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Synthesis and Characterization of an Iron(IV) Ketimide Complex

Richard A. Lewis, Guang Wu, and Trevor W. Hayton*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Received June 6, 2010; E-mail: hayton@chem.ucsb.edu

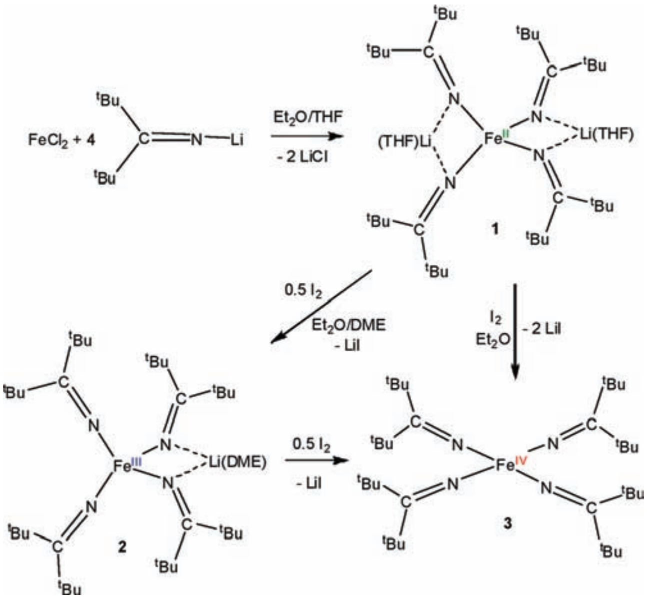
Abstract: Addition of 4 equiv of $\mathrm{LiN{=}C^{t}Bu_2}$ to $\mathrm{FeCl_2}$ in $\mathrm{Et_2O}$/THF results in the formation of $\mathrm{[Li(THF)]_2[Fe(N{=}C^{t}Bu_2)_4]}$ (**1**). Oxidation of **1** with 0.5 equiv of $\mathrm{I_2}$ in $\mathrm{Et_2O}$/DME yields $\mathrm{[Li(DME)][Fe(N{=}C^{t}Bu_2)_4]}$ (**2**) in moderate yield. Both **1** and **2** are high spin and exhibit tetrahedral geometries in the solid state. Oxidation of **1** with 1 equiv of $\mathrm{I_2}$ in $\mathrm{Et_2O}$ yields $\mathrm{Fe(N{=}C^{t}Bu_2)_4}$ (**3**) in good yield. Surprisingly, complex **3** exhibits a diamagnetic ground state and a nearly square planar geometry about the Fe center.

Interest in iron(IV) is driven by its intermediacy in several biorelevant transformations,[1−3] and in the past few years several Fe(IV) complexes containing oxo, imido, and nitrido ligands have been developed with the goal of uncovering novel bond cleavage and atom transfer reactivity.[4−10] Despite these advances, the fundamental coordination chemistry of this oxidation state remains relatively unexplored, in part because the highly oxidizing nature of many Fe(IV) complexes greatly complicates their study.[10,11] To address this problem we have endeavored to find other ligand sets which could better stabilize the 4+ state. Ketimides, in particular, have been shown to be strongly electron-donating and capable of both supporting high oxidation states and stabilizing multiple oxidation states of the same metal ion. These facets of ketimide chemistry are well illustrated by the isolation of uranium ketimides in the 3+,[12] 4+,[12,13] and 5+[14] oxidation states. In transition metal chemistry, ketimides have found application as coligands for group 4 olefin polymerization catalysts,[15−20] but their use with other transition metals is not as well established. Herein we report the synthesis of a homoleptic Fe(IV) ketimide complex and demonstrate the ability of this ligand set to stabilize high oxidation states in the later transition metals.

Addition of 4 equiv of $\mathrm{Li(N{=}C^{t}Bu_2)}$ to $\mathrm{FeCl_2}$ in $\mathrm{Et_2O}$/THF results in the formation of $\mathrm{[Li(THF)]_2[Fe(N{=}C^{t}Bu_2)_4]}$ (**1**), which can be isolated as a black crystalline solid in 60% yield (Scheme 1). Its formulation was confirmed by elemental analysis and X-ray crystallography (full details can be found in the Supporting Information). Its ^{1}H NMR spectrum in $\mathrm{C_6D_6}$ consists of a major resonance at 22.6 ppm. Also present in the ^{1}H NMR spectrum are minor peaks at 17.3 ppm and 1.27 ppm. The latter resonance is assignable to free $\mathrm{Li(NC^{t}Bu_2)}$. Additionally, the ratio of peaks is consistent from batch to batch and is independent of the method of synthesis.[21] Overall, these data suggest that complex **1** partially loses 1 equiv of $\mathrm{Li(NC^{t}Bu_2)}$ in solution, forming $\mathrm{Li[Fe(NC^{t}Bu_2)_3]}$ as the dominant Fe-containing product. Accordingly, we have assigned the resonance at 22.6 ppm to $\mathrm{Li[Fe(NC^{t}Bu_2)_3]}$ and the resonance at 17.3 ppm to **1**. Similar behavior has been observed for other "ate" complexes.[22]

Oxidation of **1** with 0.5 equiv of $\mathrm{I_2}$ in a mixture of $\mathrm{Et_2O}$, pentane, and DME yields $\mathrm{[Li(DME)][Fe(N{=}C^{t}Bu_2)_4]}$ (**2**) in 56% yield (Scheme 1). The ^{1}H NMR spectrum of **2** exhibits a single broad resonance at 30.6 ppm, assignable to the ^{t}Bu groups, and a broad singlet at 3.16 ppm is assignable to the protons in the DME moiety. No resonance was observed in the ^{7}Li{^{1}H} NMR spectrum. Complex **2** crystallizes in the triclinic space group $P\bar{1}$. In the solid state, it exhibits a tetrahedral geometry with two terminal ketimide ligands and two Li-bridged ketimide ligands (Figure 1). The single Li cation is also coordinated by a κ^{1}-DME moiety and by agostic interactions with two ketimide methyl groups (C30 and C27).[23] The terminal ketimide ligands in **2** exhibit Fe−N bond lengths of 1.885(2) and 1.886(2) Å and Fe−N−C angles of 169.6(2)° and 167.2(2)°. The Li-bridged ketimides exhibit longer Fe−N bond lengths of 1.982(2) and 1.999(2) Å and Fe−N−C angles of 144.5(2)° and 146.4(2)°. The large Fe−N−C angles for the terminal ketimides are suggestive of π donation to the Fe center.

Scheme 1



The cyclic voltammogram of **2** in THF reveals two reversible redox features at −1.63 and −0.53 V (vs Fc/Fc^{+}) (see the Supporting Information). The feature at −1.63 V is attributed to the Fe(II)/Fe(III) redox couple while the feature at −0.53 V is attributed to the Fe(III)/Fe(IV) redox couple. This latter value is similar to the Fe(III)/Fe(IV) redox potentials observed for two previously reported Fe(IV) imido complexes[5,7] and demonstrates the strongly electron-donating nature of the ketimide ligand.

The addition of 1 equiv of $\mathrm{I_2}$ to complex **1** in $\mathrm{Et_2O}$ yields $\mathrm{Fe(N{=}C^{t}Bu_2)_4}$ (**3**) in 72% yield. Complex **3** can also be synthesized by oxidation of **2** with 0.5 equiv of $\mathrm{I_2}$. Its ^{1}H NMR spectrum in $\mathrm{C_6D_6}$ consists of a sharp singlet at 1.69 ppm, assignable to the ^{t}Bu groups, while its ^{13}C{^{1}H} NMR spectrum displays a resonance at 277.0 ppm, assignable to the N═*C* carbon of the ketimide ligands. This value is shifted significantly downfield from that observed for

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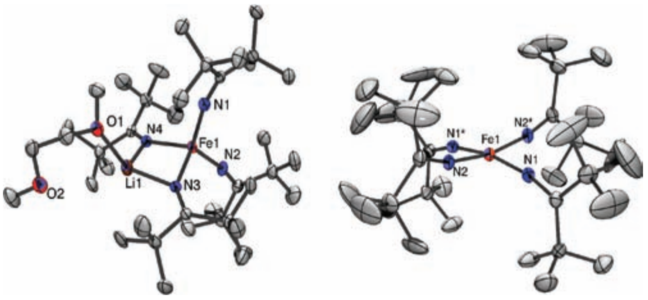

Figure 1. Solid state molecular structures of [Li(DME)][Fe(N═C^{t}Bu$_2$)$_4$] (**2**), left, and [Fe(N═C^{t}Bu$_2$)$_4$] (**3**), right.

other ketimide complexes, such as (C$_5$Me$_4$SiMe$_3$)Ti(N═C^{t}Bu$_2$)Cl$_2$ (202.1 ppm).[18] Furthermore, the cyclic voltammogram of **3** is nearly identical to that observed for **2** (see the Supporting Information). Consistent with the electrochemistry results, equimolar mixtures of **3** and **1** produce **2** via conproportionation.

Complex **3** crystallizes in the monoclinic space group *C*2/*c*. In the solid state, **3** exhibits a distorted square planar geometry about Fe (Figure 1) and nearly linear ketimide ligands (Fe1−N1−C1 = 165.5(3)°, Fe1−N2−C10 = 166.6(3)°). The N1−Fe1−N1* and N2−Fe1−N2* angles are 167.1(2)° and 167.6(2)°, respectively, while the angle between N1−Fe1−N2 and N1*−Fe1−N2* planes is 17.60(1)°. Its Fe−N bond lengths are 1.771(3) and 1.775(3) Å, which are 0.1 Å shorter than the Fe−N bond lengths of the terminal ketimides in **2**. This is consistent with removal of an electron from an Fe-based orbital. The Fe−N bonds in **3** are also shorter than those reported for the Fe(IV) tetraamido macrocyclic complex Fe(MAC*)(CN^{t}Bu)$_2$ (av. Fe−*N* = 1.91 Å),[24] and shorter than known Fe(III)−N(amide) bond lengths.[25,26] Also of note is the invariance of the C═N bond lengths in complexes **1** (av. C−N = 1.25 Å), **2** (av. C−N = 1.26 Å), and **3** (av. C−N = 1.25 Å).

The magnetic moments of complexes **1**, **2**, and **3** were investigated using SQUID magnetometry (Figure 2). At 300 K the magnetic moments of **1** and **2** are 3.16 and 4.21 cm^3·K·mol^{-1}, respectively. These values are consistent with previously reported high-spin Fe(II) and Fe(III) magnetic susceptibilities.[27] In contrast, complex **3** exhibits a small *diamagnetic* susceptibility from 300 to 29 K. At 300 K, its susceptibility is −0.064 cm^3·K·mol^{-1}. For comparison, a diamagnetic Fe(IV) alkyl, namely Fe(norbornyl)$_4$, is also known, but it has not been structurally characterized.[28]

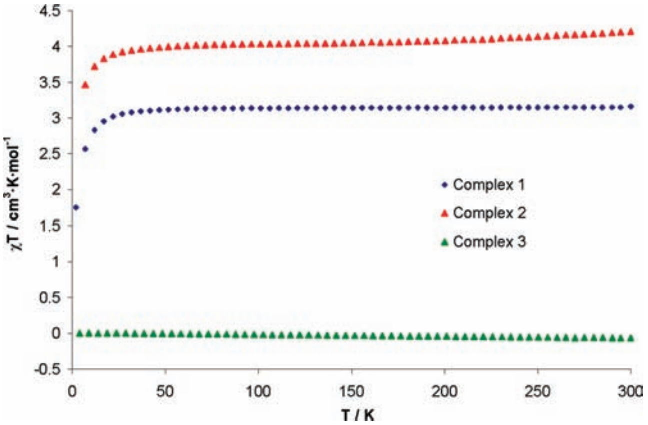

Figure 2. Magnetic susceptibilities of complexes **1**, **2**, and **3**.

The $S = 0$ ground state for complex **3** is surprising, especially considering the high-spin configuration found for other square planar d^4 complexes,[29] such as [Li(THF)$_2$]$_2$[CrPh$_4$], [Li(TMEDA)]$_2$[CrMe$_4$], and [Li(TMEDA)$_2$][MnMe$_4$].[30−32] Unlike **3** however, these complexes contain ligands solely capable of σ-donation. In contrast, the strongly π-donating nature of the ketimide ligand[18] likely enforces the low-spin electronic configuration found in **3**. In a square planar crystal field, the *d* orbitals are split into e$_g$ (d$_{yz}$, d$_{xz}$), a$_{1g}$ (d$_{z^2}$), b$_{2g}$ (d$_{xy}$), and b$_{1g}$ (d$_{x^2-y^2}$) states. In complex **3**, the ^{t}Bu groups of each ketimide are oriented perpendicular to the equatorial plane, allowing the lone pair on each nitrogen atom to interact with the d$_{yz}$ and d$_{xz}$ orbitals. Thus, a strong π interaction between the ketimide and the Fe center would push the normally low-lying d$_{yz}$ and d$_{xz}$ orbitals up in energy, forcing the four d electrons into the nonbonding d$_{z^2}$ and d$_{xy}$ orbitals. We suggest that this interaction is ultimately responsible for the observed diamagnetic ground state.

In summary, the isolation of **3**, a square planar Fe(IV) complex, reveals the utility of the ketimide platform for stabilizing unusual oxidation states and geometries in the later transition metals. Future studies will focus on exploring the reactivity of **3**, and on synthesizing other homoleptic ketimide complexes, particularly those of manganese, cobalt, and nickel. DFT calculations will also be pursued to support the proposed electronic structure of **3**.

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Supporting Information Available: Experimental procedures and crystallographic details for complexes **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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