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Communication

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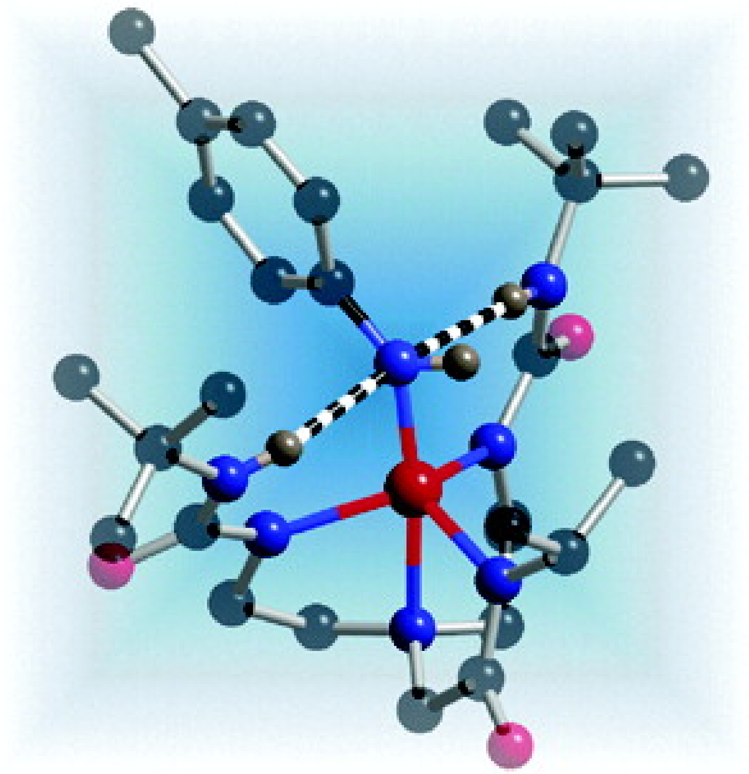

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Preparation of Iron Amido Complexes via Putative Fe(IV) Imido Intermediates

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This report describes the preparation and properties of iron(III) amido complexes ($Fe^{III}-NHR$) obtained from iron(II) precursors and aryl azides. Their isolation is facilitated with ureate/amidate tripodal ligands that create varied hydrogen bond (H-bond) networks around the $Fe^{III}-N$ unit. Results from reactivity studies suggest involvement of Fe(IV) imido intermediates.

Research on metal complexes with terminal imido and amido ligands has been stimulated by their proposed roles as intermediates in various chemical transformations.[1] For instance, metal imido complexes have been implicated as the key intermediates in metal-mediated group transfer reactions.[2] In addition, intermediary species with terminal amido ligands are linked to catalytic processes involved in N−C bond formation.[3] However, there are relatively few examples of late 3d transition metal complexes with terminal imido ligands,[4] particularly those of iron. Lee reported a stable site-differentiated 3Fe(III)/Fe(IV) cubane, where the Fe(IV) center has a terminally bonded imido ligand.[5] Peters reported the first structurally characterized monomeric Fe(III) imido ($Fe^{III}\equiv NR$) complexes using a bulky trisphosphinoborate ligand.[6] Preparative routes to these $Fe^{III}\equiv NR$ complexes occurred by reaction of an Fe(I) precursor with organic azides. Hydrogenolysis of $Fe^{III}\equiv NR$ complexes with H_2 in benzene yielded the Fe amido complex, $Fe^{II}-NHR$.[7] Wieghardt has described a low-spin Fe(III) amido species with triazacyclononane,[8] while Holland recently reported the preparation of several Fe amido complexes using β-diketiminato ligands.[9] In addition, Bergman has isolated an $Fe^{II}-NH_2$ complex using bisphosphine ligands.[10]

Analysis of the above findings suggests that during synthesis the formal oxidation states at the Fe centers range from 1+ to 3+. Que has recently provided evidence for the formation of an Fe(III) amido complex, prepared by treating an Fe(II) complex with phenyl-*N*-tosylimidoiodinane (PhI═NTs) and proposes an Fe(IV) imido species as an intermediate.[11]

We have introduced the symmetrical urea- and amide-based tripodal ligands, $H_3\mathbf{0}$ and $H_6\mathbf{3}$ (Figure 1), whose Fe(II) complexes cleave O_2 to form monomeric Fe(III) species with terminal oxo or hydroxo ligands.[12] Mechanistic studies on complexes of $[Fe^{II}H_3\mathbf{3}]^-$ suggest the involvement of an Fe(IV) oxo intermediate, showing that a two-electron process involving a high valent iron center is viable. We reasoned that a similar process could occur to prepare iron complexes with terminal imido and amido ligands. While $[Fe^{II}\mathbf{0}]^-$ and $[Fe^{II}H_3\mathbf{3}]^-$ react with organic azides, the initial products of these reactions are too unstable, and repeated attempts to isolate amido and imido complexes were unsuccessful. These observations and those reported by others[4,11] suggested to us that hybrid tripods, $H_4\mathbf{1}$ and $H_5\mathbf{2}$, with varied cavity architectures and H-bond networks, may be more conducive in producing stable monomeric imido and amido iron complexes.

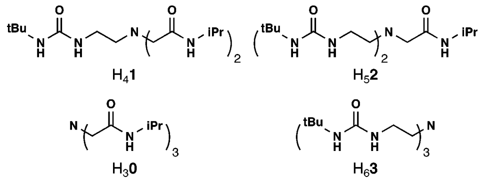
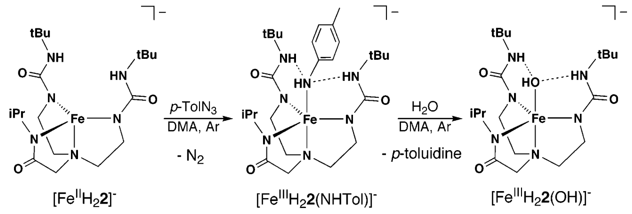


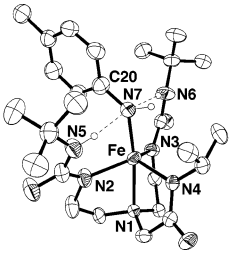
Figure 1. Tripodal ligands used in this study.

The preparative route to the Fe(III) amido complexes is illustrated in Scheme 1 for $[Fe^{III}H_2\mathbf{2}(NHTol)]^-$.[13] Treating a dimethylacetamide (DMA) solution of the high-spin iron(II) complex, $[Fe^{II}H_2\mathbf{2}]^-$, with *p*-tolyl azide ($TolN_3$) results in a rapid color change from amber to dark black-green with concomitant gas evolution that is attributed to the expulsion of N_2.[14] $K[Fe^{III}H_2\mathbf{2}(NHTol)]$ is isolated as a dark green solid with X-band EPR *g*-values of 8.65 and 4.15, values that are indicative of a monomeric Fe(III) species with an $S = {}^5/_2$ spin state. An identical reaction sequence was carried out with $[Fe^{II}H\mathbf{1}]^-$ to yield the corresponding Fe(III) amido complex $[Fe^{III}H\mathbf{1}(NHTol)]^-$ that exhibited spectroscopic properties similar to those of $[Fe^{III}H_2\mathbf{2}(NHTol)]^-$. The complexes are hygroscopic: for instance, allowing $[Fe^{III}H\mathbf{1}(NHTol)]^-$ to react with 1 equiv of water produces the Fe(III)−OH complex, $[Fe^{III}H\mathbf{1}(OH)]^-$, and *p*-toluidine in 95 and 60% yields as determined by optical spectroscopy (Scheme 1).[13,15,16]

Scheme 1



Single-crystal X-ray diffraction study on $K[Fe^{III}H_2\mathbf{2}(NHTol)]$ shows that the iron center is five-coordinate with trigonal bipyramidal geometry (Figure 2).[13] The two ureas and isopropyl group appended from N4 surround the *p*-tolyl amido ligand.



	Bond length (Å)
Fe-N7	1.968(4)
Fe-N1	2.191(3)
Fe-N2	2.056(4)
Fe-N3	2.020(4)
Fe-N4	2.029(3)
N7··N5	2.988(6)
N7··N6	2.990(6)
	Bond angle (°)
N1-Fe-N7	173.1(2)
N2-Fe-N3	127.3(1)
C20-N7-Fe	127.4(3)

Figure 2. Thermal ellipsoid plot for $[Fe^{III}H_2\mathbf{2}(NHTol)]^-$. Thermal ellipsoids are drawn at the 50% probability level, and carbon-bonded hydrogen atoms are omitted for clarity.

The Fe−N7 length is 1.968(4) Å, and a nearly linear N1−Fe−N7 angle of 173.10(15)° is observed; these findings are similar to those reported for other Fe(III) amido complexes.[9] Moreover, the

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presence of intramolecular H-bonds is supported by the average HN$\cdots$N7 distance of 2.990(6) Å. The aryl ring of the amido ligand is positioned between the urea groups, resulting in an N2−Fe−N3 angle of 127.32(14)°. A similar increase of one trigonal angle is found in related M−OH complexes of [H$_3$**3**]$^{3-}$.[12a,c] This arrangement of the tolyl moiety leaves the N−H bond of the amido ligand pointed within the cavity toward the less bulky isopropyl group of the amidate.

Examples of monomeric Fe(IV) species in synthetic systems are rare,[5,17] but we propose that the described Fe(III) amido complexes form via H-atom abstraction by Fe(IV) imido intermediates. As organic azides generally react with transition metal ions by a two-electron process to yield imido complexes,[1c,e] it is expected that starting from Fe(II) would result in formation of the Fe(IV) imido species at some point along the reaction pathway (Figure 3). Conversion of this high valent species to the Fe(III) amido could then take place by the formal transfer of a H-atom from the DMA solvent.

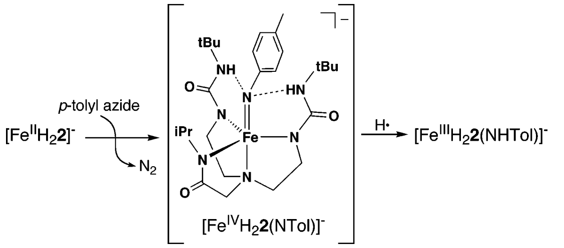
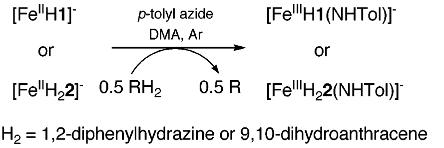


Figure 3. Proposed mechanism involving an Fe(IV) imido intermediate.

We have shown that this proposal may be viable by using 1,2-diphenylhydrazine (DPH) and 9,10-dihydroanthracene (DHA) as external H-atom sources (eq 1). Reactions using DPH result in clean conversion to azobenzene, which is produced in yields of ~90% when used with either Fe(II) complex. Although reactions with DHA do not give complete conversion to anthracene as a single product, they demonstrate C−H bond activation. Addition of TolN$_3$ to a solution of [Fe^{II}H$_2$**2**]$^-$ in DMA containing 0.5 equiv of DHA produces [Fe^{III}H$_2$**2**(NHTol)]$^-$ and a mixture of organic products with DHA starting material recovered in 73% yield, along with anthracene (14%) and the coupling product, 9,9′,10,10′-tetrahydro-9,9′-bianthracene (8%). Considerably more DHA is converted when carrying out the reaction to prepare [Fe^{III}H**1**(NHTol)]$^-$ from [Fe^{II}H**1**]$^-$: anthracene is obtained in 49% yield, with the coupling product (19%) and DHA (19%) also present.



(1)

These studies suggest that Fe(IV) imido complexes are capable of X−H bond cleavage and complement results on iron oxo complexes of [H$_3$**3**]$^{3-}$ that have a strong thermodynamic driving force to abstract H-atoms.[18] Moreover, H-atom abstraction appears to follow an intermolecular path in forming [Fe^{III}H**1**(NHTol)]$^-$ and [Fe^{III}H$_2$**2**(NHTol)]$^-$, which contrasts the intramolecular routes involving ligand modification found in other systems.[4e,f,11] In particular, Que proposes that a trigonal bipyramidal Fe(IV) imido intermediate undergoes intramolecular C−H bond insertion to an appended phenyl group in the formation of an Fe(III)−anilido complex. These differences in reactivity highlight the importance of cavity architecture (i.e., secondary coordination sphere) around reactive metal site(s). Our ability to tune cavity properties assisted in isolating [Fe^{III}H**1**(NHTol)]$^-$ and [Fe^{III}H$_2$**2**(NHTol)]$^-$. Additional studies of these effects on metal-mediated processes are ongoing.

Acknowledgment. Acknowledgment is made to the NIH (GM50781) for financial support of this work and the NSF (CHE-0079282) for funding of the X-ray diffraction instrumentation.

Supporting Information Available: Details for all experiments, spectra for the water reactions (Figures S1−S3), and crystallographic details for K[Fe^{III}H$_2$**2**(NHTol)] (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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