

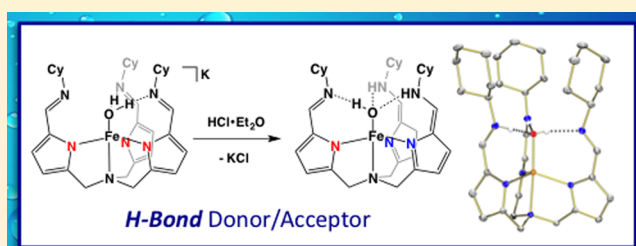
# Isolation of Iron(II) Aqua and Hydroxyl Complexes Featuring a Tripodal H-bond Donor and Acceptor Ligand

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## Supporting Information

**ABSTRACT:** A tripodal ligand platform, tris(5-cycloimino-pyrrol-2-ylmethyl)amine ( $H_3[N(\text{pi}^{\text{Cy}})_3]$ ), that features a hydrogen bond-accepting secondary coordination sphere when bound anionically to an iron center is reported. Neutral coordination to iron affords ligand tautomerization, resulting in a hydrogen bond-donating secondary coordination sphere, and formation of the tris(5-cyclohexyl-amineazafulvene-2-methyl)amine,  $H_3[N(\text{afa}^{\text{Cy}})_3]$ , scaffold. Both binding motifs result in formation of stable, high-spin iron(II) complexes featuring ancillary water, triflate, or hydroxo ligands. Structural analysis reveals that these complexes exhibit distorted trigonal-bipyramidal geometries with coordination of the apical nitrogen to iron as well as three equatorial amine or imine nitrogens, depending on the axial ancillary ligand. Formation of the aqua complex  $K[(N(\text{pi}^{\text{Cy}})_3\text{Fe}(\text{OH}_2))] \text{ (3)}$  illustrated the propensity of the ligand to be hydrogen bond-accepting, whereas the iron triflate species  $[N(\text{afa}^{\text{Cy}})_3\text{Fe}](\text{OTf})_2 \text{ (4)}$  features a hydrogen bond-donating secondary coordination sphere. The ability of each of the three arms of the ligand to tautomerize independently was observed during the formation of the iron–hydroxyl species  $[N(\text{afa}^{\text{Cy}})_2(\text{pi}^{\text{Cy}})]\text{FeOH} \text{ (5)}$  and characterized by X-ray crystallography and IR spectroscopy. The combined data for the iron complexes established that each arm of the tripodal ligand can tautomerize independently and is likely dependent on the electronic needs of the iron center when binding various substrates.



## INTRODUCTION

Analogous to the enhanced reactivity observed in metalloenzymes by appropriately positioned amino acid hydrogen bonds for the binding, orientation, and activation of substrates,<sup>1,2</sup> ligand design may be used to influence the reactivity at a metal center through secondary interactions. These interactions add structural stability to the active site of metalloenzymes and play a key role in regulating activity.<sup>2</sup> Heme and nonheme enzymes that bind and activate dioxygen for a variety of functions combine primary iron ligand fields with defined networks of hydrogen bonding interactions.<sup>3–17</sup> Although the secondary coordination sphere hydrogen bonding interactions of bioinspired metal complexes are crucial to the stabilization of coordinated oxo,<sup>18,19</sup> hydroxo,<sup>16,20–27</sup> and hydroperoxo<sup>28–32</sup> intermediates, as well as the activation of small molecules,<sup>33,34</sup> developing synthetic systems that mimic not only the structural but also the functional properties of metalloenzymes has been challenging. Synthetic difficulties arise from the necessity to involve multiple proton–electron transfers in the sustainable transformation of small molecules such as  $O_2$ ,  $H_2$ ,  $CO_2$ , and  $N_2$ .<sup>35–39</sup>

Synthetic systems capable of mediating multiple proton–electron transformations have involved highly specialized and synthetically challenging ligands such as picket-fence,<sup>40,41</sup> crown,<sup>42</sup> Pacman,<sup>43</sup> and Hangman<sup>44</sup> porphyrins, all of which feature flanking hydrogen bonding networks. One of the

earliest examples of a nonheme, ancillary ligand that includes a secondary coordination sphere of a metal ion, reported by Kitajima and co-workers<sup>45</sup> involves the formation of  $Mn(O_2)-(3,5\text{-}^i\text{Pr}_2\text{pzH})(\text{HB}(3,5\text{-}^i\text{Pr}_2\text{pz})_3)$ , in which a single hydrogen bond is shown to stabilize the Mn(III)–peroxo compound.<sup>45</sup> Borovik and co-workers have established that appropriately placed hydrogen bonds are capable of regulating the micro-environment at the metal center and that these site-specific modulations in structure can be correlated to reactivity.<sup>12,14,18–20,22,24,46</sup> For example, varying the number of hydrogen bonds (from three to zero) within a tripodal cobalt system, through the development of hybrid urea-carboxamide ligands, resulted in a variance of stability of the resultant Co–OH complexes.<sup>46a</sup> Inspired by this work, we sought to design a single ligand scaffold that, depending on substrate ligation or chemical environment, was flexible in the hydrogen bonding environment. Our goal was twofold: (1) to incorporate a secondary coordination sphere in which the hydrogen bonding to substrates was flexible in that as many as three hydrogen bonds or as few as none could be accessed for binding to the substrate, and (2) the coordination of the ligand to a metal could adapt electronically to allow the metal center to traverse various oxidation states.

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The formation of iron–hydroxyl species derived from either  $O_2$  or water has been observed; however, nonheme mononuclear Fe–OH ( $Fe^{II}/Fe^{III}$ ) species are limited<sup>16,20–27</sup> given their propensity to form multinuclear hydroxo- or oxo-bridged complexes. With the addition of very bulky ligands or secondary hydrogen bonding networks the formation of mononuclear Fe–OH species has been developed. The work by Borovik<sup>12,18,19</sup> is an elegant display of the importance of hydrogen bonding motifs in the preparation and characterization of iron complexes supported by the urea-based, tripodal ligand framework tris{(N'-tert-butylureayl)-N-ethylene]-amine.<sup>23</sup> Upon exposure to oxygen, formation of the iron(II)/iron(III)–hydroxo species is observed, stabilized by the intramolecular hydrogen bonding framework. The work by Borovik has focused on intramolecular hydrogen bonds and intermolecular hydrogen bonds;<sup>24</sup> very bulky ligands<sup>21,26b</sup> have also been used to stabilize monomeric Fe–OH complexes.

Although numerous ligands have been constructed that feature hydrogen bonding with substrates on the metal center, fewer ligand constructs feature hydrogen bond acceptors<sup>47,48</sup> in the secondary coordination sphere. Ligands that incorporate both hydrogen bond donors and acceptors are exceedingly rare.<sup>47,49</sup> Therefore, we sought to design a ligand scaffold that contains a well-defined primary coordination sphere for binding of a metal center and that features a secondary coordination sphere that, through ligand tautomerization, may be hydrogen bond donating and/or hydrogen bond accepting. To satisfy the aforementioned design criteria and electronic structure of the metal center we sought a pyrrol-based tripodal ligand framework, analogous to the tris(5-arylpyrrol-2-ylmethyl)amine ( $H_3tpa^{Ar}$ ), for the primary coordination sphere at the metal center.<sup>27,50</sup> This tripodal framework recently reported by Chang and co-workers has been shown to support a family of high-spin iron(II) complexes.<sup>51</sup> Upon oxidation of these compounds with  $Me_3NO$ , a transient Fe(IV)–oxo is formed, which is capable of functionalizing the proximal aryl-CH bonds of the ligand or abstracting H• from ethereal solvents.<sup>51</sup> This result implied that appending a secondary coordination sphere to the ligand framework may allow for the desired secondary coordination sphere interactions with metal–ligand multiple bonds.

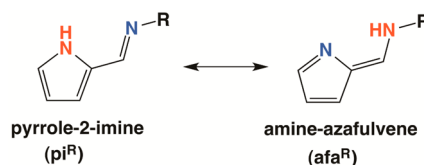
Our research program focuses on the utilization of earth-abundant metals, such as iron, to activate small molecules through the influence of ligand design. In this Report, we present the new ligand platform tris(5-cycloiminopyrrol-2-ylmethyl)amine ( $H_3[N(pi^{Cy})_3]$ ), in which the secondary coordination sphere can accommodate noncovalent interactions (hydrogen bonds) with exogenous ligands bound to the metal center. The synthesis, spectroscopic characterization, and reactivity of a new series of tripodal iron(II) complexes is discussed. This system is distinguished from other hydrogen bond cavities by its flexibility to traverse trianionic coordination to neutral coordination at the metal center while promoting a secondary coordination sphere that can be either hydrogen bond donating or accepting. This flexibility of the ligand scaffold through tautomerization allows for the isolation of stable iron(II) aqua, triflate, and hydroxyl complexes.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of  $H_3(N(pi^{Cy})_3)$ .** To generate a series of pyrrole-based tripodal ligands with a secondary coordination sphere for the stabilization of high-valent  $M=O$  complexes, we invoked modification of the parent

ligand tris(pyrrol)amine ( $H_3tpa$ ) by addition of a variety of functional groups. Chiefly, our interests focused on the selection of a pendant functional group that could serve as both a hydrogen bond donor and acceptor, depending on chemical environment and exposure to substrate. Literature precedent displays the ability of a pyrrol-2-imine to engage in tautomerization (Scheme 1).<sup>55</sup> Formation of a ligand frame-

Scheme 1

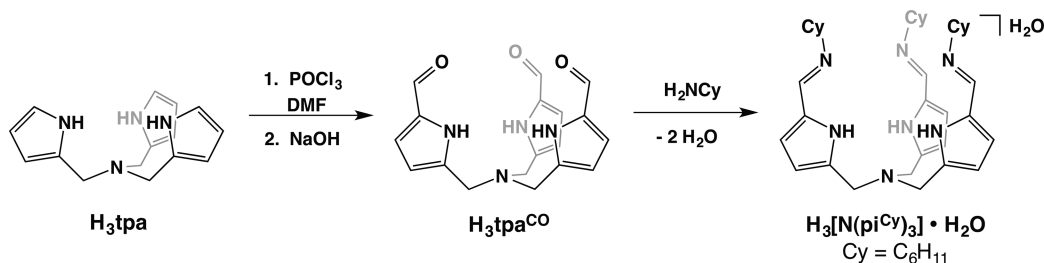


work where the metal center could bind in the pyrrol pocket gives the opportunity for a hydrogen bond-accepting secondary coordination sphere in the case of anionic coordination (abbreviated ( $pi^{Cy}$ )), while a neutral coordination environment, in the case of the amine–azafulvene tautomer (abbreviated ( $afa^{Cy}$ )) gives rise to a hydrogen bond donating periphery. The multidentate ligand architecture allows for flexibility in the secondary coordination sphere in that the various arms of the ligand may independently tautomerize to be either hydrogen bond donating or accepting, depending on chemical environment and electronic needs of the metal center.

Previous work with the development of functionalized polypyrrol compounds has illustrated a preparatory pathway for the generation of these ancillary ligands. In the case of Chang and co-workers, assembly of a tripodal pyrrole ligand framework is accomplished by triple Mannich condensations of 2-R-pyrrole (R = mesityl, 2,4,6-triisopropylphenyl, 2,6-difluorophenyl, tert-butyl, phenyl).<sup>50</sup> Following failed synthetic attempts at the generation of the desired ligand framework  $H_3(N(pi^{Cy})_3)$  by traditional routes, an alternative preparatory pathway was explored. Recent work by the Beer<sup>54</sup> and Love<sup>55</sup> research groups has shown the utility of the installation of 5'-imine substituents following the assembly of the polypyrrole framework for the functionalized tris(5-R-imino-pyrrol)ethane ligand  $H_3tpe^{NR}$  (R = cyclohexyl, benzyl) in good yields. While these ligands were suggested to afford secondary coordination spheres to metal centers possessing a pseudotetrahedral ligand field, the expected tripodal coordination of the ligand framework was sparsely observed.<sup>55</sup> We postulated installation of the functional group off the 5' carbons of the tris(pyrrol-2-methyl)amine ligand scaffold would afford the desired coordination geometry for the metal complexes.

An adapted procedure from that developed for the installation of the aldehyde functional group in the synthesis of tris(5-formylpyrrol-2-ylmethyl)ethane ( $H_3tpe^{CO}$ ) via a Vilsmeier–Haack formylation was explored for the tris(pyrrol)amine. In a similar fashion, the formyl derivative of tris(pyrrol)amine,  $H_3tpa^{CO}$ , was synthesized by the dropwise addition of  $POCl_3$  to a solution of  $H_3tpa$  in DMF at  $-10\text{ }^\circ\text{C}$  (Scheme 2). Following workup, the proligand was isolated as a brown solid in low yields (41%). While the formation of  $H_3tpa^{CO}$  was confirmed by  $^1H$  (Supporting Information, Figure S1) and  $^{13}C$  NMR and IR spectroscopies, the lack of purity of the sample due to contamination by NMR silent species and the inability to separate the compound from the residual reaction solvent, DMF, prohibited confirmation of formation by elemental analysis. Stirring  $H_3tpa^{CO}$  with an excess of

Scheme 2

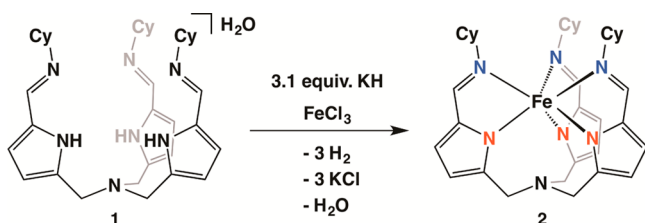


cyclohexylamine in a dry acetonitrile solution resulted in the quantitative formation of the desired imine ligand architecture via condensation (Scheme 2). The ligand could also be synthesized *in situ* by the addition of cyclohexylamine to the  $H_3tpa^{CO}$  prior to isolation.  $H_3[N(pi^{Cy})_3] \cdot H_2O$  (**1**) is isolated as a beige powder in good yields from the  $H_3tpa$  starting material (53%). Characterization of the ligand by elemental analysis revealed encapsulation of one water molecule, indicating a high affinity for substrate binding to the ligand prior to metalation. Similar behavior has been observed for the trispyrrolylethane ligand  $H_3tpe^{NCy}$ .<sup>55</sup> In the case of  $H_3tpe^{NCy}$ , crystallographic characterization also revealed binding of a water molecule within the pocket of the ligand, stabilized by hydrogen bonding.

Tautomerization of the proposed ligand system has been observed in a similar framework in the case of  $H_3tpe^{NCy}$ . Addition of  $H_3tpe^{NCy}$  to  $CoCl_2$  under aerobic conditions resulted in the oxidation of the metal center to cobalt(III), with two neutrally coordinated ligands bound to the metal center and three outer sphere chlorine atoms,  $[Co(H_3tpe^{NCy})_2][Cl]_3$ .<sup>55</sup> Structural analysis of the product revealed tautomerization of the ligand to afford the amine–azafulvene species (Scheme 1), where the amine proton is proposed to derive from a proton migration from the pyrrole nitrogen to the imine moiety.<sup>55</sup> The isomerization of this ligand indicates potential for ligand-mediated modulation of the oxidation state of a transition metal center in coordination complexes of this type and enables this ligand species to serve as both a hydrogen bond donor and acceptor.

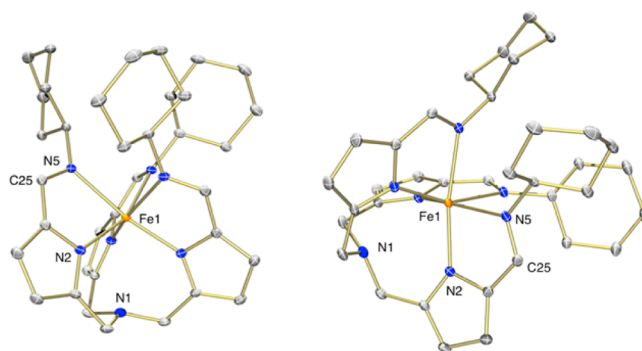
**Synthesis of  $[(N(pi^{Cy})_3)Fe]$ .** Following synthesis and characterization of the desired ligand **1**, metalation was attempted. Addition of 3.1 equiv of KH to a THF solution of complex **1** resulted in a vigorous effervescence of hydrogen and the *in situ* generation of  $K_3[(N(pi^{Cy})_3)]$ . Addition of the potassium salt of complex **1** to a THF solution of  $FeCl_3$  resulted in an immediate color change to dark brown (Scheme 3). Following workup, the product,  $(N(pi^{Cy})_3)Fe$  (**2**), was isolated as a brown powder in high yields (68%). Analysis of **2** by  $^1H$  NMR spectroscopy revealed a paramagnetic product composed of ill-defined, broad resonances ranging from  $-15.7$  to  $33.0$  ppm (Supporting Information, Figure S3). The

Scheme 3



magnetic moment of complex **2** of  $5.73 \mu_B$  was determined by Evans' method, consistent with the formation of a high spin, trivalent iron species. Characterization by IR spectroscopy revealed an intense feature located at  $1581 \text{ cm}^{-1}$ , assigned to the  $C=N$  stretch of the ligand. This IR stretch is consistent with a previously characterized Zn complex ( $C=N$  at  $1586 \text{ cm}^{-1}$ ) featuring a similar bidentate coordination of the ligand.<sup>55</sup>

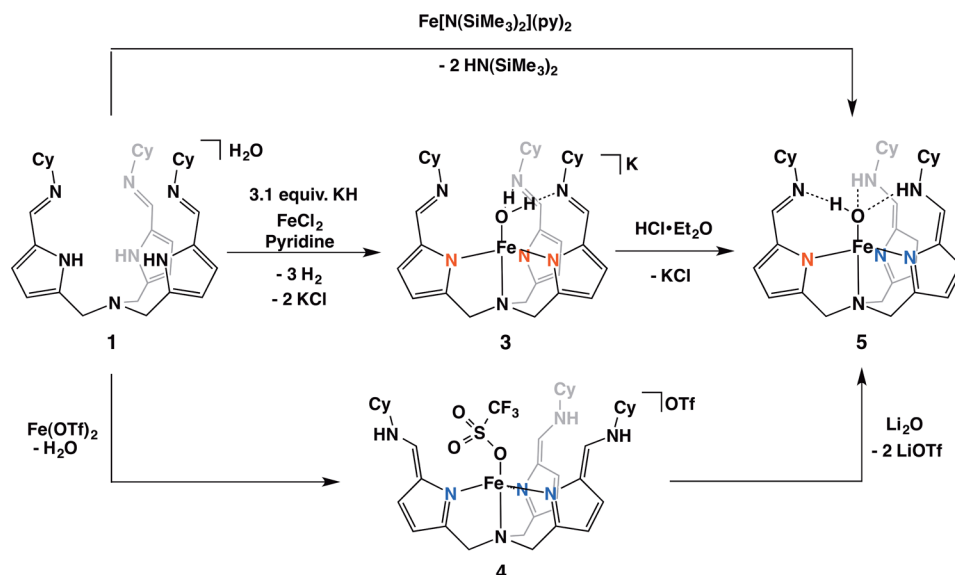
To definitively identify the molecular structure of complex **2** and better understand the coordination geometry of the tris(pyrrolyl)amine ligand framework with hydrogen bond-accepting secondary coordination sphere, crystals suitable for X-ray diffraction were grown from a concentrated solution of THF and benzene (1:1), layered with hexanes. Refinement revealed an iron(III) center in a pseudo-octahedral coordination environment. One face of the octahedron is derived from anionically coordinated pyrrole nitrogens of the ligand framework, while the other face is composed of imine nitrogens datively bound to the metal center. Complex **2** crystallizes in a hexagonal unit cell, with the  $C_3$  axis of the molecule sitting along a symmetry operation (see Figure 1). Thus, only a third



**Figure 1.** Molecular structure of **2** shown with 50% probability ellipsoids. Hydrogen atoms were removed for clarity. Left view of complex shown perpendicular to the  $Fe \cdots N1$  axis similar to subsequent complexes; right view displays pseudo-octahedral coordination geometry of **2**. Selected bond lengths (Å) and angles (deg):  $Fe1 \cdots N1$ , 2.949 58(10);  $Fe1-N2$ , 2.029 88(5);  $Fe1-N5$ , 2.263 96(6);  $N2-Fe1-N5$ , 74.976(3);  $N2-Fe1-N2a$ , 100.626(3),  $N5-Fe1-N2a$ , 158.4037(8);  $N5-Fe1-N5a$ , 85.0094(18).

of the molecule is chemically unique, with the remaining three arms generated by a symmetry operation. The iron center is removed from the traditional tris(pyrrolyl)amine pocket, with an  $Fe1-N1$  interaction of 2.949 58(10) Å, indicative of dative binding of iron to the apical nitrogen. The  $Fe1-N2$  distance of 2.029 88(5) Å is consistent with anionic  $Fe-N$  distances reported previously for pyrrolyl-based ligand frameworks.<sup>50</sup> The

Scheme 4



Fe1–N5 distance of 2.263 96(6) Å is consistent with a dative interaction.

#### Synthesis and Characterization of Iron(II) Complexes.

Since using an Fe(III) starting material afforded the coordinatively saturated and undesired octahedral iron complex, metalation of  $\text{H}_3[(\text{N}(\text{pi}^{\text{Cy}})_3)]$  was then attempted in analogy to the generation of  $[\text{Fe}(\text{tpa}^{\text{R}})]^-$ , reported by Chang and co-workers to synthesize Fe(II) derivatives.<sup>50</sup> Deprotonation of  $\text{H}_3[(\text{N}(\text{pi}^{\text{Cy}})_3)]$  was accomplished once again by addition of 3.1 equiv of KH to a THF solution of **1**. After it was stirred for 3 h at room temperature, the mixture was filtered over Celite to remove excess KH. Addition of the freshly generated  $\text{K}_3[(\text{N}(\text{pi}^{\text{Cy}})_3)]$  *in situ* to a slurry of  $\text{FeCl}_2$  in THF resulted in an instantaneous color change to yellow-orange, with concurrent dissolution of the starting material (Scheme 4). Following workup, the product  $\text{K}[(\text{N}(\text{pi}^{\text{Cy}})_3)\text{Fe}(\text{II})\text{H}_2\text{O}]$  (complex **3**) was isolated as a yellow powder in high yields (73%).

Analysis of complex **3** by <sup>1</sup>H NMR spectroscopy revealed four distinct paramagnetically shifted and broadened resonances, ranging from 0.2 to 95.6 ppm (Supporting Information, Figure S4). Signals integrating to three hydrogens located at 28.6, 32.3, and 95.6 ppm are assigned to the aryl C–H protons of the pyrrole moieties and the imine C–H protons of the ligand bound to the iron center. The six methylene hydrogens of the ligand framework are located at 12.3 ppm. Additionally, a cluster of signals ranging from 3.7 to 7.3 ppm were assigned to the cyclohexyl protons of the ligand framework. The number of <sup>1</sup>H NMR resonances is indicative of a C<sub>3</sub> symmetric molecule. IR spectroscopy further corroborated the C<sub>3</sub> symmetric ligand scaffold with a single, broad and intense  $\nu_{\text{CN}}$  signal at 1602 cm<sup>-1</sup>, indicative of a single ligand tautomer present in all three arms of the complex. The solution magnetic moment for complex **3** as determined by the Evans' method ( $\mu_{\text{eff}} = 5.39 \mu_{\text{B}}$ ) was consistent with a high-spin, Fe(II) metal center. This electronic state is similar to that observed by Chang and co-workers for their  $\text{M}[\text{Fe}(\text{tpa}^{\text{R}})]$  (M = Na, K; R = mesityl, 2,4,6-triisopropylphenyl, 2,6-difluorophenyl, *tert*-butyl, phenyl) complexes with  $\mu_{\text{eff}}$  values ranging from 5.15 to 5.42  $\mu_{\text{B}}$ .<sup>50</sup>

Orange crystals of complex **3** suitable for X-ray analysis were grown by vapor diffusion of hexanes into a concentrated THF solution of the complex. Refinement of the data revealed that

the iron(II) species is in a pseudo-trigonal bipyramidal coordination geometry with a water molecule occupying the position trans to the apical nitrogen and bound to the metal center (Figure 2, Table 1). The Fe–O1 distance of 2.080(2) Å compares favorably to that of Fe(II) aqua complexes reported in the literature, indicating a dative interaction between the two atoms.<sup>57</sup> The equatorial plane is composed of the anionically bound pyrrol nitrogen ( $\text{N}_{\text{pyr}}$ ) atoms.

Although the protons of the water molecule within the coordination sphere of the metal center were not observed on the <sup>1</sup>H NMR time scale, potentially due to proximity to the paramagnetic iron center, calculated positions indicate the protons of the water molecule are engaging in hydrogen bonding with two of the pendant imine nitrogen atoms, supported by N6···H6 and N7···H7 distances of 1.90(2) and 1.81(2) Å, respectively. The N6–O1 and N7–O1 distances of 2.739(3) and 2.650(4) Å are well within the range of donor–acceptor atoms participating in hydrogen bonding interactions. The resulting hydrogen bonding is further manifested in the elongation of two of the Fe– $\text{N}_{\text{pyr}}$  bond distances (2.108(2) and 2.118(2) Å), as compared to the third arm, which is not engaging in secondary interactions (Fe– $\text{N}_{\text{pyr}}$  bond distance of 2.044(2) Å) and more closely resembles the previously reported Fe– $\text{N}_{\text{pyr}}$  distances of  $[\text{Fe}(\text{tpa}^{\text{R}})]^-$  (R = Ph, Mes, <sup>t</sup>Bu) (2.008(3)–2.041(2) Å).<sup>50</sup> As a result, no distinct  $\nu_{\text{OH}}$  stretches were observed for the aqua complex presumably masked by the strong intramolecular hydrogen bonding within the cavity. Furthermore, the Fe–N1 distance of 2.262(3) Å is significantly elongated from that of Chang's  $[\text{Fe}(\text{tpa}^{\text{R}})]^-$  complexes (2.144(1)–2.172(2) Å),<sup>50</sup> while the N1–Fe– $\text{N}_{\text{pyr}}$  bond angles of complex **3**, ranging from 78.70(10)–80.21(10)°, further indicate a deviation from the traditional geometry, as previously characterized  $\text{M}[\text{Fe}(\text{tpa}^{\text{R}})]$  (M = Na, K) complexes have N1–Fe– $\text{N}_{\text{pyr}}$  bond angles ranging from 82.00(9)–83.84(6)°. This interaction of the Fe(II) metal center with a water molecule engaged in hydrogen bonding with the ancillary coordination environment is proposed to be responsible for perturbing the metal center from the plane of the pyrrole rings, thus giving rise to the observed distorted trigonal bipyramidal geometry.

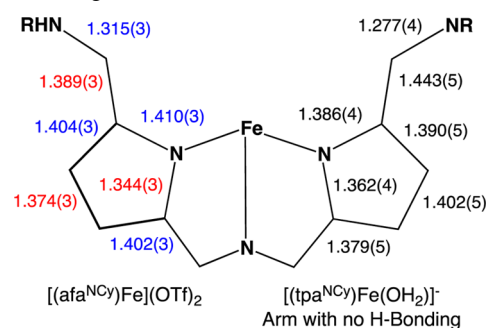
Because of our interest in probing the ability of each arm of the ligand to tautomerize independently, metalation was explored by addition of complex **1** to 1 equiv of  $\text{Fe}(\text{OTf})_2 \cdot (\text{MeCN})_2$  ( $\text{OTf} = \text{trifluoromethanesulfonate}$ ) without the addition of base. Upon addition of a THF solution of the ligand to a THF slurry of  $\text{Fe}(\text{OTf})_2$ , an instantaneous color change to yellow was noted (Scheme 4). To ensure consumption of starting materials, the reaction was stirred for 30 min before the solvents were removed under reduced pressure. Following workup, the product  $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}](\text{OTf})_2$  (**4**) was isolated as a yellow powder in quantitative yields.

Analysis of complex **4** by  $^1\text{H}$  NMR spectroscopy revealed a complicated spectrum composed of paramagnetic resonances ranging from  $-5.19$  to  $39.24$  ppm (Supporting Information, Figure S5). While the number of peaks is consistent with the desired complex  $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}](\text{OTf})_2$  adopting an unsymmetric conformation in solution, definitive peak assignment was impossible due to overlapping resonances and dynamic broadening. Characterization by  $^{19}\text{F}$  NMR revealed a signal at  $-79.59$  ppm, corresponding to the fluorine atoms of the trifluoromethylsulfonate counteranions. The single resonance indicates uniformity in the chemical environment of fluorine, suggesting dissociation of both  $(\text{OTf})^-$  moieties in solution on the NMR time scale. Characterization by IR spectroscopy revealed an intense feature centered at  $\nu_{\text{CN}}$  of  $1637\text{ cm}^{-1}$ , a value blue-shifted (by  $\sim 35\text{ cm}^{-1}$ ) from complex **3**, consistent with previously reported azafulvene derivatives of transition metal complexes.<sup>56</sup> The magnetic data from a series of independently synthesized samples of complex **4**, revealed an average  $\mu_{\text{eff}}$  of  $5.37\text{ }\mu\text{B}$ , consistent with a high-spin,  $S = 2$ , Fe(II) metal center.

Structural characterization of **4** was obtained by X-ray diffraction studies from a concentrated THF solution of the compound layered with diethyl ether. Refinement revealed a five-coordinate Fe(II) center in a pseudo-trigonal bipyramidal geometry, composed of the tripodal ligand framework with a triflate anion bound trans to the apical nitrogen (Figure 2, Table 1). The equatorial plane of complex **4** is composed of the pyrrolidone nitrogen atoms, with  $\text{Fe}-\text{N}_{\text{pyr}}$  bond distances ranging from  $2.060(2)$  to  $2.081(2)$  Å. The  $\text{Fe}-\text{N1}$  distance of  $2.268(2)$  Å is akin to complex **3**, indicating a similar displacement of the iron center from the equatorial plane.

Although the gross structural features of **3** and **4** are similar, a comparison of intraligand bond distances revealed bond contractions and elongations consistent with the formation of the amine–azafulvene tautomer in the latter complex upon coordination to the metal center (Chart 1). The bond distances compare favorably to Fe(II) complexes reported by Love and co-workers, in which tautomerization of the N-donor-extended dipyrromethane ligand framework upon coordination to  $\text{FeBr}_2$  affords the amine–azafulvene product  $\text{FeBr}_2[\text{H}_2\text{L}]$  ( $\text{L} = [2-(\text{tBu}-\text{NHCH})-\text{C}_4\text{H}_4\text{N}]_2\text{CMe}_2$ ).<sup>57</sup> This type of amino/imino ligand tautomerization was also observed in tetradentate ligand tris(2-amino-oxazoline)amine, which upon metalation tautomerizes to the 2-imino-oxazolidine.<sup>47</sup> The hydrogen atoms adjacent to the nitrogen atoms of the pendant imine moieties of **4** were located and refined, further supporting ligand tautomerization during the formation of complex **4**. The N–H functionalities are rotated away from the triflate molecule bound to the iron center and possess hydrogen bonding interactions to the outer-sphere triflate counterions, with N–O bond distances ranging from  $2.910(3)$ – $2.980(3)$  Å. A lack of

**Chart 1. Bond Length Comparisons between Complexes 4 (left) and 3 (right)<sup>a</sup>**

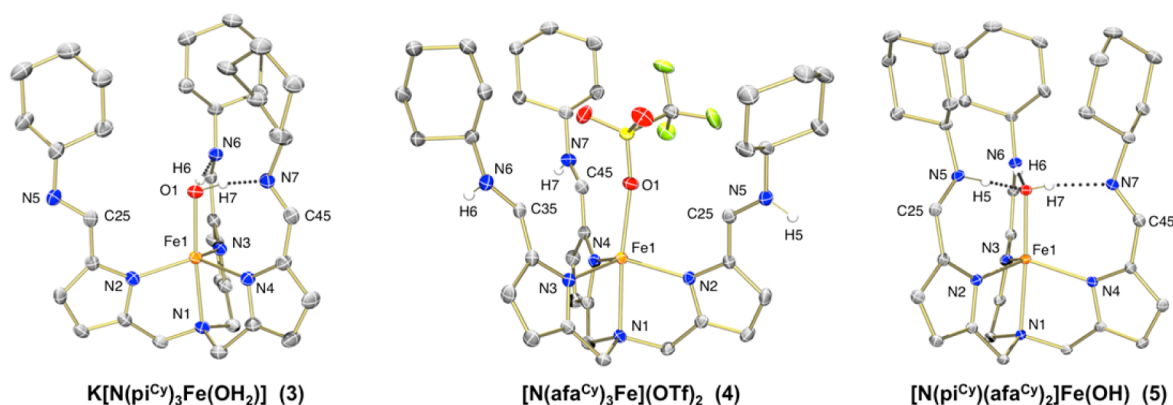


<sup>a</sup>Bond distances of the azafulvene substituent (**4**) listed in red denote contraction, while those in blue signify elongation from anionically coordinated pyrrole–imine (**3**) arm.

hydrogen bonding to the inner-sphere triflate is proposed to be a result of the steric bulk of the counterion.

To evaluate the ability of the ligand framework to engage in asymmetric tautomerization another synthetic route was sought. Exposure of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2(\text{py})_2$  to 1 equiv of complex **1** resulted in an instantaneous color change to a pale orange-brown, with concurrent formation of 2 equiv of  $\text{HN}(\text{SiMe}_3)_2$  as confirmed by  $^1\text{H}$  NMR spectroscopy (Scheme 4). Characterization of the paramagnetic, iron-containing product by  $^1\text{H}$  NMR spectroscopy revealed 10 resonances paramagnetically shifted and broadened ranging from  $-3.86$  to  $28.82$  ppm, consistent with  $\text{C}_3$  symmetry in solution (Supporting Information, Figure S6). Assignment of the signals was made possible by integration, with the three resonances located at  $-3.86$ ,  $27.71$ , and  $28.82$  ppm integrating to 3H corresponding to the imine C–H and aryl protons of the pyrrolidine moiety, respectively, while the signal integrating to 6H located at  $16.20$  ppm is assigned to the methylene protons. Resonances ranging from  $5.49$  to  $8.23$  ppm collectively integrate to 33H, which corresponds to the flanking cyclohexyl substituents adjacent to the imine nitrogens. An identical species with similar spectral features is noted upon deprotonation of  $\text{H}_3[\text{N}(\text{afa}^{\text{Cy}})_3]$  with  $\text{LiN}(\text{SiMe}_3)_2$  and addition of the solution to a THF slurry of  $\text{FeCl}_2$ .

Yellow crystals of **5** suitable for analysis by X-ray crystallography were grown from a concentrated THF solution layered with hexanes. Structural refinement revealed a pseudo-trigonal bipyramidal Fe(II) center with a hydroxyl moiety occupying the coordination site trans to the apical nitrogen (Figure 2, Table 1). The  $\text{Fe1}-\text{O1}$  bond distance of  $2.0339(12)$  Å is akin to that of  $[\text{Fe}^{\text{II}}\text{H}_3\text{L}(\text{OH})]^{2-}$  ( $\text{L} = \text{N}[\text{CH}_2\text{CH}_2\text{N}^-\text{C}(\text{O})\text{NHC}(\text{CH}_3)_3]_3$ ), previously reported by Borovik and co-workers, with Fe–O bond distances of  $2.051(3)$  and  $2.044(3)$  Å,<sup>23</sup> however, it is significantly longer than sterically unencumbered monometallic  $\text{Fe}^{\text{II}}(\text{OH})$  complexes with Fe–O bond distances ranging from  $1.830(8)$  to  $1.938(3)$  Å.<sup>13,16,21,24</sup> The equatorial plane is composed of the pyrrole nitrogens, with Fe–N bond distances ranging from  $2.1020(14)$  to  $2.1264(14)$  Å, which are significantly longer than those reported by Chang and co-workers for their family of  $[\text{Fe}(\text{tpa}^{\text{R}})]^-$  ( $\text{R} = \text{tBu}, \text{Ph}, \text{Mes}$ ) complexes ( $2.008(3)$ – $2.031(1)$  Å).<sup>50</sup> This elongation is once again attributed to the structural constraints placed on complex **5** by the interactions of the secondary coordination sphere with the hydroxyl substituent.



**Figure 2.** Molecular structures of **3**, **4**, and **5** shown with 50% probability ellipsoids. Solvent molecules, selected hydrogen atoms, potassium counteranions (**3**), and outer sphere triflate anions (**4**) were removed for clarity.

**Table 1.** Spectroscopic Data and Structural Parameters of **1**,  $\text{H}_3(\text{tpe}^{\text{NCy}})$ , **2**, **3**, **4**, and **5**

bond <sup>a</sup>	<b>1</b>	$\text{H}_3(\text{tpe}^{\text{NCy}})\cdot\text{H}_2\text{O}$	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Fe1–N1			2.94958(10)	2.262(3)	2.268(2)	2.2675(14)
Fe1–N2			2.02988(5)	2.044(2)	2.076(2)	2.1020(14)
Fe1–N3			2.26396(6)	2.118(2)	2.060(2)	2.1091(14)
Fe1–N4				2.108(2)	2.081(2)	2.1264(14)
Fe1–O1				2.080(2)	2.1603(19)	2.0339(12)
O1–H5						0.757(19)
O1–H6				0.843(19)		1.54(2)
O1–H7				0.863(19)		1.75(2)
C25–N5		1.24(2)	1.350(3)	1.277(4)	1.298(4)	1.281(2)
C35–N6		1.24(2)		1.290(4)	1.299(4)	1.297(2)
C45–N7		1.24(2)		1.281(4)	1.315(4)	1.300(2)
O1...N5		3.12(2)				2.7939(18)
O1...N6		2.89(2)		2.739(3)		2.5653(18)
O1...N7		2.87(2)		2.650(4)		2.650(2)
N1–Fe1–N2 <sup>b</sup>				78.70(10)	79.83(9)	78.04(5)
N1–Fe1–N3				80.21(9)	77.08(8)	78.16(5)
N1–Fe1–N4				79.68(10)	77.66(9)	79.09(5)
C=N stretch	1638 cm <sup>-1</sup>	1639 cm <sup>-1</sup>	1581 cm <sup>-1</sup>	1603 cm <sup>-1</sup>	1637 cm <sup>-1</sup>	1624,1655 cm <sup>-1</sup>
magnetic moment			5.73 $\mu_{\text{B}}$	5.39 $\mu_{\text{B}}$	5.37 $\mu_{\text{B}}$	5.31 $\mu_{\text{B}}$

<sup>a</sup>Bond lengths are listed in Å. <sup>b</sup>Bond angles are given in degrees.

Binding of the oxygen atom to the iron center was made possible by refinement of H5, H6, and H7 in the structure of **5**. The O1–H5 bond distance of 0.757(19) Å is consistent with a single covalent bonding interaction between these two atoms, while the O1–H6 and O1–H7 distances of 1.54(2) and 1.75(2) Å, respectively, are reminiscent of hydrogen bonding interactions. Thus, the secondary coordination sphere of complex **5** is best defined as an Fe–OH moiety with hydrogen bonding interactions to the imine nitrogen of a pyrrolidine–imine arm of the ligand. The oxygen atom is also engaged in hydrogen bonding from the adjacent, pendant N–H substituents (N6–H6 = 1.028(19) Å; N7–H7 = 0.90(2) Å) formed as a result of tautomerization to the datively coordinated amine–azafulvene. All three O1–NX (X = 5, 6, 7) distances fall within the appropriate range for hydrogen bonding interactions (2.5653(18)–2.7939(18) Å). These two distinct coordination modes of the ligand arms as pyrrol–imine and azafulvene–amine are observed in the solid-state IR spectroscopy, as denoted by the two distinct C=N stretches located at 1624 and 1655 cm<sup>-1</sup>, respectively.

**Mechanistic Considerations.** Mechanistically, two processes can be invoked for the formation of **5**. In the first, upon

exposure of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(py)<sub>2</sub> to 1 equiv of complex **1**, deprotonation of water by an amide gives rise to the transient Fe(OH)[N(SiMe<sub>3</sub>)<sub>2</sub>](py)<sub>2</sub> species. Subsequent deprotonation of a pyrrole of the ligand then coordinates the ligand to the Fe(II) center. Hydrogen bonding directs the formation of the trigonal bipyramidal structure observed for **5**. Alternatively, one can invoke the deprotonation of both pyrrole N–H bonds by the amines of the Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(py) starting material, releasing 2 equiv of amine, HN(SiMe<sub>3</sub>)<sub>2</sub>. Water then coordinates to the metal center, and the third arm binds datively, engaging in hydrogen bonding between the amine N–H and the oxygen atom of water. Finally, deprotonation of the water complex by a pendant imine gives rise to the formation of the hydroxyl species **5**.

However, we were unable to determine if the hydrogen bonding network of the ligand scaffold prevents the ligand-bound water molecule from interacting with the metal center prior to coordination of the pyrroles during formation of complexes **3** and **5**. Two different synthetic pathways were targeted to gain understanding of the mechanism for formation of **5**. When complex **4** is exposed to Li<sub>2</sub>O, a salt metathesis occurs, resulting in the release of 2 equiv of LiOTf, which can

be washed away with hexanes, and the subsequent formation of complex **5** via the deprotonation of a pendant amine by  $[O^{2-}]$ . Alternatively, the addition of  $HCl \cdot Et_2O$  to **3** cleanly resulted in formation of **5**, as assayed by  $^1H$  NMR spectroscopy. This process is chemically reversible, as addition of 1 equiv of base  $KCH_2Ph$  to complex **5** results in the quantitative conversion to the iron(II) aqua species **3**.

The formation of complex **5** illustrates the propensity of  $H_3[N(pi^{Cy})_3]$  to behave as both a hydrogen bond acceptor and donor. The anionically coordinated arm, featuring an imine–pyrrolidene extended network, makes available an imine nitrogen for hydrogen bonding with a H atom donor, such as the hydroxyl moiety in complex **5**. Ligand tautomerization to form the amine–azafulvene places hydrogen atoms on the pendant nitrogens available to engage in hydrogen bonding with the O atom acceptor. While solid-state characterization through IR and X-ray crystallography defines complex **5** as the hydroxyl species, the equivalency of the three arms of the tripod on the NMR time scale may more aptly define this compound as the hydronium species. The flexible network of hydrogen bonding results in the generation of stable Fe(II) species.

## CONCLUSION

We investigated the formation of high-spin iron(II) complexes featuring the tris(5-cyclohexyliminopyrrol)amine  $H_3[N(pi^{Cy})_3]$ , ligand (**1**). The secondary coordination sphere of **1** is capable of tautomerizing from the imine–pyrrole to the amine–azafulvene both in a symmetric and unsymmetric fashion, depending on additional axial coordination of a substrate as well as the oxidation state of iron. Trianionic coordination of the ligand to iron was achieved by prior *in situ* deprotonation of the ligand with potassium hydride and subsequent addition of  $FeCl_2$  to obtain  $K[(N(pi^{Cy})_3Fe(H_2O))] (3)$  in good yields. The propensity of the ligand scaffold to form hydrogen bonds was first exemplified in formation of the free ligand by inclusion of a single water molecule and again during formation of **3**. Formation of  $[N(afa^{Cy})_3Fe](OTf)_2$ , compound **4**, exposed the ligand's electronic flexibility as it tautomerized from the trianionic hydrogen bond-accepting pyrrole–imine platform to the neutral azafulvene–amine hydrogen bond-donating architecture. IR spectroscopy as well as crystal structure determination was consistent with the ligand tautomerization. Excitingly the various arms of the ligand can tautomerize independently, depending on substrate as well as electronic need of the iron center, which was evident in formation of the iron–hydroxyl complex  $[N(pi^{Cy})(afa^{Cy})_2]FeOH (5)$ . One arm of the ligand scaffold is the anionic pyrrole, while the other two arms of the tripodal system are coordinated to iron as the neutral azafulvene. Both complexes **3** and **4** could be converted to **5**, as well as **5** to **3**, clearly illustrating the flexibility of each arm of the ligand scaffold to engage in independent tautomerization. This insight into the dynamic nature of the ligand framework allows for the future exploration of multielectron transformations featuring the tripodal hydrogen bond donor or acceptor ligand  $H_3[N(pi^{Cy})_3]$ .

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven-dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents were dried and deoxygenated on a

Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following literature procedure prior to use. Chloroform-*d*, tetrahydrofuran-*d*<sub>8</sub>, and acetonitrile-*d*<sub>3</sub> were purchased from Cambridge Isotope Laboratories and were degassed and stored over 4 Å molecular sieves prior to use. Lithium hexamethyldisilazane was purchased from Sigma-Aldrich and recrystallized from toluene under an inert atmosphere prior to use. Potassium hydride was purchased from Sigma-Aldrich, washed with hexanes to remove mineral oil, and dried under reduced vacuum prior to use. Ferric chloride and ferrous chloride were purchased from Strem and used as received. Cyclohexylamine was purchased from Acros and used as received. Dimethylformamide (DMF) and sodium hydroxide were purchased from Fisher and used as received.  $POCl_3$  and hydrochloride etherate (2.0 M) were purchased from Sigma-Aldrich and used as received. Tris(pyrrol-2-methyl)amine<sup>52</sup> and ferrous triflate<sup>53</sup> were prepared according to literature procedures. Celite 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. NMR spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz ( $^1H$  NMR) and 126 MHz ( $^{13}C$  NMR) and referenced to the residual solvent resonance ( $\delta$  in parts per million and  $J$  in Hz). For paramagnetic molecules, the  $^1H$  NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and where possible, the peak assignment. Elemental analysis was performed by Complete Analysis Laboratories, Inc. in Parsippany, NJ and by the University of Illinois at Urbana–Champaign School of Chemical Sciences Microanalysis Laboratory in Urbana, IL.

**Preparation of  $H_3(tpa^{CO})$ .** A 100 mL three-neck round-bottom flask was charged with tris(pyrrol-2-methyl)amine ( $H_3tpa$ ) (2.000 g, 0.0079 mol) and approximately 40 mL of DMF. The tan solution was cooled to  $-10$  °C.  $POCl_3$  (4.4 mL, 0.0175 mol) was added dropwise over 10 min with vigorous stirring. Following addition of the  $POCl_3$ , the solution was dark red. The mixture was removed from the ice bath and heated to 60 °C for 2 h. The contents of the round-bottom flask were poured into an aqueous solution of NaOH (6.00 g, 0.15 mol), resulting in formation of a dark brown mixture. The contents were heated to 80 °C for 1 h. The product was subsequently extracted with dichloromethane and chloroform (1:1,  $3 \times 300$  mL). Volatiles were then removed under reduced pressure. The product was precipitated from the crude reaction mixture as a brown powder (1.471 g, 0.0043 mol, 41%) by stirring in an excess of acetonitrile for 16 h.  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  = 3.70 (s, 6H,  $-CH_2$ ), 6.18 (d,  $J$  = 5, 3H, Ar–CH), 6.92 (d,  $J$  = 5, 3H, Ar–CH), 9.40 (s, 3H, aldehyde–CH), 11.29 (br, s, 3H, pyr–NH).  $^{13}C$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  = 51.80 (methylene–C), 111.07 (pyr–C), 123.55 (pyr–C), 133.40 (pyr–C), 139.49 (pyr–C), 179.91 (aldehyde–C). IR = 1651  $cm^{-1}$  (C=O), 3304  $cm^{-1}$  (N–H).

**Preparation of  $H_3[N(pi^{Cy})_3] \cdot H_2O (1)$ .** The proligand  $H_3tpa^{CO}$  was synthesized *in situ*. The red oil is diluted with dry acetonitrile. Cyclohexylamine ( $H_2NCy$ ) (2 mL) is added, and the mixture is stirred for 16 h. The product  $H_3[N(pi^{Cy})_3] \cdot H_2O$  precipitates from solution as a tan powder, which is isolated by filtration (2.534 g, 4.17 mmol, 53%). Analysis for  $C_{36}H_{51}N_7 \cdot H_2O$ : Calcd C, 72.08; H, 8.91; N, 16.34. Found C, 72.09; H, 8.94; N, 15.83%.  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  = 1.19–1.85 (m, 30 H, Cy–CH), 3.09 (m, 3H, Cy–CH), 3.59 (s, 6H,  $-CH_2$ ), 6.02 (d,  $J$  = 4, 3H, Ar–CH), 6.89 (d,  $J$  = 4, 3H, Ar–CH), 8.02 (s, 3H, imine–CH).  $^{13}C$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  = 25.30 (Cy–C3,C5), 26.12 (Cy–C4), 35.33 (Cy–C2,C6), 50.82 (methylene–C), 69.12 (Cy–C1), 108.77 (pyr–C), 115.09 (pyr–C), 130.49 (pyr–C), 134.61 (pyr–C), 150.12 (imine–C). IR = 1638  $cm^{-1}$  (C=N), 3266  $cm^{-1}$  (N–H).

**Preparation of  $[N(pi^{Cy})_3Fe (2)$ .** A 20 mL scintillation vial was charged with  $H_3[N(pi^{Cy})_3] \cdot H_2O$  (0.050 g, 0.083 mmol) and approximately 7 mL of tetrahydrofuran (THF). KH (3.1 equiv, 0.011 g, 0.268 mmol) was weighed by difference and added as a solid to the solution of ligand, resulting in vigorous effervescence. After it was stirred for 2 h, the solution was filtered over Celite to remove excess KH and was added to a 20 mL scintillation vial charged with 1 equiv of  $FeCl_3$  (0.014 g, 0.086 mmol) and approximately 3 mL of THF. An immediate color change to dark brown was observed. The mixture was stirred for 3 h, after which time solvents were removed

under reduced pressure. The product was dissolved in benzene and filtered over Celite to remove KCl. Volatiles were removed *in vacuo* to afford the product as a dark brown powder (0.037 g, 0.059 mmol, 68%). Crystals suitable for X-ray analysis were grown from a concentrated solution of THF and benzene (1:1) layered with hexanes. IR: 1581  $\text{cm}^{-1}$  (C=N). Analysis for  $\text{C}_{36}\text{H}_{51}\text{N}_7\text{FeKCl}$ : Calcd C, 64.18; H, 7.18; N, 14.55. Found C, 64.61; H, 7.48; N, 14.21. Due to similar solubilities of KCl byproduct, complete separation was not possible.  $^1\text{H}$  NMR (THF- $d_6$ , 25 °C) Broad resonances ranging from -15.7 to 33.0 ppm could not be reliably integrated or assigned (Supporting Information, Figure S3).  $\mu_{\text{eff}} = 5.73 \mu_{\text{B}}$ .

**Preparation of  $\text{K}[\text{N}(\text{pi}^{\text{Cy}})_3\text{Fe}(\text{OH}_2)]$  (3).** A 20 mL scintillation vial was charged with  $\text{H}_3[\text{N}(\text{pi}^{\text{Cy}})_3]\cdot\text{H}_2\text{O}$  (0.050 g, 0.083 mmol) and approximately 5 mL of THF. With vigorous stirring, KH (3.1 equiv, 0.011 g, 0.268 mmol) was weighed by difference and added as a solid. Evolution of hydrogen was noted. After it was stirred for 2 h, the mixture was filtered over Celite and added to a slurry of  $\text{FeCl}_2$  (0.011 g, 0.087 mmol) in THF with two drops of pyridine (to aid in solubility). An instantaneous color change to orange was observed. Following 3 h of stirring at room temperature, solvents were removed under reduced pressure. The product was washed with hexanes to remove excess pyridine and was extracted with diethyl ether. Following the removal of volatiles, the product was isolated as an orange powder (0.042 g, 0.061 mmol, 73%). Crystals suitable for X-ray diffraction were grown from a concentrated solution of complex 3 in THF that was layered with hexanes at room temperature. Analysis for  $\text{FeK}_3\text{C}_{36}\text{H}_{50}\text{N}_7\text{O}\cdot\text{C}_4\text{H}_8\text{O}$ : Calcd C, 62.89; H, 7.65; N, 12.84. Found C, 62.45; H, 7.26; N, 13.17%.  $^1\text{H}$  NMR (THF- $d_6$ , 25 °C):  $\delta = 95.60$  (859, 3H, CH), 32.39 (60, 3H, CH), 28.56 (70, 3H, CH), 12.34 (88, 6H,  $\text{CH}_2$ ), 3.73–7.34 (33H, Cy- $\text{CH}_2$ ), 0.17 (141, 3H, CH). IR: 1603  $\text{cm}^{-1}$  (C=N).

**Preparation of  $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}(\text{OTf})_2]$  (4).** A 20 mL scintillation vial was charged with  $\text{Fe}(\text{OTf})_2(\text{MeCN})_2$  (0.043 g, 0.100 mmol) and approximately 10 mL of THF.  $\text{H}_3[\text{N}(\text{pi}^{\text{Cy}})_3]\cdot\text{H}_2\text{O}$  (0.060 g, 0.100 mmol) was weighed by difference and added as a solid to the cloudy white solution at room temperature, resulting in an instantaneous color change to yellow. After this solution was stirred for 30 min, the solvents were removed under reduced pressure, leaving a viscous yellow oil. Trituration with diethyl ether to remove excess free ligand left the product  $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}]\text{OTf}_2$  as a yellow powder (0.092 g, 0.098 mmol, 98%). Crystals suitable for X-ray analysis were grown from a concentrated solution of 4 in THF layered with diethyl ether. Analysis for  $\text{FeC}_{36}\text{H}_{51}\text{N}_7\text{O}_6\text{F}_6\text{S}_2$ : Calcd C, 48.77; H, 5.49; N, 10.48. Found C, 48.82; H, 5.39; N, 10.37%.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ , 25 °C):  $\delta = -79.59$  ( $\text{SO}_3\text{CF}_3$ ). IR: 1637  $\text{cm}^{-1}$  (C=N), 3218  $\text{cm}^{-1}$  (NH) 1739  $\text{cm}^{-1}$  (S=O).

**Preparation of  $[\text{N}(\text{pi}^{\text{Cy}})_2(\text{afa}^{\text{Cy}})]\text{FeOH}$  (5).** A 20 mL scintillation vial was charged with  $\text{Fe}[\text{N}(\text{SiMe}_3)_2(\text{py})_2]$  (0.041 g, 0.085 mmol) and approximately 3 mL of THF. In a separate vial,  $\text{H}_3[\text{N}(\text{pi}^{\text{Cy}})_3]\cdot\text{H}_2\text{O}$  (0.050 g, 0.086 mmol) was dissolved in 5 mL of THF. The solution of ligand was added dropwise to the metal complex, giving rise to an instantaneous color change to yellow-brown. After the solution was stirred for 30 min, the solvents were removed under reduced pressure, and the resulting brown residue was washed with diethyl ether. The product was isolated as a brown powder in high yields (0.055 g, 0.085 mmol, 99%). Analysis for  $\text{FeC}_{36}\text{H}_{51}\text{N}_7\text{O}\cdot\text{C}_4\text{H}_8\text{O}$ : Calcd C, 66.19; H, 8.19; N, 13.51. Found C, 66.60; H, 8.47; N, 13.45%.  $^1\text{H}$  NMR (THF- $d_6$ , 25 °C):  $\delta = 28.82$  (27, 3H, CH), 27.71 (20, 3H, CH), 16.20 (57, 6H,  $\text{CH}_2$ ), 5.49–8.23 (33H, Cy- $\text{CH}_2$ ), -3.86 (51, 3H, CH). IR: 1624, 1655  $\text{cm}^{-1}$  (C=N).

**Alternative Synthesis of 5.** A 20 mL scintillation vial was charged with  $\text{H}_3[\text{N}(\text{pi}^{\text{Cy}})_3]\cdot\text{H}_2\text{O}$  (0.050 g, 0.083 mmol) and approximately 4 mL of THF. In a separate vial, 3.1 equiv of  $\text{LiN}(\text{SiMe}_3)_2$  (0.043 g, 0.259 mmol) was dissolved in approximately 2 mL of THF. The solution was added dropwise to that of the ligand. After it was stirred for 1 h at room temperature, the deprotonated ligand  $\text{Li}_3[\text{N}(\text{pi}^{\text{Cy}})_3]$  was added dropwise to a third 20 mL scintillation vial, charged with  $\text{FeCl}_2$  (0.010 g, 0.079 mmol) and 2 drops of pyridine (to aid in solubility), with vigorous stirring. After this solution was stirred for 3 h at room temperature, the solvents were removed under reduced

pressure. The product was isolated as brown-yellow powder with LiCl as a contaminant.

**Synthesis of 5 via Addition of Acid to 3.** A 20 mL scintillation vial was charged with complex 3 (0.020 g, 0.029 mmol) and approximately 3 mL of THF. HCl (1 equiv, 2 M) in diethyl ether (0.015 mL, 0.030 mmol) was added via microsyringe with vigorous stirring. An immediate color change to yellow-brown was noted. After this solution was stirred for 30 min at room temperature, the solvents were removed under reduced pressure. The product, complex 5, was characterized by  $^1\text{H}$  NMR spectroscopy. Because of the inability to separate complex 5 from KCl, yields could not be determined via mass. The reaction was repeated in a J. Young tube in the presence of an internal standard of mesitylene. Conversion to compound 5 was found to be quantitative (>99%).

**Synthesis of 3 via Deprotonation of 5.** A 20 mL scintillation vial was charged with complex 5 (0.020 g, 0.031 mmol) and approximately 4 mL of THF and cooled to -35 °C.  $\text{KCH}_2\text{Ph}$  (1.5 equiv, 0.006 g, 0.044 mmol) was weighed by difference and added as an orange solid to the iron species with vigorous stirring. A color change to brown was noted. After this solution was stirred for 4 h at room temperature, the solvents were removed under reduced pressure. The residual oil was washed copiously with hexanes to remove residual salts and the byproduct, toluene. The product was isolated as a brown-orange powder in good yields (0.018 g, 0.026 mmol, 84%).

**Synthesis of 5 via Addition of Base to 4.** A 20 mL scintillation vial was charged with complex 3 (0.050 g, 0.053 mmol) and approximately 7 mL of THF.  $\text{Li}_2\text{O}$  (1 equiv, 0.002 g, 0.066 mmol) was weighed by difference and added as solid to the aforementioned solution. The mixture was stirred overnight at room temperature. After this time, the solution was filtered over Celite to remove excess  $\text{Li}_2\text{O}$ , the solvents were removed under reduced pressure, and the residual brown oil was washed with diethyl ether to remove  $\text{LiOTf}$  formed over the course of the reaction. The product was dried under vacuum, resulting in the isolation of a yellow brown powder (0.033 g, 0.051 mmol, 95%) identified as compound 5 via  $^1\text{H}$  NMR spectroscopy.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Spectral data for complexes 1–5; selected crystallographic data and .cif files for 2–5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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