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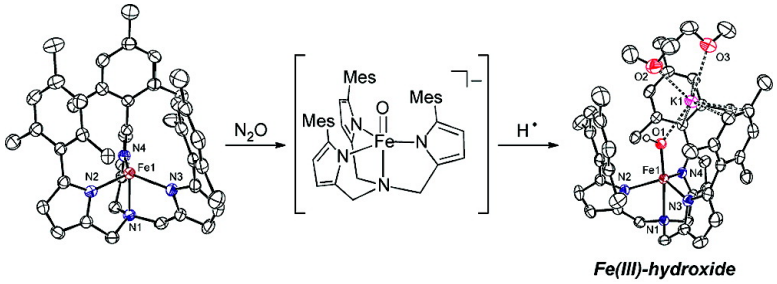

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N_2O Activation and Oxidation Reactivity from a Non-Heme Iron Pyrrole Platform

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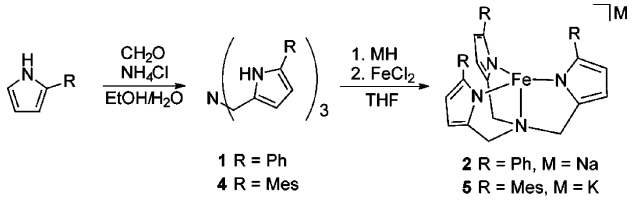
Iron occupies a central place in chemistry and biology owing in large part to its rich catalytic oxidation reactivity within heme porphyrin and non-heme environments.[1] In particular, the importance of high-valent mononuclear iron intermediates in biocatalytic transformations has stimulated interest in creating synthetic systems to probe aspects of their bonding and reactivity as well as expanding this chemistry to new applications.[2−4] We have initiated a program aimed at creating hybrid systems that incorporate key attributes of both heme and non-heme ancillary ligands, namely the η^1-pyrrole donors in hemes that can support iron in multiple oxidation states coupled with the flexibility of varying coordination geometries in non-heme frameworks. Because the majority of natural systems support iron-based oxidants in 4-fold symmetry,[1] we envisioned that exploring other geometries could allow access to high-valent iron centers with new and potentially interesting electronic, magnetic, and reactivity properties. In this regard, the activation of nitrous oxide provides a salient challenge for this general strategy. N_2O is an appealing oxidant because of its ease of handling and benign byproducts, but its kinetic stability[5] and poor properties as a ligand[6] render it a difficult molecule to activate for further transformations.[7] We now report a new 3-fold symmetric, non-heme iron pyrrole platform and its ability to activate N_2O and other oxygen-atom transfer reagents for intra- and intermolecular oxidation reactions. This work provides a rare example of oxygen transfer from N_2O to iron.[8]

The reduced π-donation of pyrrole donors compared to hard amides, combined with the ability to introduce α-substituents on pendant pyrroles, provides an attractive electronic environment for unsaturated, 3-fold symmetric compounds with mid-to-late first-row transition metals. Inspired by α-free group 4 tris(pyrrolylmethyl)amine and group 5 tris(indolylmethyl)amine complexes reported by Odom[9] and Parkin,[10] respectively, we prepared the new triply phenyl substituted tris(pyrrolylmethyl)amine derivative, H_3tpa^{Ph} (**1**), through the convergent Mannich reaction of 2-phenylpyrrole, formaldehyde, and ammonium chloride (Scheme 1). This first-generation design employs phenyl groups both as steric pickets and potential traps for high-valent electrophilic intermediates.[11]

Iron insertion into the H_3tpa^{Ph} ligand proceeds smoothly via deprotonation with NaH followed by salt metathesis with $FeCl_2$ to generate Na[tpa^{Ph}Fe] (**2**) in 82% yield. The solid-state structure of the anionic component of **2** reveals a relatively rare example of iron(II) in a four-coordinate trigonal monopyramidal geometry.[12] Fe−N bond lengths for the equatorial η^1-pyrrolide (2.010(6) Å) and apical amine (2.174(9) Å) donors are typical, and the metal center is raised by ca. 0.26 Å out of the trigonal plane defined by the three pyrrolide ligands. The solution Evans' method measurement is consistent with high-spin Fe(II) ($S = 2$). With the flanking phenyl groups able to attain a nearly coplanar arrangement with the pyrrolide donors (Scheme 2), no evidence for appreciable coordination of simple Lewis bases, including CO, pyridine, and

Scheme 1. Synthesis of [tpa^RFe]− Complexes



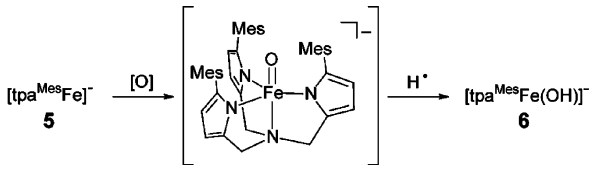


Figure 1. Proposed pathway of oxygen atom transfer to **5** involving a putative Fe(IV)-oxo intermediate with subsequent hydrogen atom abstraction.

acetonitrile, is observed in solution or in the solid state. However, treatment of **2** with the inner-sphere oxidant Me_3NO in a THF solution results in a rapid color change from bright yellow to dark brown. Subsequent workup and crystallization affords a paramagnetic, NMR-silent species in 23% yield. This product has been identified by single-crystal X-ray structural analysis, high-resolution ESI mass spectrometry, and elemental analyses as the iron(III)−phenoxide complex [tpa^{Ph2PhO}Fe]$^-$ (**3**) that results from intramolecular aryl hydroxylation (Scheme 2). Given the kinetic barriers to arene C−H hydroxylation and literature precedent for related reactions mediated by synthetic iron-oxo species,[11b] the facile generation of this oxygenated product suggests the intermediacy of a potent iron-centered oxidant.

Encouraged by the ability of our non-heme iron−pyrrole platform to effect intramolecular oxidation chemistry, we sought to promote intermolecular oxidation reactivity by providing greater access to the iron center and removing the proximate arene C−H bonds. Both of these goals can be met through the synthesis of the tris-mesityl tris(pyrrolylmethyl)amine platform, H_3tpa^{Mes} (**4**), obtained through a triple Mannich reaction starting from 2-mesitylpyrrole.[13] The synthesis of K[tpa^{Mes}Fe] (**5**) proceeds in an analogous manner to its phenyl congener and its solid-state structure displays a similar trigonal monopyramidal core. Unlike the phenyl congener, **5** reacts rapidly with small Lewis bases, including CO, acetonitrile and *tert*-butylisocyanide, to form trigonal bipyramidal adducts in solution. We suggest that the observed differential reactivity between the phenyl and mesityl tpa^R systems is due to the ability of the ortho methyl groups in the latter to gear the pendant aryl and pyrrolide rings toward a more orthogonal disposition (Scheme 2), providing greater overall access to the metal site.

Treatment of iron(II) complex **5** with pyridine-*N*-oxide in dimethoxyethane (DME) furnishes a paramagnetic, brown-colored (λ_{max} at 400 nm) species in 58% yield. Single-crystal X-ray

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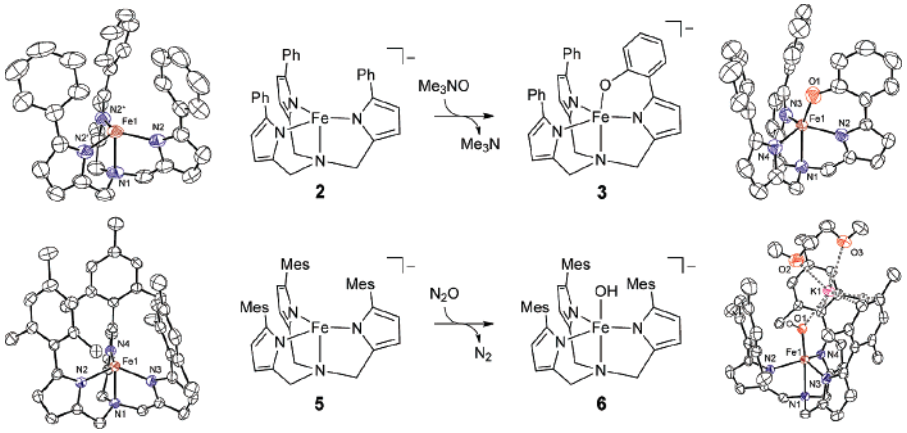
Scheme 2. Oxygen Transfer to Generate Iron(III)−Phenoxide and −Hydroxide Complexes on Non-heme Tris-Pyrrole Platforms



structural analysis, high-resolution mass spectrometry, and elemental analyses establish this product as the terminal iron(III)-hydroxide complex $[tpa^{Mes}Fe(OH)]^-$ (**6**) with no evidence for intramolecular ligand oxidation (Scheme 2). With the oxidative reactivity and coordinative unsaturation of **5** established, we next examined the activation of N_2O. Exposure of **5** to N_2O generates the same terminal hydroxide in 23% recrystallized yield. The use of two-electron oxygen-atom donors for this chemistry suggests a high-valent Fe(IV)-oxo intermediate along the reaction pathway that undergoes hydrogen atom abstraction from solvent (Figure 1). To test this proposal, we performed oxidation reactions in the presence of diphenylhydrazine (DPH) or cyclohexadiene (CHD) as external hydrogen-atom sources. Indeed, when the reaction between **5** and pyridine-*N*-oxide is carried out in the presence of DPH, azobenzene is produced in 92% isolated yield. Analogous oxidations in the presence of CHD produce benzene, although the yields are variable. Taken together, the foregoing reactivity studies establish that a putative non-heme oxoferryl species is viable and suggest an Fe(II)/Fe(IV) manifold for the observed non-heme iron pyrrole reactivity.

To close, we have presented a new non-heme iron pyrrole platform and its ability to activate N_2O for intra- and intermolecular oxidation reactions. This work represents a rare homogeneous system capable of mediating oxidative O-atom transfer from N_2O. Given the demonstrated potency of the putative oxoferryl intermediate, opportunities for stoichiometric or catalytic oxidations with N_2O are promising. In addition to probing spectroscopic and structural features of the active species generated in these oxidation reactions, we are exploring new pyrrole platforms to expand the intermolecular reactivity of these systems.

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Supporting Information Available: Synthetic and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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