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Ground State and Excited State Tuning in Ferric Dipyrin Complexes Promoted by Ancillary Ligand Exchange

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Abstract

Three ferric dipyrromethene complexes featuring different ancillary ligands were synthesized by one electron oxidation of ferrous precursors. Four-coordinate iron complexes of the type (^{Ar}L)FeX₂ [^{Ar}L = 1,9-(2,4,6-Ph₃C₆H₂)₂-5-mesityldipyrromethene] with X = Cl or ^tBuO were prepared and found to be high-spin ($S = 5/2$), as determined by superconducting quantum interference device magnetometry, electron paramagnetic resonance, and ⁵⁷Fe Mössbauer spectroscopy. The ancillary ligand substitution was found to affect both ground state and excited properties of the ferric complexes examined. While each ferric complex displays reversible reduction and oxidation events, each alkoxide for chloride substitution results in a nearly 600 mV cathodic shift of the Fe^{III/II} couple. The oxidation event remains largely unaffected by the ancillary ligand substitution and is likely dipyrin-centered. While the alkoxide substituted ferric species largely retain the color of their ferrous precursors, characteristic of dipyrin-based ligand-to-ligand charge transfer (LLCT), the dichloride ferric complex loses the prominent dipyrin chromophore, taking on a deep green color. Time-dependent density functional theory analyses indicate the weaker-field chloride ligands allow substantial configuration mixing of ligand-to-metal charge transfer into the LLCT bands, giving rise to the color changes observed. Furthermore, the higher degree of covalency between the alkoxide ferric centers is manifest in the observed reactivity. Delocalization of spin density onto the *tert*-butoxide ligand in (^{Ar}L)FeCl(O^tBu) is evidenced by hydrogen atom abstraction to yield (^{Ar}L)FeCl and HO^tBu in the presence of substrates containing weak C–H bonds, whereas the chloride (^{Ar}L)FeCl₂ analogue does not react under these conditions.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00525. General procedures and methods, experimental procedures and spectral data for 2–6, ⁵⁷Fe Mössbauer spectra, differential pulse voltammograms for 4–6, magneto-metry data, EPR spectra, solid state molecular structures and crystallographic data for 2 and 4–6, and a description of computational methods, calculated molecular orbitals, calculated electronic absorption spectra, and predicted transitions for 2–6 (PDF) Crystallographic information for 2 and 4–6 (CIF)

1.0. INTRODUCTION

During the past decade, a renewed interest in late, first-row transition-metal complexes as catalysts for C–H activation has emerged.¹ In many cases, high-spin states, resulting from compressed ligand fields, have been implicated as essential features for the unique reactivity observed.² Specifically, ancillary or spectator ligands have a pronounced influence on the electronic structure, induce orbital rearrangements, and influence bonding interactions between the metal and ligands.³ Attenuated ligand field environments favor complexes with maximum multiplicity and render the resulting metal complexes highly electrophilic.⁴ While high-spin, electron-poor transition metals act as potent Lewis acids, accepting electron density from bound ligands, they in turn can confer radical spin density upon the ligand.⁵ In these cases, it is essential to understand how communication between metal center and ligand can change the electronic structure and therefore the reactivity of the complex.

We previously reported the synthesis of ferrous dipyrinato complexes that feature compressed ligand fields, resulting in high-spin states.^{2a,b,6} Oxidation of the ferrous dipyrinato precursors with aryl azides resulted in the formation of high-spin ($S = 2$) Fe^{III} iminyl complexes.^{2a,b} These species are best described as high-spin ferric centers antiferromagnetically coupled to an iminyl ligand-based radical, an assignment supported by ⁵⁷Fe Mössbauer spectroscopy and electronic structure calculations.

To better understand how the electronic structure of a high-spin metal center can influence and be influenced by ancillary ligand substitutions, we explored single electron oxidation of a selection of ferrous precursors bearing different supporting ligands. Specifically, this study intends to address the following outstanding questions: how does ancillary ligand substitution impact (1) the resulting electronic structure, (2) molecular redox behaviors, (3) excited state phenomena, (4) ligand character contribution into the frontier orbitals, and (5) the resultant molecular reactivity profiles? Herein, we report the synthesis of a family of ferric compounds supported by the dipyrinato ligand platform with varying ancillary ligand substitution to address the foregoing questions.

2.0. EXPERIMENTAL SECTION

For general procedures and methods, see the Supporting Information.

Synthesis of [ⁿBu₄N][(^{Ar}L)FeCl₂] (2)—In a 20 mL vial, tetrabutylammonium chloride (82 mg, 0.31 mmol, 3.0 equiv) was suspended in 2 mL of benzene. A solution of (^{Ar}L)FeCl (1) (0.1 g, 0.10 mmol, 1.0 equiv) in 5 mL of benzene was added while stirring. After being

stirred at room temperature for 3 h, the reaction solution was filtered through Celite, and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield $[\text{}^n\text{Bu}_4\text{N}][(\text{}^{\text{Ar}}\text{L})\text{FeCl}_2]$ (**2**) as a purple powder (0.10 g, 99%). Crystals suitable for X-ray diffraction were grown from a concentrated solution of toluene layered with hexanes at $-35\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, 295 K, C_6D_6): δ 40.68, 19.71, 13.78, 12.17, 11.62, 8.55, 7.64, 7.31, 7.00, 5.11, 4.98, 4.56, 3.98, 3.70, 2.42, -7.38 . $\chi_{\text{M}}T$ (295 K, SQUID) = $2.9\text{ cm}^3\text{K/mol}$. Zero-field ^{57}Fe Mössbauer (90 K) (δ , $|E_{\text{Q}}|$ (mm/s)): 0.94, 3.29 ($\gamma = 0.18\text{ mm/s}$). %CHN Calcd for $\text{C}_{82}\text{H}_{85}\text{Cl}_2\text{FeN}_3$: C, 79.47; H, 6.91; N, 3.39; Found: C, 79.48; H, 6.97; N, 3.53.

Synthesis of $(\text{}^{\text{Ar}}\text{L})\text{FeCl}_2$ (4**)**—In a 20 mL vial, ferrocenium hexafluorophosphate (52 mg, 0.16 mmol, 1.0 equiv) was frozen in 3 mL of benzene. A just-thawed solution of $[\text{}^n\text{Bu}_4\text{N}][(\text{}^{\text{Ar}}\text{L})\text{-FeCl}_2]$ (**2**) in 5 mL of benzene (0.20 g, 0.16 mmol, 1.0 equiv) was added while stirring. The mixture was thawed and stirred at room temperature for 3 h. The reaction mixture was filtered through Celite, and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield a brown powder. The residue was washed with hexanes ($5 \times 3\text{ mL}$) and recrystallized at $-35\text{ }^\circ\text{C}$ from 12 mL of 3:1 ratio of hexanes to toluene. The following morning, the mother liquor was decanted, and the crystals were washed with 2 mL of hexanes and dried in vacuo to afford $(\text{}^{\text{Ar}}\text{L})\text{FeCl}_2$ (**4**) as green crystals (72 mg, 73%). ^1H NMR (500 MHz, 295 K, C_6D_6): δ 91.80 (bs), 13.70 (bs). $\chi_{\text{M}}T$ (295 K, SQUID) = $4.1\text{ cm}^3\text{K/mol}$. Electron paramagnetic resonance (EPR) (toluene, 77 K): $g_{\text{eff}} = 8.40, 5.45, 2.95$. Zero-field ^{57}Fe Mössbauer (90 K) (δ , $|E_{\text{Q}}|$ (mm/s)): 0.23, 0; Zero-field ^{57}Fe Mössbauer (4 K) (δ , $|E_{\text{Q}}|$ (mm/s)): 0.10, 0.21. %CHN Calcd for $\text{C}_{66}\text{H}_{49}\text{Cl}_2\text{FeN}_2$: C, 79.52; H, 4.95; N, 2.81; Found: C, 79.56; H, 4.77; N, 2.84.

Synthesis of $(\text{}^{\text{Ar}}\text{L})\text{FeCl}(\text{O}^t\text{Bu})$ (5**)**—In a 20 mL vial, $(\text{}^{\text{Ar}}\text{L})\text{FeCl}$ (**1**) (0.11 g, 0.11 mmol, 1.0 equiv) was frozen in 4 mL of benzene. A just-thawed solution of di-*tert*-butyl peroxide (42 mg, 0.29 mmol, 2.5 equiv) in 4 mL of benzene was added while stirring. The mixture was thawed and stirred at room temperature for 12 h. The reaction mixture was filtered through Celite, and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield a purple powder. The residue was recrystallized at $-35\text{ }^\circ\text{C}$ from a 3:1 ratio of hexanes to toluene. The following morning, the mother liquor was decanted, and the crystals washed with 2 mL of hexanes and dried in vacuo to afford $(\text{}^{\text{Ar}}\text{L})\text{FeCl}(\text{O}^t\text{Bu})$ (**5**) as purple crystals (78 mg, 66%). ^1H NMR (500 MHz, 295 K, C_6D_6): δ 93.2 (bs), 39.4 (bs), 17.7 (bs). $\chi_{\text{M}}T$ (295 K, SQUID) = $3.96\text{ cm}^3\text{K/mol}$. EPR (toluene, 77 K): $g_{\text{eff}} = 6.77, 5.87, 5.12, 1.96$. Zero-field ^{57}Fe Mössbauer (4 K) (δ , $|E_{\text{Q}}|$ (mm/s)): 0.32, 1.31 ($\gamma = 0.45\text{ mm/s}$). %CHN Calcd for $\text{C}_{70}\text{H}_{58}\text{ClFeN}_2\text{O}$: C, 81.27; H, 5.65; N, 2.71; Found: C, 81.24; H, 5.77; N, 2.95.

Synthesis of $\text{K}[(\text{}^{\text{Ar}}\text{L})\text{Fe}(\text{O}^t\text{Bu})_2]$ (3**)**—In a 20 mL vial, potassium *tert*-butoxide (35 mg, 0.31 mmol, 3.0 equiv) was suspended in 4 mL of benzene. A solution of $(\text{}^{\text{Ar}}\text{L})\text{FeCl}$ (**1**) in 6 mL of benzene (0.1 g, 0.10 mmol, 1.0 equiv) was added while stirring. After being stirred at room temperature for 3 h, the reaction mixture was filtered through Celite, and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was

frozen and removed in vacuo to yield $K[(^A\text{rL})\text{Fe}(\text{O}^t\text{Bu})_2]$ (**3**) as an orange-red powder (0.12 g, quant.) Crystals suitable for X-ray diffraction were grown from a concentrated solution of toluene layered with hexanes at $-35\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, 295 K, C_6D_6): δ 27.16, 15.86, 12.73, 11.95, 11.21, 9.17, 7.75, 7.52, 6.43, 6.30, 5.98, 5.37, 3.59, 2.38, 2.00, 1.67, 1.42, 1.21. 0.00, -2.30 . Zero-field ^{57}Fe Mössbauer (90 K) (δ , $|E_Q|$ (mm/s)): 0.97, 1.72 ($\gamma = 0.21$ mm/s). %CHN Calcd for $\text{KC}_{74}\text{H}_{67}\text{FeN}_2\text{O}_2$: C, 79.98; H, 6.08; N, 2.52; Found: C, 79.85; H, 5.97; N, 2.50.

Synthesis of $(^A\text{rL})\text{Fe}(\text{O}^t\text{Bu})_2$ (6**)**—In a 20 mL vial, $K[(^A\text{rL})\text{Fe}(\text{O}^t\text{Bu})_2]$ (**3**) (0.12 g, 0.11 mmol, 1.0 equiv) was frozen in 4 mL of THF. A just-thawed solution of silver tetrafluoroborate in 4 mL of THF (0.20 g, 0.22 mmol, 2.0 equiv) was added while stirring. The mixture was thawed and stirred at room temperature for 10 min. The reaction mixture was concentrated, dissolved in benzene, and filtered through Celite, and the filter cake was washed with excess benzene until the eluent was nearly colorless. The solvent was frozen and removed in vacuo to yield a red-pink powder. The filtration in benzene was repeated to remove traces of silver. The residue was washed with 3 mL of hexanes and recrystallized at $-35\text{ }^\circ\text{C}$ from a 4:1 ratio of hexanes to benzene. The following morning, the mother liquor was decanted, and the crystals were dried in vacuo to afford $(^A\text{rL})\text{Fe}(\text{O}^t\text{Bu})_2$ (**6**) as metallic-red crystals (75 mg, 65%). ^1H NMR (500 MHz, 295 K, C_6D_6): δ 89.9 (bs), 39.9 (bs), 25.3 (bs), 11.1 (bs). $\chi_M T$ (295 K, SQUID) = $3.93\text{ cm}^3\text{K/mol}$. EPR (toluene, 77 K): $g_{\text{eff}} = 7.48$, 5.73, 4.25, 1.81. Zero-field ^{57}Fe Mössbauer (4 K) (δ , $|E_Q|$ (mm/s)): 0.33, 1.53 ($\gamma = 0.63$ mm/s). %CHN Calcd for $\text{C}_{74}\text{H}_{67}\text{FeN}_2\text{O}_2$: C, 82.90; H, 6.30; N, 2.61; Found: C, 82.68; H, 6.44; N, 2.64.

3.0. RESULTS

3.1. Synthesis of Fe Complexes

The ferrous precursor $(^A\text{rL})\text{FeCl}$ (**1**) [$^A\text{rL} = 1,9\text{-(2,4,6-Ph}_3\text{C}_6\text{H}_2)_2\text{-5-mesityldipyrrromethene}$] was synthesized according to literature procedures.^{2a} Two oxidation procedures were attempted: (a) anion coordination followed by outer-sphere oxidation and (b) inner-sphere oxidation using an appropriate oxidant. The addition of excess tetrabutylammonium chloride (3 equiv) to **1** in a benzene solution at room temperature affords the four-coordinate ferrous salt $[\text{tBu}_4\text{N}][(^A\text{rL})\text{FeCl}_2]$ (**2**) following filtration to remove excess tetrabutylammonium chloride. Red crystals of **2** were isolated upon crystallization from toluene/hexanes at $-35\text{ }^\circ\text{C}$, and the structure was obtained by single crystal X-ray crystallography (Figure S-22). Paramagnetic **2** was analyzed by ^1H NMR and displays shifts consistent with those of other four-coordinate ferrous dipyrin complexes.^{2a,b} Oxidation of **2** with one equivalent of ferrocenium hexa-fluorophosphate at room temperature in benzene results in an instantaneous color change from red to dark brown. Isolation from the ferrocene byproduct yielded a green solid. Recrystallization of the solid from a mixture of toluene and hexanes afforded green crystals of the ferric complex $(^A\text{rL})\text{FeCl}_2$ (**4**) in 73% yield (Scheme 1). The ^1H NMR spectrum of **4** exhibits only two very broad peaks at 91.8 and 13.7 ppm.

The addition of excess potassium *tert*-butoxide (3 equiv) to **1** in a benzene solution at room temperature affords the four-coordinate salt $K[(^A\text{rL})\text{Fe}(\text{O}^t\text{Bu})_2]$ (**3**) as an orange powder

after filtration and lyophilization. The solid state molecular structure shows that the potassium counterion is coordinated to two of the dipyrin-flanking phenyl rings (Figure S-25).⁷ Reaction of **3** with a just-thawed solution of silver tetrafluoroborate (1 equiv) in THF precipitates a silver mirror over the course of 10 min. The solid byproducts were removed by repeated filtration, and the remaining product was purified via recrystallization from benzene/hexanes to afford orange-red crystals of (^{Ar}L)Fe(O^tBu)₂ (**6**) in 65% yield.

The reaction of **1** with potassium *tert*-butoxide leads to rapid oversubstitution of alkoxide, making the mixed ancillary anion [(^{Ar}L)FeCl(O^tBu)][−] inaccessible. Gratifyingly, treatment of **1** with di-*tert*-butyl peroxide at room temperature in benzene afforded a dark purple solution distinct from **1**, as ascertained by ¹H NMR. Crystallization of the new material from toluene/hexanes provides analytically pure (^{Ar}L)FeCl(O^tBu) (**5**) as purple crystals.

3.2. Crystal Structure Analysis of 4–6

Crystals suitable for X-ray diffraction analysis were typically grown from hexane-layered toluene solutions at −35 °C. The solid-state molecular structures of **4–6** are depicted in Figure 1 with the pertinent metrical parameters listed in Table 1. The Fe–N bond distances for the oxidized complexes are contracted compared to Fe^{II} precursors. For example, the Fe–N distances decrease by 5.4 and 5.8% upon oxidation of **2** to **4**, respectively (**2**: Fe–N₁ 2.089(3) Å, Fe–N₂ 2.089(3) Å; **4**: Fe–N₁ 1.967(2) Å, Fe–N₂ 1.966(2) Å). The iron center is raised above the dipyrin ligand platform in all complexes, and the geometry is best described as between trigonal-pyramidal and tetrahedral with **2** and **4** having nearly perfect trigonal-pyramidal structures ($\tau_4 = 0.84$ for **2**, $\tau_4 = 0.86$ for **4**).⁸ The geometries of **5** and **6** are closer to tetrahedral, possibly due to steric pressure from the *tert*-butoxide substituents. The dipyrin platform is nearly planar in **4** and **6**, but a substantial distortion from planarity has occurred in **5**. The distortion of the ligand can be described by the C_α–N–N–C_α torsion angle, which has been used as a measure of ruffling in porphyrin systems.⁹ The dipyrin torsion angle in **5** is 20.48(1)° and might be due to crystal packing effects.

3.3. Oxidation State Determination

Oxidation changes from the ferrous (**2** and **3**) precursor to the ferric (**4–6**) products were ascertained using zero-field ⁵⁷Fe Mössbauer spectroscopy. Complexes **2** and **3** exhibit single quadrupole doublets in their ⁵⁷Fe Mössbauer spectra at 90 K with isomer shifts (δ) of 0.94 and 0.97 mm/s and quadrupole splittings ($|E_Q|$) of 3.29 and 1.72 mm/s, respectively (Table 2, Figures S-3 and S-4). These values are typical for four-coordinate high-spin Fe^{II} complexes.¹⁰

⁵⁷Fe Mössbauer spectra of Fe^{III} complexes **4–6** at 90 K show very broad absorption peaks, and spectra were recollected at lower temperature (Figure 2).¹¹ At 4 K, the Fe^{III} complexes displayed isomer shifts (mm/s) of 0.12 for **4**, 0.32 for **5**, and 0.33 for **6**. These isomer shifts are lower than those measured for 5- and 6-coordinate iron–porphyrin systems but fall in line with reported isomer shifts for tetrahedral high-spin Fe^{III} ions.¹² The lower isomer shift for **4** can be explained by the pronounced electron deficiency of the iron center in a weaker ligand field environment compared to that of **5** and **6**. The Mössbauer spectrum for **4** shows an asymmetric singlet ($|E_Q| = 0.21$ mm/s) as would be predicted for a high-spin Fe^{III}

compound with a very small electric field gradient at the iron center. Substituting chloride for *tert*-butoxide increases the electric field gradient in these iron–dipyrrin complexes, which results in an increase in quadrupole splitting ($|E_Q| = 1.31$ mm/s for **5** and $|E_Q| = 1.53$ mm/s for **6**).

3.4. X-Band EPR Spectroscopy on 4–6

X-band EPR spectra of complexes **4–6** were recorded at 77 K in a toluene glass (Figure 3a) and exhibit features at $g_{\text{eff}} = 8.40, 5.45,$ and 2.95 (complex **4**); $g_{\text{eff}} = 6.77, 5.87, 5.12,$ and 1.96 (complex **5**); and $g_{\text{eff}} = 7.48, 5.73, 4.25,$ and 1.81 (complex **6**). All spectra can be simulated as $S = 5/2$ spin systems with an isotropic g -value of 2. The complexes show small to intermediate amounts of rhombicity, with values of $|E/D|$ of 0.13 for **4**, 0.04 for **5**, and 0.07 for **6**. In all cases, the feature between $g_{\text{eff}} = 5.5$ –6 originates from the $m_s = \pm 3/2$ Kramers doublet, and all other features are $m_s = \pm 1/2$ state transitions. No transitions originating from the $m_s = \pm 5/2$ Kramers doublet are observed.

3.5. Magnetic Measurements on 4–6

Magnetic susceptibility data were acquired for complexes **2–6** by variable-temperature (2–300 K) magnetometry and confirmed high-spin ground states for complexes **4–6**. The data show similar temperature dependencies of the magnetic susceptibility for Fe^{III} complexes (Figure 3b for **4**, Figures S-14, S-16, and S-17 for **2**, **5**, and **6**, respectively). DC magnetic susceptibility measurements at 295 K give $\chi_M T$ (cm³K/mol) values for compounds **4** (4.07), **5** (3.96), and **6** (3.93) close to the spin-only value for an $S = 5/2$ spin ground state (4.38 cm³K/mol). Notably, the susceptibility data for **2** display a downturn at a temperature higher than that of the data for **4–6**, suggestive of the presence of significant zero-field splitting (ZFS) for ferrous **2** and decreased ZFS for ferric **4–6**. Further support for the ZFS is obtained from low-temperature magnetization data at various applied dc fields. The reduced magnetization plots reveal a series of nonsuperimposable isofield curves (Figure 3c for **4**, Figures S-14, S-16, and S-17 for **2**, **5**, and **6**, respectively). Fits to the data obtained using PHI¹³ give axial and transverse zero-field splitting parameters D and $|E|$ (listed in Table 2): **4** ($D = 1.82$ cm^{−1}), **5** ($D = 1.28$ cm^{−1}), and **6** ($D = 0.99$ cm^{−1}) compared to that of **2** ($D = -12.43$ cm^{−1}).

3.6. Redox Behavior of Compounds 4–6

The electrochemical properties of complexes **4–6** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV, Figures S-11, S-12, and S-13) to determine the influence of the ancillary ligands on the electronic structure of the Fe^{III} complexes (Figure 4). All three compounds present a reversible oxidation event at $E_{1/2}$ (V): 0.81 (**4**), 0.68 (**5**), and 0.61 (**6**) that is consistent with ligand-centered oxidation, though a Fe^{IV}/Fe^{III} couple cannot be ruled out. Complex **4** also shows a reversible reduction at $E_{1/2} = -0.44$ V, which corresponds to a Fe^{III}/Fe^{II} couple. In contrast, **5** and **6** present quasi-reversible reduction events at $E_{1/2} = -1.04$ and -1.63 V, respectively. Therefore, the average cathodic shift per chloride substitution for *tert*-butoxide is 0.6 V. The potentials obtained from the CV highlight the pronounced influence of the coordinated ancillary ligands onto metal-centered

redox events. *tert*-Butoxide ligands stabilize the higher Fe^{III} oxidation state and cathodically shift the attendant reduction potentials observed.

3.7. Absorption Spectroscopy on 4–6

The UV/vis spectra (Figure 5a, Table 2) for the characteristically intense red-pink Fe^{II} complexes **1**, **2**, and **3** feature bands with maxima at 556 nm for **1**, 530 nm for **2**, and 531 nm for **3**, respectively. The bands are of similar intensity ($\epsilon = 64.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for **1**, $\epsilon = 71.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for **2**, and $\epsilon = 67.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for **3**) and are assigned as dipyrin ligand-to-ligand charge transfer bands (LLCT) akin to the Soret bands in porphyrin chromophores.¹⁴ Oxidation of dichloride **2** resulted in the immediate color change from red-pink to dark green ($\epsilon = 19.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; Figure 5a), while the oxidized **5** and **6** retain a pink color but display shifted absorption maxima (Figure 5a) and lower extinction coefficients [$\epsilon (\text{M}^{-1} \text{ cm}^{-1})$: 30.8×10^3 (**5**), 53.4×10^3 (**6**)]. To exclude possible ligand modification during the oxidation of **2** to **4**, which could result in the pronounced decrease in intensity of the LLCT and the observation of additional transitions, **4** was reduced by one electron using cobaltocene to give $[\text{Cp}_2\text{Co}][(\text{A}^{\text{L}}\text{L})\text{Fe}^{\text{II}}\text{Cl}_2]$, and complete restoration of the $\pi\text{--}\pi^*$ transition was observed (Figure 5b). Consequently, permanent ligand modification can be excluded, and the low intensity bands can be described as characteristic of **4**.

3.8. Reactivity with Cyclohexadiene

To assess the influence of the ancillary ligands on the reactivity of the Fe^{III} complexes, we investigated their activity in hydrogen atom abstraction reactions. When complex **5** was heated to 70 °C in the presence of cyclohexadiene or dihydroanthracene, complete consumption of starting material was observed. ¹H NMR spectroscopy as well as UV/vis spectroscopy confirmed formation of **1** (Figure 5c). No reaction occurred upon prolonged heating in benzene in the absence of cyclohexadiene, and the observed reactivity could therefore either be explained by ejection of *tert*-butoxyl radical or by a direct hydrogen atom abstraction (HAA) mechanism. If the first pathway were operative, HAA from toluene should be feasible (BDE (kcal/mol): $\text{PhCH}_3 = 90$; $\text{tBuO-H} = 105$),¹⁵ but substantial decay of **5** in toluene over a time-course of 24 h at 120 °C was not observed. We therefore propose a direct HAA pathway to be operative. The observed reactivity resembles the generally accepted enzymatic mechanism of lipoxygenases in which a mononuclear nonheme Fe^{III}–OH abstracts a hydrogen atom to form a Fe^{II}–H₂O species.¹⁶ Hydrogen atom abstraction reactivity from ferric species has furthermore been demonstrated using ferric alkoxide and hydroxide model complexes.¹⁷ Heating of **6** under identical conditions did not result in decay of the Fe^{III} species, and a temperature of 85 °C was necessary to induce HAA from cyclohexadiene. In contrast, if **4** was heated in cyclohexadiene to 70 °C, formation of **1** did not occur, and instead, a blue decomposition product formed, which is indicative of dipyrromethene ligand oxidation.

3.9.1. Density Functional Theory (DFT) Calculations: Ground State Electronic Structure

The electronic structure of the complexes (using the crystallographic positions of all atoms) was examined using the ORCA suite of programs.¹⁸ Single point energies were calculated using the B3LYP¹⁹ functional with TZVP as basis set on Fe, N, Cl, and O and the SVP basis set on all other atoms.²⁰ This combination of functional and basis set was chosen

because we had previously established that it accurately predicts measured Mössbauer parameters of iron–dipyrin complexes.^{2a,b} The Mössbauer parameters for all new compounds were calculated to correlate theory with experimental data and matched remarkably well.

The spectroscopically validated computational model indicates that the effective amount of spin at the iron center stays constant for all Fe^{II} complexes (**1–3**) with a calculated Mulliken spin density (MSD) on iron of 3.7 (Table 3). Upon oxidation, the MSD at iron increases as would be expected for removal of a β electron from the d-orbital manifold. However, the total MSD on iron is calculated to be 4.1 for **4–6** instead of the expected five unpaired electrons. The dipyrin ligand MSD is calculated to be 0.34 for **4**, 0.27 for **5**, and 0.19 for **6**, indicating a diminished contribution to the overall spin composition as the more electron-rich alkoxide ligands are substituted in. Indeed, the mixed Cl/O^tBu **5** is calculated to exhibit a greater MSD on the alkoxide O (0.38) compared to that of Cl (0.23) (Table 3; illustrated in Figure 6).

3.9.2. Excited State Electronic Structure Calculations—The oxidation of dichloride **2** to **4** is accompanied by a significant color change from red-pink **2** to a deep green in **4**, while both **5** and **6** largely retain the color of their ferrous precursors. To interrogate this phenomenon and the nature of the excited states in general of the Fe^{III} species, we performed time-dependent DFT (TD-DFT) calculations at the same level of theory. Single-point excited state energy calculations were used to determine the 30 lowest-energy states. The deviation between calculated and experimental optical transitions is comparable to that seen in other systems (Figures S-33, S-35, and S-42).²¹ All calculated transitions have multiconfigurational character, and predicted bands can be interpreted using difference densities between ground-state and excited-state orbitals. Although the exact energies of the calculated transitions do not align precisely with experiment, the predicted absorption spectra qualitatively reflect experimental observations (Figure 5a). TD-DFT analysis predicts one intense electronic transition for Fe^{II} complexes **1–3**, in agreement with the single, strong absorption observed experimentally. For example, the intense band calculated for **2** at 438 nm ($f_{\text{osc}} = 0.784$) has its largest contribution from dipyrin-based π – π^* (LLCT) transitions with very little metal contribution (Figures 7a and S-38) with similar observations made for **1** (Figure S-36).

The predicted transitions for the symmetric ferric complexes **4** and **6** have smaller oscillator strengths than those for their ferrous precursors, which is in agreement with experimental data. The electronic absorption spectra for **4** and **6** (Figures S-33b and c) can be correlated to the calculated transitions for those complexes. One major intense band is predicted for **6** at 413 nm ($f_{\text{osc}} = 0.384$), identified as mostly a LLCT band with some metal character mixed in (Figure 7c). The intense dipyrin π – π^* transition present in **1** and **2** is not predicted for **4**, which is consistent with the substantial color change observed. The calculation predicts a new, low-energy transition at 645 nm ($f_{\text{osc}} = 0.028$), also observed experimentally. This new, low energy transition results in the very distinct green color of **4** as opposed to the orange to pink color of all other complexes. The difference density plot shown in Figure 7b identifies the major contributor to the new band as a transition featuring significant ligand-to-metal

charge transfer (LMCT). The difference density maps for **2**, **4**, and **6** reveal a trend toward lower oscillator strengths with increasing metal character in the acceptor orbital, an observation that can be explained invoking configuration interaction between different transitions.^{14,22}

4.0. DISCUSSION

The key questions we sought to address in this study are the effects of ancillary ligand substitution on structural parameters, electronic structure, and redox and spectral properties in a series of iron dipyrinato complexes. Oxidation of the ferrous precursor **1** was achieved in one of two methods: (a) anation followed by outer-sphere oxidation in the conversion of **2** → **4** and **3** → **6**, or (b) inner sphere oxidation of **1** with di-*tert*-butyl peroxide to give the mixed ancillary ligand complex **5**. Structurally, the four coordinate complexes (ferrous **2–3** and ferric **4–6**) feature the same metrical trends observed previously with iron dipyrinato complexes.^{2a} The complexes retain the same coordination environment throughout the series, and the structural features of the ferric complexes are consistent with metal-centered oxidations without indication of extensive dipyrin or ancillary ligand redox being evident.^{2a,b}

To assess the effect of ancillary ligand substitution on the resultant electronic structure, the series of oxidized complexes **4–6** were examined by EPR, magnetometry, ⁵⁷Fe Mössbauer, cyclic voltammetry, and absorption spectroscopy. The EPR and magnetometry data suggest that **4–6** are indeed high-spin ($S = 5/2$). The variable-temperature magnetic susceptibility measurements display well-isolated spin-ground states throughout the temperature range examined (20–300 K). Minor electronic differences between **4–6** are manifest in zero-field ⁵⁷Fe Mössbauer spectroscopy. The isomer shifts observed for **4–6** fall within the typical range expected for high-spin Fe^{III} compounds,¹² and the similarity in isomer shift for **5** and **6** indicates that the electronic environment at the iron center is similar. The isomer shift for **4** is lower, which could be explained by the less π -donating character of chloride ligands compared to that of *tert*-butoxide. Comparison of the quadrupole splittings of **4–6** depicts a pronounced lattice contribution for **5** and **6** which is not apparent for **4**.²³ The chemically dissimilar ligands in **5** and asymmetric orientation of the two alkoxides in **6** lead to an inhomogeneous electric field gradient, giving rise to the nonzero quadrupole splittings observed. The qualitative trend in quadrupole splitting values is also captured by the calculated electric field gradients, lending credibility to the theoretical model employed.

We previously reported the Fe^{III/II} couples for a series of related iron–dipyrromethene complexes and found that electronic variations on the monoanionic dipyrinato ligand scaffold (halogenation of the pyrrolic β -positions, fluorinated aryl meso substituent) can shift the redox potential up to 350 mV.¹⁰ The present work illustrates a far more dramatic effect on the observed electrochemical properties upon examination of **4–6**. Substitution of the chloride ancillary ligands in **4** with the more electron-rich *tert*-butoxide ligands shows an increased stabilization of the Fe^{III} oxidation state by cyclic voltammetry, where each alkoxide substitution cathodically shifts the Fe^{III/II} couple by 600 mV. A far more modest effect is observed in the subsequent oxidative event where a separation of less than 200 mV is observed, but the oxidation is similar to those invoked for dipyrin oxidation events²⁴ and

would, consequently, bear less influence from the ancillary ligands. Similar analyses on ferric porphyrin complexes bearing alkoxide and chloride do show an anodic shifting for the primary oxidation event (~ 120 mV), though the locus of oxidation remains (iron- versus porphyrin-centered) unresolved.^{25–27}

The absorption spectra for complexes **4–6** display significant differences. Most notably, complex **2** undergoes a substantial color change upon oxidation to **4**, whereas **5** and **6** largely retain their ferrous precursor colors. The absorption spectra show a broad distribution in intensity of the absorption maxima, where the experimentally measured extinction coefficients correlate remarkably well with the calculated oscillator strengths. Not unexpectedly, the TD-DFT calculations performed suggest that highest intensity absorption bands observed in **1–3** and **5–6** are largely dipyrin-based LLCT bands akin to Soret bands observed in metal–porphyrin complexes.¹⁴ Furthermore, the results indicate that the decreasing intensity can be ascribed to increasing metal character in the acceptor orbitals invoking LMCT contributions to the excited states, which is substantial in **4**. Examples of metal–porphyrin complexes exhibiting similar Soret band broadening have been observed when the porphyrin π -system is itself being oxidized (e.g., Horseradish peroxidase), thus affecting the ground state,^{14,28,29} or when LMCT bands mix into the excited state LLCT, as is the case with d-type hyperporphyrins.³⁰

Comparing the calculated electronic structures of **4–6** reveals a systematic destabilization of the β -manifold with increasing alkoxide substitution (Figure 8). While the dipyrin π and π^* orbitals remain fairly constant across the series, the Fe-based orbitals are destabilized increasingly with each successive alkoxide substitution. The contributions to the iron–alkoxide orbital destabilization arise from the alkoxide being better matched in both σ and π capacities in terms of energy match to the iron 3d orbitals. Thus, the dichloride complex **4** displays the minimal β -manifold destabilization, effectively making the dipyrin π^* and Fe 3d β isoenergetic. As a result, the potential for LMCT excitations becomes competitive with the LLCT excitations that dominate the ferrous complexes and ferric **5** and **6**.³¹ Indeed, for complex **4**, the LMCT transitions can be mixed by configuration interaction with the dominant dipyrin LLCT, which results in the observed split low-intensity bands.³² A similar observation has been made for tetraphenylporphyrinatoiron(III) methoxide and chloride complexes.^{33,34} The effect is enhanced for the dipyrin complexes with respect to the porphyrin species as a result of the lower symmetry of the former. The cumulative effect is that, while complexes **4** and **6** are nominally electronically equivalent in the ground state, the more covalent iron–alkoxide **6** features a destabilized iron 3d β manifold (as a consequence of the higher covalency of Fe(O^{*t*}Bu) vs FeCl), resulting in blue-shifted potential LMCT pathways in the excited state, leaving the dipyrin LLCT band largely unaffected.

As a result of the alkoxide substitution progression from **4** $\rightarrow$ **6**, the alkoxides were shown to stabilize the ferric state and enhance the iron-ancillary covalency. The latter effect is evident in comparing the calculated MSDs for **4** $\rightarrow$ **6**, where the accumulated spin density on the *tert*-butoxide is maximized on the mixed ancillary **5** (Table 3). The proposed accumulation of spin density for **5** is manifest chemically by the propensity of **5** to abstract a hydrogen atom from cyclohexadiene. The concentration of spin density is subtly manifest in that the mixed ancillary **5** undergoes H-atom abstraction reactivity under conditions milder

than those for the bis-alkoxide **6**, whereas the dichloride **4** was not observed to undergo H-atom abstraction in a similar way. Given the growing interest in facilitating bond activation and subsequent bond-functionalization processes, careful attention must be paid to how metal–ligand electronic properties can be tuned to elicit the desired functional profile.

5.0. CONCLUSION

We synthesized a series of Fe^{III} dipyrromethene complexes and showed that the ancillary ligand substitution affects both spectral and reactivity properties of the ferric complexes examined. In many cases, ancillary ligands such as chloride or alkoxides are thought of as spectator ligands that will not greatly influence the characteristics of the complex. However, we observe a substantial influence for high-spin species in weak-field environments. The electron-richness of the ancillary can dramatically impact the molecular redox properties, and the degree of metal–ligand covalency can in turn alter both ground state properties (redox potentials, electronic structure, frontier orbital composition) as well as excited state phenomena (blue-shifting LMCT). Beyond the excited state spectral property changes, the reactivity profiles of the different ferric complexes display the propensity to perform H-atom abstraction as a function of the residual spin density the ancillary ligand bears.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Solid-state molecular structures for (a) $(\text{ArL})\text{FeCl}_2$ (**4**), (b) $(\text{ArL})\text{FeCl}(\text{O}^t\text{Bu})$ (**5**), and (c) $(\text{ArL})\text{Fe}(\text{O}^t\text{Bu})_2$ (**6**) at 100 K with thermal ellipsoids at 50% probability level for **4** and **6** and at 30% probability level for **5**. Color scheme: C, gray; N, blue; Cl, green; O, red; Fe, orange. H atoms and solvent molecules have been omitted for clarity.

Figure 2.
Zero-field ^{57}Fe Mössbauer spectra of **4–6** collected at 4 K.

Figure 3.

(a) EPR spectra of complexes **4–6** (X-band, 9.3298 GHz) in a toluene glass at 77 K. (b) Variable-temperature magnetic susceptibility data collected for **4** under an applied dc field of 1000 Oe. (c) Low-temperature magnetization data for **4** collected between 1.8 and 10 K under various applied dc fields. Solid lines correspond to the best fits obtained with PHI.¹³

Figure 4. Cyclic voltammograms of complexes **4–6** at room temperature in dichloromethane using 0.1 M *n*Bu₄NPF₆ as supporting electrolyte. Working electrode: glassy carbon. Reference electrode: Ag/AgNO₃. Counter electrode: Pt wire. Scan rate: 0.1 V/s.

Figure 5.

(a) UV/vis spectra for complexes **1**–**6**. Spectra obtained at room temperature in benzene; average ϵ values calculated from a minimum of four concentrations. (b) Spectral change during reduction of **4** (blue) with cobaltocene to give $[\text{Cp}_2\text{Co}][(\text{Ar}^t\text{L})\text{FeCl}_2]$ (black). (c) Spectral changes during reduction of **5** (red) to **1** (black).

Figure 6.
Mulliken spin density plot calculated for **5** (isovalue 0.01).

Figure 7.
Electron difference density map for key predicted transition for **2** (a), **4** (b), and **6** (c).
Electrons move from yellow to red areas upon excitation (isovalue 0.0025).

Figure 8. MO diagram [α (red triangle) and β (blue triangle) spin manifolds] for **4–6**, including dipyrroin-based HOMO and LUMO, and singly occupied d-orbitals.

Scheme 1.

Synthesis of Fe^{III} Complexes Supported by a Dipyrinato Ligand

Table 1Selected Bond Distances and Angles for Compounds 2 and 4–6^a

bond (Å)/angle (deg)	2	4	5	6
Fe ₁ –N ₁	2.089(3)	1.967(2)	2.031(4)	2.0253(18)
Fe ₁ –N ₂	2.086(3)	1.966(2)	1.985(4)	2.0243(19)
Fe ₁ –X ₁	2.2689(11)	2.1703(7)	2.2258(16)	1.7936(16)
Fe ₁ –X ₂	2.3027(10)	2.1890(7)	1.785(3)	1.7967(19)
τ_4^b	0.84	0.86	0.92	0.93
$\angle(\text{C}_\alpha\text{--N1--N2--C}_\alpha)$	11.065(2)	0.60814(4)	20.48(1)	1.67487(2)

^aSee Figure 1 for atom labeling.^b τ_4 is defined as $[360 - (\alpha + \beta)]/141$, with α and β being the two largest angles within the four-coordinate complex ($\tau_4 = 0$ for square-planar and $\tau_4 = 1$ for tetrahedral).⁸

Table 2

Spectroscopic Parameters Measured by ^{57}Fe Mössbauer Spectroscopy at 90 K, $\chi_M T$ at Room Temperature Derived from the Magnetization Measurements with Fitting Parameters, and UV/Vis Parameters^a

	δ (mm/s)	$ E_Q $ (mm/s)	Γ_{fwhm} (mm/s)	$\chi_M T$ (RT) (cm ³ K/mol)	g value	D (cm ⁻¹)	$ E/D $	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹) 10^3
1								556	64.4
2	0.94 (0.94)	3.29 (3.31)	0.18	2.88	2.13	-12.43	0.3	530	71.6
3	0.97 (1.03)	1.72 (1.53)	0.21					531	67.8
4^b	0.12 (0.23)	0 (-0.40)	0.64	4.07	1.96	1.82	0	469	19.0
5^b	0.32 (0.30)	1.31 (-1.54)	0.45	3.96	1.90	1.28	0	562	31.6
6^b	0.33 (0.35)	1.53 (-1.22)	0.63	3.93	1.89	0.99	0	532	53.4

^a Experimental (calculated).

^b ^{57}Fe Mössbauer spectra were recorded at 4 K.

Table 3

Calculated Mulliken Spin Densities for Complexes 1–6

	iron	dipyrrin	chloride	<i>tert</i> -butoxide
1	3.72	0.14	0.13	
2	3.71	0.08	0.10, 0.10	
3	3.68	0.07		0.09, 0.12
4	4.08	0.34	0.29, 0.28	
5	4.07	0.27	0.23	0.38
6	4.08	0.19		0.33, 0.33