=5) than they would if the ligand were acting in an *N,N'*-chelating mode. In contrast, β -diketiminate almost invariably act as *N,N'*-chelating ligands,^[1] which in the case of **2**, results in three-coordinate iron centers. It has been proposed that there is an inverse correlation between the metal coordination number and degree of N_2 ligand reduction (i.e., $\text{Fe} \rightarrow \text{N}(\pi^*)$ back-bonding) in $\text{Fe}(\text{N}_2)$ complexes.^[1d] In line with this proposal is the significant N_2 reduction observed for three-coordinate **2** (R=Me: N–N distance 1.18 Å mean; R=*t*Bu: N–N distance 1.182(5) Å^[1d,2]) and the apparently minimal reduction of the N_2 ligand of five-coordinate **5** (N–N distance 1.124(6) Å). These values can be compared to those for the only other structurally characterized dinuclear, β -diketiminate-free Fe^I complexes bearing bridging N_2 ligands, namely $[\{\text{Fe}[\text{PhB}(\text{CH}_2\text{P}i\text{Pr}_2)_3\}]_2(\mu\text{-N}_2)]$ ^[17] and $[\{\text{Fe}[\text{N}(\text{SiMe}_2\text{N}i\text{Bu})(\text{C}_2\text{H}_4\text{P}i\text{Pr}_2)_2\}]_2(\mu\text{-N}_2)]$,^[18] which are four-coordinate and display intermediate degrees of N_2 reduction (N–N distances of 1.138(6) and 1.166(3) Å, respectively).

The Raman spectrum of **5** exhibits a strong N–N stretching band centered at 2005 cm^{-1} (cf. $\nu(\text{N}_2)=2331 \text{ cm}^{-1}$), which is consistent with the proposed minimal N_2 activation in that complex (cf. other five-coordinate $\text{Fe}(\text{N}_2)$ complexes in the literature^[1d]). In comparison, the stretching bands of the low-coordinate, N_2 -activated complexes **2** appear at significantly lower frequencies (R=Me: 1810 cm^{-1} ; R=*t*Bu: 1778 cm^{-1} ^[1d,2]). Little useful information could be obtained from the NMR spectra of the paramagnetic complexes **4** and **5**, though the solution magnetic moment (Evans method) of each complex was determined. The value measured for **4** ($2.3 \mu_B$) is similar to that for **1** ($2.5 \mu_B$),^[2] and both are indicative of low-spin Fe^I systems ($S=1/2$ ground state). The value obtained for **5** ($2.6 \mu_B$ per dimer) suggests the compound possesses two low-spin ($S=1/2$) iron(I) centers, though the nature of any interaction between these centers is yet to be determined.^[19] In contrast, the low-coordinate iron complexes **2** have much higher solution magnetic moments (R=Me: $7.9 \mu_B$; R=*t*Bu: $8.4 \mu_B$ ^[1d,2]). These have

been assigned as arising from the ferromagnetic coupling of two high-spin Fe^I centers (each $S=3/2$) leading to an $S=3$ ground state.^[2] An alternative assignment also proposes an $S=3$ ground state, but resulting from strong antiferromagnetic coupling of two high-spin Fe^{II} centers ($S_A=S_B=2$; $S_{AB}=4$) with a bridging triplet N_2^{2-} ($S_C=1$) ligand.^[20]

In summary, the first amidinate–iron(I) complexes have been prepared. These can exhibit close structural similarities to related β -diketiminate complexes, but also significant differences due to the greater coordinative flexibility of the amidinate ligand. Given the emerging synthetic importance of β -diketiminate complexes of first-row transition-metals, the development of related, highly reactive species incorporating bulky, but coordinatively flexible, amidinate or guanidinate ligands is a current priority in our group. Further results from this study will appear in forthcoming reports.

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Keywords: amidinates • iron • low oxidation state • nitrogen activation • structure elucidation

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