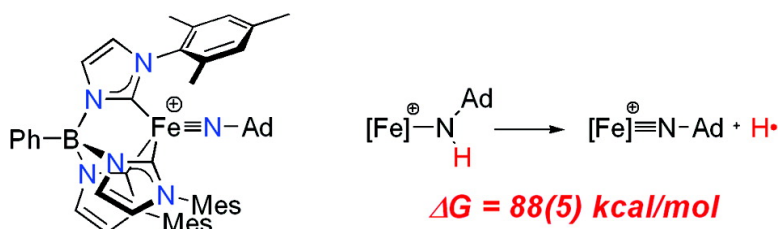


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Thermodynamics of Hydrogen Atom Transfer to a High-Valent Iron Imido Complex

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Non-heme iron dioxygenases and their model complexes hydroxylate saturated hydrocarbons via high-valent iron oxo intermediates.¹ Initial C–H bond cleavage by hydrogen atom transfer (HAT) to the reactive Fe^{IV}=O species is proposed as the first step of these hydroxylation mechanisms.² High-valent iron imidos³ may be anticipated to participate in analogous amination reactions that involve initial HAT to the imido ligand⁴ (known N–H bond-forming reactions of iron imidos include hydrogenation⁵ and NIH shift following electrophilic arene attack).⁶

Considering the thermodynamics of HAT in terms of its component steps, i.e., electron and proton transfer,⁷ can provide insight into the forces that drive the reaction. For example, these considerations have led to the proposal that the thermodynamic driving force for HAT in cytochrome P450 is provided by a highly basic reduced ferryl intermediate, allowing the enzyme to oxygenate hydrocarbons at potentials low enough to be tolerated by the protein matrix.⁸

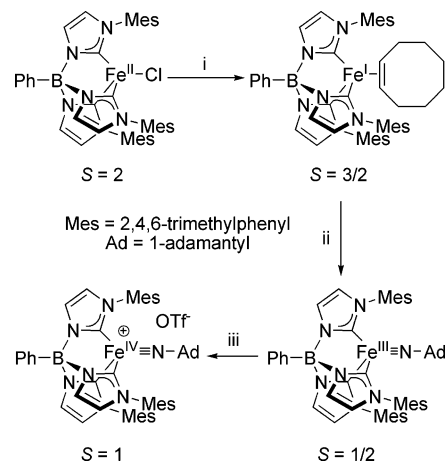
In this contribution we report the preparation of a stable high-valent iron imido complex that is supported by a bulky tris(carbene)-borate ligand. The thermal stability of this complex has allowed us to undertake studies relevant to HAT to the imido ligand. These investigations determine the propensity for HAT and show that the high basicity of the reduced imido complex provides the thermodynamic driving force.

The iron imido complex, L^{Mes}Fe≡NAd (L^{Mes} = phenyltris(1-mesitylimidazol-2-ylidene)borate), is prepared by a similar synthetic route to other iron(III) imido complexes (Scheme 1).^{9,10} The four-coordinate complex L^{Mes}FeCl, prepared from “L^{Mes}Li”¹¹ and FeCl₂(THF)_{1.5}, is reduced in the presence of cyclooctene to form the low-valent complex L^{Mes}Fe(η²-C₈H₁₄). Reaction of this complex with one equivalent of azidoadamantane results in nitrene transfer to form dark-red L^{Mes}Fe≡NAd. All of these complexes have been spectroscopically and crystallographically characterized, see Supporting Information (SI) for details.

Oxidation of L^{Mes}Fe≡NAd by [Cp₂Fe]OTf results in formation of the high-valent imido complex [L^{Mes}Fe≡NAd]OTf. The metrical parameters of this complex (characterized as the BPh₄[−] salt) are very similar to those of its precursor (Figure 1). The Fe–N bond distance in L^{Mes}Fe≡NAd⁺ (1.618(3) Å) is also comparable to other crystallographically characterized four-coordinate iron(IV) imido complexes.^{3a,b} The ¹H NMR spectrum of [L^{Mes}Fe≡NAd]OTf is consistent with the X-ray crystal structure, and distinct from that of L^{Mes}Fe≡NAd. The magnetic moment, determined by the Evans method (μ_{eff} = 2.7(3) BM), is consistent with S = 1 Fe(IV).

Air-stable [L^{Mes}Fe≡NAd]OTf can be heated for days at 100 °C with no evidence of decomposition. This unusual thermal stability has allowed us to undertake thermodynamic investigations relevant to HAT. In particular, we have determined the barriers toward

Scheme 1. Synthesis^a of L^{Mes}Fe≡NAd and [L^{Mes}Fe≡NAd]OTf



^a Conditions and reagents: (i) cyclooctene, K₂S₂O₈, THF, 81%; (ii) N₃Ad, THF, 79%; (iii) [Cp₂Fe]OTf, THF, 60%.

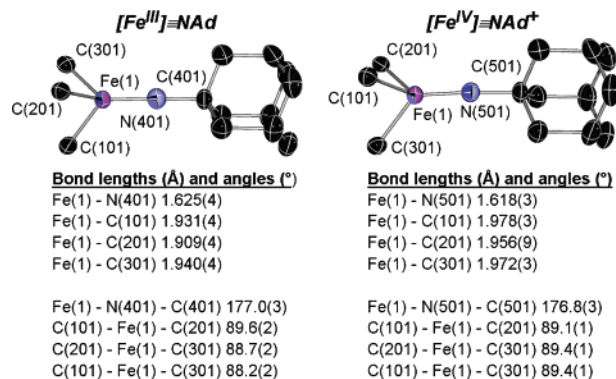


Figure 1. X-ray crystal structures of L^{Mes}Fe≡NAd and [L^{Mes}Fe≡NAd]OTf. Thermal ellipsoids are shown at 50% probability; hydrogen atoms and most of the tris(carbene)borate ligand have been omitted for clarity.

electron and proton transfer, allowing the thermodynamic barrier to HAT to be calculated.

Electron transfer from [L^{Mes}Fe≡NAd]OTf is reversible. The cyclic voltammogram of [L^{Mes}Fe≡NAd]OTf (MeCN, 0.10 M NBu₄PF₆) reveals a wave at E_{1/2} = −0.98 V relative to Cp₂Fe^{+/0}/Cp₂Fe, which we have assigned to the Fe^{IV}/Fe^{III} couple.¹² Consistent with this low barrier toward electron transfer, weak oxidants, such as I₂, cleanly oxidize L^{Mes}Fe≡NAd to [L^{Mes}Fe≡NAd]⁺. Therefore, [L^{Mes}Fe≡NAd]OTf is a weak oxidant.

The two imido complexes, L^{Mes}Fe≡NAd and [L^{Mes}Fe≡NAd]OTf, undergo rapid electron transfer on the ¹H NMR time scale. Line-shape analysis¹³ of a mixture of the two complexes in THF-d₈ has allowed us to determine the second-order rate constant for self-exchange to be k₂ = 7.6(5) × 10⁷ M^{−1} s^{−1} at 308 K. This

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