

Article

## Direct comparison of C–H bond amination efficacy through manipulation of nitrogen-valence centered redox: imido versus iminyl

Matthew J.T. Wilding, Diana A. Iovan, Alexandra T Wrobel, James T. Lukens, Samantha N. MacMillan, Kyle M. Lancaster, and Theodore A. Betley

*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • Publication Date (Web): 22 Sep 2017

Downloaded from <http://pubs.acs.org> on September 22, 2017

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

# Direct comparison of C–H bond amination efficacy through manipulation of nitrogen-valence centered redox: imido versus iminyl

Matthew J.T. Wilding<sup>†</sup>, Diana A. Iovan<sup>†</sup>, Alexandra T. Wrobel<sup>†</sup>, James T. Lukens<sup>‡</sup>, Samantha N. MacMillan<sup>‡</sup>, Kyle M. Lancaster<sup>‡</sup>, and Theodore A. Betley<sup>\*†</sup>.

<sup>†</sup> Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge MA 02138, United States

<sup>‡</sup> Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca NY 14853, United States

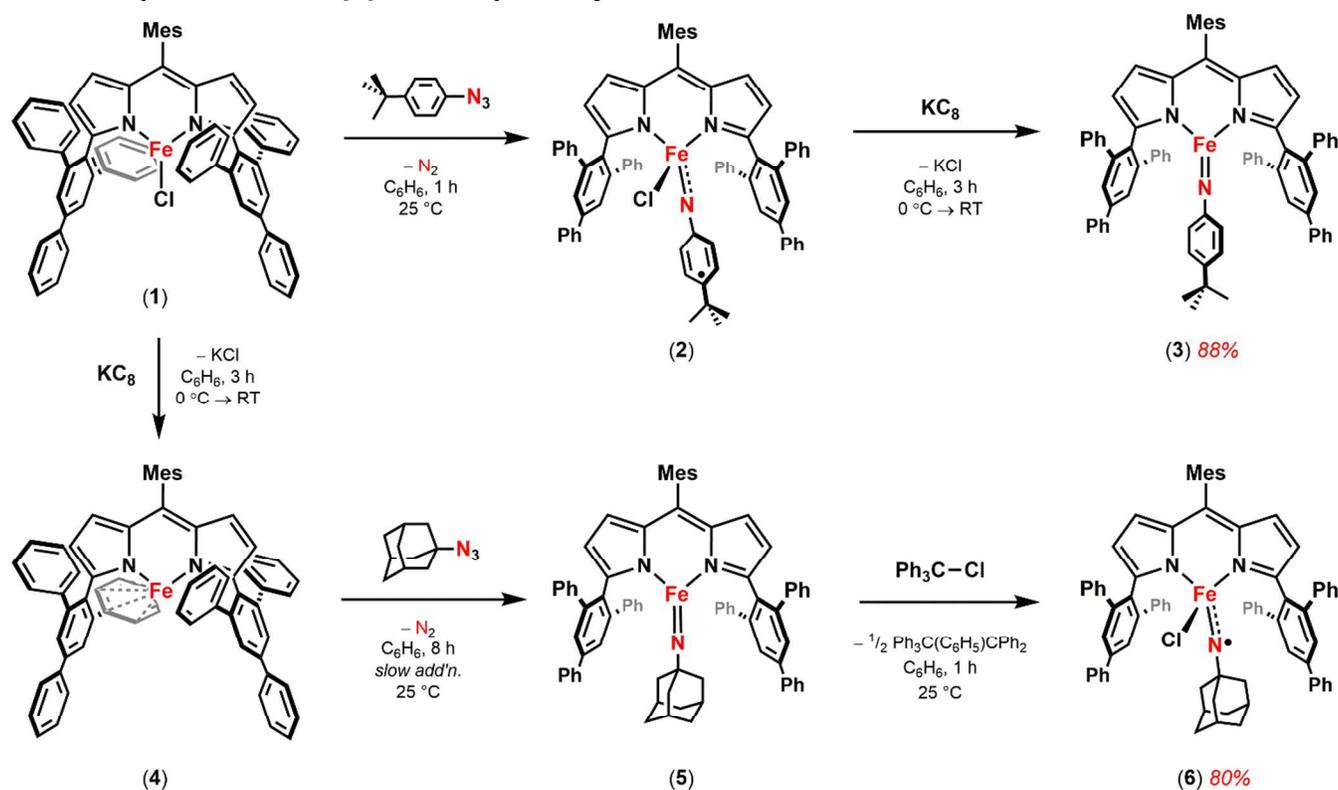
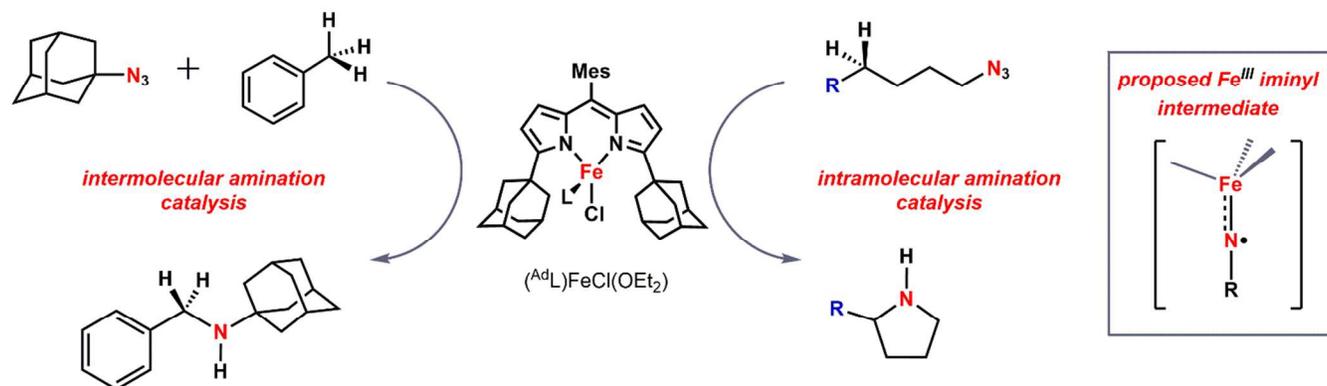
**ABSTRACT:** Reduction of previously reported iminyl radical (<sup>Ar</sup>L)FeCl(N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)) (**2**) with potassium graphite furnished the corresponding high-spin ( $S = 5/2$ ) imido (<sup>Ar</sup>L)Fe(N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)) (**3**) (<sup>Ar</sup>L = 5-mesityl-1,9-(2,4,6-Ph<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)dipyrrin). Oxidation of the three-coordinate imido (<sup>Ar</sup>L)Fe(NAd) (**5**) with chlorotriphenylmethane afforded (<sup>Ar</sup>L)FeCl(NAd) (**6**) with concomitant expulsion of Ph<sub>3</sub>C(C<sub>6</sub>H<sub>5</sub>)CPh<sub>2</sub>. The respective alkyl/aryl imido/iminyll pairs (**3**, **2**; **5**, **6**) have been characterized by EPR, zero-field <sup>57</sup>Fe Mössbauer, magnetometry, single crystal X-ray diffraction, XAS, and EXAFS for **6**. The high-spin ( $S = 5/2$ ) imidos exhibit characteristically short Fe–N bonds (**3**: 1.708(4) Å; **5**: 1.674(11) Å), whereas the corresponding iminylls exhibit elongated Fe–N bonds (**2**: 1.768(2) Å; **6**: 1.761(6) Å). Comparison of the pre-edge absorption feature (1s → 3d) in the X-ray absorption spectra reveal that the four imido/iminyll complexes share a common iron oxidation level consistent with a ferric formulation (**3**: 7111.5 eV, **2**: 7111.5 eV; **5**: 7112.2 eV, **6**: 7112.4 eV) as compared with a ferrous amine adduct (<sup>Ar</sup>L)FeCl(NH<sub>2</sub>Ad) (**7**: 7110.3 eV). N K-edge X-ray absorption spectra reveal a common low-energy absorption present only for the iminyll species **2** (394.5 eV) and **6** (394.8 eV) that was assigned as a N 1s promotion into a N-localized, singly occupied iminyll orbital. Kinetic analysis of the reaction between the respective iron imido and iminyll complexes with toluene yielded the following activation parameters:  $E_a$  (kcal/mol) **3**: 12.1, **2**: 9.2; **5**: 11.5, **6**: 7.1. The attenuation of the Fe–N bond interaction on oxidation from an imido to an iminyll complex leads to a reduced enthalpic barrier [ $\Delta(\Delta H^\ddagger) \sim 5$  kcal/mol]; the alkyl iminyll **6** has a reduced enthalpic barrier (1.84 kcal/mol) as compared with the aryl iminyll **2** (3.84 kcal/mol), consistent with iminyll radical delocalization into the aryl substituent in **2** as compared with **6**.

## 1. Introduction

Late transition metal complexes featuring metal-ligand multiple bonds are investigated intensely to probe their efficacy for functional group transfer to organic substrates.<sup>1–15</sup> Within this class of coordination complexes, iron complexes to which the nitrene functional group (R–N) is bound have now been characterized spanning a large range of oxidation states and electronic structures (Fe<sup>II</sup>  $S = 0$ ,<sup>16</sup> Fe<sup>III</sup>  $S = 1/2$ ,  $S = 3/2$ ,<sup>17–23</sup>  $S = 5/2$ ,<sup>24</sup> Fe<sup>III</sup>(NR)  $S = 2$ ,<sup>25–26</sup> Fe<sup>IV</sup>  $S = 0$ ,  $S = 1$ ,<sup>27–31</sup> Fe<sup>V</sup>  $S = 1/2$ ,<sup>32,33</sup>). Of these examples, only the high-spin, ferric imido<sup>24</sup> and iminyll complexes<sup>25–26</sup> have been demonstrated to be competent for nitrene group transfer into aliphatic or olefinic substrates. The unique electronic configuration of the two amination agents warrants further investigation into how the electronic structure of the reactive intermediate impacts functional group transfer from complexes bearing metal-ligand multiple bonds.

Key to the success of the two examples for which C–H bond amination is observed is the utilization of a weak-

field ancillary ligand, <sup>Ar</sup>L, where <sup>Ar</sup>L = 5-mesityl-1,9-(2,4,6-Ph<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)dipyrrin.<sup>26</sup> We previously have shown that reaction of the ferrous chloride precursor (<sup>Ar</sup>L)FeCl (**1**) with aryl azide N<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu) results in formation of the ferric iminyll complex (<sup>Ar</sup>L)FeCl(N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)) (**2**) (Scheme 1), where evidence of the iminyll radical can be seen in disruption of the iminyll aryl substituent.<sup>25–26</sup> For example, reaction of **1** with N<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>) results in bimolecular, radical coupling of the phenyl iminyll ligands to afford the diferric product [(<sup>Ar</sup>L)FeCl]<sub>2</sub>(μ-N(Ph)(C<sub>6</sub>H<sub>5</sub>)N), allowing for unambiguous spectroscopic assignment of the ferric state. A room temperature solution magnetic moment determination of **2** (5.3(1) μ<sub>B</sub>) in conjunction with agreement of the spectroscopic Mössbauer parameters between **2** and the bimolecularly-coupled product suggest the quintet **2** is comprised of a high-spin ferric center, antiferromagnetically coupled to an iminyll radical [ $S_{\text{total}} = (S_{\text{ferric}} = 5/2) - (S_{\text{iminyl}} = 1/2) = 2$ ]. Although this electronic structure had been suggested previously,<sup>34–37</sup> **2** constitutes the first structurally and

**Scheme 1.** Synthesis of imido (3, 5) and iminyl (2, 6) species.**Scheme 2.** Inter- and intramolecular amination reactions.

spectroscopically authenticated example of a transition metal stabilized iminyl complex. The isolated iminyl **2** was competent for both intermolecular amination of toluene as well as azirdination of styrene in stoichiometric reactions.<sup>26</sup> Employing the less sterically demanding 1,9-adamantyl substituted dipyrin ligand ( $\text{AdL}$ ) allowed for the nitrene-transfer reaction to be run catalytically using  $\text{N}_3\text{Ad}$  as an oxidant (Scheme 2).<sup>26, 38-39</sup> Although no reactive intermediate could be isolated or observed during catalysis, the similarity between the kinetic isotope effects observed for both the stoichiometric and catalytic amination processes suggested a common ferric iminyl reactive intermediate was operative.

We have previously demonstrated that oxidative group

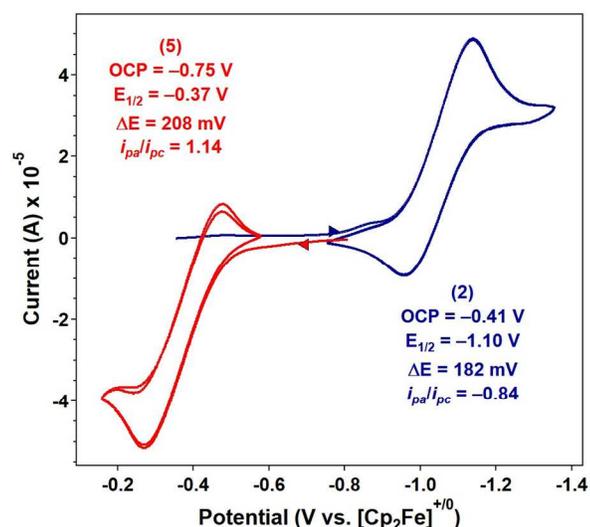
transfer with both alkyl ( $\text{N}_3\text{Ad}$ ) and aryl ( $\text{N}_3\text{Mes}$ ) azides to the monovalent iron complex ( $\text{ArL}$ )Fe (**4**) resulted in isolable ferric imido products ( $\text{ArL}$ )Fe( $\text{NAd}$ ) (**5**) (Scheme 1) and ( $\text{ArL}$ )Fe( $\text{NMes}$ ).<sup>24</sup> The imido complexes were characterized and described as possessing metal ligand multiple bond character with structural features similar to those reported for ferric imidos.<sup>17-23</sup> Unlike those literature precedents, the imido complexes were spectroscopically determined to be high-spin ( $S = 5/2$ ). Akin to their ferric iminyl congeners,<sup>25-26</sup> these imido species were shown to be competent for both H-atom abstraction and nitrene transfer to C-H bond substrates.

Given the common core electronic structure ( $S_{\text{ferric}} = 5/2$ ) between the imido and iminyl molecular species previously characterized,<sup>24-26</sup> we sought to address the

following questions through a comparative examination of the two distinct molecular oxidation levels: (1) what are the redox stabilities of iminyl **2** and imido **5**? Are their respective imido and iminyl congeners electrochemically or chemically accessible? (2) We proposed that the aryl-substituent in iminyl **2** is critical to stabilization of the iminyl functionality via delocalization of the radical throughout the aromatic ring.<sup>26</sup> If chemical oxidation of the alkyl imido **5** is possible, would the oxidation of the complex be iron-borne resulting in a Fe<sup>IV</sup> oxidation state akin to the hydroxylating ferryl compound I in cytochrome P450?<sup>40-41</sup> Or would a similar ferric-stabilized iminyl radical [e.g., Fe<sup>III</sup>(<sup>•</sup>NR)] be observed without the ability to delocalize the radical, as proposed for the intra- and intermolecular amination catalysts? Furthermore, can the two redox resonance forms be spectroscopically distinguished [Fe<sup>IV</sup>(NR) ↔ Fe<sup>III</sup>(<sup>•</sup>NR)]? (3) Lastly, if the redox isomers are accessible for both alkyl and aryl imido/iminyll moieties, how is the change in molecular oxidation level manifested in C–H bond amination efficacy? Herein we report our findings concerning the interconversion of the imido/iminyll redox forms, describe their comparative metal oxidation states using X-ray absorption spectroscopy, and provide a kinetic assessment of their reactivity in intermolecular amination.

## 2. Results and Discussion

### 2.1 Redox stability of the imido/iminyll units



**Figure 1.** Cyclic voltammograms of **2** (blue) and **5** (red) obtained in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C, with 0.1 M (<sup>n</sup>Bu<sub>4</sub>N)(PF<sub>6</sub>); 100 mV/s; referenced to [Cp<sub>2</sub>Fe]<sup>+ / 0</sup> couple.

Cyclic voltammetry (CV) was performed on iminyl **2** and imido **5** to assess their redox stability (Figure 1). CV examination of iminyl **2** in dichloromethane shows a quasi-reversible reduction event at -1.10 V versus [Cp<sub>2</sub>Fe]<sup>+ / 0</sup> (Figure 1). The anticipated imido complex will well dissociate the chloride ligand, akin to the three-coordinate (<sup>Ar</sup>L)Fe(NMes).<sup>24</sup> The quasi-reversible couple suggests a chemical process indeed occurs following reduction. The electrochemical behavior of imido **5** was

also investigated and its cyclic voltammogram reveals a quasi-reversible oxidation event at -374 mV versus [Cp<sub>2</sub>Fe]<sup>+ / 0</sup> (Figure 1). Given the reduction of **2** and oxidation of **5** constitute the same nominal redox couple, it is worth noting the large cathodic shift afforded by coordination of the chloride ligand and the aryl iminyl moiety (Δ = -0.676 V). The redox potential for adamantyl imido **5** (E<sub>1/2</sub> = -0.37 V) is also mildly anodically shifted as compared with the more electron rich analogues reported ([tris(carbeno)borate)Fe(NAd)]<sup>+</sup> -0.64 V,<sup>27</sup> [(bis(phosphino)pyrazolylborate)Fe(NAd)]<sup>+</sup> -0.72 V<sup>29</sup>), though the comparison is not straightforward given the coordination number change between species (three- vs. four-coordinate).

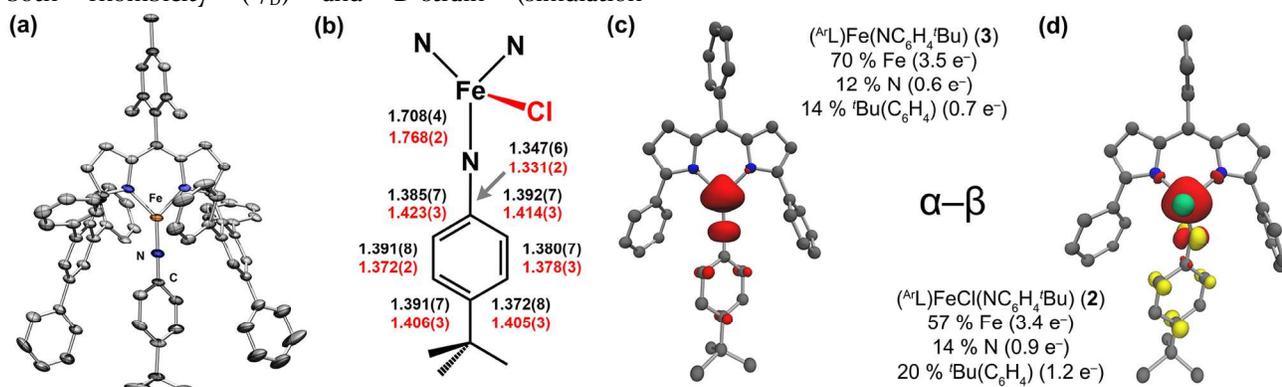
### 2.2 Synthesis and spectroscopic characterization of imido Fe(N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu) and iminyl FeCl(<sup>Ar</sup>N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu) pair

While oxidative group transfer to monovalent **4** can afford imido complexes with sterically encumbered alkyl and aryl azides,<sup>24</sup> no terminal imido complex could be obtained upon treatment of **2** with N<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu) and only the tetraazide adduct was obtained (<sup>Ar</sup>L)Fe(N<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)<sub>2</sub>) from net consumption of two equiv of azide.<sup>42</sup> Given the mild reduction potential for **2** (-1.10 V vs [Cp<sub>2</sub>Fe]<sup>+ / 0</sup>), chemical reduction was thus pursued as a means for generation of the terminal imido analogue. Accordingly, reduction of **2** with KC<sub>8</sub> in thawing benzene-*d*<sub>6</sub> resulted in the formation of a new paramagnetic complex via <sup>1</sup>H NMR. The molecular structure of three-coordinate iron imido (<sup>Ar</sup>L)Fe(N(C<sub>6</sub>H<sub>4</sub>-*p*-<sup>t</sup>Bu)) (**3**) was obtained by X-ray diffraction studies on single crystals grown from a concentrated toluene solution layered with pentane at -35 °C (Figure 2a). The molecular structure features a distorted trigonal planar iron(III) center supported by the dipyrin ligand and the aryl imido. The Fe–N<sub>3</sub> distance of 1.708(4) Å in **3** is longer than the iron imido bond in **5** (1.674(11) Å), and nearly identical to that found in the mesityl imido (<sup>Ar</sup>L)Fe(NMes) (1.708(2) Å), though far shorter than the corresponding distance in **2** (1.768(2) Å). The pertinent bond distances to compare **2** and **3** are presented in Figure 2b. Notably, all of the carbon-carbon bonds within the imide aryl ring in **3** are equivalent within error, indicating the aromaticity of the imido aryl framework has been restored from the iminyl **2** upon reduction.

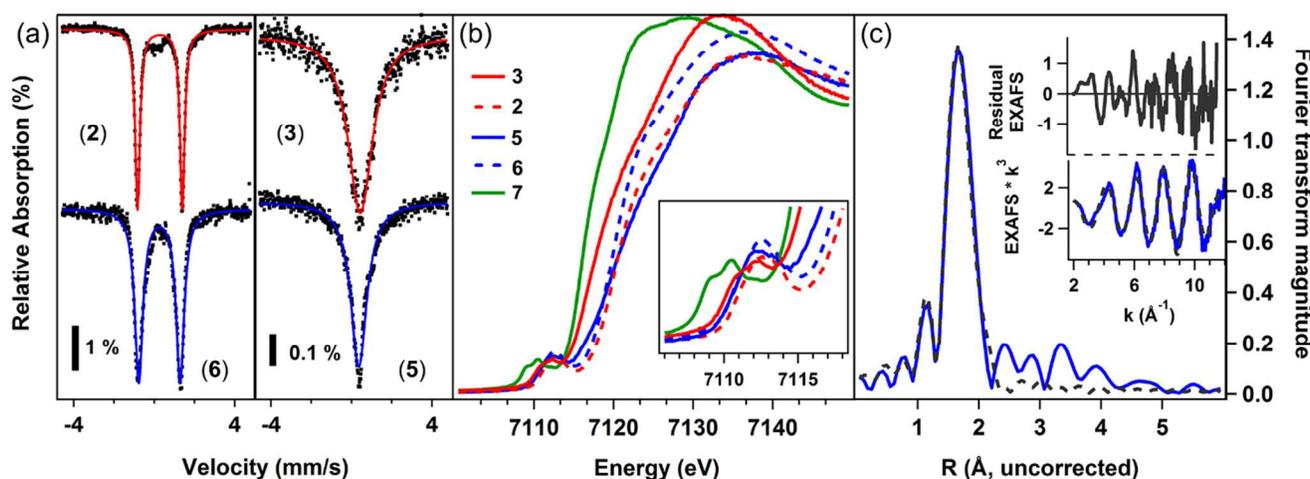
Further spectroscopic characterization of **3** affords data in line with that observed for the alkyl imido **5**.<sup>24</sup> Akin to **5**, complex **3** features a symmetric electric field gradient, displaying a zero-field <sup>57</sup>Fe Mössbauer spectrum with a single transition (δ: 0.44 mm/s, |ΔE<sub>Q</sub>|: 0.00 mm/s) at 200 K that becomes broad and weakly absorbing at lower temperature (Figure 3a). In accordance with the observed temperature dependent phenomena (*vide supra*), **3** does not exhibit an EPR signal above ca. 50 K. The frozen toluene EPR spectrum of **3** (2.8 K) displays a rhombic signal (g<sub>eff</sub> = 8.62, 5.35, 3.10), well reproduced by an S = 5/2 simulation treating each intra-doublet

transition as an effective  $S = 1/2$  system (in accordance with the weak-field limit) and including the effects of both rhombicity ( $E/D$ ) and  $D$ -strain (simulation

parameters:  $g = 2.0$ ,  $|E/D| = 0.05$ , linewidth = 15 G). The inclusion of  $D$ -strain is necessary to



**Figure 2.** (a) Solid state molecular structure of **3** with thermal ellipsoids at the 35% probability level. Positional disorder, solvent molecules, and H atoms are removed for clarity. Color scheme: Fe, orange; N, blue; C, gray. (b) Selected bond metrics (Å) for iminyl **2** in red and imido **3** in black. Mulliken spin density plots ( $\alpha-\beta$ ) and values calculated for **3** (c) and **2** (d).



**Figure 3.** (a) Zero-field  $^{57}\text{Fe}$  Mössbauer spectra [δ, |ΔE<sub>Q</sub>|, Γ (mm/s)] of iminyl **2** (top left, red trace: 0.28, 2.22, 0.14), iminyl **6** (bottom left, blue trace: 0.26, 2.05, 0.24); imido **3** (top right, red trace: 0.44, 0.00, 0.74), and imido **5** (bottom right, blue trace: 0.37, 0.00, 0.50). (b) Overlaid Fe K-edge XANES with inset Fe 3d pre-edge features for **3** (solid red), **2** (dashed red), **5** (solid blue), **6** (dashed blue), **7** (solid green). (c) EXAFS for **6** with data shown in blue and theoretical fit in black dashes.

account for the randomness in spatial conformation of the frozen solution and provide an effective powder pattern for a given  $S$  and  $E/D$ .<sup>43</sup> The data and corresponding simulation are shown in Figure S5. Accordingly, solid-state magnetometry of **3** is consistent with a high spin state as evidenced by a  $\mu_{\text{eff}}$  of  $4.6 \mu_{\text{B}}$  ( $\chi_{\text{M}}T = 4.76 \text{ cm}^3 \text{ K/mol}$ ) at 295 K (Figure S4). The value of  $\chi_{\text{M}}T$  over the temperature range surveyed is consistent with an  $S = 5/2$  configuration (spin-only value anticipated is  $4.38 \text{ cm}^3 \text{ K/mol}$ ). The spin state suggested by the magnetic susceptibility data is further corroborated by variable-temperature, variable-field magnetization data collected on heating from 1.8 to 10 K and at increasing fields of 1–7 T (Figure S4 inset). Magnetization saturation occurs at  $3.5 \mu_{\text{B}}$  at 1.8 K and 7 T. The lower than expected saturation ( $5 \mu_{\text{B}}$  for an ideal  $S = 5/2$  with  $g = 2$ ) and the observation of non-superimposable isofield curves indicate the presence

of zero-field splitting and rhombicity, which was quantified by fitting the data to the spin Hamiltonian  $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g_{\text{iso}}\mu_{\text{B}} \mathbf{S} \cdot \mathbf{H}$ . The fit parameters considering an  $S = 5/2$  system that best reproduce the data are  $g = 2.00$ ,  $D = 13.4.0 \text{ cm}^{-1}$ ,  $|E/D| = 0.29$ .<sup>44</sup>

The original spin-state assignment for iminyl **2** was based on room temperature, solution magnetic moment determination.<sup>26</sup> Thus, we sought to probe the ground spin state electronic structure for this molecule to corroborate the quintet assignment. Solid-state magnetometry was collected on a sample of **2**, cleanly isolated following removal of H-atom sources via treatment of reaction glassware with trimethylsilylchloride, use of perdeuterated solvents, and immediate purification of azide prior to synthesis. The magnetic susceptibility reveals a well-isolated ground state with no thermal transitions apparent between 50 K

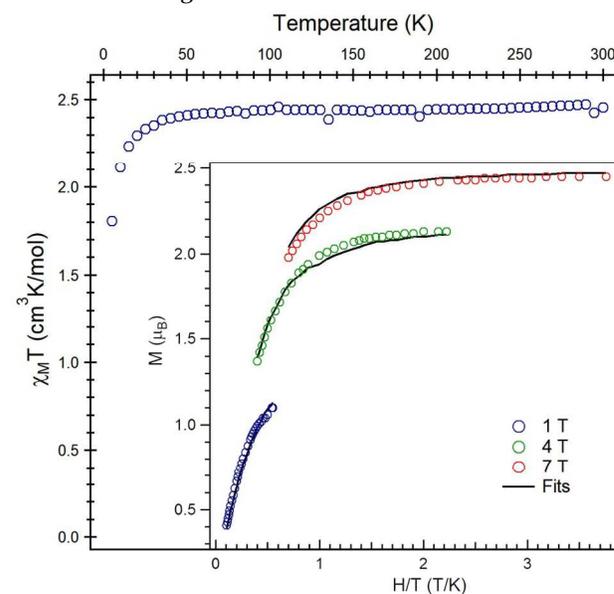
and 300 K. Both the room temperature effective magnetic moment of  $5.1 \mu_B$  ( $\chi_M T = 3.6 \text{ cm}^3 \text{ K/mol}$ ) and reduced magnetization data can be well modeled as an  $S = 2$  spin system (Figure S1). The spin state suggested by the magnetic susceptibility data is further corroborated by variable-temperature, variable-field magnetization data collected on heating from 1.8 to 10 K and at increasing fields of 1 to 7 T (Figure S1 inset). Magnetization saturation occurs at  $3.5 \mu_B$  at 1.8 K and 7 T. The lower than expected saturation ( $4 \mu_B$  for an ideal  $S = 2$  with  $g = 2$ ) and the observation of non-superimposable isofield curves indicate the presence of zero-field splitting and rhombicity, which was quantified by fitting the data to the spin Hamiltonian  $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g_{\text{iso}}\mu_B \mathbf{S} \cdot \mathbf{H}$ . The fit parameters considering an  $S = 2$  system that best reproduce the data are  $g = 2.12$ ,  $D = -8.8 \text{ cm}^{-1}$ ,  $|E/D| = 0.33$ .<sup>44</sup> As noted above, the magnetic susceptibility for **2** plateaus between 50 K and 300 K without variation in the susceptibility. Thus, the strength of the antiferromagnetic coupling between the ferric site ( $S_{\text{Fe}} = 5/2$ ) and iminyl moiety must exceed ca.  $200 \text{ cm}^{-1}$ , in line with the value predicted via DFT methods<sup>45</sup> and supporting a broken-symmetry electronic structure of **2** ( $J_{\text{calc}} = -673 \text{ cm}^{-1}$ ).<sup>26</sup>

For the iminyl/imido pair of **2** and **3**, respectively, the data collectively support an assignment of **2** as a high-spin  $\text{Fe}^{\text{III}}$  center antiferromagnetically coupled to an iminyl centered radical. Upon reduction of **2**, the added electron populates an orbital that is principally imide-based to restore aromaticity to the imide aryl  $\pi$ -system, maintaining the ferric oxidation state. The unusual stability of the ferric iminyl state can potentially be attributed to the resonance stabilization afforded via  $\pi$ -delocalization within the iminyl aryl unit. To gain insight into the location of the redox, single-point DFT<sup>45</sup> calculations on the iminyl **2** and imido **3** complexes were performed. The calculated spin density plots ( $\alpha - \beta$ ) for **2** and **3**, shown in Figure 2c-d, illustrate the contributions to the total spin contributed by iron (**2**: 57%; **3**: 70%) and the imido unit (**2**: 34%; **3**: 26%). The total spin localization within the imido aryl substituent in **3** is equal to the spin contribution from the imido N (12% N, 14% Ar), but increases upon oxidation to the iminyl **2** (14% N, 20% Ar). Based on these findings, the aryl component of the imido/iminyl fragment can play a critical role in spin delocalization, though it was as of yet unclear if an alkyl iminyl complex could adopt a similar electronic configuration to **2** without a means for stabilizing the  $N$ -centered radical.

### 2.3 Synthesis and spectroscopic characterization of an alkyl iminyl ( $^{\text{Ar}}\text{L}$ )FeCl( $^{\text{NAd}}$ )

To synthesize the alkyl iminyl analogue of **2**, a solution of chlorotriphenylmethane was added to a solution of imido **5** in thawing benzene- $d_6$  and allowed to stir for 1 h at room temperature. After 1 h elapsed and the reaction solution changed in color from pink to maroon, assessment of the reaction progress by  $^1\text{H}$  NMR revealed consumption of **5** with concomitant formation of a new paramagnetic species and  $\text{Ph}_3\text{C}(\text{C}_6\text{H}_5)\text{CPh}_2$ . The reaction volatiles were removed *in vacuo* and the resultant

precipitate was washed with pentane. Dissolution of the maroon solids in benzene followed by lyophilization yielded a maroon powder (80% yield). The zero-field  $^{57}\text{Fe}$  Mössbauer spectrum of the new material displayed a clean quadrupole doublet ( $\delta$ : 0.26 mm/s,  $|\Delta E_Q|$ : 2.05 mm/s) with parameters very similar to those observed for **2** ( $\delta$ : 0.28 mm/s,  $|\Delta E_Q|$ : 2.22 mm/s) (Figure 3a). The similar Mössbauer spectra suggest a common iron oxidation state, spin state, and geometric configuration between **2** and the oxidation product of **5**, leading us to formulate the product as ( $^{\text{Ar}}\text{L}$ )FeCl( $^{\text{NAd}}$ ) (**6**). The magnetic susceptibility of **6** is shown in Figure 4, revealing a  $\mu_{\text{eff}}$  of  $4.4 \mu_B$  at 295 K ( $\chi_M T = 2.46 \text{ cm}^3 \text{ K/mol}$ ) consistent with an  $S = 2$  ground state electronic configuration. The spin state suggested by the magnetic susceptibility data is further corroborated by variable-temperature, variable-field magnetization data collected on heating from 1.8 to 10 K and at increasing fields of 1–7 T (Figure 4, inset). Magnetization saturation occurs at  $2.6 \mu_B$  at 1.8 K and 7 T. The lower than expected saturation ( $4 \mu_B$  for an ideal  $S = 2$  with  $g = 2$ ) and the observation of non-superimposable isofield curves indicate the presence of zero-field splitting and rhombicity, which was quantified by fitting the data to the spin Hamiltonian  $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g_{\text{iso}}\mu_B \mathbf{S} \cdot \mathbf{H}$ . The fit parameters considering an  $S = 2$  system that best reproduce the data are  $g = 1.95$ ,  $D = 6.9 \text{ cm}^{-1}$ , and  $|E/D| = 0.33$ .<sup>44</sup> Thus, the data support a view of **6** as an  $\text{Fe}^{\text{III}}$  iminyl complex even in the absence of an iminyl aromatic  $\pi$ -framework throughout which the nitrogen centered radical can delocalize.



**Figure 4.** Variable-temperature susceptibility data of ( $^{\text{Ar}}\text{L}$ )FeCl( $^{\text{NAd}}$ ) (**6**) collected at 1.0 T, with  $\chi_M T = 2.46 \text{ cm}^3 \text{ K/mol}$  at 295 K. (Inset) Reduced magnetization data collected at 3 fields (1, 4, 7 T) over the temperature range 1.8 K–10 K. Magnetization fit parameters obtained with PHI<sup>44</sup>:  $S = 2$ ,  $g = 1.95$ ,  $D = 6.9 \text{ cm}^{-1}$ ,  $|E/D| = 0.33$ .

#### 2.4.1 Extended X-ray absorption fine structure analysis of iminyl **6**

The reactive nature of **6** precluded obtaining suitable single crystals for X-ray diffraction analysis. Thus, XAS and EXAFS analysis on a benzene solution of **6** was undertaken. The Fourier transform of the EXAFS region of the XAS spectrum for **6** to  $k=10 \text{ \AA}^{-1}$  (resolution =  $0.15 \text{ \AA}$ ) is well-modeled via a first shell simulation considering two pyrrole nitrogens, one chloride, and one iminyl nitrogen scattering paths (Figure 3c). The values are shown in Table 1 and are nearly identical to the crystallographically determined bond lengths of **2** (Fe–N<sub>pyrrole</sub> 2.013(1) Å, 1.997(1) Å; Fe–Cl 2.20(1) Å; Fe–N<sub>iminyl</sub> 1.768(2) Å). The resolution of the data is sufficient to differentiate the N<sub>pyrrole</sub> and N<sub>iminyl</sub> scattering paths, although it is not sufficient to detect asymmetry in the individual Fe–N<sub>pyrrole</sub> scattering paths. The close structural similarity of **6** to **2** strongly suggests that oxidation of imido **5** occurs at the imido nitrogen, preserving the high-spin ferric electronic configuration at iron.

**Table 1.** EXAFS simulation of **6**<sup>a</sup>

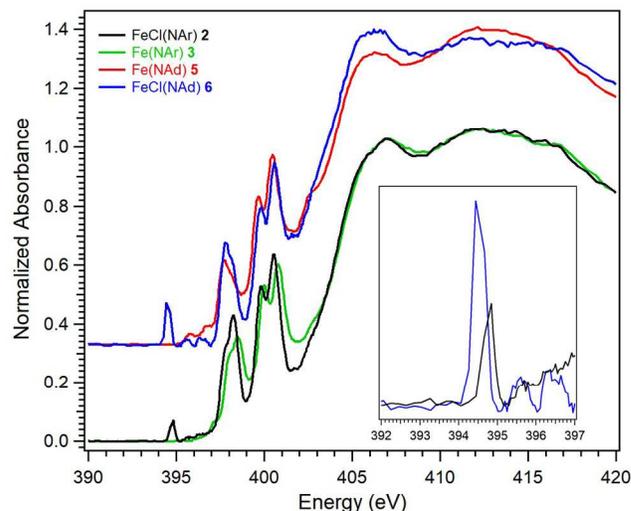
path	CN	R, Å	$\sigma^2$ , Å <sup>2</sup>	E <sub>0</sub>	F, %
Fe–N <sub>pyrrole</sub>	2	1.987(8)	0.0003(6)	-7.61	29.5
Fe–Cl	1	2.222(5)	0.0011(4)		
Fe–N <sub>iminyl</sub>	1	1.761(6)	0.0004(7)		

<sup>a</sup>EXAFS were fit in OPT using paths calculated by FEFF7. Coordination numbers (CN) were held constant while distances (R) and Debye-Waller factors ( $\sigma^2$ ) were allowed to float. Parenthetical values correspond to fitting errors in R and  $\sigma^2$  in the final significant digit. Errors in coordination number are estimated at 25%. Fits were performed over the entire (0 to 6.0 Å) Fourier transform window. Goodness of fit is measured by F, defined as  $[(\sum_i [k_i^3(\text{EXAFS}_{\text{obs}} - \text{EXAFS}_{\text{calc}})]^2 / n)]^{1/2}$ . Additional fitting details are included in the Supporting Information.

#### 2.4.2 Fe and N K-edge X-ray absorption near edge spectroscopy on imidos (**3**, **5**) and iminyls (**2**, **6**)

In light of the challenges associated with assignment of metal oxidation state in the presence of high-lying ligand-based molecular orbitals, samples of both imido/iminyll pairs (**3** and **2**; **5** and **6**) were investigated by X-ray absorption near edge spectroscopy and the results shown in Figure 3b. Note that, given the coordination number change as well as potential change in iron-imido/iminyll covalency, comparison of the rising edge energy will not unambiguously reflect the respective metal oxidation levels for the three-coordinate imido and four-coordinate iminyll complexes. Iron K-edge pre-edge absorption features are typically assigned to Fe 1s → 3d excitations, although in the present case appreciable ligand character can be expected in the acceptor molecular orbitals. Nevertheless, the maxima of the resolved pre-edge features demonstrate that upon reduction of iminyll **2** (711.5 eV) to imido **3** (711.5 eV), or oxidation of imido **5** (712.2 eV) to iminyll **6** (712.4 eV), very little change in Fe physical oxidation state is inferred.

For comparison, the energy-weighted maximum of the resolved pre-edge bands of the ferrous product of **1** and adamantyl amine, (<sup>Ar</sup>L)FeCl(NH<sub>2</sub>Ad) (**7**), is shifted to lower energy (710.3 eV), consistent with a more reduced iron center in this complex as compared to the other species studied. Comparing the aryl and alkyl imido/iminyll pairs, the pre-edge absorption features for the alkyl species (**5**, **6**) are shifted to higher energy relative to those of the aryl congeners (**3**, **2**). These shifts are 0.7 eV for the imido complexes and 0.9 eV for the iminyll complexes. These energy differences are nearly as great as the difference between the ferrous complex examined (**7**) and the ferric imidos (~1.2 eV).

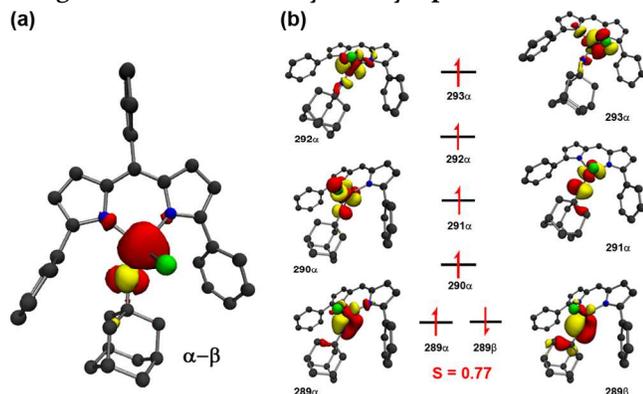


**Figure 5.** N K-edge XAS for imido (**3**, **5**) and iminyll (**2**, **6**) complexes; (Inset) N 1s → iminyll N 2p pre-edge features for **2** (black) and **6** (blue).

To provide further evidence for the iminyll radicals in **2** and **6**, the nitrogen orbital containing the iminyll was probed directly using nitrogen K-edge X-ray absorption spectroscopy. As seen in Figure 5, pre-edge features at 400.5 and 399.8 eV are observed for all species (**2**, **3**, **5**, and **6**) that can be assigned as transitions into high-lying antibonding molecular orbitals of N 2p parentage. Additional lower energy features present at 398.3 and 397.7 eV for the aryl (**3** and **2**) and alkyl (**5** and **6**) imido/iminyll pairs, respectively, represent transitions into the Fe 3d-based antibonding singly occupied molecular orbitals that are predicted to contain substantial mixing with N 2p orbitals (both dipyrroin and imido/iminyll N-donors). Most importantly, new pre-edge features found at lowest energy at 394.5 and 394.8 eV are observed exclusively in the iminyll species **6** and **2**, respectively. In a recently reported N K-edge XAS calibration and study of [(PNP)<sup>+</sup>Ni<sup>II</sup>Cl][OTf], a similar low energy pre-edge feature present upon oxidation from its neutral congener was identified.<sup>46</sup> This new pre-edge feature present at 396.4 eV was assigned, through collaboration with TDDFT calculations, as a transition from N 1s into the nitrogen localized aminyl-based SOMO on the PNP ligand framework. Hence, we assign the pre-edge features

observed here at 394.5 and 394.8 eV as transitions into the nitrogen-localized iminyl radicals present in **6** and **2**, respectively.

### 2.4.3 Electronic structure calculations corroborate assignment of **6** as an alkyl iminyl species



**Figure 6.** Calculated Mulliken spin density (a) and qualitative molecular orbital scheme (b) for **6**. Spin density is plotted at an isovalue of 0.009 au. Molecular orbitals are plotted at isovalues of 0.04 au.

A geometry optimization<sup>45</sup> of **6** was carried out to produce coordinates from which to carry out electronic structure calculations. The complete structure of **6** including full aryl substituents was optimized using the BP86<sup>47-48</sup> functional with the segmented all-electron relativistically contracted (SARC) Ahlrich's def2-TZVP-ZORA basis set.<sup>49-50</sup> Optimization of **6** employed the broken symmetry (BS) approach, assuming partitioning between 5 Fe-based and 1 ligand-based spin (BS 5,1). The structure produced at this level of theory closely reproduces the experimental bond lengths, yielding the following primary coordination sphere interatomic distances: Fe–N<sub>pyrrole</sub> 2.002 Å, 1.981 Å; Fe–Cl 2.200 Å; Fe–N<sub>iminyl</sub> 1.707 Å (Figure 6a). These coordinates, along with optimized structures for **2**, **3**, **5**, and **7**, were used in B<sub>3</sub>LYP calculations of Mössbauer  $\delta^{51}$  values as well as time-dependent DFT (TDDFT) calculations of Fe K-edge XAS<sup>52</sup> pre-edge bands (Table 2, Figure S21). Calculated spectroscopic parameters accord strongly with experiment – after calibration with the remaining compounds in the test set (Figures S22, S23), the value of  $\delta$  for **6** is matched by theory, and the error in the  $1s \rightarrow 3d$  excitation is 0.1 eV.

**Table 2. Experimental and Calculated Spectroscopic Parameters**

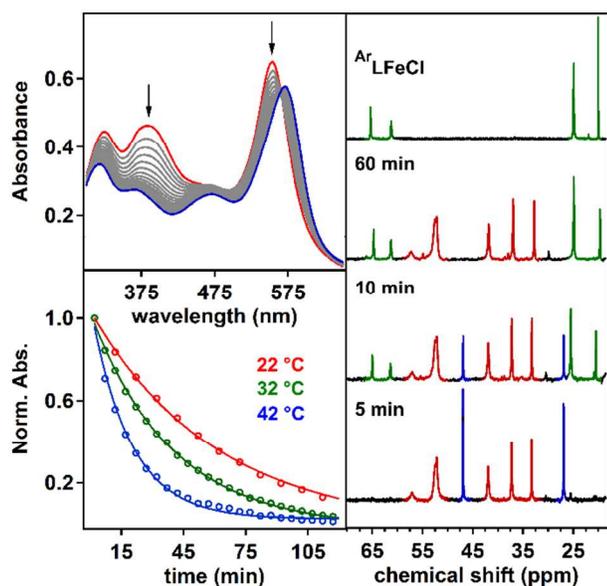
Complex	$\delta$ (Exp), mm·s <sup>-1</sup>	$\delta$ (Calc) <sup>a</sup> , mm·s <sup>-1</sup>	Pre-edge (Exp), eV	Pre-edge (Calc) <sup>b</sup> , eV
<b>2</b>	0.28	0.23	7111.5	7111.7
<b>3</b>	0.44	0.44	7111.5	7111.6
<b>5</b>	0.37	0.42	7112.2	7112.0
<b>6</b>	0.26	0.26	7112.4	7112.5

7            0.91            0.90            7110.3            7110.3  
<sup>a</sup>DFT: B<sub>3</sub>LYP,<sup>53</sup> CP(PPP)<sup>51</sup> on Fe, def2-TZVP-ZORA<sup>49-50, 54-56</sup> on all other atoms. <sup>b</sup>TDDFT: B<sub>3</sub>LYP, CP(PPP) on Fe, def2-TZVP-ZORA on all other atoms.

Accord between calculated and experimental geometric and electronic structural parameters further supports assignment of **6** as a stable alkyl analogue of iminyl **2**. Electronic structure calculations support preservation of a high-spin d<sup>5</sup> Fe<sup>III</sup> that is strongly antiferromagnetically coupled to AdN<sup>•</sup> (calculated  $J = -2204$  cm<sup>-1</sup>) (Figure 6b).<sup>57-58</sup> Moreover, comparison of the orbital mixing coefficients (UCOs) in the calculated unrestricted corresponding orbitals for iminyl species **2** and **6** that is localized to the N-centered  $\beta$  SOMO of the antiferromagnetically-coupled pair reveals a ratio of 1.91 (62.3% in **6** vs. 32.6% in **2**). This ratio corresponds well to the experimental 2.02 (0.141 in **6** vs. 0.071 in **2**) ratio of intensities of the iminyl pre-edge features found in the N K-edge XAS.

### 2.5 Comparative kinetic analysis for the imido/iminyl complexes undergoing C–H bond activation with toluene

The isolation of iron imido/iminyl redox pairs provides a unique opportunity to investigate the effect of altering the valence of the transferred atom during a C–H functionalization reaction without affecting the transition metal oxidation state. Dissolution of iminyl complexes **2** or **6** in toluene results in immediate reaction, as demonstrated by the change in UV/Vis absorption over time (Figure 7). The change in absorbance at  $\lambda_{\max}$  was fit as an exponential decay and the resulting observed rate constant is shown in Table 3. In contrast, the UV/Vis spectrum of the imido complexes **3** or **5** in toluene is identical to that observed in benzene and does not change over the course of four hours at room temperature. In fact, a similar rate of reaction to those exhibited by the iminyl species is not achieved until the solution is heated to 80 °C, indicating a substantially higher barrier towards reactivity with toluene for the imidos **3** and **5**. Assuming a simple kinetic profile wherein the change in absorbance at  $\lambda_{\max}$  is directly related to the consumption of starting material (imido or iminyl) and the reaction course is not significantly altered by temperature, the activation energy can be extracted from these data for each complex and is presented in Table 3.



**Figure 7.** (Top left) UV/Vis traces of the reaction of **2** with toluene at 22 °C with spectra recorded every 10 minutes for 4 hours. (Bottom left) Normalized absorbance at  $\lambda_{max}$  (554 nm) during the course of the reaction at various temperatures. (Right) <sup>1</sup>H NMR spectra progression of a toluene solution of equimolar imido **5** and iminyl **6** at 60 °C at the time elapsed indicated. Chemical shifts corresponding to **5** are highlighted in red, **6** in blue, and (<sup>Ar</sup>L)FeCl (**1**) in green.

Upon oxidation of the nitrogen atom from the imide to the iminyl state, the barrier for reaction with toluene decreased by an average of 3.7 kcal/mol. The additional radical density present on the nitrogen atom can account for the enhancement of reactivity, more closely resembling the electronic structure at the transition state for hydrogen atom abstraction. This simple Hammond-type analysis is in line with the higher activation energy for the aryl imido and iminyl complexes **3** and **2**, respectively, which feature electron delocalization through the aromatic fragment as opposed to the localized spin density at the transferring nitrogen atom of **5** and **6**. Alternatively, the higher molecular oxidation state may also contribute to the increase in reactivity via a Bell-Evans'-Polanyi-type correlation,<sup>59</sup> wherein the rate enhancement upon oxidation is attributable to the increased driving force of the reaction as a result of a higher oxidation potential or enhanced N-H bond strength of the metal-amide product. Regardless, the activation parameters for reaction of these iron imide complexes with toluene demonstrate a higher enthalpic barrier upon reduction or upon substitution with an aromatic imide substituent, suggesting that both a higher metal-imide bond order and delocalization through the aromatic  $\pi$ -system stabilize the iron imide with respect to hydrogen atom abstraction.

**Table 3. Rate constants, half-lives, and activation energies for reaction of iron complexes with toluene<sup>a</sup>.**

Complex	T (°C)	k (s <sup>-1</sup> )	t <sub>1/2</sub> (min)	E <sub>a</sub> (kcal/mol)
---------	--------	----------------------	------------------------	---------------------------

<b>5</b>	80	0.0264	26	11.5
	90	0.0427	16	
	100	0.0633	11	
<b>3</b>	80	0.0195	36	12.1
	90	0.0343	20	
	100	0.0745	9	
<b>6</b>	22	0.0299	23	7.1
	32	0.0433	16	
	42	0.0722	10	
	42	0.0528	13	
<b>2</b>	22	0.0166	42	9.2
	32	0.0256	27	
	42	0.0528	13	

<sup>a</sup>Exponential decay of  $\Delta(\lambda_{max})$  versus time was fit independently at each temperature.

Comparison of the independent rates of reaction for **5** and **6** suggests that a rate enhancement of two orders of magnitude occurs upon oxidation. Indeed, heating an equimolar ratio of **5** and **6** to 60 °C in toluene results in selective consumption of the iminyl complex **6** and formation of a new set of paramagnetic resonances via <sup>1</sup>H NMR (Figure 7). The appearance of these chemical shifts can be attributed to the formation of (<sup>Ar</sup>L)FeCl (**1**) and occurs concomitantly with a peak at 3.72 ppm corresponding to *N*-benzyl-adamantylamine. The competition experiment validates the independent rate studies and demonstrates that the iminyl complex **6** is significantly more reactive towards C-H bonds than its imido congener **5**. The increased reactivity of **6** is not limited to C-H amination: imido **5** is stable in neat styrene up to 100 °C, whereas iminyl **6** reacts smoothly with 200 equiv. styrene at room temperature to yield the desired aziridine in 36% yield. Further, hydrogen atom abstraction from cyclohexene occurs at room temperature with iminyl **6** to produce the H<sub>2</sub>NAd adduct (<sup>Ar</sup>L)FeCl(H<sub>2</sub>NAd) (**7**) quantitatively, whereas the imido congener **5** requires heating to 80 °C and arrests at formation of the amide adduct (<sup>Ar</sup>L)Fe(HNAd).<sup>24</sup>

## 2.6. Reaction pathways and thermodynamic considerations

### 2.6.1 Frontier molecular orbital considerations

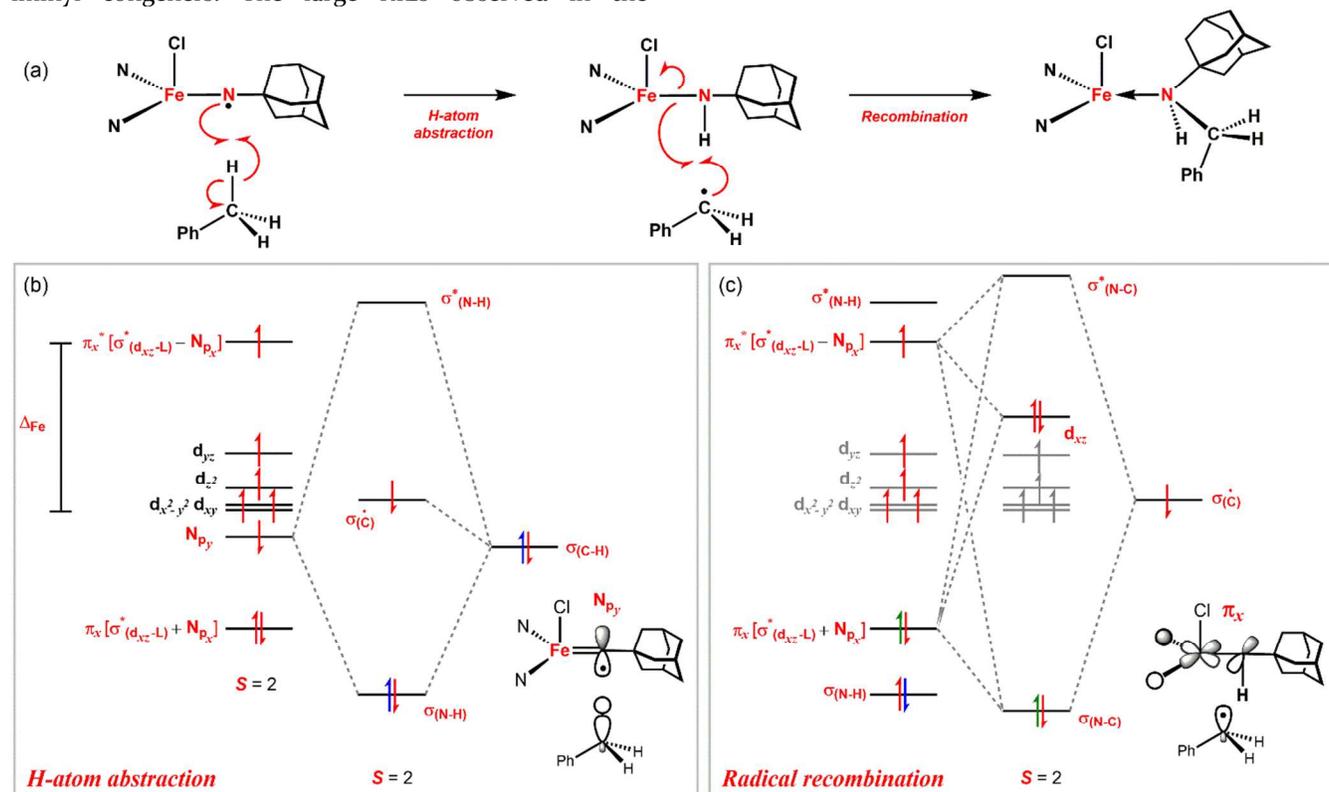
The electronic structure of the imido and iminyl differ in the extent to which both *N* 2p orbitals engage in  $\pi$ -bonding with iron orbitals of appropriate symmetry. The imido complexes feature nearly linear Fe-N-C bond linkages, signifying maximal, though non-degenerate,  $\pi$  interactions:  $\pi_x$  [ $\sigma_{(dxz - L\sigma)} \pm Np_x$ ] which includes a Fe-L<sub>dipyrrin</sub>  $\sigma^*$  component, and the orthogonal  $\pi_y$  (Fe  $d_{yz} \pm Np_y$ ). The high-spin imido complexes give rise to a  $(\pi_x)^2(\pi_y)^2(\pi_y^*)(\pi_x^*)$  configuration. The iminyl complexes, however, lack conjugation of the two  $\pi$  manifolds. Indeed, a simple description for the iminyl consistent with the iron oxidation levels observed by <sup>57</sup>Fe Mössbauer and XAS, consists of only the  $\pi_x$  interaction, leaving a largely *N*-centered radical for **6**. While the iminyl radical lacks the enhanced stabilization afforded by delocalization in

the aromatic ring of **2**, the radical is nonetheless stabilized by coupling antiferromagnetically to the five iron  $\alpha$  spins (see Figure 6). This electronic configuration manifests in the larger Fe–N bond lengths observed, as well as the enhanced reactivity of the iminyl with respect to the imido congener.

We have previously proposed a reaction sequence for intermolecular amination using imido **5**. We can amend that orbital description to describe qualitatively the reactivity differences observed between the imido and iminyl congeners. The large KIEs observed in the

reactions of both imido (**3**, **5**) and iminyls (**2**, **6**) with toluene suggest that the C–H bond breaking event contributes significantly to the rate limiting step of the reaction sequence illustrated for **6** in Figure 8a.

A consideration of the frontier molecular orbitals (FMOs) that complete this process include the Fe–N  $\pi$  interaction ( $\pi_x$ ), the N  $2p_y$  orbital containing the iminyl radical, and the toluene C–H  $\sigma$  bond (Figure 8b). The N-radical ( $2p_y$ )<sup>1</sup> dictates the primary orbital interaction with the incoming toluene C–H substrate given its steric



**Figure 8.** Frontier molecular orbital description of (<sup>ArL</sup>)FeCl(NAd) (**6**) reaction profile (a) for H-atom abstraction from PhCH<sub>3</sub> (b) and the subsequent radical rebound event (c).

accessibility and more favorable energetic overlap. Thus the frontier orbital interaction with respect to the iron-iminyl is lower in energy than the analogous imido amination reaction which proceeds from the ( $\pi_y$ )<sup>1</sup> orbital.

The H-atom abstraction step is highlighted in Figure 8b, where the homolyzed C–H orbital (yielding PhC<sup>•</sup>H<sub>2</sub> and H is) combine with N  $2p_y$  to yield three orbital combinations: ( $\sigma_{N-H}$ )<sup>2</sup> (C<sup>•</sup>H<sub>2</sub>Ph)<sup>1</sup>( $\sigma_{N-H}^*$ )<sup>0</sup>. Unlike the imido amination sequence where H-atom abstraction leads to metal reduction, the H-atom abstraction step for the iminyl is completely N-centered, leaving the iron oxidation level unchanged. The H-atom abstraction step conserves total spin-angular momentum as the resulting radical pair complex remains in a quintet spin configuration. The recombination step (Figure 8c) should proceed combining the benzylic radical with the remaining  $\pi_x$  [ $\sigma_{(dxz-L)}^* \pm Np_x$ ] pair yielding three product orbitals: ( $\sigma_{N-C}$ )<sup>2</sup>(Fe  $3d_{xz}$ )<sup>2</sup>( $\sigma_{N-C}^*$ )<sup>0</sup>, constituting a net reduction of the iron center, yet again conserving the total spin-angular momentum for the entire reaction

sequence.

That the iminyl complexes will activate the C–H bonds of toluene at lower temperatures than their respective imido congeners is a direct result of the diminished Fe–N bond order. Thus, the oxidizing orbital (N  $2p_y$ )<sup>1</sup> is lower in energy than the corresponding imido reaction partner ( $\pi_y$ ), leading to a better energetic overlap between H-atom donor and acceptor orbitals. Furthermore, the entire amination sequence for the iminyls conserves the total spin angular momentum while the imido complexes must change their electronic configurations ( $S = 5/2 \rightarrow S = 3/2$ ) concomitantly with iron reduction.

The presence of metal-stabilized iminyl radicals have now been observed<sup>9, 36</sup> or implicated in H-atom abstraction reactivity<sup>12-13, 21, 37</sup> and nitrene transfer catalysis<sup>7-8, 10-11, 60-61</sup> in a number of systems.<sup>15</sup> The supporting organic moiety on the bound nitrene can promote stabilization via hetero-atom donation, akin to Fischer-type carbene ligands,<sup>10-11</sup> or promote reactivity by

concentration of radical density on the iminyl *N*-atom as is the case in **6**.

### 2.6.2 Thermodynamic Considerations

In considering a stepwise mechanism for C–H amination, the initial hydrogen atom abstraction from substrate can be represented via a thermodynamic square scheme that partitions the driving force of the reaction into the constituent proton and electron transfer contributions, as shown in equation 1:

$$\Delta G_{\text{HAT}} \text{ (kcal/mol)} = 23.06 E^{\circ} + 1.37 \text{ p}K_{\text{a}} + 59.5 \text{ (eq 1)}$$

where the final constant represents the standard potential for proton reduction in aprotic solvent.<sup>62</sup> Electrochemical analysis of **2** revealed a quasi-reversible reduction potential of  $-1.05$  V versus  $[\text{Cp}_2\text{Fe}]^{+/0}$ . Given this reduction potential, the productive activation of toluene (C–H BDE:  $90$  kcal/mol)<sup>63</sup> by **2** would require a  $\text{p}K_{\text{a}}$  of  $40$  in the resulting  $(^{\text{ArL}}\text{FeCl}(\text{NH}(\text{C}_6\text{H}_4\text{-}i\text{Pr}))$  complex. This estimation is in line with both the experimentally determined  $\text{p}K_{\text{a}}$  of Smith's iron(III)–amide ( $\text{p}K_{\text{a}} = 37(3)$ )<sup>27</sup> and the calculated  $\text{p}K_{\text{a}}$  of Borovik's manganese(II)–hydroxide ( $\text{p}K_{\text{a}} \geq 36$ ) complexes,<sup>64</sup> as well as others. The higher calculated  $\text{p}K_{\text{a}}$  value for **2** as compared to Smith's cationic tris(carbeno)borate-supported iron(IV) imide can be rationalized via the difference in overall charge between these molecules, and permits the activation of the stronger C–H bond of toluene.

The ability of **6** to functionalize toluene allows a rough estimation of the Fe=N bond strength via equation 2:

$$\Delta H^{\circ}_{(\text{Fe}=\text{N})} = \Delta H^{\circ}_{(\text{N}-\text{H})} + \Delta H^{\circ}_{(\text{C}-\text{N})} - \Delta H^{\circ}_{(\text{C}-\text{H})} - 2 * 23.06 E^{\circ} \text{ (eq 2)}$$

where  $E^{\circ}$  is the standard reduction potential of **6**. Although the appropriate bond dissociation energies have not been determined for *N*-benzyl-adamantyl amine, experimental values for *N*-methyl-benzyl amine are readily available<sup>65</sup> and provide an Fe–N bond strength of approximately  $94$  kcal/mol. This value is similar to the experimentally determined  $\Delta H^{\circ}_{(\text{Fe}=\text{O})}$  range of Nocera's pacman iron(IV) oxo porphyrin system of  $65$ – $85$  kcal/mol which can promote two-electron oxidation of substrate, but not C–H hydroxylation chemistry.<sup>65</sup>

A comparison of the activation energies for the imide/iminyll pairs demonstrated a lower barrier for reaction with toluene at the iminyll state. A Bell-Evans-Polanyi correlation between the rate of reaction and thermodynamic driving force would suggest that hydrogen atom transfer is therefore less favorable at the lower valent state. The higher Fe–N bond order, coupled with the absence of electrochemical reduction of **5** under experimental conditions (to  $-2.3$  V versus  $[\text{Cp}_2\text{Fe}]^{+/0}$ ), indicate that the overall functionalization process is likewise less favorable at the imide state. These data support that the enhancement of reactivity at the iminyll state is both kinetic and thermodynamic in nature, due to the higher radical density present at the *N*-atom and weaker iron–nitrogen interaction via the broken

symmetry electronic structure, respectively.

### 2.5 Conclusions

We have previously demonstrated that the (dipyrrin)iron platform is capable of stabilizing both high-spin ferric imido species, as well as the highly unusual ferric iminyll complex which features a high-spin iron center antiferromagnetically coupled to the iminyll radical. Both of the high-spin complexes are capable of effecting nitrene transfer to C–H bonds and olefinic substrates. The foregoing results demonstrate that the imido/iminyll redox isomers are chemically interchangeable. Furthermore, the elusive alkyl iminyll intermediate  $(^{\text{ArL}}\text{FeCl}(\text{NAd}))$ , implicated in both inter- and intramolecular C–H bond functionalization catalytic processes, was isolated and spectroscopically characterized. Comparison of the Mössbauer spectroscopy, magnetometry, and bond lengths of the alkyl iminyll complex with the aryl iminyll congener revealed striking similarities, suggesting a common electronic structure and indicating the nitrene aryl component is not necessary to stabilize the iminyll oxidation level via radical delocalization. Furthermore, oxidation of the imido complexes to their iminyll redox isomers largely localizes the oxidation event to the NR fragment. The iminyll complexes feature N K-edge pre-edge absorptions found to be characteristic for these N radical based ligands, arising from N  $1s$  promotion into a singly occupied N  $2p$  iminyll orbital. Lastly, having access to both alkyl and aryl NR redox isomers, we were able to assess how the change in molecular oxidation level manifests in changes to C–H bond amination efficacy. Oxidation of the imido complexes to their iminyll redox isomer results in a rate enhancement of two orders in magnitude. The rate enhancement is largely enthalpic (entropic barriers are nearly equal). The ability of the imido or iminyll component to delocalize the spin-density throughout an aryl substituent also results in a greater barrier towards functional group transfer. We infer this latter to mean that concentration of radical density upon the transferring group can play a large role in C–H bond functionalization processes.

### Associated Content

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. X-ray crystal structure images; magnetic data; cyclic voltammograms; X-ray absorption spectra; Mössbauer, UV-vis, and  $^1\text{H}$  NMR spectra (PDF). Crystallographic data (CIF).

### Author Information

#### Corresponding Author

\*betley@chemistry.harvard.edu

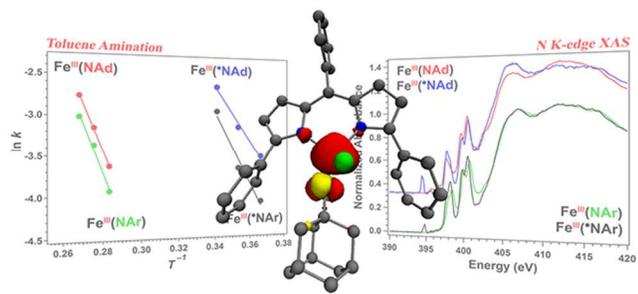
### Acknowledgments

1 T.A.B. gratefully acknowledges support by grants from the  
2 NSF (CHE-0955885) and NIH (GM-115815), and from  
3 Harvard University. M.W. would like to thank the NSF for  
4 a Predoctoral Graduate Fellowship. K.M.L. gratefully  
5 acknowledges support from the NSF in the form of a  
6 CAREER award (CHE-1454455) and from the ACS  
7 Petroleum Research Fund (55181-DNI6). This work is  
8 based in part on research conducted at the Stanford  
9 Synchrotron Radiation Lightsource (SSRL), which is  
10 supported by the U.S. Department of Energy, Office of  
11 Science, Office of Basic Energy Sciences under Contract  
12 No. DE-AC02-76SF00515. The SSRL Structural Molecular  
13 Biology Program is supported by the Department of  
14 Energy's Office of Biological and Environmental Research,  
15 and by NIH/HIGMS (including P41GM103393). The  
16 content of this publication is solely the responsibility of  
17 the authors and does not necessarily represent the official  
18 views of NIGMS or NIH.

## References

- (1) Nugent, W. A.; Mayer, J. M., *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, or Alkylidyne Ligands*. Wiley-Interscience: New York, 1988.
- (2) Saouma, C. T.; Peters, J. C. *Coord. Chem. Rev.* **2011**, *255*, 920.
- (3) Berry, J. F. *Comments Inorg. Chem.* **2009**, *30*, 28.
- (4) Zhang, L.; Deng, L. *Chin. Sci. Bull.* **2012**, *57*, 2352.
- (5) Bess, E. N.; Deluca, R. J.; Tindall, D. J.; Oderinde, M. S.; Roizen, J. L.; Du Bois, J.; Sigman, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 5783.
- (6) Liu, W.; Groves, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 12847.
- (7) Bagh, B.; Broere, D. L. J.; Sinha, V.; Kuijpers, P. F.; van Leest, N. P.; de Bruin, B.; Demeshko, S.; Siegler, M. A.; van der Vlugt, J. I. *J. Am. Chem. Soc.* **2017**, *139*, 5117.
- (8) Fujita, D.; Sugimoto, H.; Shiota, Y.; Morimoto, Y.; Yoshizawa, K.; Itoh, S. *Chem. Commun.* **2017**, *53*, 4849.
- (9) Goswami, M.; Lyaskovskyy, V.; Domingos, S. R.; Buma, W. J.; Woutersen, S.; Troepfner, O.; Ivanović-Burmazović, I.; Lu, H.; Cui, X.; Zhang, X. P.; Reijerse, E. J.; DeBeer, S.; van Schooneveld, M. M.; Pfaff, F. F.; Ray, K.; de Bruin, B. *J. Am. Chem. Soc.* **2015**, *137*, 5468.
- (10) Kuijpers, P. F.; Tiekink, M. J.; Breukelaar, W. B.; Broere, D. L. J.; Van Leest, N. P.; van der Vlugt, J. I.; Reek, J. N. H.; De Bruin, B. *Chem. Eur. J.* **2017**, *23*, 7945.
- (11) Kuijpers, P. F.; van der Vlugt, J. I.; Schneider, S.; De Bruin, B. *Chem. Eur. J.* **2017**, DOI: 10.1002/chem.201702537.
- (12) Spasyuk, D. M.; Carpenter, S. H.; Kefalidis, C. E.; Piers, W. E.; Neidig, M. L.; Maron, L. *Chem. Sci.* **2016**, *7*, 5939.
- (13) Zhou, W.; Patrick, B. O.; Smith, K. M. *Chem. Commun.* **2014**, *50*, 9958.
- (14) Prier, C. K.; Zhang, R. K.; Buller, A. R.; Brinkmann-Chen, S.; Arnold, F. H. *Nat. Chem.* **2017**, *9*, 629.
- (15) Olivos Suarez, A. I.; Lyaskovskyy, V.; Reek, J. N. H.; van der Vlugt, J. I.; De Bruin, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 12510.
- (16) Brown, S. D.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 1913.
- (17) Bart, S. C.; Lobkovsky, E.; Bill, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 5302.
- (18) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782.
- (19) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322.
- (20) Cowley, R. E.; DeYonker, N. J.; Eckert, N. A.; Cundari, T. R.; DeBeer, S.; Bill, E.; Ottenwaelder, X.; Flaschenriem, C.; Holland, P. L. *Inorg. Chem.* **2010**, *49*, 6172.
- (21) Cowley, R. E.; Holland, P. L. *Inorg. Chem.* **2012**, *51*, 8352.
- (22) Lu, C. C.; Saouma, C. T.; Day, M. W.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 4.
- (23) Scepaniak, J. J.; Young, J. A.; Bontchev, R. P.; Smith, J. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3158.
- (24) Wilding, M. J. T.; Iovan, D. A.; Betley, T. A. *J. Am. Chem. Soc.* **2017**, *139*, 12043.
- (25) Iovan, D. A.; Betley, T. A. *J. Am. Chem. Soc.* **2016**, *138*, 1983.
- (26) King, E. R.; Hennessy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917.
- (27) Nieto, I.; Ding, R.; Bontchev, R. P.; Wang, H.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2716.
- (28) Searles, K.; Fortier, S.; Khusniyarov, M. M.; Carroll, P. J.; Sutter, J.; Meyer, K.; Mindiola, D. J.; Caulton, K. G. *Angew. Chem. Int. Ed.* **2014**, *53*, 14139.
- (29) Thomas, C. M.; Mankad, N. P.; Peters, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 4956.
- (30) Verma, A. K.; Nazif, T. N.; Achim, C.; Lee, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 11013.
- (31) Wang, L.; Hu, L.; Zhang, H.; Chen, H.; Deng, L. *J. Am. Chem. Soc.* **2015**, *137*, 14196.
- (32) Ni, C.; Fettinger, J. C.; Long, G. J.; Brynda, M.; Power, P. P. *Chem. Commun.* **2008**, 6045.
- (33) Hong, S.; Sutherlin, K. D.; Vardhaman, A. K.; Yan, J. J.; Park, S.; Lee, Y.-M.; Jang, S.; Lu, X.; Ohta, T.; Ogura, T.; Solomon, E. I.; Nam, W. *J. Am. Chem. Soc.* **2017**, *139*, 8800.
- (34) Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 9961.
- (35) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248.
- (36) Lu, C. C.; De Beer George, S.; Weyhermüller, T.; Bill, E.; Bothe, E.; Wieghardt, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 6384.
- (37) Shay, D. T.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem. Int. Ed.* **2005**, *44*, 1508.
- (38) Hennessy, E. T.; Betley, T. A. *Science* **2013**, *340*.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
- (39) Hennessy, E. T.; Liu, R. Y.; Iovan, D. A.; Duncan, R. A.; Betley, T. A. *Chem. Sci.* **2014**, *5*, 1526.
- (40) Mehn, M. P.; Peters, J. C. *J. Inorg. Biochem.* **2006**, *100*, 634.
- (41) Ortiz de Montellano, P. R., *Cytochrome P450 : Structure, Mechanism, and Biochemistry*. 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2005.
- (42) Wilding, M. J. T. *Electronic structure/function relationship in metal ligand multiple bonds for C-H functionalization chemistry*. Harvard University, 2016.
- (43) Hagen, W. R. *Mol. Phys.* **2007**, *105*, 2031.
- (44) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. *J. Comput. Chem.* **2013**, *34*, 1164.
- (45) Neese, F. *ORCA - An ab initio, Density Functional and Semi-empirical Electronic Structure Package, 2.7*; Universität Bonn: Bonn, Germany, 2009.
- (46) Lukens, J. T.; Kurogi, T.; Mindiola, D. J.; Lancaster, K. M. *Unpublished data*.
- (47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (48) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (49) van Lenthe, E.; van der Avoird, A.; Wormer, P. E. S. *J. Chem. Phys.* **1998**, *108*, 4783.
- (50) van Wüllen, C. *J. Chem. Phys.* **1998**, *109*, 392-399.
- (51) Neese, F. *Inorg. Chim. Acta* **2002**, *337*, 181.
- (52) De Beer George, S.; Petrenko, T.; Neese, F. *J. Phys. Chem. A* **2008**, *112*, 12936.
- (53) Devlin, F. J.; Finley, J. W.; Stephens, P. J.; Frisch, M. J. *J. Phys. Chem.* **1995**, *99*, 16883.
- (54) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
- (55) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
- (56) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- (57) Soda, T.; Kitagawa, Y.; Onishi, T.; Takano, Y.; Shigeta, Y.; Nagao, H.; Yoshioka, Y.; Yamaguchi, K. *Chem. Phys. Lett.* **2000**, *319*, 223.
- (58) Yamaguchi, K.; Takahara, Y.; Fueno, T., *Applied Quantum Chemistry*. Springer: Dordrecht, 1986.
- (59) Mayer, J. M. *Acc. Chem. Res.* **2011**, *44*, 36.
- (60) Thacker, N. C.; Lin, Z.; Zhang, T.; Gilhula, J. C.; Abney, C. W.; Lin, W. *J. Am. Chem. Soc.* **2016**, *138*, 3501.
- (61) Broere, D. L.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; Dechert, S.; van der Vlugt, J. I. *J. Am. Chem. Soc.* **2014**, *136*.
- (62) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961.
- (63) Luo, Y.-R., *Handbook of Bond Dissociation Energies in Organic Compounds*. CRC Press LLC: Boca Raton, FL, 2003.
- (64) Parsell, T. H.; Yang, M.-Y.; Borovik, A. S. *J. Am. Chem. Soc.* **2009**, *131*, 2762.
- (65) Rosenthal, J.; Pistorio, B. J.; Chng, L. L.; Nocera, D. G. *J. Org. Chem.* **2005**, *70*, 1885.



TOC graphic