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# Synthesis of Functionalized Hexadentate Iminopyridine $Fe^{II}$ Complexes – Toward Anion-Dependent Spin Switching in Polar Media



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We report the syntheses and characterizations of low-spin  $Fe^{II}$  complexes of hexadentate ligands poised for aniontriggered spin-state switching in polar solutions:  $[Fe(L^{5-OH})]$ - $(BF_4)_2$  (1) and  $[Fe(L^{5-ONHtBu})](BF_4)_2$  (3), in which  $L^{5-OH}$  and  $L^{5-ONHtBu}$  are tripodal iminopyridine ligands that contain methanolic or *tert*-butylamide functional groups, respectively, bound *meta* to the pyridyl N donor atom. Solid-state evidence for strong hydrogen bonding between  $CI^-$  anions and all three amide functional groups in  $[Fe(L^{5-ONHtBu})]^{2+}$  is provided by the crystal structure of  $\{[Fe(L^{5-ONHtBu})] \subset CI\}_2^-$ 

# Introduction

We and others are interested in understanding the factors that control spin-state switching in solution so as to develop new applications for spin-crossover (SC) based materials.<sup>[1]</sup> As small energy differences separate high-spin (HS) and low-spin (LS) states in a typical Fe<sup>II</sup> SC system, noncovalent interactions between a complex and its environment significantly impact the observed spin states. Under the right conditions – a suitably balanced ligand field, complex solution stability, and sufficiently perturbing host–guest interactions – spin-state switching may act as a reporter in a chemical sensing scheme.

Anions provide an attractive substrate for sensing as they play important roles in biology and the environment.<sup>[2]</sup> In recognition of their impacts on living systems, interest in effective anion sensing has spurred the design of molecular sensors.<sup>[2a,3]</sup> The incorporation of metal atoms into sensing architectures has become increasingly widespread; they are used to influence complex geometry, add additional reporting functionality (e.g., optical, electrochemical, or magnetic differences in the anion-free and -associated states), or to be the site of anion binding itself.<sup>[2a,4]</sup> Specific to spin-

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[FeCl<sub>4</sub>] (2). In ambient-temperature acetonitrile solutions of 1 and 3, chloride ion titrations produce marked changes in the <sup>1</sup>H NMR spectra, including large downfield shifts for the amide NH and hydroxy OH resonances, which indicates strong anion binding events. Interestingly, for amide-containing 3, we observe small changes in magnetic susceptibility as  $(nBu_4N)$ Cl is added, which suggests that spin-state control by anion-cation interactions may be accessible for related compounds with weaker ligand fields.

state switching schemes, it appears that anion-sensing and spin-crossover complexes are a natural fit, because an electrostatic cation–anion interaction offers a strong chemical trigger for SC property perturbation, and most SC complexes are cationic.

Recently, we have demonstrated that homo- and heteroleptic Fe<sup>II</sup> complexes featuring the bidentate ditopic ligand H<sub>2</sub>bip demonstrate solution-phase anion-dependent spin switching.<sup>[5]</sup> However, to minimize ligand exchange in solution, these studies must be performed in dichloromethane, a solvent of low polarity. The extension of this proof-ofconcept work into more polar media (such as alcohols, acetonitrile, or water) would be more relevant to the aqueous conditions of biological media or environmental samples. To do this, ligand lability must be minimized. Hexadentate ligands based on the Schiff-base condensation of tris(2-aminoethyl)amine (tren) with pyridinecarbaldehydes combine with Fe<sup>II</sup> to produce SC species;<sup>[6]</sup> a variety of Fe<sup>II</sup> complexes with related tripodal ligands also demonstrate tunable SC behavior. However, none of these complexes have been shown to act as anion receptors,<sup>[7]</sup> which is unsurprising given the absence of anion-binding functional groups.

Competent anion binding is optimized when multiple hydrogen-bonding groups are oriented toward a single binding site or pocket and when hydrogen bonding is coupled with electrostatic interactions.<sup>[8]</sup> Poised NH and OH groups can encourage direct anion–ligand interactions in tripodal complexes (Scheme 1). Metal-based anion receptors can ef-

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fectively combine these two binding modes, as shown in the recent work by Fabbrizzi and co-workers on a (tris)imidazolium cage organized around an Fe<sup>II</sup> ion, which is capable of binding spherical and linear anions.<sup>[9]</sup> A second example uses Cu<sup>II</sup> ions to preorganize a tripodal ligand to sense phosphates.<sup>[10]</sup>



Scheme 1. Tripodal ditopic ligand family targeting anion-triggered spin-state switching.

To observe  $Fe^{II}$  anion-dependent spin switching in solution, several criteria need to be met. The complex must competently bind anions, and the host–guest association must sufficiently perturb the ligand field to prompt spin-state switching. The spin-switching event must take place in a relatively narrow temperature range between 0 and 100 °C for aqueous solutions and in slightly larger windows for polar organic solvents such as methanol or acetonitrile. These last two criteria are highly dependent on the ligand field.

In this work, we targeted ligands based on pyridines functionalized at the 5-position as shown in Scheme 1; our recent efforts on the HS and SC 6-position analogues have been reported elsewhere.<sup>[11]</sup> Chelation of the ligand to an

Fe<sup>II</sup> center would provide positive charge to attract anions and also organize the hydrogen-bond donor groups into a pocket where anions could bind. The ligand field provided by the diimine ligand arms would be near the SC regime.<sup>[11a,12]</sup> Distinct from the more commonly observed behavior of HS (6-position) complexes, in which successful anion binding increases ligand-field strength to cause HS $\rightarrow$ LS switching,<sup>[5,13]</sup> here anion binding to LS 5-position complexes could cause geometric perturbation of the Fe<sup>II</sup> center by pushing the ligand arms out, which would lead to lengthening of the Fe-N bonds and a transition to the HS state. Herein, we report on the anion-binding behavior of Fe<sup>II</sup> complexes of L<sup>5-OH</sup> and L<sup>5-ONHtBu</sup>, in which we find competent cation-chloride interactions in polar solution and potential evidence for spin-state switching as a result of anion binding.

## **Results and Discussion**

#### Syntheses

The preparation of  $L^{5-OH}$  is relatively straightforward and necessitates only one or two steps from precursors found in the literature, as shown in Scheme 2.

The 5-hydroxy-substituted aldehyde starting material reacts cleanly with tren to afford the desired tripodal ligand; it does not precipitate from solution and is isolated as an oil. In contrast, the methyl ester functionalized ligand<sup>[14]</sup> and the amide-based ligand  $L^{5-ONHtBu}$  are isolated as free flowing powders.

The synthesis of L<sup>5-ONH/Bu</sup> is more challenging. We aimed to produce an amide-functionalized aldehyde precursor by converting a 5-position methyl ester to an amide by



Scheme 2. Synthetic pathway for L<sup>5-OH</sup>.



Scheme 3. Synthetic pathway for ligand  $L^{5-ONH/Bu}$ . The steps in the top row of the synthetic scheme are modified from ref.<sup>[17]</sup> The steps in the middle row are adapted from ref.<sup>[14]</sup>



modification of a published synthetic route.<sup>[15]</sup> This was unsuccessful, perhaps because of increased steric bulk of the tert-butylamine group relative to the diaminopropane group. A successful alternative synthetic path (Scheme 3) was adapted from a set of published procedures and starts from pyridine-2,5-dicarboxylic acid. Protection at the 2-position as a methyl ester<sup>[16]</sup> is followed by generation of an acyl chloride from an unprotected acid at the 5-position.<sup>[17]</sup> The acyl chloride for L<sup>5-ONH*t*Bu</sub> is produced by using thio-</sup> nyl chloride and reacts readily with tert-butylamine to generate the desired amide functionalization.<sup>[17]</sup> The amide groups are unaffected by the reduction and oxidation steps needed to convert the 2-position ester to the aldehyde in a way analogous to the steps described for the synthesis of L<sup>5-OH</sup>, and final condensation to produce L<sup>5-ONH/Bu</sup> proceeds smoothly.

Both of the new ligands were characterized by <sup>1</sup>H NMR spectroscopy and positive-ion ESI-MS. The major ESI-MS peak for each of the isolated ligands corresponds to the sodium adduct of the ligand. The <sup>1</sup>H NMR spectrum for each ligand clearly shows loss of the aldehyde resonance downfield of  $\delta = 10$  ppm and a new resonance in the  $\delta = 8.0-8.4$  ppm region owing to imine formation. In each ligand, the three arms tethered to the apical N atom of tren are equivalent on the <sup>1</sup>H NMR timescale, and the resonances are split in ways consistent with the expected three-fold symmetry. The ligands were used in subsequent steps without further purification.

Metalation of the ligands by Fe<sup>II</sup> is straightforward, and the resulting compounds are shown in Scheme 4. Solutions of Fe<sup>II</sup> salts react rapidly with solutions of the free ligand to form the desired complexes. The salts [Fe(L<sup>5-OH</sup>)]X [X = (BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (1), SO<sub>4</sub><sup>2-</sup> (S1), (BPh<sub>4</sub><sup>-</sup>)<sub>2</sub> (S2)] and [Fe(L<sup>5-ONH/Bu</sup>)]X {X = (Cl<sup>-</sup>)[(FeCl<sub>4</sub>)<sup>2-</sup>]<sub>0.5</sub> (2), (BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (3), (BPh<sub>4</sub><sup>-</sup>)<sub>1.5</sub>(Cl<sup>-</sup>)<sub>0.5</sub> (S3)} are purple and are all stable in air. Interestingly, attempts to directly prepare the chloride salt of [Fe(L<sup>5-ON/Bu</sup>)]<sup>2+</sup> result instead in the formation of a salt that contains both chloride and [FeCl<sub>4</sub>]<sup>2-</sup> anions. Evans-method room-temperature <sup>1</sup>H NMR spectra indicate that all the Fe<sup>II</sup> centers in these salts (except for [FeCl<sub>4</sub>]<sup>2-</sup>) are LS. This



Scheme 4. Tripodal Fe<sup>II</sup> iminopyridine complexes with anion-binding substituents. is consistent with the behavior of the 5-position methyl ester complex, which is also LS at room temperature even though an electron-withdrawing substituent is present and is expected to weaken the ligand field.<sup>[14]</sup>

#### Solid-State Structural Characterization

To explore anion–cation interactions in the solid state, crystals of  $1 \cdot CH_3CN$  and  $2 \cdot 3CH_3CN \cdot (CH_3CH_2)_2O$  were structurally characterized at 100 and 120 K, respectively. An Fe-containing cation for each complex is shown in Figure 1; full renderings are shown in Figures S1 and S2 (Supporting Information). The Fe–N bond lengths for the 5-position functionalized  $1 \cdot CH_3CN$  and  $2 \cdot 3CH_3CN \cdot$ 



Figure 1. One complex cation and hydrogen-bonded anion from the asymmetric unit cell in the structures of  $1 \cdot CH_3CN$  (top) and  $2 \cdot 3CH_3CN \cdot (CH_3CH_2)_2O$  (bottom), shown at 40% probability. First coordination sphere and atoms participating in hydrogen-bonding interactions are labeled. Dark red, blue, red, gray, green, and white atoms correspond to Fe, N, O, C, Cl, H atoms, respectively. Hydrogen atoms bonded to carbon atoms and minor disordered components have been omitted for clarity.



(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O are typical of low-spin Fe<sup>II</sup> and range from 1.948(3) to 1.996(3) Å and 1.848(3) to 1.991(3) Å, respectively.<sup>[12]</sup> The apical nitrogen atom of the podand ligand lies 3.460(4) Å from the Fe center in 1·CH<sub>3</sub>CN and has nearly planar geometry with C-N-C angles of 119.3(4) to 120.9(4)°. Similarly, the apical nitrogen atom in 2·3CH<sub>3</sub>CN·(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O is also nearly planar and lies 3.489(3) Å from the Fe center with C-N-C angles of 118.9(3)-120.6(3)°. These values contrast with the 6-position-functionalized [Fe(L<sup>6-OH</sup>)](BPh<sub>4</sub>)<sub>2</sub>, which remains high spin at 100 K.<sup>[11a]</sup> There, the Fe-N bonds are longer than those found in low-spin Fe<sup>II</sup> complexes (ca. 1.9 Å) and range from 2.159(3) to 2.277(3) Å. The apical N atom is also clearly pyramidalized with more acute C-N-C angles that range from 116.90(17) to  $117.28(17)^{\circ}$  and a shorter N-Fe distance of 3.242(2) Å. Key Fe-N distances and the angles around the apical N atom for each of the structures are tabulated in Table S1 (Supporting Information).

The complex cations in each of the structures participate in hydrogen-bonding interactions in the solid state (Table 1). For 1·CH<sub>3</sub>CN, in which no free halide ions are present, all but one of the hydroxy groups participate in hydrogen-bonding interactions with hydroxy groups on adjacent cations. The O-O distances compare closely to an average reported O-O distance of 2.76(10) Å for OH···OH hydrogen-bonding interactions.<sup>[18]</sup> In the structure of  $2 \cdot 3 CH_3 CN \cdot (CH_3 CH_2)_2 O$ , which contains a halide ion, there are multiple direct hydrogen bonds between the anions and the amide functional groups of the ligands. The N-Cl distances in  $2 \cdot 3 CH_3 CN \cdot (CH_3 CH_2)_2 O$  are very close to the reported mean N-Cl distance of 3.181(6) Å for sp<sup>2</sup> NH···Cl interactions.<sup>[19]</sup> These interactions are comparable to those found in the previously reported [Fe(L<sup>6-OH</sup>)]Br<sub>2</sub> structure,<sup>[11a]</sup> in which the mean O-Br distance for an OH···Br interaction is 3.254(8) Å.<sup>[19]</sup>

Table 1. Hydrogen-bonding interactions in the crystal structures of  $1 \cdot CH_3CN$  and  $2 \cdot 3CH_3CN \cdot (CH_3CH_2)_2O$ .

Complex	Interacting atoms (DH-A)[a]	Distance [Å]
1-CH <sub>3</sub> CN	O1–O4	2.744(5)
	O3–O6	2.882(5)
	04–05	2.755(5)
2·3CH <sub>3</sub> CN·(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	N4–Cl1	3.169(4)
	N7C11	3.186(3)
	N10-Cl1	3.194(4)
	N14-Cl2	3.199(4)
	N17-Cl2	3.220(4)
	N20-Cl2	3.201(3)

[a] Complete labeling for donor and acceptor atoms is presented in Figure S3 (Supporting Information).

There are several close contacts between the  $BF_4^-$  anions and the hydroxy groups on the complex cation in  $1 \cdot CH_3CN$ [Table S2 (Supporting Information)], but none of these interactions have distances short enough to be considered hydrogen bonds. In  $2 \cdot 3CH_3CN \cdot (CH_3CH_2)_2O$ , many of the close contacts occur between the 6-position hydrogen atom on the pyridine moiety and the bound Cl<sup>-</sup> ion; however, these hydrogen atoms are not pointing directly into the cavity holding the chloride ion. Additionally, there are close contacts between the imine group and the Cl atoms of the  $[FeCl_4]^{2-}$  anion.

#### **Solution Anion-Binding Studies**

Although cation–anion interactions have been observed in the solid state for Fe<sup>II</sup> complexes with 5- or 6-positionfunctionalized tripodal ligands and salts of  $[Fe(L^{6-OH})]^{2+}$ show temperature-dependent changes in solid-state interactions and spin state,<sup>[11a]</sup> neither anion binding in solution nor anion-dependent spin-state behavior has been observed in solution for tripodal ligand Fe<sup>II</sup> complexes. Intrigued by the evidence of strong chloride binding in the solid-state structure containing **2**, we explored the solution behavior of these tripodal complexes toward anion interaction.

The degree of interaction can be probed by <sup>1</sup>H NMR spectroscopy. In diamagnetic compounds, strong interactions between anions and the OH or NH protons result in downfield shifts of the proton resonances owing to electrostatic deshielding. The addition of excess Cl<sup>-</sup> ions to Ru<sup>II</sup>-based amide anion receptors in CD<sub>3</sub>CN produces downfield shifts of nearly 2 ppm for protons involved in hydrogen bonding.<sup>[20]</sup> Similar shifts are observed for hydrogen-bonding protons in LS Fe<sup>II</sup>-based imidazolium anion receptors.<sup>[9]</sup> The LS nature of complexes such as 1 and 3 should allow for the unambiguous detection of anion binding. If spin-state switching accompanies anion binding, magnetic susceptibility increases can be detected by the Evans method.

The <sup>1</sup>H NMR spectrum of the  $Fe(BF_4)_2$  salt of  $L^{5-OH}$ , 1, in CD<sub>3</sub>CN does not display paramagnetic peak shifting or broadening, which indicates that the complex remains LS in solution. All of the peaks in the <sup>1</sup>H NMR spectrum can be assigned, including that of the OH proton at  $\delta$  = 3.38 ppm. The position of this peak is not shifted greatly from the chemical shift for the OH proton in the free ligand  $(\delta = 3.50 \text{ ppm in CDCl}_3)$ . The similarity of the peak positions suggests that the tetrafluoroborate ions do not interact strongly with the hydroxy groups in solution. However, upon addition of excess  $(nBu_4N)Cl$  to a solution of 1, the <sup>1</sup>H NMR spectrum changes [Figures 2 and S4 (Supporting Information)]. Small downfield shifts of 0.05 and 0.22 ppm are observed for the imine proton  $(H^3)$  and the proton at the 6-position  $(H^6)$ , respectively. More dramatically, the OH proton (H<sup>8</sup>) shifts 1.6 ppm downfield to  $\delta = 5.0$  ppm. The magnitude of this shift indicates that there is strong interaction in solution between the OH proton and the added Clions. In addition to the large  $\delta$  shift, the signal splittings of the OH proton and the adjacent methylene protons  $(H^7)$ change: they now each appear as a doublet of doublets and have integrations of three protons, which indicates that the methylene protons are no longer equivalent. A likely explanation for this is that the interacting Cl<sup>-</sup> ion effectively locks the methanol group into a single conformation, which orients one hydrogen atom on the methylene group toward the metal center and the other away from it, resulting in magnetically inequivalent positions.



Figure 2. 300 MHz <sup>1</sup>H NMR spectra of  $[Fe(L^{5-OH})](BF_4)_2$  (1) in CD<sub>3</sub>CN at 24.9 °C (top) and after the addition of 2 equiv. of  $(nBu_4N)Cl$  (bottom). The signal marked with \* is due to diethyl ether.

Complexes of L<sup>5-ONH/Bu</sup> show similar anion dependence in their <sup>1</sup>H NMR spectra. For both {[Fe(L<sup>5-ONH/Bu</sup>)] $\subset$ -Cl}<sub>2</sub>[FeCl<sub>4</sub>] (**2**) and [Fe(L<sup>5-ONH/Bu</sup>)](BF<sub>4</sub>)<sub>2</sub> (**3**), all proton resonances can be assigned, including those of the NH protons, which lie at  $\delta = 9.12$  and 6.79 ppm, respectively. Alteration of the counteranion does not obviously influence the spin state of the [Fe(L<sup>5-ONH/Bu</sup>)]<sup>2+</sup> complex cation at room temperature, but the large difference in NH chemical shift implies anion binding is operative in solutions containing Cl<sup>-</sup> ions.

To further study the solution interaction between chloride ions and  $[Fe(L^{5-ONHtBu})]^{2+}$ ,  $(nBu_4N)Cl$  was used to titrate 1.27 equiv. of Cl<sup>-</sup> ions to a solution of 3, and the proton shifts were monitored by <sup>1</sup>H NMR spectroscopy [Figures 3 and S5 (Supporting Information)]. From the titration data, downfield shifts are seen for the amide proton, as expected from comparison of the separately collected spectra of 2 and 3. The amide peak ultimately shifts +2.2 ppm, which indicates very strong cation-anion interactions. The proton at the 6-position also shows modest downfield shifts upon chloride titration, which is consistent with its proximity to the bound anion. The other aromatic protons on the pyridine and the imine proton all show small upfield shifts, as shown in Figure 3. Similar upfield shifts for protons pointing away from the anion-containing cavity were observed for the tris(imidazolium) Fe<sup>II</sup> complex studied by Fabbrizzi and co-workers.<sup>[9]</sup>

Focusing on the large downfield shifts, it is useful to compare this result to the heteroleptic  $Ru^{II}$  complex reported by Beer and co-workers (also studied in  $CD_3CN$ ), in which a bipyridine ligand decorated with two *tert*-butyl amide groups is poised for selective anion chelation.<sup>[20]</sup> For this  $Ru^{II}$  complex, the amide NH signal undergoes a +1.62 ppm shift upon addition of 1 equiv. of Cl<sup>-</sup> ions, and quantitative analysis of the titration data gives a stability constant of 6700 m<sup>-1</sup>. In the Fe<sup>II</sup> systems described here, we expect comparable association constants for the L<sup>5-OH</sup> system and even stronger association for the L<sup>5-ONH/Bu</sup> system. This improved anion binding is likely because of the tripodal pocket created by Fe<sup>II</sup> complexation, in contrast to the bidentate chelation available in the Ru<sup>II</sup> system. Fab-



Figure 3. Chemical-shift changes for the aromatic protons in  $[Fe(L^{5-ONH/Bu})](BF_4)_2$  (3) during titration of  $(nBu_4N)Cl$ . The <sup>1</sup>H NMR spectra were collected in CD<sub>3</sub>CN at 400 MHz and 23.5 °C. Red: amide H<sup>7</sup>, green: imine H<sup>3</sup>, blue: 3-position H<sup>4</sup>, purple: 4-position H<sup>5</sup>, black: 6-position H<sup>6</sup>; H atoms labelled as in Figure S10 (Supporting Information). Lines are provided as a visual guide.

brizzi's tris(imidazolium) Fe<sup>II</sup> system has also been studied through <sup>1</sup>H NMR titrations, and association constants have been calculated [6300 m<sup>-1</sup> for Cl<sup>-</sup> in CD<sub>3</sub>CN/D<sub>2</sub>O (4:1)].<sup>[9]</sup> However, direct comparison to our iminopyridine systems is difficult, because anion binding is highly sensitive to solvent polarity and competing hydrogen-bonding interactions. Titrations with a very similar tris(imidazolium) Fe<sup>II</sup> complex have been done in CD<sub>3</sub>CN: these give imidazolium C–H peak shifts of  $\delta = 2.67$  ppm after addition of 1 equiv. of (*n*Bu<sub>4</sub>N)Cl and yield an association constant for Cl<sup>-</sup> of  $1.4 \times 10^6 \text{ m}^{-1.[21]}$  It is likely that [Fe(L<sup>5-ONH/Bu</sup>)]<sup>2+</sup> would not bind anions as strongly as these systems as it is a dicationic species, whereas the tris(imidazolium) Fe<sup>II</sup> complex cations have charges of 5+.

One intriguing observation from the chloride titration study of 3 is that the capillary and bulk solvent TMS peaks are split upon addition of (nBu<sub>4</sub>N)Cl [Figures S6 and S7 (Supporting Information)]. It is tempting to conclude that such behavior is indicative of an anion-triggered increase in magnetic susceptibility. We note that slight increases in  $\chi_{\rm M}T$ for 3 by itself when heated above room temperature in the solid state (Experimental Section) suggest that the compound is close to the spin-crossover region, and anion-cation interactions could further perturb the HS/LS ratio. Several possible origins of this behavior are discussed in detail in the Supporting Information. Briefly, the shifts are small, do not appear to increase at higher temperatures in acetonitrile solution [Figure S8a (Supporting Information)], and the apparent  $\chi_M T$  changes depend on the concentration of the species, which indicates interference from experimental conditions [e.g., inhomogeneous fields for the capillary standard; see also Figure S8 (Supporting Information)]. However, real susceptibility increases cannot be ruled out for [Fe(L<sup>5-ONHtBu</sup>)]<sup>2+</sup> when combined with chloride; this

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suggests that similar complexes with slightly weaker ligand fields may show a strong spin-state response to added anions.

# Conclusions

Two new tripodal iminopyridine ligands and their  $Fe^{II}$  coordination complexes have been synthesized. Ligands with functionalization at the 5-pyridine position form exclusively LS complexes at room temperature; they are airstable in the solid state and in solution. The complexes interact strongly with anions in the solid state and in solution. Structural characterization of **2** clearly shows a chloride anion bound by the three amide protons in the pocket created by  $Fe^{II}$  coordination to the ligand. The addition of chloride ions to **1** and **3** produces large downfield shifts for the hydroxy and amide protons, respectively, in the NMR spectra, which indicates strong cation–anion interactions in solution.

The observation of apparent magnetic susceptibility changes in solutions of [Fe(L<sup>5-ONH/Bu</sup>)]<sup>2+</sup> titrated with chloride ions suggests that anion-triggered spin-state switching may emerge in Fe<sup>II</sup> complexes with a slightly weaker ligand field. For tripodal iminopyridine ligands, the available results<sup>[6,11a,14]</sup> demonstrate that functionalization at all three 6- and 5-positions generate exclusively HS and LS Fe<sup>II</sup> complexes, respectively. Moving toward the spincrossover regime may be achieved by employing mixed-arm tripodal ligands: Drago and co-workers have demonstrated HS-LS tunability by adjusting steric bulk at the 6-position;<sup>[6]</sup> the incorporation of anion-binding moieties has not been explored. Alternatively, changing trigonal twisting<sup>[22]</sup> by modification or substitution of the tren backbone may afford spin-crossover complexes without impacting an already demonstrated robust anion binding pocket. Both of these strategies are being pursued in our laboratory to target anion-triggered spin-state switching in polar media.

# **Experimental Section**

Preparation of Compounds: Unless otherwise noted, compound manipulations were performed either inside a dinitrogen-filled glovebox (MBRAUN Labmaster 130) or by Schlenk techniques on an inert-gas (N<sub>2</sub>) manifold. The preparations of diethyl pyridine-2,5-dicarboxylate,<sup>[23]</sup> 2,5-pyridinedimethanol,<sup>[24]</sup> and 6-(methoxycarbonyl)nicotinic acid<sup>[16]</sup> have been described previously. Literature procedures for generating amides from acyl chlorides<sup>[17]</sup> were modified to use 6-(methoxycarbonyl)nicotinic acid as the starting material and tert-butylamine as the reagent to give methyl 5-(tert-butylcarbamoyl)picolinate. N-(tert-Butyl)-6-formylnicotinamide was synthesized analogously to methyl 6-formylnicotinate.<sup>[14]</sup> Pentane was distilled from sodium metal and subjected to three freeze-pump-thaw cycles. Other solvents were sparged with dinitrogen, passed through molecular sieves, and degassed prior to use. All other reagents were obtained from commercial sources and were used without further purification.

**5-(Hydroxymethyl)picolinaldehyde:** A synthesis using  $SeO_2$  as the oxidant has been reported in a patent;<sup>[25]</sup> here,  $MnO_2$  was used as

the oxidizing agent, because it allows for easier isolation of the product. 2,5-Pyridinedimethanol (0.486 g, 3.49 mmol) was dissolved in CHCl<sub>3</sub> (100 mL). Activated MnO<sub>2</sub> (6.07 g, 69.9 mmol) was added, and the suspension was stirred at room temperature. After 45 min, the mixture was filtered through Celite, the solids were washed with CHCl<sub>3</sub> (3 × 100 mL), and the filtrate was collected. The solvent was removed by rotary evaporation to give a yellow solid, which was purified by column chromatography (EtOAc on silica gel) to give 0.165 g (34%) of light yellow powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.86 (s, 2 H, CH<sub>2</sub>OH), 7.90 (d, 1 H, 3-H), 7.96 (d, 1 H, 4-H), 8.75 (s, 1 H, 6-H), 10.05 (s, 1 H, CHO) ppm. These values qualitatively match previously reported chemical shifts.<sup>[25]</sup>

{6,6',6''-[(1*E*,1'*E*,1'*E*)-{[Nitrilotris(ethane-2,1-diyl)]tris(azanylylidene)}tris(methanylylidene)]tris(pyridine-6,3-diyl)}trimethanol (L<sup>5-OH</sup>): In air, 5-(hydroxymethyl)picolinaldehyde (0.203 g, 1.46 mmol) was dissolved in methanol (6 mL). A methanolic solution (5 mL) of tris(2-aminoethyl)amine (tren, 0.071 g, 0.49 mmol) was added, and the resulting yellow solution was heated at reflux for 14 h. The solvent was removed by rotary evaporation to leave 0.237 g (97%) of an orange oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.94 (t, 6 H, 1-H), 3.50 (t, 3 H, 8-H), 3.70 (t, 6 H, 2-H), 4.73 (s, 6 H, 7-H), 7.62 (dd, 3 H, 5-H), 7.82 (d, 3 H, 4-H), 8.08 (s, 3 H, 3-H), 8.54 (d, 3 H, 6-H<sup>6</sup>) ppm. ESI-MS (MeOH): *m*/*z* = 526.27 [M + Na]<sup>+</sup>. The compound was used in subsequent metalation reactions without further purification.

**[Fe(L<sup>5-OH</sup>)](BF<sub>4</sub>)<sub>2</sub> (1):** Solid Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (50.3 mg, 0.149 mmol) was added to a stirring methanolic solution (3 mL) of L<sup>5-OH</sup> (73.4 mg, 0.146 mmol), which resulted in an immediate color change to violet-plum. The mixture was stirred for 2 h, and a dark plum precipitate formed. The precipitate was collected by filtration to give 94.5 mg (88%) of plum-colored solid. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 3.08 (m, 6 H, 1-H), 3.39 (m, 3 H, 8-H), 3.53 (m, 6 H, 2-H), 4.50 (d, 6 H, 7-H), 6.96 (s, 3 H, 3-H), 8.06 (d, 3 H, 5-H), 8.19 (d, 3 H, 4-H), 9.09 (d, 3 H, 6-H) ppm. ESI-MS (CH<sub>3</sub>CN): m/z = 279.67 [Fe(L<sup>5-OH</sup>)]<sup>2+</sup>. C<sub>27</sub>H<sub>33</sub>B<sub>2</sub>F<sub>8</sub>FeN<sub>7</sub>O<sub>3</sub> (733.05): calcd. C 44.24, H 4.54, N 13.38; found C 43.70, H 5.02, N 13.36, and C 43.56, H 4.80, N 13.25. Crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile.

**6,6',6''-[(1***E***,1'***E***,1''***E***,1''***E***)-{[Nitrilotris(ethane-2,1-diyl)]tris(azanylylidene)}tris(methanylylidene)]tris[***N***-(***tert***-butyl)nicotinamide] (L<sup>5-ONH/Bu</sup>): A solution of tren (0.131 g, 0.896 mmol) in acetonitrile (2 mL) was added to a solution of** *N***-(***tert***-butyl)-6-formylnicotinamide (0.600 g, 2.91 mmol) in acetonitrile (8 mL). Upon addition, the reaction mixture darkened to a dark yellow color. The reaction mixture was stirred at room temperature for 16 h, and then the solvent was removed in vacuo to afford 0.520 g (85%) of yellow powdered product. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): \delta = 1.45 (s, 27 H, 8-H), 2.92 (t, 6 H, 1-H), 3.72 (t, 6 H, 2-H), 6.86 (s, 3 H, 7-H), 7.85 (d, 3 H, 4-H), 8.00 (dd, 3 H, 5-H), 8.22 (s, 3 H, 3-H), 8.78 (d, 3 H, 6-H) ppm. ESI-MS (CH<sub>3</sub>OH):** *m***/***z* **= 733.53 [M + Na]<sup>+</sup>. The compound was used in subsequent metalation reactions without further purification.** 

**{[Fe(L<sup>5-ONH/Bu</sup>)]**⊂**Cl}<sub>2</sub>[FeCl<sub>4</sub>] (2):** A solution of L<sup>5-ONH/Bu</sup> (0.070 g, 0.098 mmol) in acetonitrile (3 mL) was added to a stirred mixture of FeCl<sub>2</sub> (0.019 g, 0.15 mmol) in acetonitrile (1 mL). The resulting dark purple solution was stirred at room temperature for 2 h, and then the solvent was removed in vacuo to give a purple residue. This solid was triturated with diethyl ether (10 mL) to give a dark purple powder. The powder was collected by filtration and washed with diethyl ether (3 × 3 mL) to give 0.064 g (72%) of product. <sup>1</sup>H



NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  = 1.23 (27 H, 8-H), 3.08 (6 H, 1-H), 3.42 (3 H, 2-H), 3.56 (3 H, 2-H), 7.56 (3 H, 6-H), 8.22 (3 H, 4-H), 8.34 (3 H, 5-H), 8.98 (3 H, 7-H), 9.07 (3 H, 3-H) ppm. ESI-MS (CH<sub>3</sub>CN): m/z = 801.33 [Fe(L<sup>5-ONH/Bu</sup>)C]]<sup>+</sup>, 383.27 [Fe-(L<sup>5-ONH/Bu</sup>)]<sup>2+</sup>. C<sub>78</sub>H<sub>108</sub>Cl<sub>6</sub>Fe<sub>3</sub>N<sub>20</sub>O<sub>6</sub> (1802.10): calcd. C 51.99, H 6.04, N 15.55; found C 51.87, H 6.16, N 15.33. Crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile.

 $[Fe(L^{5-ONH/Bu})](BF_4)_2$  (3): A solution of  $Fe(BF_4)_2 \cdot 6H_2O$  (0.024 g, 0.076 mmol) in acetonitrile (3 mL) was added to a solution of L<sup>5-ONHtBu</sup> (0.054 g, 0.076 mmol) in acetonitrile (2 mL). The resulting dark purple solution was stirred at room temperature for 2 h, and then the solvent was removed in vacuo to give a purple residue. This solid was triturated with diethyl ether (10 mL) to give a dark purple powder. The powder was collected by filtration, washed with diethyl ether  $(3 \times 3 \text{ mL})$ , and dried in vacuo to give 0.061 g (85%) of product. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  = 1.31 (27 H, 8-H), 3.09 (6 H, 1-H), 3.56 (3 H, 2-H), 3.71 (3 H, 2-H), 6.79 (3 H, 7-H), 7.37 (3 H, 6-H), 8.34 (3 H, 4-H), 8.45 (3 H, 5-H), 9.27  $(3 \text{ H}, 3 \text{ -H}) \text{ ppm. ESI-MS} (CH_3CN): m/z = 853.0 \text{ [Fe-}$ (L<sup>5-ONH/Bu</sup>)(BF<sub>4</sub>)]<sup>+</sup>, 383.27 [Fe(L<sup>5-ONH/Bu</sup>)]<sup>2+</sup>. Magnetic susceptibility (SQUID, 295 K):  $0.62 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 1.80 \mu_{\text{B}}$ ); (395 K):  $0.95 \text{ cm}^3 \text{ K mol}^{-1}$  ( $\mu_{\text{eff}} = 2.22 \,\mu_{\text{B}}$ ).  $C_{39}H_{56}B_2F_8\text{FeN}_{10}O_4$  (3·H<sub>2</sub>O) (958.38): calcd. C 48.88, H 5.89, N 14.61; found C 48.94, H 5.74, N 14.35.

**Structure Determinations:** Crystals suitable for X-ray analyses were coated with Paratone-N oil and supported on a Cryoloop before being mounted on a Bruker Kappa Apex II CCD diffractometer under a stream of dinitrogen. Data collection was performed at 100 or 120 K with Mo- $K_{\alpha}$  radiation and a graphite monochromator, targeting complete coverage and fourfold redundancy. Initial lattice parameters were determined from at least 500 reflections harvested from 36 frames; these parameters were later refined against all data. Crystallographic data and metric parameters are presented in Table 2. Data were integrated and corrected for Lorentz and polar-

ization effects by using SAINT, and semiempirical absorption corrections were applied by using SADABS.<sup>[26]</sup> The structure was solved by direct methods and refined against  $F^2$  with the SHELXTL 6.14 software package.<sup>[27]</sup> Unless otherwise noted, thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at the ideal positions and were refined by using a riding model where the thermal parameters were set at 1.2 times those of the attached carbon atom (1.5 for methyl protons). In the structure of 1·CH<sub>3</sub>CN, positional disorder in one of the BF<sub>4</sub> anions was treated by splitting atoms F15 and F16 over two positions (refined to a 56:44 ratio); all thermal parameters were treated anisotropically. Solvate molecule disorder in the structure of  $2 \cdot 3 CH_3 CN \cdot (CH_3 CH_2)_2 O$  was modeled in the following manner. Two acetonitrile molecules were modeled at full occupancy. The occupancy of the third acetonitrile molecule was originally tied to a free variable that refined to 70-80% occupancy; this was rounded to full occupancy to give a chemically more reasonable value. Positive residual electron density near the terminal C atom (C82) may be due to further disorder. SAME, DELU and SIMU restraints were used on each of the acetonitrile molecules with the acetonitrile containing N21, C79, and C80 as the model for SAME. Meanwhile, the diethyl ether molecule is disordered over two positions at two sites. Because of the large amount of disorder in this solvent molecule, H atoms were not added to the model. Both disordered solvent molecules were treated isotropically. CCDC-901283 (for 1·CH<sub>3</sub>CN) and CCDC-901284 [for 2·3CH<sub>3</sub>CN·(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Other Physical Methods:** Absorption spectra were obtained with a Hewlett–Packard 8453 spectrophotometer in glass cuvettes with 1 cm path lengths in air and near-IR spectra were recorded with a Cary 500 spectrophotometer; all experiments were performed at room temperature. Mass spectrometric measurements were performed in either the positive-ion or negative-ion mode with a Fin-

Table 2. Crystallographic data<sup>[a]</sup> for 1 and 2.

	1·CH <sub>3</sub> CN	$2\cdot 3CH_3CN\cdot (CH_3CH_2)_2O$	
Empirical formula	$C_{29}H_{36}B_2F_8FeN_8O_3$	C <sub>88</sub> H <sub>117</sub> Cl <sub>6</sub> Fe <sub>3</sub> N <sub>23</sub> O <sub>7</sub>	
Formula mass	774.13	1989.30	
Color, habit	purple parallelepiped	purple plate	
Crystal size [mm]	$0.25 \times 0.19 \times 0.15$	$0.39 \times 0.18 \times 0.14$	
Crystal system	orthorhombic	triclinic	
Space group	$Pna2_1$	PĪ	
Ż	8	2	
<i>a</i> [Å]	15.4403(3)	11.9443(11)	
<i>b</i> [Å]	12.2839(2)	21.0685(18)	
c [Å]	34.8855(6)	21.1533(18)	
a [°]	90	73.208(4)	
$\beta$ [°]	90	89.076(4)	
γ [°]	90	84.615(4)	
V [Å <sup>3</sup> ]	6616.6(2)	5073.4(8)	
$d_{\text{calcd.}} [\text{g/cm}^3]$	1.554	1.302	
T [K]	100(2)	120(2)	
<i>F</i> (000)	3184	2084	
No. of unique reflections	11691	21768	
No. of observed reflections	89312	72359	
No. of parameters	947	1117	
$\mu(\text{Mo-}\bar{K}_{\alpha}) \text{ [mm^{-1}]}$	0.547	0.643	
GOF	1.056	1.023	
$R_1 (wR_2) [\%]^{[b]}$	4.42 (10.28)	6.00 (14.33)	

[a] Obtained with graphite-monochromated Mo- $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation. [b]  $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ ,  $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$  for  $F_o > 4\sigma(F_o)$ .



nigan LCQ Duo mass spectrometer, equipped with an analytical electrospray ion source and a quadrupole ion trap mass analyzer. <sup>1</sup>H NMR spectra were measured with Varian INOVA 300 MHz or 400 MHz instruments. Magnetic susceptibilities in solution were determined by the Evans method.<sup>[28]</sup> Magnetic susceptibility measurements in the solid state were performed with a Quantum Design model MPMS-XL superconducting quantum interference device (SQUID) magnetometer in the temperature range 295–395 K under a field of 1000 Oe. One square inch of aluminum foil and six inches of copper wire were used as the sample holder. The data were corrected by subtracting the measured susceptibility of an empty sample holder. Diamagnetic corrections were applied by using Pascal's constants.<sup>[29]</sup>

**Supporting Information** (see footnote on the first page of this article): Preparations of compounds S1–S3; key bond/internuclear distances and angles; <sup>1</sup>H NMR spectra including chloride titrations.

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