**Spectroscopic and Reactivity Comparisons between Nonheme Oxoiron(IV) and Oxoiron(V) Species Bearing the Same Ancillary Ligand**

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**ABSTRACT:** This work directly compares the spectroscopic and reactivity properties of an oxoiron(IV) and an oxoiron(V) complex that are supported by the same neutral tetradentate N-based PyNMe₃ ligand. A complete spectroscopic characterization of the oxoiron(IV) species (2) reveals that this compound exists as a mixture of two isomers. The reactivity of the thermodynamically more stable oxoiron(IV) isomer (2b) is directly compared to that exhibited by the previously reported 1e⁻-oxidized analogue [Fe⁵⁻(O)(OAc)(PyNMe₃)]²⁻ (3). Our data indicates that 2b is 4 to 5 orders of magnitude slower than 3 in hydrogen atom transfer (HAT) from C–H bonds. The origin of this huge difference lies in the strength of the O–H bond formed after HAT by the oxoiron unit, the O–H bond derived from 3 being about 20 kcal mol⁻¹ stronger than that from 2b. The estimated bond strength of the FeIV–O–H bond of 100 kcal mol⁻¹ is very close to the reported values for highly active synthetic models of compound I of cytochrome P₄₅₀. In addition, this comparative study provides direct experimental evidence that the lifetime of the carbon-centered radical that forms after the initial HAT by the high valent oxoiron complex depends on the oxidation state of the nascent Fe–OH complex. Complex 2b generates long-lived carbon-centered radicals that freely diffuse in solution, while 3 generates short-lived caged radicals that rapidly form product C–OH bonds, so only 3 engages in stereoretentive hydroxylation reactions. Thus, the oxidation state of the iron center modulates not only the rate of HAT but also the rate of ligand rebound.

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**INTRODUCTION**

High valent oxoiron species are the oxidizing agents in a variety of iron-dependent oxygenases. For example, in the heme enzyme cytochrome P₄₅₀, a high-valent oxoiron(IV)-porphyrin radical (Cpd 1) is responsible for the hydroxylation of aliphatic C–H bonds and of arene moieties, as well as the epoxidation of olefins, among other reactions. In Rieske oxygenases, a family of bacterial nonheme iron enzymes, a yet undetected oxoiron(V) species has been proposed as the oxidizing agent, while an S = 2 oxoiron(IV) species breaks strong C–H bonds via hydrogen atom transfer (HAT) in other nonheme oxygenases such as taurine dioxygenase, prolyl hydroxylase, tyrosine hydroxylase, phenyl alanine hydroxylase, as well as in α-ketoglutarate dependent halogenases. Due to the biological relevance of these high valent oxoiron compounds, intense research efforts have been devoted to the preparation of synthetic analogues that can reproduce both the structural properties and the reactivity of the biological systems. These synthetic models aim to provide detailed insight into the enzymatic mechanisms, and helpful information for the design of catalysts with potential application in environmentally friendly oxidation technologies.

Resulting from these research efforts, a large number of synthetic oxoiron(IV) complexes has been described. The reported systems typically consist of iron complexes based on tetra- and pentadentate nitrogen-based ligands, although complexes incorporating O atom donors or organometallic moieties are also known. Reactivity studies have disclosed that in most cases these synthetic oxoiron(IV) complexes are competent to perform hydrogen-atom abstraction of weak C–H bonds.

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H bonds and oxygen atom transfer (OAT) to sulfides.

Examples in which such species can break stronger C–H bonds are scarce, and moderate reaction rates are observed in most of these cases. In sharp contrast to the plentiful examples of well-defined synthetic oxoiron(IV) species, the preparation of the one-electron oxidized oxoiron(IV) analogues has remained elusive. This can be attributed to the higher oxidizing abilities of these species that make them especially reactive and thus difficult to trap. The first example of a nonporphyrinic oxoiron(V) complex was reported by Collins and co-workers using a tetraanionic macrocyclic tetramide ligand (TAML). The structurally related compound was characterized by several spectroscopic means, and reactivity studies demonstrated that it was competent in OAT to sulfides and alkenes and in HAT from alkanes. The structurally related compound was reported a few years later, and it exhibited remarkably higher stability at room temperature. Nevertheless, these oxoiron(V) species are far less reactive than cytochrome P450 Cpd I, which is considered as their biological heme analogue, suggesting that the tetraanionic character of TAML and related ligands attenuate the electrophilicity of the complex, significantly limiting their oxidation reactivity.

It was recently reported that the reaction of peracids with the iron(II) complex bearing a neutral N-based PyNMe₃ ligand, [Fe⁶(PyNMe₃)(CH₃CN)₂]²⁺, generates an oxoiron(V) species, [Fe⁶(V)(O)(PyNMe₃)(CH₃CN)]²⁺ (3, Scheme 1), which exhibits fast reaction rates in the stereoretentive hydroxylation of unactivated C–H bonds of alkanes and in the epoxidation of olefins. Even approaching the values reported for P450 Cpd I. The exact electronic structure of 3 has been a matter of debate. Münch, Costas and Que, on the basis of a thorough spectroscopic data, describe the species as an oxoiron(V) core attached to carboxylate ligand, generated after heterolytic O–O cleavage of a cyclic Fe(III)-peracetate moiety. In contrast, Ye, Neese, and co-workers claim that the compound is best characterized as an iron(IV) center antiferromagnetically coupled to an O–O radical, so that O–O bond has not been completely broken. Thus, this is a fascinating molecule with a very intriguing electronic structure. However, the interest in compound 3 goes beyond its unique bonding structure, as it shows reaction rates and selectivity patterns fully congruent with those of related iron complexes used as efficient catalysts in C–H and C=C oxidation reactions. Indeed, low temperature EPR studies performed along the catalytic reactions of some of these related systems during catalysis display the transient formation of small (<2%) amounts of species with the characteristic spectroscopic features of 3. These data strongly suggest that 3 may constitute a representative example of the oxidizing agents operating with these catalysts.

In this work, the spectroscopic and reactivity properties of 3 are compared with those of its oxoiron(IV) counterpart [Fe⁴(V)(O)(PyNMe₃)(CH₃CN)]²⁺ (2). This oxoiron(IV) species has been characterized by several spectroscopic techniques and, remarkably, two isomers can be identified. The HAT and OAT reactivity of the more thermodynamically stable isomer (2b, Scheme 1) has been studied and compared to 3. By comparing the reactivity of these two complexes with the same tetradentate ligand architecture, the current work provides valuable insight into the impact of the iron oxidation state in defining the unusual reactivity properties of 3.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of 2. The oxoiron(IV) complex [Fe⁴(V)(O)(PyNMe₃)(CH₃CN)]²⁺ (2) can be prepared by reaction of the iron(II) precursor [Fe⁴(II)(PyNMe₃)(CH₃CN)]²⁺ with either 1.1 equiv Bu₄NIO₄ or 4 equiv 2-tBuSO₃H-C₆H₄IO, albeit with low yields (<40%) as previously determined by Mössbauer spectroscopy. However, the addition of 0.8 equiv triflic acid (TfOH) or 1 equiv HClO₄ together with 1.1 equiv Bu₄NIO₄ to 1 affords the target complex 2 with significantly higher yields, as determined by the increased intensity of the two absorption bands characteristic of 2 at ~800 and ~980 nm.

UV–vis spectral monitoring of the generation of 2 shows that the relative intensities of these two low energy bands change over time (Figure 1). Thus, the initially more intense ~800 nm band decreases concomitantly with the increase in the intensity of the ~980 nm band, which then becomes the more intense of the two near-IR bands (Figure 1). These
observations suggest that two species are formed along the reaction pathway and an isosbestic point at 940 nm becomes apparent in the conversion between them. Interestingly, when the reaction of 1 with IO₄⁻/THOH is performed at −60 °C using a 1:1 CH₃CN:CH₂Cl₂ solvent mixture, the initial compound (2a) remains stable at this temperature. However, when the same reaction is carried out at −20 °C, the direct formation of the second species (2b) is observed (Figure S8).

Spectroscopic analyses have been carried out in order to validate the iron oxidation states of 2a and 2b and characterize their electronic structures (Table 1). Mössbauer samples of the two species were prepared by freezing the reaction mixture of Fe-N subshell is observed at 2.17 Å, which we assign to Fe−N bonds of the diferric byproduct, that represents 50% of the Fe in samples of 3.

<table>
<thead>
<tr>
<th>UV−vis−NIR</th>
<th>2a</th>
<th>2b</th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>λmax nm (ε, M⁻¹cm⁻¹)</td>
<td>792 (−)²</td>
<td>805 (230)²</td>
<td>490 (4500)²</td>
</tr>
<tr>
<td>Mössbauer</td>
<td>δ, mm/s (ΔE_Q, mm/s)</td>
<td>0.07 (0.98)</td>
<td>0.09 (0.24)</td>
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<tr>
<td>rRaman</td>
<td>k (Fe−O), cm⁻¹</td>
<td>822</td>
<td>829</td>
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<tr>
<td>XAS</td>
<td>K-edge energy, eV</td>
<td>7124.8</td>
<td>7124.4</td>
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<tr>
<td></td>
<td>pre-edge energy, eV</td>
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<td>pre-edge area, units</td>
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<td>19.6</td>
</tr>
<tr>
<td></td>
<td>r(Fe=O), Å</td>
<td>1.66</td>
<td>1.65</td>
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<tr>
<td></td>
<td>average r(Fe−N), Å</td>
<td>2.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>

²Reliable extinction coefficient for 2a could not be obtained due to the unavoidable contamination of this compound by 2b. Extinction coefficient values (ε) determined from the purity calculated by Mössbauer (for 2b) or EPR analyses (for 3). Spectroscopic data for 3 was obtained from refs 22, 28. Mössbauer and XAS parameters were obtained from samples of 3 generated using cyclohexyl peroxycarboxylic acid instead of peracetic acid.

A second Fe−N subshell is observed at 2.17 Å, which we assign to Fe−N bonds of the diferric byproduct, that represents 50% of the Fe in samples of 3.

Figure 2. Mössbauer spectra of 2a and 2b at various temperatures and magnetic fields. The stacked spectra in the top panel were recorded from the sample frozen at t = 2 min. The high-spin ferric species and species 2b have been removed to highlight the pattern for species 2a (35% of total iron). The stacked spectra on the bottom panel were recorded from the sample frozen at t = 30 min. The high-spin ferric species has been removed to highlight the pattern of species 2b (60% of total iron). Raw Mössbauer data can be found in Figure S6.
Scheme 2. (a) Different Ligands (X) Can Be Coordinated cis to the Oxo Group in 2a and 2b; (b) Possible Structure of the Two Geometrical Isomers of the Oxoiron(IV) Species, 2a and 2b

![Diagram](image_url)

**Figure 3.** Resonance Raman spectra of 2a (black line) and 2b (red line) in frozen acetonitrile solutions at 77 K ($\lambda_{exc} = 457$ nm). Band marked with # corresponds to solvent.

**Figure 4.** Fourier-transformed k-space EXAFS data of 2a (left) and 2b (right) in acetonitrile at 10 K. Insets show the k-space spectra.

Table 2. $^1$H NMR Paramagnetic Shifts Observed for Pyridine Protons of Oxoiron(IV) Complexes$^a$

<table>
<thead>
<tr>
<th>compound</th>
<th>$^1T$ (k)</th>
<th>$^\beta_1$</th>
<th>$^\beta_{12}$</th>
<th>$^\gamma$</th>
<th>ref</th>
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<tr>
<td>[Fe$^\text{IV}$(O)(N4Py))$]^{2+}$</td>
<td>298</td>
<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
<td>$^\gamma$</td>
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<td>[Fe$^\text{IV}$(O)(BnTPEN)]^{2+}$</td>
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<td>$^\gamma$</td>
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<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
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<td>298</td>
<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
<td>$^\gamma$</td>
<td>1.4</td>
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<tr>
<td>[Fe$^\text{IV}$(O)(TMC-py)]^{2+}$</td>
<td>298</td>
<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
<td>$^\gamma$</td>
<td>6.3</td>
</tr>
<tr>
<td>[Fe$^\text{IV}$(O)(TMC-py)]^{2+}$</td>
<td>298</td>
<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
<td>$^\gamma$</td>
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<td>[Fe$^\text{IV}$(O)(TMC-py)]^{2+}$</td>
<td>298</td>
<td>$^\beta_{12}$</td>
<td>$^\beta_{12}$</td>
<td>$^\gamma$</td>
<td>-11.6</td>
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</table>

$^a$Relative to pyridine at 7 ppm.
The $^1$H NMR spectrum of the more stable $2b$ isomer recorded at $-65^\circ$C in 1:1 CD$_3$CN/CD$_2$Cl$_2$ exhibits relatively sharp and well-resolved paramagnetically shifted signals due to the $S = 1$ Fe$^{IV}$═O center (Figure 5). The number of signals observed is consistent with the presence of a mirror plane of symmetry that bisects the pyridine ring. Due to their longer distances from the Fe center, the pyridine protons give rise to the sharpest signals in the spectrum of $2b$, which are found at $-25$ ppm (1H) and $15$ ppm (2H) (Figure 5). These peaks can be assigned respectively to the single $\gamma$ and the two $\beta$ protons of the pyridine based on their relative intensities. The remaining broader spectral features can be reasonably associated with benzylic CH$_2$ (-42 and $-63$ ppm (2H), CH$_3$ peaks at $-39$ ppm (2H) and $-147$ ppm (2H), and CH$_3$ protons at $-67$ ppm (9H). The chemical shift pattern observed for the pyridine $\beta$ protons and the two $\beta$ protons of the pyridine ligand relative to the Fe═O unit, based on comparisons with the most published examples have pyridines bound cis to the Fe═O unit and oriented parallel to the Fe═O axis, namely Fe$^{IV}$═O complexes in the literature. Most published complexes supported by the macrocyclic ligand with deuterated benzylic protons ($2b-d_5$) (Figure S7). The chemical shift pattern observed for the pyridine $\gamma$ and $\beta$ protons of $2b$ can shed light on the orientation of the pyridine ligand relative to the Fe═O unit, based on comparisons with the patterns associated with structurally well characterized Fe$^{IV}$═O complexes in the literature.

Neither of the shift patterns described above matches that observed for $2b$, which exhibits a relatively small downfield paramagnetic shift of 8 ppm for the $\beta$ protons and a larger upfield paramagnetic shift of 32 ppm for the $\gamma$ proton. Such a pattern is associated with a pyridine bound trans to the oxo atom, as reported for the pendant pyridine ligand trans to the oxo unit in [Fe$^{IV}$═O(TM-py)]$^{2+}$ (TM-py = 1-(pyridyl-2-methyl)-4,8,11-trimethyl-1,4,8,11-tetrazacyclotetradecane). For the latter complex, the two pyridine $\beta$ protons exhibit quite small paramagnetic shifts of $-0.5$ ppm and $+3.6$ ppm (actual peaks observed at $6.5$ and $10.6$ ppm) and a larger paramagnetic shift of nearly $-11.6$ ppm for the $\gamma$ proton found at $-4.6$ ppm. Although there is a difference in the magnitudes of the paramagnetic shifts of the pyridine protons between these two complexes, the directions of the shifts agree. The larger paramagnetic shifts observed for $2b$ versus [Fe$^{IV}$═O(TM-py)]$^{2+}$ (Table 2) likely arise from two factors: (a) the $90^\circ$C difference in temperature at which the NMR data were obtained, which will decrease when this difference is taken into account, and (b) the shorter Fe−N$_{py}$ bond length of $2.03 \, \text{Å}$ calculated for $2b$ (see Supporting Information, Figure S27, for more details) versus the $2.118(3) \, \text{Å}$ value determined crystallographically for [Fe$^{IV}$═O(TM-py)]$^{3+}$, which results in greater unpaired spin density delocalized onto the pyridine in the former.

The $^1$H NMR spectrum of $2a$ in 1:1 CD$_3$CN:CD$_2$Cl$_2$ at $-65$ $\circ$C shows significant contamination from the more stable $2b$ isomer, as shown by the Mössbauer results discussed earlier (Figure 2). On the basis of the above assignment of $2b$ as the $\text{trans}$ isomer, $2a$ should correspond to the $\text{cis}$ isomer with the pyridine perpendicular to the Fe═O axis. From a careful inspection of the composite $2a$ + $2b$ spectrum and comparison with the spectrum of pure $2b$, we can identify sharper features with a relative 2:1 intensity ratio at $-19$ and $12$ ppm that we assign to the $\beta$ and $\gamma$ protons of $2a$, respectively. The shift pattern with upfield shifted $\beta$ protons and a downfield shifted $\gamma$ proton is fully consistent with a cis-bound pyridine perpendicular to the Fe═O unit (Scheme 2b), as found for the pyridines perpendicular to the Fe═O units of [Fe$^{IV}$═O] (BNTPEN)$^{2+}$ and [Fe$^{IV}$═O(P$_2$MeTACN)]$^{2+}$ (Table 2).

Interestingly, in line with the experimental observations, DFT calculations predict that the isomer with the oxo group trans to the pyridine ring is slightly energetically favored by $0.9 \, \text{kcal/mol}$ over the isomer with the oxo group cis to the pyridine (see Supporting Information for more details). This further supports the NMR results pointing out that the most stable isomer $2b$ contains the pyridine trans to the oxo group, and they show a relative cis orientation in the kinetically favored geometric isomer $2a$.

Oxidative Reactivity of $2a$ versus $2b$ and Comparison to $3$. The oxidizing abilities of $2a$ and $2b$ were compared at $-60^\circ$C. Isomer $2a$ was directly synthesized at $-60^\circ$C in 1:1 CH$_3$CN:CH$_2$Cl$_2$. Of note, this compound is obtained together with approximately equimolar amounts of isomer $2b$ according to spectroscopic studies (see above). Compound $2b$ was first generated at $-40^\circ$C and then cooled down to $-60^\circ$C for reactivity comparisons with $2a$. Reaction rates were determined by monitoring the decay of the near-IR absorption bands characteristic of $2a$ and $2b$ (at $792$ and $990 \, \text{nm}$, respectively) upon addition of an excess of a particular substrate (Figure S12 and S13). In the case of $2b$, its decay at $990 \, \text{nm}$ could be fitted to single exponential functions, from which observed reaction rates ($k_{obs}$) and the corresponding
second order rate constants ($k_2$) could be extracted. Reactions of 2a with substrates were “contaminated” by the presence of approximately equimolar quantities of 2b. Thus, the contribution of 2b to the decay of the most intense absorption band of 2a at 792 nm was subtracted to obtain the decay of “pure” compound 2a. Gratifyingly, the reaction of this species with substrates could also be nicely fitted to a single exponential function and reaction rates for 2a could be extracted (see Supporting Information for more details). Both species exhibited hydrogen-atom transfer (HAT) and oxygen atom transfer (OAT) reactivity typically observed for most S = 1 oxoiron(IV) complexes but they showed different reactivity trends. Isomer 2a reacted approximately 18 times faster than 2b in HAT reactions with 9,10-dihydroanthracene ($k_2 = 9.5 \times 10^6$ M$^{-1}$ s$^{-1}$ for 2a and 0.53 M$^{-1}$ s$^{-1}$ for 2b) but was about 4 times less reactive than 2b in OAT reactions with thioanisole ($k_2 = 0.038$ M$^{-1}$ s$^{-1}$ for 2a and 0.14 M$^{-1}$ s$^{-1}$ for 2b). These results further support the notion that 2a and 2b correspond to two different oxoiron(IV) species that exhibit different relative reactivity.

Further reactivity studies of the oxoiron(IV) species were carried out using isomer 2b. On the one hand, this compound corresponds to the thermodynamic product, so that it can be obtained without contamination from 2a and is thermally stable at −40 °C, which makes it easier to manipulate. On the other hand, the relative disposition of the oxo group trans to the pyridine in 2b is also observed in 3. For the latter, spectroscopic analysis did not show the presence of two different isomers, and the detected signals were assigned to the isomer with the oxo group trans to the pyridine as it was slightly more stable than the corresponding cis isomer on the basis of DFT calculations. Thus, 2b and 3 likely represent the same geometric isomer making reactivity comparisons more straightforward.

First, the reactivity of 2b with thioanisole and its para-substituted derivatives (X = OMe, Me, Cl, CN) at −40 °C was evaluated. Upon substrate addition, the absorption bands associated with 2b disappeared (Figure S14), and this decay was also accompanied by the recovery of the UV–vis absorption features of 1 (Figure S16), which was also supported by MS (Figure S17). Moreover, analysis of the oxidized products in the reaction with thioanisole revealed the formation of the corresponding sulfoxide in S4% yield with respect to 2b. Under conditions of excess substrate, the decay of the absorption band of 2b at 990 nm could be fitted to a single exponential and second-order rate constants could be extracted. As expected, the Hammett analysis supported the electrophilic character of 2b ($\rho = -1.77$, Figure S15) as previously observed for other well-defined oxoiron(IV) complexes (see SI for more details). The reaction of the oxoiron(V) species 3 with sulfides is exceedingly fast, and reaction rates could not be determined even when analyzed at −45 °C by stopped flow methods.

Therefore, a direct comparison between the OAT ability of 2b and 3 cannot be made, but the accumulated data indicate that 2b behaves like a common oxoiron(IV) complex, while under the same reaction conditions 3 exhibits extraordinarily fast OAT rates. Under the assumption that the possible contributions of spin state changes to these reactions are either (i) insignificant or (ii) are very similar for the two compounds, the comparison highlights the extreme electrophilicity of the Fe$^\equiv$O unit.

The HAT ability of 2b was also measured by studying its reaction with hydrocarbons. In this case, kinetic studies were carried out at −40 °C in order to establish a direct comparison with the reaction rates reported for 3 at this temperature (see below).22 Substrates with relatively weak C–H bonds (BDE = 75–85 kcal mol$^{-1}$) were used, because substrates with stronger bonds turned out to be unreactive toward 2b at this temperature. Due to the limited solubility of the chosen substrates (xanthene, 1,4-cyclohexadiene, 9,10-dihydroanthracene, and fluorene) in CH$_2$CN at −40 °C, reactions were run in a 1:1 CH$_2$CN:CH$_2$Cl$_2$ mixture. Reactions produce [Fe$^{IV}(OH)(CF_3SO_2)(PyNMe_3)]^+$ (ascertained by MS, Figure S19) and organic products. Reactions were monitored by UV–vis absorption spectroscopy by following the decay of the band at 990 nm characteristic of 2b upon addition of the substrate (Figure S18). Under these experimental conditions reactions 41 showed pseudo-first-order behavior and second-order reaction rates ($k_2$) could be extracted by plotting the observed rate constants ($k_{obs}$) as a function of the substrate concentration (Figure S20). These rate constants were then adjusted for the reaction stoichiometry to yield $k_2$ based on the number of abstractable hydrogen atoms of substrates. As expected, reaction rates decreased with the increase of the C–H BDE and more interestingly the log($k_2$) values correlated linearly with the C–H BDE values, giving a slope of approximately −0.25 (kcal/mol)$^{-1}$ (Figure S21).

HAT reactions with compound 2b also exhibit a normal kinetic isotope effect (KIE), so deuterated substrates react more slowly than their proton analogues. Using xanthene-d$_2$ and 9,10-dihydroanthracene-d$_4$, KIE values of 24 and 28 were obtained, respectively (Figure S23).48 These high values are commonly observed in HAT processes carried out by oxoiron(IV) complexes. For example, a KIE value of 36 (at −40 °C) was reported for the oxidation of xanthene with the oxoiron(IV) complex bearing the 13-TMC ligand and a KIE value of 27 (at −15 °C) was described for the oxidation of 9,10-dihydroanthracene using the [Fe$^{IV}$(O)(CH$_3$CN)].

Altogether, the good correlation between reaction rates and the C–H BDE values and the large KIE values provides strong evidence for a rate-determining HAT process in the reactions of hydrocarbons with 2b.

Activation parameters for HAT reactions of 2b with xanthene and cyclohexadiene were determined by measuring reaction rates between 273 and 293 K. The corresponding Eyring plot for xanthene afforded $\Delta H^\ddagger = 6.4 \pm 0.6$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -27.2 \pm 2.6$ cal K$^{-1}$ mol$^{-1}$, while $\Delta H^\ddagger = 7.3 \pm 0.5$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -25.6 \pm 2.1$ cal K$^{-1}$ mol$^{-1}$ were determined for cyclohexadiene (Figure S24). These values are very close to the ones previously reported for the reaction of a tetracarbene ligated oxoiron(IV) with 1,4-cyclohexadiene and 9,10-dihydroanthracene.52

It has been observed that the reactivity of oxoiron(IV) complexes depends dramatically on the ligand set.53−55 The combination of the above-described data for 2b and the recently described reactivity of 32 represents a unique opportunity to compare the oxidizing abilities of a pair of oxoiron(IV) and oxoiron(V) compounds bearing exactly the same ligand architecture. A first notable observation is that reactions with substrates bearing strong C–H bonds (BDE $\sim$89–100 kcal mol$^{-1}$) can only be studied for 3 because 2b
does not appear to be powerful enough to carry out HAT reactions with these strong C–H bonds. On the other hand, rates for HAT reactions with substrates containing weak C–H bonds can only be measured for 2b, because the reaction with 3 exhibited extremely fast reaction rates, too fast even at −40 °C to be extracted by stopped flow methods.22 Therefore, reaction rates for a common substrate are not available.

In order to establish a quantitative comparison between reaction rates, we performed regression analyses of the log($k_s$) vs BDE correlations experimentally determined for 2b and 3. Regression analyses provide correlation lines with a slope of −0.25 (kcal/mol)−1 in both cases (using a linear free energy relationship a unitless slope of 0.34 is obtained in both cases. Figures S22). This coincidence in the slopes of these correlations strongly suggests that HAT of 2b and 3 proceed via very similar transition states. Extrapolation of the straight lines obtained in these correlations permitted us to estimate hypothetical second order reaction rates for substrates containing strong C–H bonds in the case of 2b, and for the fast reactions of 3 against substrates with weak C–H bonds.

Results are shown in Figure 6 and Table 3. As anticipated, the

![Figure 6](image)

**Figure 6.** Correlation of log($k_s$) with the BDE of different substrates at −40 °C for 2b (blue line) and 3 (red line). Filled circles correspond to experimentally determined data and empty circles correspond to extrapolated values. The extrapolation made for compound 3 should be taken with a caveat, since a loss of linearity is likely to occur at BDE values below 90 kcal·mol−1, as previously reported for other highly reactive HAT reagents (see text for more details).

**Table 3.** Experimental and Extrapolated $k_s$ Values for 2b and 3 at −40 °C

<table>
<thead>
<tr>
<th>substrate</th>
<th>BDE (kcal mol−1)</th>
<th>compound 2b $k_s$ (M−1 s−1)</th>
<th>compound 3 $k_s$ (M−1 s−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xanthene</td>
<td>75.2</td>
<td>2.1 ± 0.2</td>
<td>1.4 × 10^5</td>
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<tr>
<td>cyclohexadiene</td>
<td>76.0</td>
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<td>9,10-dihydroanthracene</td>
<td>76.3</td>
<td>0.77 ± 0.05</td>
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<tr>
<td>fluorene</td>
<td>82.2</td>
<td>0.030 ± 0.004</td>
<td>2.5 × 10^3</td>
</tr>
<tr>
<td>toluene</td>
<td>89.7</td>
<td>4.2 × 10^−4</td>
<td>55 ± 1 b</td>
</tr>
<tr>
<td>tetralinolufuran</td>
<td>92.1</td>
<td>1.0 × 10^−4</td>
<td>7.2 ± 0.2 b</td>
</tr>
<tr>
<td>cyclooctane</td>
<td>95.7</td>
<td>1.4 × 10^−5</td>
<td>0.34 ± 0.01 b</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>99.5</td>
<td>1.7 × 10^−6</td>
<td>0.23 ± 0.01 b</td>
</tr>
</tbody>
</table>

“Extrapolated values are shown in italics. 6Ref 22.

Gathered data show that 3 is four to 5 orders of magnitude more reactive than 2b. It is important to note that extrapolation of the log($k_s$) vs BDE correlations must be done with caution. While linear correlations over a wide range of BDEs have been reported for several oxoiron(IV) complexes with moderate reactivities,5,38,55,56 a loss of linearity below 90 kcal/mol has been observed for a highly reactive peroxygenase compound 1 and t-butoxy radicals.27,57,58 Such a loss of linearity might not be discarded for the highly reactive oxoiron(V) species 3 for substrates with low BDEs, thus challenging the direct extrapolation at low BDEs for this compound. Thus, while loss of linearity may happen for compound 3 at low BDE values, this is not likely to occur at high BDEs for 2b according to literature precedents. This way, extrapolation of the straight line is reliable for 2b and the statement that 3 is four to 5 orders of magnitude more reactive than 2b can be more strongly defended for strong C–H bonds.

Reactivity comparisons between oxoiron(IV) and oxoiron(V) species have been reported in very few systems. In fact, the only precedent for nonheme iron systems is for the complexes of the tetraionic bTAML ligand. In this case, the reaction of [FeIV(O)(bTAML)]− toward benzyl alcohol (BDE < 80 kcal mol−1) at pH 7 was found to be 2500 times faster than for its 1-e−-reduced counterpart [FeV(O)(bTAML)]2− at pH 12.59 Of note, reactions toward stronger C–H bonds were precluded due to the attenuated electrophilicity of this system.

In contrast, van Eldik and co-workers found that a Cpd I mimic, [(TMPS)*FeIV(O)(H2O)]3+ reacted with benzyl alcohols only a hundred times faster than its 1-e−-reduced counterpart [(TMPS)FeV(O)(OH)]3+. The different degrees of protonation of the OH/OH2 ligand in these two compounds should be noted.60 Even more interestingly, a Cpd I model compound reported by Groves [(4-TMPyP)*FeIV(O)+] exhibited a very high second order rate constant of 3.6 × 106 M−1 s−1 for the oxidation of xanthene, but negligible reactivity was observed when the 1-e−-reduced analogue [(4-TMPyP)FeV(O)] was used.61 Indeed, the extrapolated reaction rate for the oxidation of xanthene calculated for 3 (Table 3) is only 10 times slower than that observed for Groves’ model compound without accounting for the 50 °C difference in the measurements (reaction rates in the Groves system were measured at +10 °C, while reactions for 3 were recorded at −40 °C), thus suggesting that 3 compares well in HAT reactivity with the most active cytochrome P450 mimics.

The KIE’s determined for 2b and 3 are also significantly different. 2b exhibits very large KIE’s (~28), in agreement with the large values observed for synthetic and enzymatic oxoiron(IV) species, which are commonly rationalized on the basis of large tunneling contributions.5,30,62,63 In contrast, KIE’s determined for 3 of ~5–6 are significantly smaller than those determined for 2b, so they can still be accommodated by a classical treatment of the C–H cleavage. Notably, these “classical” values resemble those obtained for catalytic C–H37 oxidation systems with bioinspired iron catalysts.64

Activation parameters in representative HAT reactions performed by 2b and 3 are collected in Table 4. Activation entropies are large and negative, consistent with a bimolecular process, and those determined for 2b are systematically more negative. This pattern reflects a later and more ordered transition state for the less reactive 2b. This provides some clues about the origin of the differences in the magnitude of the KIE’s; tunneling contributions require close proximity between the hydrogen-donor and the hydrogen-acceptor and activation parameters indeed provide evidence for the necessary closer contact between the oxoiron(IV) (2b) and the substrate C–H bond with respect to the same situation in the more reactive oxoiron(V) (3).51
The linear free energy correlation between log $k_2'/$ and differences in enthalpy free for the present system (Figure 6) provides interesting insights into the origin of the fast HAT reactivity of 3. With few exceptions, such a correlation is commonly observed for HAT reactions as described by the Bell–Evans–Polyani model. The enthalpy change of the present reactions corresponds to the difference between the energy that is required to break the C–H bond (BDE$_{C-H}$) and the energy provided by the formation of the Fe–O–H bond (BDE$_{FeO-H}$) (eq 2). Considering that cyclohexadiene reacts with 2b at a reaction rate ($k_2' = 0.70$ M$^{-1}$ s$^{-1}$) that is only 2.05 times the rate of reaction of 3 with cycloctane ($k_2' = 0.34$ M$^{-1}$ s$^{-1}$), we can estimate that both reactions have similar activation free energies given the observed Bell–Evans–Polyani correlation (Figure 6). Therefore, the 20 kcal-mol$^{-1}$ difference in BDE$_{C-H}$ between these two substrates (76.0 kcal-mol$^{-1}$ for cyclohexadiene and 95.7 kcal-mol$^{-1}$ for cyclooctane) should approximately correspond to the difference in energy between the BDE of Fe$^{III}$O–H and Fe$^{IV}$O–H.

$$\text{Fe}^{III}==\text{O} + \text{C–H} \xrightarrow{\text{HAT reaction}} \text{Fe}^{IV}==\text{O} + \text{C–H}.$$  

(1)

On the other hand, acetate is an anionic sigma donor ligand that should favor higher oxidation states. Therefore, the extraordinarily higher reactivity of 3 when compared with 2b is likely to be even tamed by the different ligand. In other words, if the two complexes would share exactly the same ligand set, differences in reaction rates are expected to be even larger.

It is also remarkable that the hydrogen-atom abstraction reactions carried out by 2 and 3 entail changes in the spin state along the reaction. HAT reactions from 3 (which has a $S = 1/2$ ground state) form an iron(IV)-hydroxo species, which possesses a $S = 1$ or $S = 2$ spin state, together with an alkyl radical. After the hydroxyl ligand rebound, an iron(III) complex with a $S = 2$ is formed concomitantly with the hydroxylation product. Thus, a change in the spin state occurs along this reaction path. Indeed, we and others have investigated the spin state changes along the reaction of oxoiron(IV) with alkanes by computational methods and disclosed that reactions usually occur at the $S = 1/2$ or $S = 3/2$ surfaces, depending on which of the two spin states has the lower energy barriers. In some instances, a spin crossover before reaching the first transition state is necessary to access the most energetically favored path. The $S = 2$ reaction path is usually much higher in energy with larger kinetic barriers. However, this is the most stable spin state for the reaction products, so that a spin crossover is necessary after the ligand rebound. A similar situation occurs with the HAT reactions carried out by oxoiron(IV) species analogous to 2. In this case, most frequently reaction takes place at the quintet spin state even though the most stable spin configuration of the oxoiron(IV) is the triplet ($S = 1$). (for a notable exception see ref S2. Thus, a spin crossover occurs before the transition state. In spite of the fact that spin-state changes are involved along the course of the reaction, spin–orbit couplings and spin–spin interactions remove the associated forbiddance. Thus, the feasibility of the HAT reactions carried out by oxoiron(IV) and oxoiron(V) species appears to be dictated by ground state thermodynamics rather than by multiple state reactivities.

### Differences in Chemoselectivity between 2b and 3.

The oxidation of cyclohexene constitutes a very informative mechanistic probe. Indeed, cyclohexene has been used as a substrate probe to study the reaction mechanism of oxidation reactions in enzymes and model systems. This molecule provides the oxidant with two possible channels of reactivity: abstraction of an allylic C–H bond and OAT to the C–C bond. Analysis of the oxidized products formed upon reaction of 2b or 3 with 100 equiv cyclohexene at $-40^\circ$C in CH$_3$CN showed completely different outcomes (Scheme 3). Under aerobic conditions, the oxoiron(IV) complex 2b afforded mainly allylic oxidation (31% yield of allylic ketone and 5% yield of allylic alcohol with traces of epoxide), while the oxoiron(IV) compound 3 afforded mainly cyclohexene oxide (60% yield) with minor amounts of allylic products (6% combined yield of allylic alcohol and ketone products). This comparison clearly indicates that 2b is a sluggish OAT reagent.

### Table 4. Activation Parameters for the Reactions of 2b and 3 with C–H Bonds

<table>
<thead>
<tr>
<th>compound</th>
<th>substrate</th>
<th>BDE (kcal mol$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (cal K$^{-1}$ mol$^{-1}$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>xanthene</td>
<td>75.2</td>
<td>$6.4 \pm 0.6$</td>
<td>$-27.2 \pm 2.6$</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>cyclohexadiene</td>
<td>76.0</td>
<td>$7.3 \pm 0.5$</td>
<td>$-25.6 \pm 2.1$</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>89.7</td>
<td>$6.5 \pm 0.2$</td>
<td>$-19.6 \pm 1.2$</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>cyclohexane</td>
<td>99.5</td>
<td>$8.8 \pm 0.7$</td>
<td>$-18.2 \pm 1.9$</td>
<td>22</td>
</tr>
</tbody>
</table>
Scheme 3. Product Distribution in the Reaction of 2b and 3 with Cyclohexene at −40 °C in CH₃CN under Aerobic Conditions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Conditions</th>
<th>Products</th>
<th>Yield (%)</th>
<th>Isotope Labeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>−40 °C, CH₃CN, air</td>
<td>31%</td>
<td>5%</td>
<td>&lt;1% (82% ¹⁸O)</td>
</tr>
<tr>
<td>3</td>
<td>−40 °C, CH₃CN, air</td>
<td>3%</td>
<td>3%</td>
<td>60% (0% ¹⁸O)</td>
</tr>
</tbody>
</table>

Yield with respect to Fe

(¹⁸O incorporation under ¹⁸O₂ atmosphere)

Scheme 4. Hydrogen Atom Transfer from C−H Bonds by Oxoiron(IV) and Oxoiron(IV) Species

Scheme 4. In striking contrast, 3 hydrosylates alkenes with a C−H bond. Of note, cyclohexene with 2b performed under ¹⁸O₂ atmosphere indicates that the hydroxyl ligand formed after HAT reforms bond with the newly formed carbon-centered radical, which diffuses out of the solvent cage, producing long-lived carbon-centered radicals that can interact with dioxygen to give rise to the observed ¹⁸O-labeling of the allylic ketone (Scheme 4). Conversely to what was observed in the oxidation of cyclohexene by 2b, the oxoiron(IV) to the C−H bond has been done to exclude the formation of hydroxyl radicals (Figure S25), which indicates that after hydrogen atom abstraction by the newly formed allylic radical does not undergo rapid rebound and has a long enough lifetime to interact with gaseous dioxygen (Scheme 4).

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**CONCLUSIONS**

In this work we have described the synthesis and characterization of an oxoiron(IV) species with a neutral tetradentate N-based ligand, Fe⁴⁺(O)⁺(PyNMe₃)(CH₃CN)²⁺, that according to our spectroscopic studies exists as a mixture of two isomers (2a and 2b). The reactivity of the thermodynamically more stable isomer (2b) toward C−H bonds has been directly compared to that exhibited by the previously reported 1e⁻ oxidized species Fe³⁺(O)(OAc)(PyNMe₃)³⁻ (3). Our data show that the oxoiron(IV) species 2b is 4 to 5 orders of magnitude slower than 3 in hydrogen atom abstraction reactions from C−H bonds. Analysis of the collected kinetic data indicates that the origin of this huge difference lies in the strength of the O−H bond formed after hydrogen-atom abstraction by the oxoiron unit and we estimate that the O−H bond formed upon reaction of 3 with a C−H bond is about 20
Materials. Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Solvents were purchased from Scharlab, Acros or Sigma-Aldrich and used without further purification. Preparation and handling of air-sensitive materials were carried out in an N₂ drybox (Jacomex) with O₂ and H₂O purchased from Scharlab, Acros or Sigma-Aldrich and used without available reagent quality unless otherwise stated. Solvents were of HAT but also the rate of ligand rebound.

Resonance Raman spectra were obtained on frozen samples of 2a and 2b at 77 K with excitation at 457 nm laser (50 mW at source, Cobalt Lasers) through the sample in a NMR tube using a 135° scattering arrangement (parallel to the slit direction). The collimated Raman scattering was collected using two plano convex lenses (f = 10 cm, placed at an appropriate distance) through appropriate long-pass edge filters (Semrock) into an Acton AM-506M3 monochromator equipped with a Princeton Instruments ACTON PyLON LN/CCD-1340 × 400 detector. The detector was cooled to −120 °C prior to the experiments. Spectral calibration was performed using the Raman spectrum of acetone/toluene 50:50 (v/v). Each spectrum was 80 accumulated, typically 60 times with 5 s acquisition time, resulting in a total acquisition time of 5 min per spectrum. The collected data was processed using Spectrgryph, and a multipoint baseline correction was performed for all spectra.

Mössbauer spectra were recorded on a Bruker Avance III HD naneobay 400 MHz spectrometer or on a Bruker Ultrashield Avance III-400. Temperatures for low temperature experiments were determined by calibration using a solution of methanol and TMS as the standard. 0.5 mL 4-mM solution of 1 was prepared for NMR experiments and the corresponding oxoiron(IV) samples were prepared by adding 1.1 mL BuNIO₄ and 1 equiv HClO₄ to this solution in an NMR tube at 235 K.

Mössbauer spectra were recorded with two spectrometers using the WMOSS software package (SEE Co, Edina, MN). The figures of Mössbauer spectra were plotted in SpinCount (provided by Prof. M. P. Hendrich of Carnegie Mellon University).

Synthesis of [Fe(PyNMe₂)(CH₃CN)]²⁺(SbF₆). In the glovebox, PyNMe₂ (41.3 mg, 0.17 mmol) was dissolved in CD₃CN (2 mL). Afterward FeCl₂ (21.1 mg, 0.17 mmol) was added directly as a solid and the mixture was stirred for 24 h. A color change from pale yellow to deep orange was observed. Then, AgSbF₆ (121 mg, 0.34 mmol) was added, which caused the immediate formation of a white precipitate corresponding to AgCl and the solution turned dark green. After stirring for 2 h the solution was filtered over Celite to remove precipitated AgCl. Then, direct addition of diethyl ether (10 mL) caused the precipitation of the complex which was separated and dried. Finally, the resulting solid was dissolved using a mixture of CH₂Cl₂ (1.5 mL) and CH₃CN (0.5 mL). Slow diethyl ether diffusion over the resulting solution in the anaerobic box afforded 41.8 mg (0.05 mmol, 32% yield) of dark brown crystals corresponding to [Fe(II)SbF₆] suitable for X-ray diffraction (see SI). 1H NMR (CD₃CN, 400 MHz, 298 K) δ, ppm 114, 99, 87, 77, 66, 56, 55, 12, −24, −35. ESI-QTOF-MS (m/z) calcd for [Fe(PyNMe₂)](CH₃CN)²⁺172.5802, found 172.5806. [Fe(PyNMe₂)](SbF₆)²⁻ 539.0295, found 539.0294. Anal. Calcd for C₁₅H₁₇F₂₄N₂S₂: C, 25.20; H, 3.35; N, 9.80. 98.80. C, 25.18; H, 3.21; N, 9.72.

NMR (CD₃CN, 400 MHz, 298 K) δ, ppm 7.58 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.7 Hz, 2H), 2.55–2.46 (m, 14H), 2.21 (s, 3H). 13C NMR (CD₃CN, 100 MHz, 298 K) δ, ppm 157.4, 136.8, 122.2, 61.9. [Fe(CF₃SO₃)(CH₃CN)]²⁺ (91.9 mg, 0.21 mmol) was added directly as a solid to a vigorously stirred solution of PyNMe₂-d₅ (53.2 mg, 0.21 mmol, 60:40:4 to ensure the complete elution of PyNMe₂-d₅ in a two-necked round flask inside the glovebox. The mixture was taken out the glovebox and stirred at 50 °C under an inert atmosphere for 24 h. Then D₂O (2 mL) was added to quench the reaction. Upon removal of CD₃CN under vacuum, the residue was extracted with CH₂Cl₂ (4 × 10 mL) and the organic layer was dried with MgSO₄ and filtered. The solvent was removed under reduced pressure obtaining a brown oil. The product was further purified by column chromatography over silica using an initial mixture of CH₂Cl₂-MeOH-NH₄ ₂O:5:00:40 and slowly raising the polarity to 80:40:0 to ensure the complete elution of PyNMe₂-d₅. The resulting compound was isolated (53.3 mg, 0.21 mmol, 54% yield) of the pure deuterated ligand were obtained. 1H NMR (CD₃CN, 400 MHz, 298 K) δ, ppm 7.56 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 7.7 Hz, 2H), 2.65–2.44 (m, 14H), 2.20 (s, 3H).

Synthesis of [Fe(CF₃SO₃)₂(PyNMe₂-d₅)]·[Fe(CF₃SO₃)₂(THF)]. Synthesis of [Fe(CF₃SO₃)₂(PyNMe₂)]·[Fe(CF₃SO₃)₂(THF)].

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monitored upon substrate addition and the decay was fitted to a single exponential after subtraction of the contribution from 2b (see Supporting Information for more details).

**Oxidation of Sulphides and Hydrocarbons with 2b at −60 °C in a 1:1 Mixture of CH3CN:CH2Cl2.** A solution of 2b was obtained at −40 °C in a 1:1 mixture of CH3CN:CH2Cl2 (see above for more details) after isomerization of 2a. The solution of 2b was cooled down to −60 °C and 100 μL of a solution containing the desired amount of substrate (10−46 equiv) in a 1:1 mixture of CH3CN:CH2Cl2 were added. Disappearance of the UV−vis absorption band characteristic of 2b at 990 nm was monitored upon substrate addition and the decay was fitted to a single exponential function from which the reaction rate could be extracted.

**Oxidation of Cyclohexene with 2b and 3 at −40 °C.** Once 2b or 3 were fully formed in pure CH3CN, 200 μL of a solution containing 100 equiv of cyclohexene in CH3CN were added. After total decay of the UV−vis absorption band of 2b at 990 nm or 3 at 490 nm, biphenyl was added as internal standard and the reaction mixture was rapidly filtered through a silica plug and subsequently washed with ethyl acetate. At this point an aliquot of the solution was analyzed by GC and GC×MS. To the remaining solution, an excess of solid PPh3 was added and analyzed by GC to exclude the formation of hydroperoxides, as previously reported. 76 This experiment was carried out under different atmospheres, namely N2, air and O2.

**Oxidation of Cyclohexene by 3 at −40 °C.** Once 3 was fully formed in CH3CN, 100 μL of a solution containing 45 equiv of cyclohexene in CH3CN were added. After total decay of the UV−vis absorption band of 3 at 490 nm, the reaction mixture was rapidly filtered through a silica plug and subsequently washed with ethyl acetate. At this point an aliquot of the solution was analyzed by GC and GC×MS. This experiment was carried out under N2 and O2 atmospheres.

**Eyring Plot for the Reaction of 2b with Cyclohexadiene and Xanthene.** Once 2b was fully formed in a 1:1 mixture of CH3CN:CH2Cl2, 100 μL of a solution containing 10 equiv of cyclohexadiene or xanthene in a 1:1 mixture of CH3CN:CH2Cl2 were added. The decay of the absorption band of 2b at 990 nm was monitored and fitted to a single exponential function from which the observed rate constant (kobs) could be extracted. This experiment was repeated at five different temperatures (233−273 K) for each substrate, in order to calculate the activation parameters (ΔH* and ΔS*) by plotting the ln(kobs/T) values as a function of 1/T.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b05758.

Characterization of PyNMe3−d4, 1-CF3SO3−d4, and 1-SbF6−XAS analysis for 2a and 2b, raw Mössbauer spectra for 2a and 2b, 1H NMR characterization of 2b and 2b−d6, UV−vis spectroscopy of the conversion of 2a to 2b and comparison of their reactivities in OAT and HAT processes, UV−vis spectroscopy of the reaction of 2b in OAT and HAT processes, MS spectra for the reactions of 2b and 3 with cyclohexene and cyclohexane, DFT calculations for the structure of 2a and 2b including predicted 1H NMR chemical shifts and geometry coordinates (PDF).

Crystal data ( CIF).

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Modeling the cis-Oxo-Labile Binding Site Motif of Non-Heme Que, L., Jr. Crystallographic Evidence for a Sterically Induced Ferryl Fan, R.; Guo, Y.; Ozerov, M.; Nehrkorn, J.; Krzystek, J.; Telser, J.; Sons, 2016; pp 1


Notice that 9,10-dihydroanthracene-d14 could be synthesized with only a 98% D enrichment. If this is taken into account, a much higher KIE should have been obtained.


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