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Synthesis and Characterization of Sterically Encumbered β-Ketoiminate Complexes of Iron(II) and Zinc(II)‡

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The synthesis, structure, and spectroscopic signatures of a series of four-coordinate iron(II) complexes of β -ketoiminates and their zinc(II) analogues are presented. An unusual five-coordinate iron(II) triflate with three oxygen bound protonated β -ketoimines is also synthesized and structurally characterized. Single-crystal X-ray crystallographic analysis reveals that the deprotonated bis(chelate)metal complexes are four-coordinate with various degrees of distortion depending on the degree of steric bulk and the electronics of the metal center. Each of the high-spin iron(II) centers exhibits multiple electronic transitions including ligand π to π^* , metal-to-ligand charge transfer, and spin-forbidden *d-d* bands. The ¹H NMR spectra of the paramagnetic high-spin iron(II) centers are assigned on the basis of chemical shifts, longitudinal relaxation times (T_1), relative integrations, and substitution of the ligands. The electrochemical studies support variations in the ligand strength. Parallel mode EPR measurements for the isopropyl substituted ligand complex of iron(II) show low-field resonances (g > 9.5) indicative of complex aggregation or crystallite formation. No suitable solvent system or glassing mixture was found to remedy this phenomenon. However, the bulkier diisopropylphenyl substituted ligand exhibits an integer spin signal consistent with an isolated iron(II) center [S = 2; $D = -7.1 \pm 0.8$ cm⁻¹; E/D = 0.1]. A tentative molecular orbital diagram is assembled.

Introduction

Iron is an attractive metal for catalysis due to its low cost and relatively low toxicity. In particular, imine ligand scaffolds support iron catalysts for ethylene polymerization,¹⁻⁶ support unusual three coordinate iron centers with unique electronic structures giving rise to unusual reactivity with small molecules,⁷⁻¹² and in certain instances show redox non-innocent behavior.^{13,14} High-spin four-coordinate iron(II) complexes are dominated by tetrahedral geometries.¹⁵⁻²¹ Multiple examples of square planar iron(II) complexes have been reported with sterically encumbered or macrocyclic ligands.²²⁻³³ Recent reports of trigonal monopyramidal high-spin iron(II) complexes supported by multidentate ligands have

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unusual magnetic and physical properties.^{34–37} Ligands that impose a *cis*-divacant octahedral (or sawhorse) geometry have also been invoked as key intermediates for *cis*-dihydroxylation catalysts for higher formal oxidation states,^{38–40} but are usually found in clusters for iron(II).^{41,42} Highly distorted four-coordinate high-spin iron(II)

centers exhibit unique physical properties and chemical reactivity. Seminal work by Holm and coworkers demonstrates that deprotonated α , β -unsaturated- β -ketoamines (or β -ketoiminates) support four-coordinate metal geometries,^{43,44} resist coordination polymer formation,44-47 and allow facile tuning of both steric and electronic constraints. Furthermore, the stereochemical preferences of these bidentate monoanionic ligands in their reactions with cobalt, nickel, iron, chromium, copper, and zinc have been described.43,44,47-51 Due to our interest in generating catalysts of earth abundant metals for small molecule activation featuring sterically encumbered β -ketoiminate ligands, we have revisited this classic coordination chemistry with bulkier ligand scaffolds. In this work, the role of the steric bulk of these ligands in modulating the physical properties of divalent metal centers is explored. The full assignment of the ¹H NMR spectra of the paramagnetic $[Fe^{II}(L^R)_2]$ complexes (where $L^R = a$ deprotonated α,β -unsaturated- β -ketoamine or β -ketoiminate) is provided as well as the electronic spectra into the near-infrared. Additionally, electrochemical studies of the iron(II) and zinc(II) complexes are presented. Interestingly, while the solid state structure of

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[‡] Electronic supplementary information (ESI) available: Tables comparing NMR features and bond distances of ligands, schemes of prevalent tautomers and resonance contributors for the ligands, and figures showing preliminary molecular orbital diagrams, zinc cyclic voltammograms and electronic changes under dioxygen. CCDC reference numbers 807200– 807204. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10024f

 $[Fe^{II}(L^{iPr})_2]$ reflects a monometallic complex, the frozen solventglass EPR spectra of this complex indicate formation of molecular aggregates (or microcrystallites) in solution. These studies provide a basis for ongoing work on the catalysts for the activation of small molecules.

Results and discussion

Following standard synthetic routes for the preparation of α . β unsaturated-B-ketoamines, condensation of a B-diketone with a primary amine and a catalytic amount of acid afforded the desired ligands in high yield (Scheme 1).52-55 Although three tautomeric forms are possible (i.e.; Schiff base, ketamine, and enimine), the ¹H NMR spectra for each of the reaction products exhibits a singlet between 4.9 and 5.2 ppm with an integration of one proton. This observation is consistent with a methine proton (See ESI, Schemes S1 and S2, and Tables S1 and S2[‡]). Furthermore, each product exhibits a highly deshielded broad singlet between 10.7 and 12.5 ppm with an integration of one proton. This suggests either the presence of an intramolecular hydrogen bond between the amine and the adjacent ketone or the presence of an iminium proton. Collectively, these observations are inconsistent with the Schiff base or ketoimine tautomer, which would have a methylene feature. Furthermore, the ¹³C NMR chemical shift for the α carbon is observed between 90 and 100 ppm, which is indicative of some alkene character. The insensitivity of the acid dissociation constants to aniline substitution led Martin and coworkers to suggest that the enimine tautomer may predominate for aromatic amines.⁵⁶ However, the feature between 194–196 ppm in the ¹³C NMR spectra of each ligand is consistent with the ketone formulation. The highly deshielded feature in the ¹H NMR (10.7 to 12.5 ppm) is not as highly shifted as the enol proton of acetylacetone. which appears at 15.5 ppm. Furthermore, this feature can be split by benzylic amines (e.g., when $R = CH_2C_6H_5$) further emphasizing the prevalence of the ketamine tautomer.54 Yet, the ¹³C NMR spectra of each product exhibits a peak between 160 and 163 ppm, which is consistent with significant C-N multiple bond character. Zwitterionic resonance forms with iminium cation character are undoubtedly resonance contributors in this delocalized π -system. Therefore, departing from the literature precedent naming these species as α , β -unsaturated- β -ketoamines, ^{54,55} we will describe these species as protonated β-ketoiminates.



Scheme 1

One equivalent of metal(II) triflate reacts with two equivalents of protonated β -ketoiminate and base to afford the mononuclear bis(chelate)metal(II) complexes. We have utilized a number of different iron sources (*i.e.*; [FeCl₄](NEt₄)₂, FeCl₂, Fe(OTf)₂, or [Fe(Mes)₂]₂) and bases (*i.e.*, KO'Bu, NaH, or Li(N'Pr₂)) to obtain intensely-colored yellow crystals of [Fe(L^{iPr})₂] in high yield, which are related to the deep red com-

plex [{PhC(O)CHC(N*i*Pr)CH₃}₂Fe^{II}] reported by Holm and coworkers.⁴⁴ Sodium hydride deprotonation is the preferred synthetic method due to the limited introduction of byproducts, which are potential metal center ligands, and the increased yield of the product. Additionally, the bis(chelate)metal complex also forms (albeit in lower amounts) when one equivalent of deprotonated ligand is added to a single equivalent of iron(II). The reaction of HL^{*i*Pr} and NaH with zinc(II) triflate affords colorless crystals of the analogous [Zn(L^{*i*Pr})₂].

One surprising experimental observation is that mixing HL^{dipp} and sodium hydride does not immediately evolve hydrogen gas. Initially, upon addition of iron(II) triflate, a deep red complex is formed which, after a few minutes, evolves a gas resulting in a deep emerald green $[Fe(L^{dipp})_2]$ complex. The identity of the transient red species remains unknown, and attempts at the production of the anionic tris-chelate complex have not been successful. The reaction of three equivalents of HL^{dipp} with iron(II) triflate in the absence of base affords the pale yellow [Fe(HL^{dipp})₃(OTf)₂]. Titration of this complex with sodium hydride yields the emerald green bis(chelate) metal complex without observation of the deep red transient species. The treatment of HL^{dipp} with Li(NⁱPr₂) followed by the addition of iron(II) triflate proceeds immediately to the emerald green product, therefore on the basis of limited literature precedent,⁵⁷⁻⁵⁹ we speculate that a sodium complex forms prior to the formation of the emerald green [Fe(L^{dipp})₂]. Few other examples of sodium and iron(II) heterobimetallic dimers are known.^{57,60}

The structures of the $[Fe(L^{iPr})_2]$ and $[Zn(L^{iPr})_2]$ reveal isomorphous four-coordinate divalent metal centers each supported by two bidentate β -ketoiminate ligands (Fig. 1, Tables 1 and 2). Whether using Alvarez's continuous symmetry measurements^{61,62} or Hauser's qualitative τ_4 measurements (Table 2),⁶³ the [M^{II}(L^{iPr})₂] complexes all show similar degrees of distortion from tetrahedral. The τ_4 values indicate a distorted trigonal pyramidal geometry about each metal center. The bond distances and angles compare well with those reported previously for high-spin iron(II) complexes⁶⁴⁻⁶⁸ and comparable zinc complexes.⁶⁹⁻⁷¹ The nearest Fe \cdots H–C contact is at 2.72 Å and no evidence supports agostic interactions with the isopropyl groups. The chelate bite angles are similar (average N–M–O ~ 96°) and are typical of those observed for other $\beta\text{-ketoiminates}$ with various divalent metals. $^{53,71-73}$ The ligand backbones (O1-C2-C3-C4-N1) of both complexes have bond distances with the range of 1.293-1.433 Å, consistent with delocalized π -systems (Table S3[‡]). The ionic radii of the iron and



Fig. 1 ORTEP plot of one of the two unique molecules in the crystals of $[Fe(L^{Pr})_2]$ and $[Zn(L^{Pr})_2]$ showing 50% probability thermal ellipsoids and the labeling scheme for unique atoms. All hydrogen atoms are omitted for clarity.

Table 1 Summary of the crystallographic data for $[Fe(L^{iPr})_2]$ (1), $[Zn(L^{iPr})_2]$ (2), $[Fe(HL^{dipp})_3(OTf)_2] \cdot C_6H_6$ (3a), $[Fe(L^{dipp})_2]$ (3b), and $[Zn(L^{dipp})_2]$ (4)

	1	2	3a	3b	4
chemical formula	$C_{16}H_{28}FeN_2O_2$	$C_{16}H_{28}N_2O_2Zn$	$C_{59}H_{81}F_6FeN_3O_9S_2$	$C_{34}H_{48}FeN_2O_2$	$C_{34}H_{48}ZnN_2O_2 \\$
Formula weight/g mol ⁻¹	336.25	345.77	1210.24	572.59	582.11
Space group	Iba2	Iba2	$P\overline{1}$	C2/c	$P\overline{1}$
a/Å	10.6628(2)	10.6260(2)	10.9902(9)	23.7223(2)	9.9587(1)
b/Å	15.7409(3)	15.6935(3)	15.5889(13)	12.0690(1)	10.9893(1)
c/Å	20.5025(4)	20.6601(4)	18.9999(15)	11.7799(1)	16.4658(1)
$\alpha /^{\circ}$	90	90	76.706(4)	90	84.78
$\beta/^{\circ}$	90	90	86.343(4)	107.93(1)	76.17
$\gamma/^{\circ}$	90	90	83.931(4)	90	65.85
$V/Å^3$	3441.2(1)	3445.3(1)	3147.6(4)	3208.93(5)	1596.52(2)
Ζ	8	8	2	4	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.298	1.333	1.277	1.185	1.211
T/K	150	150	150	150	150
Absorption/cm ⁻¹	8.82	1.432	3.78	5.00	8.00
$R_1, \mathrm{w}\hat{R}_2 (I > 2\sigma(I))^a$	0.0283/0.0710	0.0256/0.0616	0.0392/0.0937	0.0376/0.0888	0.0262/0.0702
R_1 , w R_2 (all data)	0.0356/0.0747	0.0364/0.0656	0.0572/0.1037	0.0537/0.0965	0.0305/0.0727

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|/\Sigma ||F_{o}| \cdot wR_{2} = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]]^{1/2} \text{ where } w = q/\sigma^{2}(F_{o}^{2}) + (a^{*}P)^{2} + b^{*}P.$

Table 2Selected bond lengths (Å) and angles (°) for 1, 2, 3, and 4

	1		2		3	4
	$[\operatorname{Fe}(L^{i\operatorname{Pr}})_2]$		$[Zn(L^{iPr})_2]$		$[Fe(L^{dipp})_2]$	$[Zn(L^{dipp})_2]$
M–O#	1.9407(8)	1.9419(8)	1.9479(8)	1.9481(8)	1.9270(8)	1.9617(9), 1.9570(8)
M–N#	2.0447(8)	2.0373(9)	2.0000(9)	1.9915(9)	2.0508(8)	1.9818(9), 1.9792(9)
N#-M-O#	93.92(3)	94.31(3)	97.67(3)	98.09(3)	91.38(3)	96.69(4), 95.91(4)
N#-M-N#A	120.32(5)	122.52(5)	122.00(6)	123.82(6)	139.80(5)	134.11(4)
N#-M-O#A	113.72(3)	112.80(3)	111.98(4)	111.23(4)	100.39(3)	96.69(4), 114.24(4)
O#–M–O#A	123.54(5)	122.50(5)	116.87(5)	115.44(5)	145.40(6)	105.65(4)
N#…O#	2.914	2.918	2.972	2.975	2.848	2.923, 2.947
Ring dihedrals	81.9	80.7	82.61(2)	81.86(2)	59.41(3)	88.90(3)
$S(T_{d})^{61,87}$	2.08	2.06	1.27	1.27	8.29	9.02
$S(D_{4h})^{61,87}$	23.96	24.53	25.94	25.72	10.56	14.89
$ au_{4}^{63}$	0.82	0.81	0.86	0.86	0.53	0.79

zinc are similar and few meaningful differences can be found in these similar structures.

Crystallographic analysis of the yellow crystals of [Fe(HL^{dipp})₃(OTf)₂] reveals a mononuclear five-coordinate iron(II) center with an oxygen rich coordination sphere (Fig. 2, and Tables 1 and 3). The distorted square pyramidal iron(II) center ($\tau_5 = 0.23$)⁷⁴ is supported by two *trans* triflates and three oxygen bound protonated ligands. The triflate ligands have the longest Fe–O bonds whilst the Fe–O bonds to the protonated ligand are shorter. This type of monodentate oxygen-coordination for a protonated HL^{dipp} has been previously observed in [Mg(HL^{dipp})(L^{dipp})₂].⁷³ The bond distances of the protonated β -ketoiminate backbone are indicative of delocalization across the π -system (Table S3[‡]). The aromatic π -system of the phenyl ring is orthogonal to the π -system of the protonated ligands.

The structures of the iron(II) and zinc(II) complexes of L^{dipp-} , deviate significantly from one another (Fig. 3, Tables 1 and 2). While both show four-coordinate metal centers with bidentate β -ketoiminates and similar degrees of distortion on the basis of continuous symmetry measurements, the mean planes determined by the six-membered chelate rings intersect at 88.90(3)° for the zinc complex, while the same metric in the iron(II) complex is 59.41(3)°. While the continuous symmetry measurements place



Fig. 2 ORTEP plot of $[Fe(HL^{dipp})_3(OTf)_2]$ showing 50% probability thermal ellipsoids and the labeling scheme for unique atoms. All hydrogen atoms and the benzene solvate are omitted for clarity. The exceptions are the three hydrogens associated with protonated ligands. Dashed lines indicate hydrogen bonding interactions. No agostic interactions were found.

both complexes along the D_{2d} spread distortion pathway, a τ_4 value of 0.53 for [Fe(L^{dipp})₂] is indicative of a seesaw or sawhorse

	3a
	[Fe(HL ^{dipp}) ₃ (OTf) ₂]·benzene
Fe-O1	2.0258(11)
Fe–O2	2.0132(11)
Fe–O3	2.0460(10)
Fe–O4	2.1266(12)
Fe–O7	2.1883(12)
O1–Fe–O2	148.58(4)
O1–Fe–O3	104.73(4)
O2–Fe–O3	106.57(4)
O4–Fe–O7	162.08(5)
${\tau_{5}}^{74}$	0.23



Fig. 3 ORTEP plot of $[Fe(L^{dipp})_2]$ and $[Zn(L^{dipp})_2]$ showing 50% probability thermal ellipsoids and the labeling scheme for unique atoms. All hydrogen atoms are omitted for clarity.

geometry for the iron(II) center (with C_{2v} symmetry). Similar bond distances are observed in both complexes and the iron-nitrogen and iron-oxygen distances are typical of high-spin iron(II) centers. The closest Fe···H–C distance is 3.341 Å in the iron complex [Fe(L^{dipp})₂] with no evident agostic interactions. Due to the similar ionic radii of the divalent metal centers and the structure of the zinc complex, steric bulk must not be the sole factor governing the distortion in the iron complex. The orthogonality of the diisopropylphenyl substituent relative to the N,O-chelate π -system negates any electron-withdrawing resonance effect from the phenyl ring leaving only the electron-releasing inductive effect.

Both the iron and zinc complexes undergo no noticeable color changes between the solid state and solution. Furthermore, the electronic spectra have been collected in a variety of solvents (toluene, THF, benzene) and over a wide temperature range without observing any dramatic change in the appearance or the position of the spectral features. All of the β -ketoiminate complexes exhibit an intense feature at approximately 310 nm $(\varepsilon \approx 20\,000 \text{ M}^{-1} \text{ cm}^{-1})$, which we have attributed to a ligand π - π^* transition. The zinc complexes are spectroscopically silent above 400 nm. The electronic spectrum of $[Fe(L^{iPr})_2]$ exhibits an intense group of features centered at 410 nm (*i.e.*, 24400 cm⁻¹ with $\varepsilon = 2600 \text{ M}^{-1} \text{ cm}^{-1}$) and a much weaker set of near-IR bands at 920 nm and 1120 nm (i.e., 11 000 and 9000 cm-1 with $\varepsilon = 30$ and 20 M⁻¹ cm⁻¹, respectively, Fig. 4). On the basis of the extinction coefficients, the high energy features are proposed to be charge-transfer bands whereas the lower energy features are *d*-*d* bands. Holm's high-spin iron(II) β -ketoiminate complexes each exhibit near-IR features near 10000 cm⁻¹, which are split



Fig. 4 Electronic spectra of $[Fe(L^{IPr})_2]$ (—) and $[Fe(L^{dipp})_2]$ (---) in THF at room temperature. The extinction coefficients for the high energy features are on the left, while the extinction coefficients for the low energy features are on the right.

by approximately 2000 cm⁻¹.⁴⁴ This observation is more in line with six-coordinate ferrous centers than distorted tetrahedral complexes, which generally exhibit two bands in the 4000-7000 cm⁻¹ region.^{75,76} These near-infrared features suggest the solid state structures do not accurately convey the solution constitution of these iron(II) complexes. Notably, [Fe(L^{dipp})₂] shows a similar charge transfer band at 420 nm (*i.e.*, 23 800 cm⁻¹ with $\varepsilon = 1400 \text{ M}^{-1}$ cm⁻¹) and two weak low energy features at 680 and 1470 nm (*i.e.*, 14700 and 6800 cm⁻¹, respectively). The splitting in the dd bands is consistent with the higher degree of distortion from an ideal tetrahedral geometry that is observed crystallographically for $[Fe(L^{dipp})_2]$. The mineral gillespite is an example of a square planar ferrous site which exhibits two transitions at 8000 and $20\,000\,\mathrm{cm}^{-1}$.⁷⁵ However, the near-infrared spectrum of [Fe(L^{dipp})₂] is not consistent with a square planar geometry for the iron(II) center. The near-infrared features of a trigonal monopyramidal iron(II) center supported by a trianionic ligand exhibits two features at 1636 nm and 1911 nm ($\varepsilon = 250$ and 180 M⁻¹ cm⁻¹, respectively).³⁷ Regardless of the geometry, these low energy features are likely spin-forbidden d-d bands.

Each iron complex exhibits paramagnetically shifted ¹H NMR peaks providing further support for the paramagnetic nature of these species in benzene solution (Fig. 5, Table 4). The spectra show little deviation in THF, chloroform, or benzene. The assignments have been made on the basis of chemical shifts, longitudinal relaxation measurements (T_1) , relative integration, and substitution studies. [Fe(L^{iPr})₂] exhibits several paramagnetically broadened and shifted peaks (Fig. 5A). The proximity of the hydrogen atoms observed in the solid state structures is consistent with the short relaxation times (< 1 ms) observed in solution. While the overlapping nature of the peaks complicates the assignments, the relatively low number of peaks is consistent with the ligands appearing in symmetric environments on the NMR time scale at room temperature. This could also be due to aggregation in solution to form dimers, trimers, or oligomers, as has often been observed in acetylacetonate chemistry.46,77-80 If the interaction of the trigonal monopyramidal iron centers with the oxygen or nitrogen of another complex results in dimers,66,67 most of the postulated equilibria would remove the magnetic equivalence of the chelated ligands. Therefore, an equilibrium between the

 Table 4
 Summary of ¹H NMR Parameters^a

	$C(O)$ - CH_3	- <i>CH</i> -	$C(N)$ - CH_3	ⁱ Pr-	ortho-H	meta-H	para-H
	δ /ppm	δ /ppm	δ /ppm	δ /ppm	δ /ppm	δ /ppm	δ /ppm
[Fe(L ^{iPr}) ₂]	-64.5 (1.4)	-21	-54 (1.0)	-19 (0.3, -CH) $-24 (0.4, -CH_3)$			
$[Fe(L^{Ph})_2]$	-72(0.9)	-17(0.5)	-55 (0.9)	_	-63 (0.3)	15 (6.3)	-38 (6.1)
$[Fe(L^{dipp})_2]$	-28(0.7)	Ь	-22 (0.9)	0.28(5.3, 6H), -16 (0.9, 6H), -24(3.6)	_	15 (9.3)	-43 (1.9)
$[Fe(L^{3,5-Me_2})_2]$	-71.8	-8.9	-55.9	_	-63.4	-15.5 (-CH ₃)	-37.6
[Fe(L ^{Mes}) ₂]	-55.5	-12.5	-52.8	_	36.8 (-CH ₃)	13.3	1.5 (-CH ₃)



Fig. 5 ¹H NMR spectrum of (A) [Fe(L^{Pr})₂], (B) [Fe(L^{Ph})₂], (C) [Fe(L^{dipp})₂], (D) [Fe($L^{3,5-Me_2}$)₂], and (E) [Fe(L^{Mes})₂] in benzene- d_6 at room temperature. Spectra are referenced to the residual protic solvent peak at 7.16 ppm. Dashed lines identify the peak associated with benzene.

aggregated and monometallic species would have to be rapid to be consistent with the spectra reported.

[Fe(L^{Ph})₂] reveals five well resolved resonances and the assignment of these features will be discussed as an example of the process used for the other complexes (Fig. 5B). The very broad peak at -72 ppm with the rapid relaxation time (1.0 ms) integrates to three hydrogens and is consistent with the methyl group next to the ketone functionality of the β-ketoiminate complex. The other broad resonance at -55 ppm with a similarly short T_1 and integration of 3 protons is assigned to the other methyl group of the L^{Ph} anion. The peak with the largest downfield shift (+15 ppm) has a relative long T_1 and integrates for two protons. This is consistent with the *meta*-position of the phenyl group. In further support of the assignment of the *meta* proton, the spectrum of [Fe(L^{3,5-Me₂})₂] (Fig. 5D) displays a new feature at -15 ppm.

The change in paramagnetic shift is consistent with a dominant π -delocalization pathway for the arene ring. The peak at -63 ppm has a very short relaxation time (0.3 ms) indicative of close proximity to the metal center and has an integration of nearly two protons. These properties are consistent with the *ortho*-protons of the phenyl ring. This feature is absent in both [Fe(L^{dipp})₂] and [Fe(L^{Mes})₂] (Fig. 5C and E, respectively). In [Fe(L^{Ph})₂], the feature at -38 ppm has an integration of one proton and the similar relaxation time leads us to assign this peak to the *para*-position of the phenyl ring. The remaining feature at -17 ppm must be the methine at the α -position of the β -ketoiminate. Unfortunately, attempts to obtain correlated spectra have been unsuccessful due to the rapid relaxation processes. Collectively, the ¹H spectra of the iron(II) β -ketoiminates are consistent with the ligands appearing in identical magnetic environments on the NMR time scale.

Electrochemical investigation of the bis(β -ketoiminate)metal complexes has been carried out in THF (Fig. 6). Both iron complexes exhibit a quasi-reversible one-electron oxidative wave (Fig. 6A and B). The position of the anodic peak potentials differ with the substitution of the β -ketoiminate ligand. For [Fe(L^{ipr})₂], this feature is centered at -185 mV vs. Fc^{+/0} or +345 mV vs. SCE, while for [Fe(L^{dipp})₂] the wave is centered at -245 mV vs. SCE, while for [Fe(L^{dipp})₂] the wave is centered at -245 mV vs. Fc^{+/0} ($\Delta E = 120$ mV) or +285 mV vs. SCE. The positive potential shift (60 mV) of the Fe^{II/III} couple indicates that the [Fe(L^{dipp})₂] is more easily oxidized. This shift in potential suggests a stronger ligand field effect for the L^{dipp} anion than for the L^{iPr} anion- if the complexes have identical constitutions in solution. The orthogonality of the diisopropylphenyl π -system to the ligand backbone removes the electron-withdrawing resonance effect and leaves the electron-releasing inductive effect resulting in a stronger ligand.

Interestingly, the zinc complexes show both irreversible oxidative and quasi-reversible reductive waves, which must be ascribed to ligand oxidation and reduction (Fig. S1[‡]). Similar features are observed in the iron complexes and are assigned to the oxidation and reduction of the ligand anion. The ligand oxidation and reduction features become less reversible at low scan rates, which is consistent with rapid chemical steps following the electrochemical process.

All EPR data were collected using a variety of solvents and glassing-solvent mixtures to ensure homogeneous samples (Fig. 7). The 7 K X-band perpendicular (1a) and parallel (1b) mode spectra of 1 show more resonances than are theoretically possible for an isolated S = 2 paramagnetic species. Moreover, the signals



Fig. 6 Cyclic voltammogram of (A) 1.0 mM $[Fe(L^{ipr})_2]$ and (B) 1.0 mM $[Fe(L^{ipp})_2]$ in THF at room temperature under nitrogen with 0.4 M (ⁿBu₄N)(ClO₄) as the supporting electrolyte at a scan rate of 200 mV s⁻¹.

observed at g > 9.5 (1b) shift upon rotation of the sample within the EPR cavity thus indicating that these signals can be attributed to molecular aggregates within the sample. This behavior was observed for all solvents and glassing solvent mixtures attempted. Therefore, no meaningful interpretation of these spectra can be made. However, the increased steric bulk of the Ldipp ligand to produce the $[Fe(L^{dipp})_2]$ complex (2) adequately prevents molecular crowding as indicated by EPR spectroscopy. The X-band EPR spectra of 2 taken under identical conditions as shown for 1 show a strong parallel mode (2b) resonance and a weak signal in perpendicular mode (2a). Both of these can be attributed to an isolated high-spin ferrous iron (S = 2) species. Spectra **2b** exhibits homogeneous saturation behavior with a power at halfsaturation ($P^{1/2}$) of 490 mW at 10 K. When normalized for Curie law dependence, the intensity of 2b decreases with increasing temperature thus indicating that this signal originates from within the ground $(m_s = \pm 2)$ doublet. By fitting the temperaturenormalized intensity of this signal to a Boltzman population distribution for a three level system (S = 2), both the sign and magnitude for the axial zero-field splitting term was determined, $D = -7.1 \pm 0.8$ cm⁻¹ (refer to Fig. S2 and Eqn S1[±]). Simulations for spectra 2a and 2b are provided in Fig. 8.

A molecular orbital diagram can be hypothesized for $[Fe(L^{dipp})_2]$ (Fig. S3[‡]). The electronic spectra provide relative positions for the π , d, and π^* orbitals. Noting the energies of the MLCT band, we postulate the relative positions for the lowest energy d-orbital. The low energy spin-forbidden *d*-*d* transitions of $[Fe(L^{dipp})_2]$ observed are consistent with removal of the degeneracy of the e_g orbitals.



Fig. 7 7 K perpendicular mode (**a**) and parallel mode (**b**) X-band EPR spectra of 1.3 mM [Fe(L^{ipr})₂] (**1**) and 1.7 mM [Fe(L^{ipp})₂] (**2**) in CH₂Cl₂-toluene. All signals are normalized for concentration. Instrumental parameters: microwave frequency, (**a**) 9.64 GHz, (**b**) 9.38 GHz; microwave power, (**1a**) 0.02 mW, (**1b**) 0.06 mW, (**2a**) 0.02 mW, (**2b**) 0.63 mW; temperature, 7 K; modulation amplitude, 0.9 mT. The small $g \sim 4$ feature observed in parallel mode is from trace O₂ (S = 1) condensing on top of the frozen sample and can be ignored.

A descent in symmetry from the ideal tetrahedral configuration (for instance, D_{2d} spread as suggested by continuous symmetry measurements) is expected for the high-spin d^6 iron(II) complexes. However, positive zero-field splitting values are observed for square planar and flattened tetrahedral complexes.^{75,76} Only elongated tetrahedral,⁷⁵ a C_3 -symmetric tripodal thiolate rich iron(II) methyl,⁸¹ and a trigonal monopyramidal iron(II) complex³⁶ are known to exhibit negative zero field splittings. While the sawhorse geometry is unusual for iron(II), a precedent for this geometry exists in a cluster and the complex has a negative zero-field splitting value.⁴¹

Preliminary oxygenation studies have been undertaken and both high-spin iron(II) complexes react readily with dioxygen even at low temperature to give brick red or orange products (Fig. S3[‡]). The electronic spectra of the product(s) are dominated by a broad band, which tails into the visible. Holm and coworkers reported a brick red iron(II) complex, [{PhC(O)CHC(NiPr)CH₃}₂Fe^{II}].⁴⁴ The comparable extinction coefficient ($\varepsilon \sim 40 \text{ M}^{-1} \text{ cm}^{-1}$) in the near-infrared bands would not be obtained if the complex was partially oxidized. We attribute the difference in color to the electronic tuning of the β-ketoiminate backbone by replacement of a methyl group with a phenyl group. Preliminary studies indicate multi-step kinetic processes in the formation of the red oxidation products, which we are attempting to unravel. Mechanistic studies are ongoing and will be the topic of a separate manuscript along with the reactivity of these complexes with other small molecules.



Fig. 8 10 K X-band perpendicular (**2a**) and parallel (**2b**) mode spectra of $[Fe(L^{dipp})_2]$. Quantitative simulations (*dashed lines*) are overlaid on the spectra for comparison. Instrumental parameters: microwave frequency, (**a**) 9.64 GHz, (**b**) 9.38 GHz; microwave power, (**a**) 0.06 mW, (**b**) 0.20 mW; temperature, 10 K; modulation amplitude, 0.9 mT. Simulation parameters: S = 2; $g_{x,y,z} = 2.02 \ 2.07 \ 2.19$; $D = -7.1 \pm 0.8 \ \text{cm}^{-1}$; E/D = 0.096; $\sigma_D = \sigma_{E/D} = 0.01$; $\sigma_B = 0.9 \ \text{mT}$.

Experimental

General considerations

Materials. All manipulations were carried out using standard Schlenk or glove box techniques under a dinitrogen atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial vendors and used as received unless otherwise noted. THF, toluene, benzene, and diethyl ether were distilled under nitrogen from Na/benzophenone and subsequently dried over activated alumina. Diisopropylamine was vacuum distilled under nitrogen prior to use. Acetonitrile was distilled from calcium hydride under nitrogen. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. $Fe(OTf)_2 \cdot 2CH_3CN$ (OTf = $-OSO_2CF_3$) was prepared according to literature precedent utilizing Me₃Si(OTf).^{82,83} [Fe(Mes)₂]₂ was prepared according to literature precedent.^{84,85} All chemical reactions were performed at high altitude conditions (~7200 feet or ~2200 m).

Ligand Synthesis. HL^{iPr} (R = -^{*i*}Pr), HL^{Ph} (R = -C₆H₅) and HL^{dipp} (R = -2,6-^{*i*}Pr₂C₆H₃) were prepared according to literature methods.^{48,53} $HL^{3.5Me2}$ (R = 3,5-Me₂-C₆H₃) was prepared from acetylacetone (14.6 g, 0.146 mol), 3,5-dimethylaniline (17.6 g, 0.146 mol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (150 mL). The solution was heated to reflux for 48 h under N₂, while H₂O was removed using a Dean–Stark apparatus. The solvent was removed under reduced pressure, leaving a red-

orange oil. Yield: 23.7 g, (0.117 mol, 80.1%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 12.42 (s, 1H), 6.82 (s, 1H), 6.73 (s, 1H), 5.15 (s, 1H), 2.29 (s, 6H), 2.08 (s, 3H), 1.98 (s, 3H). HL^{Mes} was prepared from acetylacetone (15.4 g, 0.154 mol), 2,4,6-trimethylaniline (20.1 g, 0.149 mol), and a catalytic amount of p-toluenesulfonic acid in toluene (125 mL). The solution was heated to reflux for 4 d under N₂, while H₂O was removed using a Dean–Stark apparatus. The solvent was removed under reduced pressure, leaving a dark redorange oil. Crystallization from the slow evaporation of hexane led to the isolation of clear colorless crystals. Yield: 4.52 g (0.64 mmol, 14.0%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 11.88 (s, 1H), 6.92 (s, 2H), 5.21 (s, 1H), 2.30 (s, 1H), 2.18 (s, 6H), 2.12 (s, 3H), 1.64 (s, 3H).

Complexes. [Fe(L^{*i*Pr})₂], (1). NaH (0.0488 g, 2.03 mmol) was added to a solution of HL^{*i*Pr} (0.285 g, 2.02 mmol) in THF and stirred until the evolution of hydrogen ceased. Fe(OTf)₂(CH₃CN)₂ (0.437 g, 1.00 mmol) was added and the mixture was stirred overnight. A bright yellow solution was isolated *via* filtration of the inorganic salts. Bright yellow blocks of 1 suitable for single-crystal X-ray diffraction were obtained by slow evaporation of the THF from the filtrate. This procedure led to the isolation of 0.300 g (0.893 mmol, 89.3%) of diffraction quality crystals. Anal. calcd for 1, C₁₆H₂₈FeN₂O₂: C 57.15, H 8.39, N 8.33. Found: C 57.13, H 8.21, N 8.14. UV-vis [λ_{max} , nm (ε , M⁻¹ cm⁻¹) in THF] 410 (2600), 916 (30), 1120 sh (20). ESI/MS (THF, 200 °C): *m*/*z* = 336 ([M]⁺, *i.e.*, [Fe(L^{*i*Pr})₂]⁺).

 $[Zn(L^{Pr})_2]$, (2). NaH (0.0495 g, 2.06 mmol) was added to a solution of HL^{iPr} (0.291 g, 2.06 mmol) in THF and stirred until the evolution of hydrogen ceased. Zn(OTf)₂ (0.372 g, 1.02 mmol) was added and the mixture was stirred overnight. A pale yellow solution was isolated *via* filtration of the inorganic salts. Bright yellow blocks of 2 suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of the THF from the filtrate. This procedure led to the isolation of 0.116 g (0.335 mmol, 32.9%) of diffraction quality off-white crystals. Anal. calcd for 2, C₁₆H₂₈ZnN₂O₂: C 55.57, H 8.16, N 8.10. Found: C 55.74, H 8.03, N 7.93. ESI/MS (THF, 200 °C): *m*/*z* = 367 ([M + Na]⁺, *i.e.*, [Zn(L^{iPr})₂Na]⁺).

[Fe(HL^{dipp})₃(OTf)₂]·C₆H₆, (**3a**). Fe(OTf)₂(CH₃CN)₂ (0.869 g, 1.99 mmol) was added to a suspension of HL^{dipp} (1.559 g, 6.01 mmol) in THF. The solution was stirred vigorously for 90 min. The solvent was removed from the resultant dark yellow solution and the residue dissolved in benzene. Filtration yielded a dark yellow solution which was evaporated to dryness. Bright yellow blocks of **1** suitable for single-crystal X-ray diffraction were obtained from slow cooling of a concentrated benzene solution of this compound. This procedure led to the isolation of 1.64 g (1.35 mmol, 68.1%) of diffraction quality crystals. Anal. calcd for **3a**, C₅₉H₈₁F₆FeN₃O₉S₂: C 60.24, H 8.44, N 3.47, F 9.42. Found: C 60.24, H 8.44, N 3.38, F 9.3. UV-vis [λ_{max} , nm (ε , M⁻¹ cm⁻¹) in benzene] 420 (480). ESI/MS (THF, 200 °C): m/z = 1232 ([M+ Na]⁺, *i.e.*, [Fe(OTf)₂(HL^{dipp})₃]Na⁺).

 $[Fe(L^{dipp})_2]$, (**3b**). NaH (0.0974 g, 4.06 mmol) was added to a solution of HL^{dipp} (1.04 g, 4.01 mmol) in THF and stirred for over 1 h. Fe(OTf)₂(CH₃CN)₂ (0.872 g, 2.01 mmol) was added and the mixture was stirred overnight. The solvent was removed from the resultant brown solution and the residue dissolved in toluene. Filtration yields a dark green solution which was evaporated

to dryness. Bright green blocks of **3** suitable for single-crystal X-ray diffraction were obtained by layering acetonitrile on a concentrated THF solution of this compound. This procedure led to the isolation of 0.683 g (1.19 mmol, 59.2%) of diffraction quality crystals. Anal. calcd for **3b**, $C_{34}H_{48}FeN_2O_2$: C 71.32, H 8.45, N 4.89. Found: C 71.82, H 8.45, N 4.89. UV-vis [λ_{max} , nm (ε , M^{-1} cm⁻¹) in THF] 420 (1400), 680 (50), 1470 (7). ESI/MS (THF, 200 °C): m/z = 572 ([M]⁺, *i.e.*, [Fe(L^{dipp})₂]⁺).

Two additional synthetic methods were used to produce $[Fe(L^{dipp})_2]$. In the first, HL^{dipp} (0.519 g, 1.99 mmol) was added to an excess of [Fe(Mes)₂]₂ (0.589 g, 1.00 mmol) in benzene. Solvent and byproducts were removed under vacuum to yield a green solid. NMR and UV-vis of the product are identical to those listed above. The second method used 2.5 M "BuLi in hexane (0.99 mL, 2.48 mmol) added via syringe to a solution of HNⁱPr₂ (0.295 mL, 2.10 mmol) in 20 mL of THF chilled with dry ice. A solution of HLdipp (0.488 g, 1.88 mmol) in 10 mL of THF was transferred via cannula to the LiNⁱPr₂ solution and stirred for 2 h at dry ice temperature. Next, a solution of Fe(OTf)₂·2CH₃CN (0.4090 g, 0.94 mmol) in 20 mL of THF was cannula transferred to the deprotonated ligand with immediate formation of a green solution. After stirring for 1 h the solution was evaporated to dryness. The residue was dissolved in 10 mL of toluene and solids removed by filtration. Spectroscopic data was identical to those obtained by other synthetic methods.

 $[Zn(L^{dipp})_2]$, (4). NaH (0.0965 g, 4.02 mmol) was added to a solution of HL^{dipp} (1.04 g, 4.00 mmol) in THF and stirred for over 1 h. Zn(OTf)₂ (0.730 g, 2.01 mmol) was added and the mixture was stirred overnight. A pale yellow solution was isolated *via* filtration of the inorganic salts. Off-white blocks of 4 suitable for single-crystal X-ray diffraction were obtained by slow evaporation of the THF from the filtrate. This procedure led to the isolation of 0.405 g (0.696 mmol, 34.8%) of diffraction quality crystals. Anal. calcd for 4, C₃₄H₄₈ZnN₂O₂: C 70.15, H 8.31, N 4.81. Found: C 70.51, H 8.51, N 5.01. ESI/MS (THF, 200 °C): m/z = 580 ([M]⁺, *i.e.*, [Zn(L^{dipp})₂]⁺).

[Fe(L^{Ph})₂]. NaH (0.048 g, 2.00 mmol) was added to a solution of HL^{Ph} (0.350 g, 2.00 mmol) in THF and stirred until the evolution of hydrogen ceased. Fe(OTf)₂·2CH₃CN (0.436 g, 1.00 mmol) was added and the mixture was stirred overnight. The solvent was removed from the resultant dark brown solution and the residue dissolved in toluene. Filtration gave a dark orange solution, which was evaporated to dryness. Modification of literature procedures^{44,48} was used to produce this complex. NaH (0.096 g, 4.0 mmol) was added to a solution of HL^{Ph} (0.703 g, 4.01 mmol) in THF and stirred until the evolution of hydrogen ceased. FeCl₂ (0.252 g, 2.00 mmol) was added and the resulting suspension was allowed to stir overnight. A brown solution was obtained after filtration. Electronic and ¹H NMR features of the products obtained from the two syntheses were identical.

 $[Fe(L^{3,5-Me_2})_2]$. NaH (0.0543 g, 2.26 mmol) was added to a solution of HL^{3,5-Me_2} (0.411 g, 2.02 mmol) in THF and stirred. Fe(OTf)₂·2CH₃CN (0.432 g, 0.991 mmol) was added, resulting in the slow formation of bubbles, and the solution was allowed to stir overnight. THF was removed under reduced pressure, the remaining oil was dissolved in toluene, and filtered to remove inorganic salts. Toluene was then removed under reduced pressure, and the remaining oil/solid was dissolved in minimal THF and

layered with CH₃CN. No crystals have been obtained, however a green/yellow precipitate formed in the bottom of the vial.

 $[Fe(L^{Mes})_2]$. NaH (0.0557 g, 2.32 mmol) was added to a solution of HL^{Mes} (0.433 g, 1.99 mmol) in THF and stirred, resulting in a rapid formation of bubbles. Fe(OTf)₂·2CH₃CN (0.429 g, 1.11 mmol) was added and the solution was allowed to stir overnight. THF was removed under reduced pressure, the remaining oil was dissolved in toluene, and filtered to remove inorganic salts. Toluene was then removed under reduced pressure, and the remaining oil/solid was dissolved in a minimal amount of hot THF and layered with CH₃CN, leading to the isolation of pure, light green/yellow crystals.

Physical Methods. Elemental analyses were carried out at Columbia Analytical Services, Inc., Tucson, AZ. Electronic spectra were recorded in quartz cuvettes on an Agilent 8453 diodearray spectrophotometer (250-1100 nm), which was equipped with a liquid nitrogen cryostat (Unisoku). The near-IR data were collected on a Perkin-Elmer Lamba 950 STD detector module (up to 2500 nm). ¹H and ¹³C NMR were collected on a Bruker Avance DRX-400 NMR spectrometer at room temperature and referenced to the residual protic solvent peak (at 7.16 ppm for benzene). Special care was taken with paramagnetic samples to ensure that the delay between pulses was greater than five times the longest proton longitudinal relaxation time (T_1) for proper integration of the peaks. IR spectra were recorded as KBr pellets at room temperature on a Varian 800 FTIR (Scimitar Series) set to 1 cm⁻¹ resolution. Electrochemical measurements were carried out in a drybox under N₂ in THF solution with 0.4 M (Bu₄N)(ClO₄) as the supporting electrolyte using a model ED401 computer controlled potentiostat (eDAQ). A three-electrode configuration with a glassy carbon working electrode, either a non-aqueous Ag/Ag⁺ reference electrode or a Ag wire quasi-reference electrode with a Fc^{+/0} internal reference, and a platinum wire auxiliary electrode was used. The potential values were referenced to an internal ferrocenium/ferrocene couple which is reported to be +0.53 V vs. SCE in [NBu₄][ClO₄] in THF.⁸⁶ The peak separations are reported with a scan rate of 200 mV s⁻¹ (Fc^{+/0} peak separation was 90 mV under these conditions). The low resolution electrospray ionization mass spectral data for the complexes were obtained using an LCQ mass spectrometer (Finnigan MAT) on THF solutions that were directly infused into the spectrometer via a syringe pump. The heated capillary was set at 200 °C. X-band (9 GHz) EPR spectra were recorded on a Bruker EMX Plus spectrometer equipped with a bimodal resonator (Bruker model 4116DM). Low-temperature measurements were made using an Oxford ESR900 cryostat and an Oxford ITC 503 temperature controller. A modulation frequency of 100 kHz was used for all EPR spectra. All experimental data used for spin-quantitation were collected under non-saturating conditions. EPR spectra were simulated and quantified using SpinCount (ver. 3.1.2), created by Professor M.P. Hendrich at Carnegie Mellon University. The simulations were generated with consideration of all intensity factors, both theoretical and experimental, to allow concentration determination of species. The only unknown factor relating the spin concentration to signal intensity was an instrumental factor that depended on the microwave detection system. However, this was determined by the spin standard, Cu(EDTA), prepared from a copper atomic absorption standard solution purchased from Sigma–Aldrich. Preliminary kinetic measurements were carried out using distilled THF which was shaken over activated alumina and stored over 3A molecular sieves under nitrogen. Crystalline materials were dissolved in THF at room temperature. Oxygen was bubbled into the solutions and oxygen saturation was assumed in these experiments but was not directly measured.

 $[Zn(L^{iPr})_2],$ analysis. $[Fe(L^{iPr})_2],$ X-Rav diffraction $[Fe(HL^{dipp})_3(OTf)_2] \cdot C_6H_6$, $[Fe(L^{dipp})_2]$, and $[Zn(L^{dipp})_2]$ were characterized using single-crystal X-ray diffraction. A translucent intense-yellow rectangular prismatic crystal of $[Fe(L^{iPr})_2]$, pale white crystals of $[Zn(L^{iPr})_2]$, yellow rectangular prism of $[Fe(HL^{dipp})_3(OTf)_2] \cdot C_6H_6$, emerald green rectangular prism of $[Fe(L^{dipp})_2]$, and a colorless rectangular plate of $[Zn(L^{dipp})_2]$ were glued to either a MiTeGen micromount or a Hampton Research CryoLoop using Paratone N oil and mounted on a Bruker Smart Apex II CCD area detector for data collection at 150 K using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. A summary of the crystallographic details for 1, 2, 3a, 3b, and 4 is given in Table 1. All non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Two of the crystals (1 and 2) are isomorphous. The asymmetric unit consists of two crystallographically dissimilar half-molecules of $M[L_1]_2$. The iron centers are located on two-fold symmetry axes. In 3a, the asymmetric unit consists of a [Fe(HLdipp)3(OTf)2] molecule and a solvated benzene molecule. Both molecules are located on general positions and are well separated from one another. The protons from the HL^{dipp} lignad (i.e., N-H) were located in the Fourier maps and refined isotropically. In 3b, the asymmetric unit consists of half of the complex molecule with the iron center located on a two-fold symmetry axis. In 4, the asymmetric unit consists of a well ordered $[Zn(L^{dipp})_2]$ molecule. The final full matrix least squares refinement converged to $R_1 = 0.0283$ and $wR_2 = 0.0709$ for 1, $R_1 = 0.0256$ and $wR_2 = 0.0656$ for 2, $R_1 = 0.0392$ and $wR_2 =$ 0.01037 for **3a**, and $R_1 = 0.0376$ and $wR_2 = 0.0965$ for **3b**, and $R_1 = 0.0376$ 0.0262 and $wR_2 = 0.0727$ for 4.

Conclusions

In conclusion, we have explored multiple pathways for the production of β-ketoiminate complexes of iron. Characterization of the iron and analogous zinc β -ketoiminate complexes has shown that both sterics and electronics lead to distortion from the ideal tetrahedral geometries in the solid state. Despite the monometallic nature of the solid state structures, the EPR supports the formation of higher order aggregates of unknown identity in solution for $[Fe(L^{iPr})_2]$. Furthermore, the presence of spin-forbidden d-d transitions at ~10,000 cm⁻¹ for $[Fe(L^{iPr})_2]$ is also more consistent with an octahedral metal center, providing further evidence for the alteration of composition on dissolution. Increasing the steric bulk of the ligand in $[Fe(L^{dipp})_2]$ leads to spectra that are more consistent with the retention of the solid state composition in solution. The features in the electronic spectra allow the assembly of a tentative molecular orbital diagram for $[Fe(L^{dipp})_2]$, which is consistent with either a severely distorted elongated tetrahedral, a sawhorse, or a trigonal monopyramidal geometry. Finally, ascertaining the spectroscopic signatures of the bis(chelate) complexes will enable us to better interpret the reactivity of these complexes with small molecules.

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