Published in final edited form as:

Eur J Inorg Chem. 2016 July ; 2016(20): 3344–3355. doi:10.1002/ejic.201600112.

Effects of Ligand Halogenation on the Electron Localization, Geometry and Spin State of Low-Coordinate (β -Diketiminato)iron Complexes

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Abstract

This contribution explores the influences of incorporating electron-withdrawing CF_3 and halide groups into β -diketimate iron complexes of tetrazene and isocyanide. The synthesis of a new halogenated β -diketimine ($\text{L}^{\text{CF}_3, \text{ClH}}$) was accomplished via two different methods, including a novel microwave-assisted synthesis that improves the yield of the difficult condensation. Treatment of an iron(II) complex of this ligand with reductant and azide gives two diiron complexes with novel tetrazenes as bridging ligands. Structural and Mössbauer data show that the bridging tetrazene is a radical anion. The halogenation of the supporting ligand also influences iron(I) complexes of the type $\text{LFe}(\text{CN}^t\text{Bu})_2$, which are low-spin and square-planar with alkyl substituents but high-spin and pseudotetrahedral with halogen substituents. DFT calculations suggest that the changes from halogenation come from a combination of steric and electronic effects, and that the electronic influence of ligand halogenation is minor.

Keywords

Diketimate; fluorination; tetrazene; isocyanide; redox-active

Introduction

In coordination chemistry, the supporting ligand has several roles: to limit the binding sites on the metal, to increase the reactivity of the metal for a given reaction, and to remain unreactive during synthesis and catalysis. One problem with the popular *N*-aryl β -diketimate ligands with ortho substituents on the aryl rings is that they have weak C-H bonds that are susceptible to abstraction by electrophilic oxo or imido ligands.^[1] One way to eliminate the reactivity of such C-H bonds is to substitute them with oxidation-resistant C-F or C-Cl bonds.^[2] However, halogenation can influence the β -diketimate complexes,

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Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

Supporting Information: Spectra and computational information. The crystallographic data are available from the Cambridge Crystallographic Data Centre with deposition numbers 1477165-1477171.

affecting the electron density on the metal and its reactivity.^[3] Thus it is important to evaluate the influence of ligand halogenation on the properties of β -diketiminato metal complexes.^[4]

One potential influence of halogenation of the supporting ligand is in the balance of electron density between the metal and a “redox-active” co-ligand that can be reduced or oxidized by the metal.^[5] Typically, the oxidation states of the ligand and the metal are determined experimentally. For iron complexes, Mössbauer spectroscopy is particularly useful for characterizing the metal’s oxidation level,^[6] while the oxidation level of the redox active ligand can be determined using the bond lengths from a high resolution crystal structure. For example, in tetrazene complexes (Figure 1), the neutral tetrazene ligand can have two N=N double bonds (1.28(4) Å)^[7] and an N-N single bond (1.45 Å), a radical anionic tetrazene with NN bond lengths between single and double bonds (~1.35 Å), or a dianionic tetrazene ligand with two N-N single bonds and one N=N double bond. Each reduction of the tetrazene ligand results from an electron being donated from the metal; therefore the metal and ligand oxidation levels are linked.

In a previous study, we evaluated the β -diketiminato iron tetrazene complex $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$, where $L^{\text{Me,iPr}} = 2,4\text{-bis}(2,6\text{-diisopropylphenylimido})\text{-3-pentyl}$.^[8] The Mössbauer spectrum of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ indicated a high-spin electronic configuration at iron(II), and the N-N bond lengths within the N_4Ad_2 ligand were between single and double bonds (N1-N2, 1.317(2) Å; N2-N3, 1.334(2) Å; N3-N4, 1.309(2) Å), corresponding to resonance structure **B** in Figure 1. Together, these data led to a self-consistent picture of a high-spin iron(II) ion ($S_{\text{Fe}} = 2$) with strong antiferromagnetic coupling to the radical anion N_4Ad_2 ($S_{\text{tetrazene}} = 1/2$) to give an overall $S = 3/2$ spin state. Cyclic voltammetry of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ revealed a reversible, one-electron reduction at 1.84 V (versus $\text{Cp}_2\text{Fe}^{+/0}$) to give an isolable product, $[\text{K}(\text{cryptand-222})][L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)]$.^[8] The Mössbauer parameters remained consistent with a high-spin iron(II) ion, but the reduced compound had NN bond lengths more consistent with a dianionic tetrazene (resonance structure **C** of Figure 1); thus, the reduction had occurred at the ligand.

Here, we present a new β -diketiminato ligand with F and Cl substituents, and we evaluate the electronic effects on iron complexes in two ways. First, we present several new iron-tetrazene complexes and specify the redox level of the metal and ligand. Second, we present the influence of the ligand fluorination on iron(I)-isocyanide complexes, where the electron density at the iron site is probed using both the C-N stretching frequency and DFT calculations. Both facets of this work help to understand the relay effect of the supporting ligand on the electronics of the other ligands on the same iron center.

Results and Discussion

Ligand synthesis and characterization

A new fluorinated β -diketimine, with trifluoromethyl groups on the backbone and 2,6-dichlorophenyl groups on the nitrogen atoms, was synthesized through two different procedures (Scheme 1). The first method is a one-pot synthesis that begins by adding TiCl_4 to 2,6-dichloroaniline in decane, followed by addition of hexafluoroacetylacetone (HfAcH)

and 1,8-bis(dimethylamino)-naphthalene (Proton Sponge®). After heating to 70 °C for 1 d, the temperature was raised to 140 °C for 1 d to afford a keto-imine (**1**) in 57% yield and $\text{L}^{\text{CF}_3, \text{Cl}}\text{H}$ (**2**) in 14% yield. This procedure could be repeated using **1** in place of HfacH to afford **2** in 40% yield, giving an overall yield of 38%. Each one-pot procedure takes about 7 days to complete, including drying and vacuum distillation of the large amount of decane needed.

The second method uses two steps. The first step is acid-catalyzed condensation of 2,6-dichloroaniline and HfacH with *p*-toluenesulfonic acid in toluene heated by microwave radiation to 210 °C for 30 min to produce **1** in 40% yield. The second step is the addition of TiCl_4 to excess aniline in decane followed by the addition of **1**. This mixture was heated by microwave radiation to 210 °C for 4 hours to produce **2** in 52% yield, with a combined yield of 21%. This two-step procedure takes a total of 5 days and uses one-fifth the amount of decane.

The ^1H NMR spectrum of **2** displays four resonances, with one downfield at δ 11.5 ppm for the -NH proton of the enaminoimine tautomer of **2**. This -NH resonance is more upfield than the β -diketimines with β -Me groups by about 1 ppm, presumably due to deshielding by the electron withdrawing trifluoromethyl groups.^[9] The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **2** displays a single resonance at δ -68.9 ppm. The vibrant yellow color of **2** corresponds to a strong absorption at 330 nm with a molar absorptivity of $22,000 \text{ M}^{-1} \text{ cm}^{-1}$. The color is reminiscent of $\text{L}^{\text{Me}, \text{Ph}_3\text{H}}$, which is yellow and has an absorption band at 377 nm ($25,000 \text{ M}^{-1} \text{ cm}^{-1}$),^[10] while other *N*-aryl β -diketimines are white in color.

Synthesis and characterization of a (β -diketiminate)iron(II) complex of the fluorinated ligand

Deprotonation of **2** by potassium hexamethyldisilazide ($\text{KN}(\text{SiMe}_3)_2$) produced a yellow-orange solution, which was added to 1.2 equiv $\text{FeCl}_2(\text{THF})_{1.5}$ in THF to produce a purple mixture. After drying and washing with pentane, a red powder was isolated in 80% yield. Crystallization from concentrated Et_2O at -40 °C gave red single crystals of $\text{L}^{\text{CF}_3, \text{Cl}}\text{FeCl}(\text{Et}_2\text{O})$ (**3•Et₂O**). The molecular structure of **3•Et₂O** is shown in Figure 2. Diethyl ether is typically a weak ligand, and there are relatively few crystallographically characterized examples of it coordinating to iron.^[11] Removal of diethyl ether from **3•Et₂O** was facile, as drying the crystals under vacuum gave an ether-free chloride dimer $[\text{LFe}(\mu\text{-Cl})_2]$ (**4**) as shown by elemental analysis of the powder and by X-ray crystallography of a crystal grown from a toluene solution. Zero-field Mössbauer spectroscopy of solid **4** at 80 K revealed a doublet at $\delta = 0.92(2) \text{ mm/s}$ with a quadrupole splitting of $|E_Q| = 2.30(2) \text{ mm/s}$. The Mössbauer parameters of the related iron(II) complex $^{\text{Me}}\text{L}^{\text{Me}, \text{Me}}\text{Fe}(\mu\text{-Cl})\text{Li}(\text{ether})_2$ ($\delta = 0.90 \text{ mm/s}$, $|E_Q| = 2.40 \text{ mm/s}$)^[12] and $[\text{L}^{\text{Me}, \text{Me}}\text{Fe}(\mu\text{-Cl})_2]$ ($\delta = 0.91 \text{ mm/s}$, $|E_Q| = 2.38 \text{ mm/s}$), which have methyl groups on the backbone and the ortho aryl positions, are very similar to the parameters of **4** ($^{\text{Me}}\text{L}^{\text{Me}, \text{Me}}$ is $\text{MeC}[\text{C}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]_2^-$). The similarity of the isomer shifts suggests that the halogenation does not have a marked effect on the electron density at the iron nucleus in this tetrahedral geometry.

A Mössbauer spectrum of **4** dissolved in THF had a similar isomer shift of $\delta = 0.88(2)$ mm/s with a significantly different quadrupole splitting of $|E_Q| = 2.06(2)$ mm/s. This change in Mössbauer parameters between the solid state and the THF solution of **4** suggests that dimeric **4** breaks up to give a monomeric complex $L^{CF_3, Cl}FeCl(THF)$. The 1H NMR spectrum of **4** in C_6D_6 exhibits three sharp, paramagnetically shifted resonances having integrations consistent with one symmetric ligand environment with C_{2v} local symmetry. Its $^{19}F\{^1H\}$ NMR spectrum has a single resonance at $\delta -165.0$ ppm that is also consistent with one symmetric ligand environment. The red hue of **4** is different than the yellow analogues of **4** that have $\beta-CH_3$ instead of $\beta-CF_3$.

The crystal structure of **4** gives an opportunity to compare bond lengths and angles to other four-coordinate iron(II) β -diketiminate complexes (Table 1), in order to gain insight into the steric and electronic effects of ligand halogenation. Increased steric bulk of the β -substituent typically increases the $C_\beta-N_L-C_{aryl}$ angles because of nonbonded interactions between the β -substituent and the aryl rings.^[13,14] With β - t Bu groups, the aryl rings create enough steric hindrance around the iron to inhibit dimerization, and no coordination of Et_2O was observed.^[15] The size of the $\beta-CF_3$ substituent in **4** is between that of the β - t Bu groups on monomers like $L^{tBu, iPr}Fe(Cl)(X)$ ($X = 3$ -methylpyridine) and the β -Me groups on dimers like $[MeL^{Me, Me}FeCl]_2$.^[12,15] The substituents decrease in size in the order $tBu > CF_3 > CH_3$ and the $C_\beta-N_L-C_{aryl}$ angles are 124° , 121° , and 119° , respectively, indicating that the CF_3 groups push the aryl rings toward the metal, but not as much as *tert*-butyl groups. Determining the electronic effects of ligands can be difficult to disentangle from the steric effects. Thus, we compare the Fe-N and $C_\beta=N$ bond lengths of **4** to $[MeL^{Me, Me}FeCl]_2$ which has similarly sized *ortho*-substituents (CF_3 vs. CH_3). The average Fe-N bond lengths for **4** and $[MeL^{Me, Me}FeCl]_2$ are $1.999(2)$ Å and $1.973(2)$ Å, respectively and the average $C_\beta=N$ bond lengths are $1.327(2)$ Å and $1.336(4)$ Å. Thus, the CF_3 substituents appear to slightly lengthen the Fe-N bonds, primarily from a steric effect.

Synthesis and characterization of iron- and diiron-tetrazene complexes

One of our initial goals was to create an iron(III) imido complex, since we have shown two examples of these complexes, and they are capable of abstracting hydrogen atoms from hydrocarbons.^[16] Because these are generated from addition of azides to iron(I) species, we desired a source of iron(I) analogous to $L^{Me, iPr}Fe(N_4Ad_2)$. However, adding KC_8 to **4** under various conditions gave intractable mixtures of products, probably from attack of reducing agent (or reduced iron) on carbon-chlorine bonds. Fortunately, it was possible to generate an (unidentified) iron(I) species *in situ* using KC_8 in THF at $-108^\circ C$. As will be shown below, this gave tetrazene products rather than imido complex. This may indicate the formation of a transient imidometal intermediate that undergoes an addition of a second equivalent of azide, which this is the most accepted mechanism for tetrazene formation.^[17]

In initial experiments with a 1:1 ratio of iron to azide, KC_8 (2.3 equiv) was added to the dimer **4** in THF at $-108^\circ C$, followed by 2 equiv of adamantylazide (N_3Ad) as shown in Scheme 2. X-ray quality crystals were obtained from pentane in 47% yield. The crystal structure revealed a diiron complex (**5**) with a bridging 1,4-bis(adamantyl)tetrazene ligand (Figure 4a). The tetrazene ligand is coordinated to the Fe1 atom through the N1 and N4

atoms to form a five-membered FeN₄ ring. The other iron atom (Fe2) is coordinated by the N2 and N3 atoms in an η^2 binding mode, and lies very close to the iron-tetrazene plane. This “edge-on” coordination to Fe2 is reminiscent of a known diketiminate-supported iron(II)-pyrazolate complex.^[18] Each iron atom has a tetrahedral geometry, when considering the side-on coordination of N2 and N3 as two single bonds to Fe2. Since the two iron atoms and the bridging tetrazene ligand are almost coplanar, the idealized geometry of the FeN₄Fe core is C_{2v} . However, Fe1 is above the plane of its β -diketiminate ligand by 0.82 Å, breaking the horizontal mirror plane that would otherwise be perpendicular to the FeN₄ ring. The ¹H NMR spectrum of **5** was complicated, and solution samples were always contaminated with variable amounts of **6** (see below), which prevented us from drawing reliable conclusions about its solution structure.

The ¹⁹F{¹H} NMR spectrum of **5** exhibits two resonances at δ –117.4 and –122.3 ppm, corresponding to the supporting ligands on the two inequivalent iron atoms. The solution magnetic moment of **5** is 5.2(1) BM at room temperature. The Mössbauer spectrum of **5** at 80 K displays four peaks of nearly equal intensity, consistent with two unique iron environments that each give a doublet. Unfortunately, the presence of two equally-populated iron environments inevitably leads to ambiguity in fitting. Figure 5 presents the data fit with two possibilities. Below, we will present evidence that fit A is more likely to be correct.

Another diiron-tetrazene complex crystallized as **5•THF**, where a THF molecule is coordinated to Fe2 of **5**. In the molecular structure of **5•THF** (Figure 4b) both iron atoms are out of their β -diketiminate planes. In **5•THF**, five-coordinate Fe2 is still very close to the Fe1-tetrazene plane. Coordination of THF to Fe2 causes a lengthening of the bonds from Fe2 to the N atoms of the tetrazene from 2.00–2.02 Å to 2.04–2.08 Å. The ¹⁹F{¹H} NMR spectrum of **5•THF** displays two resonances at –116.3 and –124.4 ppm. The chemical shifts of these resonances are very similar to those of **5**, which suggests that **5** and **5•THF** are in equilibrium. To determine the binding strength of the THF ligand to **5**, the ¹⁹F{¹H} NMR spectrum of **5** in C₆D₆ was monitored with varying amounts of added THF, and the peaks shifted as expected for a THF-binding equilibrium that is fast on the NMR time scale. A plot of the change in chemical shift versus [THF] (see Supporting Information) yielded $K_{eq} = 15(2) \text{ M}^{-1}$ for binding at 298 K.

In order to force the formation of a mononuclear complex, the KC₈ reduction of **4** at –65 °C was followed by addition of 4 equiv of N₃Ad, and then stirred for 18 h at room temperature. The ¹⁹F{¹H} NMR spectrum showed a mixture of products, and red-orange crystals could be isolated from pentane in 13% yield. These were crystallographically characterized as L^{CF₃,Cl}Fe(N₄Ad₂) (**6**), which is shown in Figure 4c. The structure of **6** is similar to L^{Me,iPr}Fe(N₄Ad₂)^[8] with N-N distances within 0.002 Å (see Table 2). The Fe of **6** is out of the β -diketiminate plane by 0.815 Å whereas the Fe in L^{Me,iPr}Fe(N₄Ad₂) is out of the plane by 0.855 Å. The ¹H NMR spectrum of **6** has only five detectable signals (the other two expected signals may be broadened). This can be compared to the 19 signals for L^{Me,iPr}Fe(N₄Ad₂)^[8]. The relative simplicity of the ¹H NMR spectrum of **6** is attributed to flipping the iron to both sides of the tetrazene plane (like in **5•THF** above), which is not possible in the more crowded literature complex. The ¹⁹F{¹H} NMR spectrum of crystallized **6** has a single resonance at δ –158.2 ppm.

The Mössbauer spectrum of **6** (Figure 6) exhibits two doublets, one with $\delta = 0.75(4)$ mm/s and $|E_Q| = 1.55(4)$ mm/s (82%), and an apparent impurity with $\delta = 0.42(8)$ mm/s and $|E_Q| = 0.80(10)$ mm/s (18%). (We have been unable to purify **6** to a level where this apparent iron(III) impurity is not observed by Mössbauer spectroscopy.) The major species has similar parameters to $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ ($\delta = 0.69(2)$ mm/s, $|E_Q| = 1.32(4)$ mm/s),^[8] and is thus consistent with the tetrazene complex **6**. The spectrum of **6** is useful in distinguishing the two possible assignments of the Mössbauer data of **5** (Figure 5b)). In fit A, the doublet with larger intensity is the same within error as the Mössbauer parameters of **6**, which agrees with the very similar environment of one of the iron atoms in **5**. The unequal intensities of the two doublets in fit A for **5** is consistent with the presence of **6** as a 30% impurity, which is not observed as a separate signal because of its very similar parameters. Impurities were also evident in the ^1H NMR spectrum of **5** that are consistent with the presence of an impurity.

Determination of ligand and metal oxidation states in tetrazene complexes

Through X-ray crystallography, Mössbauer spectroscopy, EPR spectroscopy, and magnetometry studies, $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ was previously determined to have an electronic structure in which there is a high-spin iron(II) ion antiferromagnetically coupled to a radical monoanion tetrazene ligand.^[8] The NN bond lengths and Mössbauer parameters of **5** and **6** are compared to those of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ in Table 2, in an effort to assign metal and ligand oxidation states.

The Fe1-N_{diketimate} bond lengths of **5** are 2.03 Å, consistent with the average $\text{Fe}^{2+}\text{-N}_\text{L}$ bond length of four-coordinate, β -diketimate iron(II) complexes of 2.03 Å.^[19] The NN bond lengths of **5** are 1.331(5), 1.323(6), and 1.316(5) Å and the NN bond lengths of **6** are 1.316(6), 1.332(6), and 1.309(6) Å. These are similar to one another, and are similar to those of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ (Table 2). These NN bond lengths are between those expected for a NN single (1.45 Å) and double (1.25 Å) bond.^[20] These bond lengths suggest resonance form **B** (Figure 1).

The similarity in the Mössbauer parameters of one of the doublets in **5**, the doublet of **6**, and the doublet of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ suggest that all three complexes have an iron site with the same oxidation state (high-spin iron(II)) and same geometry (pseudo-tetrahedral). The crystal structures corroborate the similar geometries. Since a combination of spectroscopic and computational studies showed that iron(II) is the best description of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$, the similar Mössbauer data of **5** and **6** suggest that Fe1 is in the +2 oxidation state and therefore resonance structure **B** is most appropriate (Figure 1). Thus, the electron-withdrawing groups on the supporting ligands have little effect on the electron localization in the tetrazene. It is notable that **5** and **5**•**THF** are the first examples of a tetrazene ligand bridging two metals in an $\eta^2:\kappa^2$ binding mode. In these complexes, the much higher isomer shift of 1.21 mm/s suggests that Fe2 in **5** is high-spin iron(I). The Fe2-N_L bond lengths are 1.99 Å and consistent with the average of 1.97 Å for $\text{Fe}^{1+}\text{-N}_\text{L}$ bond lengths of β -diketimate complexes with π -bound ligands.^[21] Thus **5** has one iron(I) site and one iron(II) site, with a radical tetrazene ligand between the irons.

The reduction potential of $L^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ was reported to be -1.84 V (versus $\text{Cp}_2\text{Fe}^{+/0}$), and the reduction was assigned to the tetrazene $^{\bullet/-}$ since the iron stayed as iron(II).^[8] Cyclic voltammetry of its halogenated analogue **6** in THF gives a one-electron quasireversible reduction at -1.85 V (versus $\text{Cp}_2\text{Fe}^{+/0}$). Thus, the halogens on the β -diketiminate ligand do not affect the redox potential. This supports the idea that reduction occurs at the tetrazene ligand, which is fairly unresponsive to substitution on the diketiminate.

Synthesis and characterization of (β -diketiminate)iron(I)-isocyanide complexes

To query the electronic effects of the electron-withdrawing β -diketiminate ligand on other coordinated ligands, *tert*-butyl isocyanide complexes of the $L^{\text{CF}_3,\text{Cl}}\text{Fe}$ system were synthesized to compare to the known diketiminate-supported iron(I) compounds $\text{Me}_2\text{L}^{\text{Me,Me}}\text{Fe}(\text{CN}^t\text{Bu})_3$, $L^{\text{Me,iPr}}\text{Fe}(\text{CN}^t\text{Bu})_3$, and $L^{\text{Me,iPr}}\text{Fe}(\text{CN}^t\text{Bu})_2$.^[22,23,24] Complex **4** was reduced with KC_8 at $-65\text{ }^\circ\text{C}$, and an excess of *tert*-butyl isocyanide was added to produce a dark red mixture. The excess $^t\text{BuNC}$ was removed under vacuum to form a dark green powder in 86% yield. A single crystal was obtained from a 1:1 toluene/pentane solution and was crystallographically characterized as $L^{\text{CF}_3,\text{Cl}}\text{Fe}(\text{CN}^t\text{Bu})_3$ (**7**, Figure 7). The Fe-C bonds are distinctly longer in this complex than in the analogues with the smaller $\text{Me}_2\text{L}^{\text{Me,Me}}$ ligand or the larger $L^{\text{tBu,iPr}}$ ligand (Table 3), indicating a potential electronic effect of the halogenated ligand. The Mössbauer spectrum of **7** showed a doublet at $\delta = 0.25(2)\text{ mm/s}$ and $E_Q = 0.63(2)\text{ mm/s}$, which is similar to the parameters of $\text{Me}_2\text{L}^{\text{Me,Me}}\text{Fe}(\text{CNXyl})_3$ of $\delta = 0.17\text{ mm/s}$ and $E_Q = 0.81\text{ mm/s}$. The larger isomer shift in **7** corroborates the longer Fe-C distances, because the bond distances and isomer shift are typically correlated.^[25] The CN stretching vibrations of the CN^tBu ligands for **7** have a large frequency range of $1991\text{--}2122\text{ cm}^{-1}$ compared to the range for $L^{\text{tBu,iPr}}\text{Fe}(\text{CN}^t\text{Bu})_3$ of $2012\text{--}2096\text{ cm}^{-1}$, but the comparison is difficult because of the overlap between an indeterminate number of peaks. The EPR spectrum of **7** as a frozen toluene solution at 10 K exhibits a nearly rhombic signal with $g = [2.067, 2.076, 1.998]$, which is similar to other β -diketiminate iron(I) tris(isocyanide) complexes.^[20–22]

It was also possible to make a bis(isocyanide)iron(II) complex with the halogenated ligand. Compound **4** was reduced with KC_8 at $-108\text{ }^\circ\text{C}$, and only 2 equiv of CN^tBu were added to the cold solution. Warming and filtration gave a quantitative yield of a blue-green powder (**8**) that was used without further purification. **8** was identified by elemental analysis and X-ray diffraction (see below) as $L^{\text{CF}_3,\text{Cl}}\text{Fe}(\text{CN}^t\text{Bu})_2$, and even though it had consistent elemental analysis the spectroscopy showed some impurities (see below). This material was too sensitive for us to successfully purify it; attempts to crystallize **8** typically resulted in the formation of an unidentified red oil, though on one occasion we obtained a single crystal of **8** for structural characterization (see below).

The IR spectrum of crude **8** exhibits three bands at 2180 , 2126 , and 2108 cm^{-1} in the region of CN stretches. Decomposition of **7** in the presence of air resulted in a red powder with one band at 2176 cm^{-1} , suggesting that the peak at 2180 cm^{-1} in **8** is due to the presence of a decomposition product. Thus, **8** has two CN stretching vibrations (2126 and 2108 cm^{-1}) as expected for symmetric and antisymmetric combinations.

The Mössbauer spectrum of **8** displays two doublets with a major species (82%) at $\delta = 0.64(2)$ mm/s, $|E_Q| = 2.36(3)$ mm/s and a minor species (18%) at $\delta = 0.14(4)$ mm/s, $|E_Q| = 0.58(10)$ mm/s (Figure 9b). The doublet of the minor species is similar to the tris(isocyanide) complex $L^{CF_3, Cl}Fe(CN^tBu)_3$ (**7**) (discussed above) which has Mössbauer parameters of $\delta = 0.25(2)$ mm/s, $|E_Q| = 0.63(2)$ mm/s (Figure 9a), suggesting that it is the small impurity in this sample. The putative presence of **7** as an impurity could not be confirmed by IR, because the bands for **7** (see below) overlap with those in the IR spectrum of **8**. Note that the compound passed elemental analysis, suggesting that elemental analysis is not sufficiently sensitive to establish the purity of **8**. The UV-vis spectrum of **8** exhibits a prominent absorbance at 710 nm with an extinction coefficient of $\sim 3,000\text{ M}^{-1}\text{cm}^{-1}$. The solution magnetic moment of **7** is $3.6(2)$ BM and consistent with an $S = 3/2$ spin state. Table 3 compares the CN stretching frequencies in the IR spectra of **8** to those of $L^{Me, iPr}Fe(CN^tBu)_2$.^[27] The lowest energy stretching band of **8** and $L^{Me, iPr}Fe(CN^tBu)_2$ are 2108 and 2050 cm^{-1} , respectively, with a significant difference of 58 cm^{-1} that indicates that backbonding is less in **8**. It is not easy to relate this change to the changes in the supporting ligand, because the change in spin state is expected to be a large perturbation on backbonding.

A blue-green single crystal of **8** was obtained from Et_2O and characterized by X-ray crystallography. There is a large difference in the Fe-C bond lengths, which are $0.17\text{ \AA}$ longer in **8** than in $L^{Me, iPr}Fe(CN^tBu)_2$. This large change correlates with a change in geometry: the structure of **8** is tetrahedral ($\tau_4 = 0.94$) at the iron and has linear CN^tBu ligands, whereas $L^{Me, iPr}Fe(CN^tBu)_2$ is square-planar ($\tau_4 = 0.10$) with bent CN^tBu ligands.^[32,26] The change in geometry begs the question of whether this is a steric or an electronic effect. There are two steric differences between $L^{Me, iPr}$ and $L^{CF_3, Cl}$: (a) the increase in size in the β -substituent from β -Me to β - CF_3 and (b) the decrease in size of the N -aryl ortho-substituents from iPr to Cl . The change of the β -substituent could push the N -aryl rings toward the iron and destabilize the square planar geometry. However, this must not be a major destabilizing factor, because $L^{tBu, iPr}Fe(CO)_2$ is also square planar even though tBu groups are much larger than CF_3 groups.^[27] With respect to the second steric change, the N -aryl rings are perpendicular to the β -diketiminato plane causing the *ortho*-substituents to lie above and below the N_2Fe plane. It is possible for the large out-of-plane iPr groups to push the CN^tBu ligands into a square planar geometry. Of course, an electronic effect is also possible. Thus, density functional theory calculations were performed to evaluate the electronic effects of the CF_3 groups on the geometry of the metal by a stepwise replacement of a CF_3 group with a methyl group for each spin state.

Calculations utilized the B3LYP level of theory with triple-zeta basis sets (def2-TZVP) on the iron and atoms coordinated to the iron, and double-zeta basis sets on all other atoms, as in earlier calculations on β -diketiminato iron complexes.^[28] The B3LYP functional was chosen over BP86 and revPBE based on the superior agreement of the optimized structures (particularly the Fe-C and C-N bond lengths; see Supporting Information) with the crystal structure of the literature precedent $L^{Me, iPr}Fe(CN^tBu)_2$ and with **8**. The doublet spin states of each complex optimized to a pseudo-square planar geometry. This is consistent with the square planar $L^{Me, iPr}Fe(CN^tBu)_2$ having a doublet spin state as determined by EPR

spectroscopy.^[22] The quartet spin states of each complex optimized to a tetrahedral geometry consistent with the $S = 3/2$ spin state of **8**, supporting the magnetic susceptibility results shown above and indicating that **8** indeed has a $S = 3/2$ ground state.

The difference in electronic (E), enthalpic (H), and free (G) energies between the doublet and quartet states are compared in Figure 10 for each ligand variant. The high-spin state is clearly overstabilized by the B3LYP functional, but we can still interpret the trends upon ligand variation. Each CF_3 substitution (right side of graph) lowers the electronic energy of the quartet state relative to the doublet state by *ca.* 1.2 kcal/mol. This result indicates that the CF_3 groups make the tetrahedral geometry more favored over the square planar geometry, but not enough to account for the geometry difference between **8** and $\text{L}^{\text{Me,iPr}}\text{Fe}(\text{CN}^t\text{Bu})_2$. Instead, the influence of the ortho substituents appears to be the most important (left side of graph), where changing from isopropyl to methyl to chloro gives much greater changes. Since methyl and isopropyl are electronically similar but give a drastic change, it is most reasonable to attribute the difference to the relative size of the substituents.

Summary and Conclusions

New, heavily halogenated β -diketiminato supporting ligands can be synthesized by a one-pot synthesis or by a 2-step microwave synthesis, where the latter method produces less waste. Use of this ligand afforded an iron(II) chloride complex with a coordinated diethyl ether ligand. Diethyl ether can be removed easily under vacuum to form the dimer, $[\text{L}^{\text{CF}_3,\text{Cl}}\text{FeCl}]_2$ (**4**).

Reduction of complex **4** is difficult, presumably because the halogenated substituents are susceptible to attack by reducing agents. We solved this issue by reducing at low temperature and adding substrates to the cold solution; however, in many cases the products were difficult to purify well, and the ^1H NMR spectra indicate impurities. Despite these difficulties, single crystals could be obtained on rare occasions which elucidated the nature of the products. When N_3Ad is added to reduced **4**, the azides couple to form a bis(adamantyl)tetrazene, and this is reduced by one electron to give $\text{N}_4\text{Ad}_2^{\bullet-}$ in iron(II) complexes. These tetrazene radical anion complexes can be coordinated to one iron, or bridge between two iron ions (one iron(I) and one iron(II)) in a new binding mode for dialkyltetrazene ligands. The crystallographic and spectroscopic evidence indicate that the influence of ligand halogenation is small, because the single-electron reduction of the tetrazene is very similar between the halogenated tetrazene complex and its alkylated analogues.

When iron(I) complexes with two or three isonitrile ligands were synthesized with the new halogenated ligand, interestingly the bis(isonitrile) complex is high-spin and tetrahedral in contrast to the square-planar, low-spin $\text{L}^{\text{Me,iPr}}\text{Fe}(\text{CN}^t\text{Bu})_2$. DFT calculations suggest that these structural differences and change in spin state are mostly from steric influences, and the electronic differences are again relatively small. This is consistent with more general observations on β -diketiminato complexes, where steric effects are greater than electronic effects.^[3] Therefore, substitution of halogens for the purposes of ligand protection is likely to be a useful strategy that will not cause major electronic changes at the metal, but it will be

important to make the supporting ligand isosteric for closer concurrence between the spin state, structure, and nuclearity of analogous complexes.

Experimental Section

General considerations

Unless otherwise specified, all manipulations were performed under an inert atmosphere using standard Schlenk techniques or in an M. Braun Unilab N₂-filled glovebox maintained at or below 1 ppm O₂ and H₂O. Glassware was dried at 150 °C overnight. Celite was dried at 250 °C under vacuum overnight. Toluene, diethyl ether and pentane were purified by passage through activated alumina and Q5 columns from Glass Contour Co. (Laguna Beach, CA). THF was dried by distilling from Na/benzophenone. THF-*d*₈ and C₆D₆, were dried over CaH₂, then over Na/benzophenone, vacuum transferred, and stored over 3 Å molecular sieves. Decane was dried by filtering through activated alumina and placed over 3 Å molecular sieves for 24 h two times, and stored over sieves.

Adamantylazide was purchased from Sigma Aldrich and crystallized from pentane. Potassium hexamethyldisilazide, titanium tetrachloride, *p*-toluenesulfonic acid monohydrate, and 1,8-bis(dimethylamino)naphthalene (Proton Sponge®), were purchased from Sigma Aldrich and 2,6-dichloroaniline from Oakwood Products, Inc. Hexafluoroacetylacetone (HfACH) was purchased from Sigma Aldrich (colorless liquid) and dried by distillation from calcium sulfate twice (yellow liquid). FeCl₂(THF)_{1.5} was synthesized by a literature procedure.^[29] KC₈ was prepared by heating potassium and graphite at 150 °C under an argon atmosphere. Reactions at –65 °C were performed in a glovebox with a cold well with an external Dewar filled with dry ice and acetone.

¹H NMR and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer at room temperature; ¹⁹F{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Shifts (δ) are reported in ppm, relative to residual protiated solvent in C₆D₆ (δ 7.15 ppm) or THF-*d*₈ (δ 1.73, 3.58 ppm) and ¹⁹F chemical shifts are reported in ppm relative to an added reference compound of trifluorotoluene (δ –63.7 ppm) or hexafluorobenzene (δ –164.9 ppm). Peaks were singlets unless otherwise noted. Overlapping peaks are reported together with one integration. Solution magnetic susceptibilities were determined by Evans' method.^[30] Microwave reactions were performed with a CEM Discover SP (2450 MHz) reactor in a 10 mL pressure vessel (note that the cap is not air-tight). Infrared data were obtained on a Shimadzu FT-IR Prestige-21 spectrometer using KBr pellets. Electronic spectra were recorded between 400 and 1000 nm on a Cary 50 UV-visible spectrophotometer, using Teflon-sealed air-free cuvettes of 0.1 cm optical path length. Elemental analyses were performed by the CENTC Elemental Analysis Facility at the University of Rochester. Electrochemical data were obtained under an Ar atmosphere using a Cypress Systems 3100 potentiostat. The working electrode was glassy carbon with a 1 mm diameter working area and Ag wires were used as the pseudoreference electrode and the auxiliary electrode. All spectra were taken using a [NBu₄][BAr^F] electrolyte solution in THF. The scan rate was 500 mV/s. All measurements were referenced to the Cp₂Fe⁺/Cp₂Fe couple using an internal ferrocene standard.

Computational Methods

DFT calculations were performed with the ORCA program package, version 2.8.0.^[31] Calculations reported here employed the B3LYP^[32] functional. The Ahlrichs triple- ζ -quality basis set with one set of polarization functions, def2-TZVP, was used for the iron atom, atoms directly coordinated to it, and all atoms of the alkyl ligand.^[33] The smaller polarized Ahlrichs double- ζ -quality basis set, def2-SVP, was used on all other atoms. The auxiliary basis set def2-SVP/J was used to speed the calculations through the resolution of identity (RIJCOSx) approximation.^[34] An empirical van der Waals correction was applied to the DFT energy (VDW10).^[35] The SCF calculations were tightly converged (TightSCF) with unrestricted spin (UKS) and geometry optimizations converged normally (Opt). Numerical frequency (NumFreq) calculations were performed on each complex to obtain the Gibbs free energy (in kcal/mol at STP). Ground states had no imaginary frequencies.

X-ray Crystallography

Single crystals were placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(1) K. A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with appropriate frame times ranging from 25–120 seconds with a detector distance of approximately 4.00 cm. The structures **4** and **4**•THF were solved using SIR97^[36] and refined using SHELXL-97.^[37] The structures of **3**, **3**•Et₂O, **5**, **6**, and **7** were solved using SIR2011^[38] and refined using SHELXL-2013.^[39] A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

One-pot Synthesis of L^{CF3,Cl}H (2)—Under an N₂ atmosphere, a three-neck flask was loaded with 2,6-dichloroaniline (12.5 g, 77.2 mmol) and decane (400 mL). A dropping funnel was loaded with a solution of 1,8-bis(dimethylamino)naphthalene (16.5 g, 77.2 mmol) in decane (100 mL) and attached to the three-neck flask. Another dropping funnel loaded with TiCl₄ (16.9 mL, 154 mmol) and attached to the three-neck flask. The aniline solution was cooled to 0 °C and the TiCl₄ was added dropwise. The resulting red mixture was warmed to ambient temperature and stirred for 18 h. The empty dropping funnel was replaced with a septum, the mixture was cooled to 0 °C, and Hf^{ac}H (2.80 mL, 19.9 mmol) was added via syringe followed by the dropwise addition of the 1,8-bis(dimethylamino)-naphthalene solution. The septum was replaced with a condenser and the yellow mixture was warmed to 70 °C for 24 h, then 140 °C for 24 h. The mixture was cooled to room temperature and filtered through Celite to remove a dark brown solid and isolate a deep yellow solution. The solid was washed with Et₂O until the wash was colorless. Et₂O was removed under vacuum, and the decane was removed by vacuum distillation at 45 °C to produce an orange solid. Excess aniline and **1** were removed via Kügelrohr sublimation at 75 °C under dynamic vacuum. The remaining orange solid was crystallized from hot hexane

to afford **2** (1.39 g, 2.80 mmol, 14%). The second fraction from the Kugelrohr sublimation was isolated as **1** (3.87 g, 11.0 mmol, 57%). The above procedure was repeated using **1** in place of HfacH to produce **2** (2.2 g, 4.44 mmol, 40%) for an overall yield of 38%. Spectroscopic data for **1** and **2** are below.

Two-step Microwave Synthesis of L^{CF3,Cl}H (2). Keto-imine (1)—Under an atmosphere of N₂, a 10 mL tube was loaded with 2,6-dichloroaniline (300 mg, 1.8 mmol), *p*-toluenesulfonic acid (180 mg, 0.92 mmol), HfacH (250 L, 1.8 mmol), and toluene (3 mL) and heated to 210 C via microwave radiation (P_{max} = 300 W) for 30 min. Under air, the mixture was filtered, and the solid was washed with hexane until the wash was colorless. Volatile materials were removed under vacuum and excess aniline was removed via sublimation at 40 C under dynamic vacuum to afford **1** (250 mg, 0.72 mmol, 41%). ¹H NMR (500 MHz, CDCl₃): 11.2 (1H, s, *NH*), 7.4 (4H, d, *J* = 8 Hz, *m*-Ar), 7.3 (2H, t, *J* = 8 Hz, *p*-Ar), 6.1 (1H, s, β*CH*) ppm. ¹³C{¹H} NMR (125.7 MHz, CDCl₃): 181.6 (q, *J* = 36 Hz, O=CCF₃), 154.0 (q, *J* = 33 Hz, N=CCF₃), 135.8 (s, N*C*_{Ar}), 132.0 (s, *p*-*C*_{Ar}), 130.8 (s, *o*-*C*_{Ar}), 128.8 (s, *m*-*C*_{Ar}), 117.7 (2 overlapping quartets, N=CCF₃ and O=CCF₃), 89.6 (s, β*C*) ppm. ¹⁹F{¹H} NMR (376.3 MHz, CDCl₃): 68.5 (N=CCF₃), 78.4 (O=CCF₃) ppm. IR (KBr): 1946 (w), 1871 (w), 1663 (s), 1601 (s), 1568 (m), 1508 (m), 1441 (m), 1381 (m), 1325 (m), 1267 (s), 1209 (s), 1148 (s), 1090 (s), 935 (w), 849 (w), 820 (s), 783 (s), 748 (w), 727 (m), 671 (w) cm^{1}. MS (EI⁺): *m/z* (relative intensity): 351 (100%), 352 (12%), 353 (61%), 354 (7%), 355 (10%), 356 (1.2%). Anal. Calcd for C₁₁H₅Cl₂F₆NO: C, 37.53, H, 1.43, N, 3.98. Found: C, 37.52, H, 1.43, N, 3.91.

L^{CF3,Cl}H (2)—Under an atmosphere of N₂, a 10 mL tube was loaded with 2,6-dichloroaniline (300 mg, 1.8 mmol) and decane (2 mL) and cooled to 30 C. TiCl₄ (33 L, 0.3 mmol) was added to form a red-orange mixture and stirred for 24 h. As a solid, **1** was added and the vial was rinsed with 1 mL decane. This procedure was performed with 6 10-mL reaction tubes. Each tube was heated to 210 C using variable microwave power (P_{max} = 300 W) for 4 h. Under air, each reaction tube was washed with 7 mL hexane, 5 mL toluene, and 5 mL hexane and combined. The yellow mixture was filtered through Celite and the volatile materials were removed under vacuum. The decane was vacuum distilled under dynamic vacuum at 40 C. The excess aniline and unreacted **1** were sublimed from the product under dynamic vacuum at 65 C. The orange and yellow solid was dissolved in hexane (15 mL) and filtered through a pipette column of silica gel (2.7 cm 5 cm) in hexane and the yellow solution was dried under vacuum to afford yellow crystals of **2** (463 mg, 0.930 mmol, 52%). ¹H NMR (500 MHz, CDCl₃): 11.5 (1H, s, *NH*), 7.4 (4H, d, *J* = 10 Hz, *p*-Ar), 7.1 (2H, t, *J* = 10 Hz, *m*-Ar), 6.0 (1H, s, β*CH*) ppm. ¹³C{¹H} NMR (100.5 MHz, CDCl₃): 152.3 (q, *J* = 31 Hz, CCF₃), 138.2 (s, N*C*_{Ar}), 130.8 (s, *p*-*C*_{Ar}), 128.2 (s, *m*-*C*_{Ar}), 127.6 (s, *o*-*C*_{Ar}), 118.8 (q, *J* = 283 Hz, CF₃), 89.3 (s, β*C*) ppm. ¹⁹F{¹H} NMR (376.3 MHz, CDCl₃): 68.9 ppm. MS (EI⁺): *m/z* (relative intensity): 494 (78%), 495 (14%), 496 (100%), 497 (19%), 498 (48%), 499 (10%), 500 (9%). IR (KBr): 2924 (w), 2855 (w), 1645 (s), 1589 (s), 1564 (s), 1514 (s), 1495 (m), 1439 (s), 1406 (m), 1387 (m), 1331 (m), 1283 (s), 1229 (m), 1186 (s), 1142 (s), 1109 (m), 1092 (m), 1065 (m), 943 (w), 874 (w), 791 (s), 773 (s), 745 (m) cm^{1}. UV-vis (toluene, in mM^{1}cm^{1}): 330(22) nm. Anal. Calcd for C₁₇H₈Cl₄F₆N₂: C, 41.16, H, 1.63, N, 5.65. Found: C, 41.20, H, 1.55, N, 5.58.

[L^{CF3,Cl}FeCl]₂ (4)—A solution of potassium hexamethyldisilazide (161 mg, 0.808 mmol) in Et₂O (5 mL) was added to a solution of **2** (402 mg, 0.811 mmol) in Et₂O (10 mL) at a rate of 2–4 drops per second. The dark yellow solution was stirred for 2 h at RT and completely dried under vacuum at 35 °C as determined by a vacuum gauge. The dark yellow solid was dissolved in THF (10 mL) and added to a mixture of FeCl₂(THF)_{1.5} in THF (5 mL) to produce a dark purple mixture which was stirred at RT for 18 h. Volatile materials were removed under vacuum, and the solid was heated under dynamic vacuum at 60 °C for 6 h to afford a bright red powder. Toluene (50 mL) was added to the red powder and the suspension was stirred at 90 °C for 18 h. The dark red mixture was filtered through Celite and dried under vacuum to produce a dark red solid which was washed with pentane (7 mL) three times. The resulting bright red powder of **4** (380 mg, 0.324 mmol, 80%) was collected. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 10.4 (8H, *m*-Ar), –29.5 (2H, βCH), –53.7 (4H, *p*-Ar) ppm. ¹H NMR (500 MHz, THF-*d*₈, 25 °C): δ 18.2 (4H, *m*-Ar), –50.1 (2H, *p*-Ar), –61.4 (1H, βCH) ppm. ¹⁹F{¹H} NMR (376.3 MHz, C₆D₆, 25 °C): δ –63.7 (CF₃) ppm. ¹⁹F{¹H} NMR (376.3 MHz, THF, 25 °C): δ –165.0 (CF₃) ppm. μ_{eff} (THF-*d*₈, 25 °C) = 5.6(2) BM per Fe. IR (KBr): 1562 (m), 1541 (m), 1435 (s), 1420 (s), 1321 (m), 1296 (m), 1234 (m), 1188 (s), 1159 (s), 1146 (s), 1109 (m), 1096 (w), 955 (w), 887 (w), 806 (m), 787 (m), 772 (m), 775 (w) cm^{–1}. UV-vis (THF, ε in mM^{–1}cm^{–1}): 254(21), 365(36), 515(1.9) nm. Anal. Calcd for C₂₁H₁₇Cl₅F₆FeN₂O (**3**•Et₂O): C, 38.19, H, 2.59, N, 4.24. Calcd for C₁₇H₇Cl₅F₆FeN₂ (**4**): C, 34.82, H, 1.20, N, 4.78. Found: C, 35.02, H, 1.18, N, 4.55. Zero-field Mössbauer (solid, 80 K): δ = 0.92(2) mm/s, | *E*_Q | = 2.30(2) mm/s; Zero-field Mössbauer (THF solution, 80 K): δ = 0.88(2) mm/s, | *E*_Q | = 2.06(2) mm/s.

L^{CF3,Cl}Fe(N₄Ad₂)FeL^{CF3,Cl} (5)—A solution of **4** (100 mg, 0.086 mmol) in THF (5 mL) was cooled to –108 °C and KC₈ (27 mg, 0.20 mmol) as a solid was added and stirred for 1 min. N₃Ad (30 mg, 0.17 mmol) in THF (3 mL) was cooled to –108 °C, added to the mixture, and stirred for 10 min. Volatile materials were removed under vacuum. The residue was dissolved in pentane, filtered through Celite, concentrated to 5 mL (a dark red precipitate formed), filtered, and cooled to –40 °C to afford dark red-orange crystals of **5** (60 mg, 0.040 mmol, 47%). ¹H NMR (500 Hz, C₆D₆, 25 °C) δ 11.5 (2H), 9.6 (2H), 5.1 (3H), –0.9 (2H), –1.7 (4H), –6.5 (1H), –7.2 (3H), –14.2/–14.5 (6H), –24.5 (1H), –24.9 (1H), –25.9 (1H) ppm. The integrations given above are rough estimates (see ESI, section S-4). The ¹H NMR spectrum showed some impurities including **6**, consistent with the deviations in microanalysis. ¹⁹F{¹H} NMR (376.3 MHz, C₆D₆, 25 °C): δ –117.4, –122.5 ppm. μ_{eff} (C₆D₆, 25 °C) = 5.2(1) BM. IR (KBr): 2907 (m), 2849 (m), 1558 (w), 1535 (w), 1435 1312 (m), 1288 (m), 1234 (m), 1186 (s), 1152 (s), 1103 (m), 1070 (w), 955 (w), 883 (w), 789 (m), 771 (m), 746 (w), 698 (w) cm^{–1}. Anal. Calcd for C₅₄H₄₄Cl₈F₁₂Fe₂N₈: C, 45.41, H, 3.10, N, 7.84. Found: C, 45.93, H, 3.15, N, 7.24. Zero-field Mössbauer (solid, 80 K): δ = 0.73(2) mm/s, | *E*_Q | = 1.45(2) mm/s (57%) and δ = 1.21(2) mm/s, | *E*_Q | = 2.08(2) mm/s (43%).

L^{CF3,Cl}Fe(N₄Ad₂) (6)—A solution of **4** (90 mg, 0.15 mmol) in THF (15 mL) was cooled to –65 °C and a suspension of KC₈ (24 mg, 0.18 mmol) in 1 mL THF was added. The dark green mixture was stirred for 15 min at –65 °C and N₃Ad (0.38 mL, 0.80 M in THF) was added, giving a color change to dark red. The mixture continued to stir at –65 °C for 30 min, warmed to RT, and stirred overnight. The mixture was filtered through Celite and volatile

materials were removed under vacuum. The residue was dissolved in pentane, filtered through Celite, concentrated, and cooled to $-40\text{ }^{\circ}\text{C}$ to afford red crystals of **6** (17 mg, 0.020 mmol, 13%). ^1H NMR (500 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 4.5 (12H), -0.9 (6H), -6.4 (6H), -23.9 (2H), -24.4 (6H) ppm. Two expected peaks are absent. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ -158.2 (CF_3) ppm. μ_{eff} (C_6D_6 , $25\text{ }^{\circ}\text{C}$) = $3.4(1)$ BM. IR (KBr): 3063 (w), 2908 (s), 2851 (m), 2088 (w), 1559 (w), 1532 (w), 1434 (s), 1410 (s), 1317 (w), 1283 (m), 1234 (m), 1205 (m), 1183 (s), 1151 (s), 1131 (w), 1107 (w), 1097 (w) cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{37}\text{Cl}_4\text{F}_6\text{FeN}_6$: C, 50.65, H, 4.25, N, 9.58. Found: C, 50.41, H, 4.30, N, 8.69. Zero-field Mössbauer (solid, 80 K): δ = $0.75(2)$ mm/s, $|E_Q|$ = $1.55(2)$ mm/s.

$\text{LCF}_3\text{ClFe}(\text{CN}^t\text{Bu})_3$ (7)—A solution of **4** (47 mg, 0.080 mmol) in THF (5 mL) was cooled to $-65\text{ }^{\circ}\text{C}$. KC_8 (12 mg, 0.089 mmol) suspended in THF (1 mL) was added dropwise while stirring. After stirring for 10 min, an excess of $^t\text{BuNC}$ (0.050 mL, 0.44 mmol) was added, and the mixture was stirred for 30 min at $-65\text{ }^{\circ}\text{C}$. The dark brown mixture was warmed to ambient temperature and filtered through Celite. Volatile materials were removed under vacuum to give a dark red-orange residue. The residue was dissolved in toluene (5 mL) and placed under dynamic vacuum. As the solution became more concentrated, the color changed from dark red to dark green and resulted in a dark green residue that was taken up in pentane and dried to form **7** as a dark green powder (55 mg, 0.069 mmol, 86%). ^1H NMR (500 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): silent. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): silent. EPR (toluene, 10 K): g_{eff} = 2.076, 2.067, 1.998. IR (KBr): 2982 (m), 2112 (s), 2043 (s), 1991 (m), 1543 (w), 1431 (s), 1368 (w), 1298 (m), 1231 (m), 1207 (m), 1171 (s), 1132 (s), 1069 (w), 1036 (w), 959 (w), 889 (w), 783 (m), 743 (w) cm^{-1} . Anal. Calcd for $\text{C}_{32}\text{H}_{34}\text{Cl}_4\text{F}_6\text{FeN}_5$: C, 48.03, H, 4.28, N, 8.75. Found: C, 48.37, H, 4.32, N, 8.58. Zero-field Mössbauer (solid, 80 K): δ = $0.25(2)$ mm/s, $|E_Q|$ = $0.63(2)$ mm/s.

$\text{LCF}_3\text{ClFe}(\text{CN}^t\text{Bu})_2$ (8)—A solution of **4** (50 mg, 0.085 mmol) in THF (3 mL) was cooled to $-108\text{ }^{\circ}\text{C}$ and KC_8 (14 mg, 0.10 mmol) was added followed by *tert*-butylisocyanide (19 μL , 0.17 mmol). The bright blue-green mixture was stirred for 30 min at ambient temperature, filtered through Celite, and dried under vacuum to produce a blue-green powder of **8** (61 mg, 0.085 mmol, 100%). ^1H NMR (500 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ 29.4 (4H, *m*-Ar), -49.8 (2H, *p*-Ar), -147.2 (1H, βCH) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.3 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ -65.1 (major), -67.5 , -120.2 ppm. We assume that the latter two peaks correspond to the small impurities observed in the Mössbauer spectra. μ_{eff} (C_6D_6 , $25\text{ }^{\circ}\text{C}$) = $3.6(2)$ BM. IR (KBr): 2986 (m), 2938 (w), 2870 (w), 2180 (m), 2126 (s), 2108 (s), 1578 (w), 1555 (w), 1516 (w), 1433 (s), 1369 (m), 1296 (s), 1242 (m), 1169 (s), 1146 (s), 1113 (s), 1067 (m), 950 (w), 887 (m), 808 (m), 773 (m), 743 (w), 719 (w) cm^{-1} . UV-vis (THF, ϵ in $\text{mM}^{-1}\text{cm}^{-1}$): 255(14), 285(15), 710(3) nm. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{Cl}_4\text{F}_6\text{FeN}_4$: C, 45.22, H, 3.51, N, 7.81. Found: C, 45.21, H, 3.58, N, 7.63. Zero-field Mössbauer (solid, 80 K): δ = $0.64(2)$ mm/s, $|E_Q|$ = $2.36(3)$ mm/s.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Institutes of Health (GM065313). We thank Megan Reesbeck and Stephanie Daifuku for assistance with EPR spectroscopy.

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Figure 1.
Resonance structures of a tetrazene complex, where the oxidation states of the tetrazene ligand and the metal change.

Figure 2.

Molecular structure of **3•Et₂O**, showing 50% thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)-N(11), 2.012(1); Fe(1)-N(21), 2.017(1); Fe(1)-Cl(1), 2.2425(5); Fe(1)-O(14), 2.092(1); N(11)-Fe(1)-N(21), 92.97(5); O(14)-Fe(1)-Cl(1), 101.60(4).

Figure 3.

Molecular structure of **4**, showing 50% thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)-N(11), 1.9947(15); Fe(1)-N(21), 2.0034(14); Fe(1)-Cl(1), 2.3201(5); N(11)-Fe(1)-N(21), 93.01(6).

Figure 4.

(a) Molecular structure of **5**, showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Fe(1)-N(11), 2.032(4); Fe(1)-N(21), 2.033(4); Fe(2)-N(14), 1.987(4); Fe(2)-N(24), 1.988(4); Fe(1)-N(1), 1.975(4); Fe(1)-N(4), 2.004(4); Fe(2)-N(2), 2.019(4); Fe(2)-N(3), 1.983(4); N(1)-N(2), 1.331(5); N(2)-N(3), 1.323(6); N(3)-N(4), 1.316(5); N(11)-Fe(1)-N(21), 90.20(17); N(24)-Fe(2)-N(14), 93.75(17). (b) Molecular structure of **5•THF**, showing 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Fe(1)-N(14), 2.046(2); Fe(1)-N(24), 2.039(2); Fe(2)-N(11), 2.064(2); Fe(2)-N(21), 2.077(2); Fe(2)-O(19), 2.208(2); Fe(1)-N(1), 2.008(2); Fe(1)-N(4), 1.962(2); Fe(2)-N(2), 2.081(2); Fe(2)-N(3), 2.043(2); N(1)-N(2), 1.323(3); N(2)-N(3), 1.311(3); N(3)-N(4), 1.341(3); N(24)-Fe(1)-N(14), 89.26(9); N(11)-Fe(2)-N(21), 87.91(9). (c) Molecular structure of **6**, showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Fe(1)-N(11), 2.028(4); Fe(1)-N(21), 2.012(4); Fe(1)-N(1), 2.002(4); Fe(1)-N(4), 1.972(4); N(1)-N(2), 1.316(6); N(2)-N(3), 1.332(6); N(3)-N(4), 1.309(6); N(11)-Fe(1)-N(21), 90.42(17). In each, hydrogen atoms are omitted for clarity.

Figure 5.

Two fits of the zero-field Mössbauer spectrum of solid **5** at 80 K. The black circles are the data points. (a) Fit A: The blue and green solid lines show fitted components with $\delta = 0.73(2)$ mm/s, $|E_Q| = 1.45(2)$ mm/s and $\delta = 1.21(2)$ mm/s, $|E_Q| = 2.08(2)$ mm/s in a 1.3:1 ratio, and the solid red line is the sum of the two. (b) Fit B: The solid lines show fitted components with $\delta = 0.80(2)$ mm/s, $|E_Q| = 1.30(2)$ mm/s (blue) and $\delta = 1.11(2)$ mm/s, $|E_Q| = 2.27(2)$ mm/s (47%, green) in a 1.1:1 ratio, and the solid red line is the sum of the two components.

Figure 6.

Zero-field Mössbauer spectrum of solid **6** at 80 K. The black circles are the data points. The blue and green solid line show fitted components for a major (82%) species with $\delta = 0.75(4)$ mm/s and $|E_Q| = 1.55(6)$ mm/s and a minor (18%) species with $\delta = 0.42(8)$ mm/s and $|E_Q| = 0.80(10)$ mm/s. The solid red line is the sum of the two components.

Figure 7.

Molecular structure of **7**, showing 50% thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)-N(11), 1.9940(18); Fe(1)-N(21), 2.0045(18); Fe(1)-C(14), 1.952(2); Fe(1)-C(15), 1.846(2); Fe(1)-C(16), 1.843(2); C14(1)-N(14), 1.166(3); C(15)-N(15), 1.169(3); C(16)-N(16), 1.169(3); N(11)-Fe(1)-N(21), 91.11(7).

Figure 8.

Molecular structure of **8**, showing 50% thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)-N(11), 1.937(5); Fe(1)-C(14), 1.988(6); N(11)-Fe(1)-N(11A), 97.31(3); C(14)-N(14), 1.158(8).

Figure 9.

(a) Zero-field Mössbauer spectrum of solid **7** at 80 K. The black circles are the data points and the solid red line is the total fit. The blue and green solid lines show fits to the data for a major species ($\delta = 0.25(2)$ mm/s, $|E_Q| = 0.63(2)$ mm/s, 88%, green) and a minor species ($\delta = 0.59(3)$ mm/s, $|E_Q| = 2.35(7)$ mm/s, 12(3)%, blue). (b) Zero-field Mössbauer spectrum of solid **8** at 80 K. The black circles are the data points and the solid red line is the total fit. The blue and green solid lines show fits to the data for a major species ($\delta = 0.64(2)$ mm/s, $|E_Q| = 2.36(3)$ mm/s, 82(3)%, blue) and a minor species ($\delta = 0.14(4)$ mm/s, $|E_Q| = 0.58(10)$ mm/s, 18%, green).

Figure 10. (top) Computed favorability of tetrahedral to square planar interconversion with varying R, R', and R'' groups. (bottom) Plot of energy differences (in kcal/mol) between tetrahedral and square planar complexes with varying R, R', and R'' groups.

Scheme 1.
Synthetic routes to a new halogenated β -diketimine.

Scheme 2.
Preparation of iron-tetrazene complexes.

Table 1

Bond lengths (Å) and angles (°) of tetrahedral iron(II) β -diketiminate complexes. Averages were taken when applicable.

Complex	C β -N-C _{Ar} (°)	C β =N (Å)	Fe-N (Å)
[Me ^t L ^{Me,Me} FeCl] ₂ ^a	119	1.336(4)	1.973(2)
4 , [L ^{CF3,Cl} FeCl] ₂	121	1.327(2)	1.999(2)
L ^{tBu,iPr} Fe(Cl)(L) ^b	124	1.327(3)	2.012(2)

^aRef 12.

^bRef 15, L = 3-methylpyridine.

Table 2

The NN bond lengths (Å) and Mössbauer parameters of **5**, **6**, and $\text{L}^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$.^[8]

		Mössbauer Parameters
	NN (Å)	δ (mm/s), E_Q (mm/s)
5	1.331(5), 1.323(6), 1.316(5)	Fe1: 0.73(2), 1.45(2) Fe2: 1.21(2), 2.08(2)
6	1.316(6), 1.332(6), 1.309(6)	0.75(4), 1.55(6)
$\text{L}^{\text{Me,iPr}}\text{Fe}(\text{N}_4\text{Ad}_2)$ ^[8]	1.317(2), 1.334(2), 1.309(2)	0.69(2), 1.32(4)

Table 3

Key bond lengths (Å) and Mössbauer parameters of isocyanide complexes for comparison to **7**. The axial isocyanides are listed first.

L	Fe-C (Å)	C-N (Å)	Mössbauer Parameters
Me ₂ L ^{Me,Me} (tris, ref 22)	1.885(1), 1.798(1), 1.822(1)	1.170(2), 1.185(2), 1.173(2)	0.17, 0.81
L ^{tBu,iPr} (tris, ref 21)	1.912(4), 1.824(4), 1.833(4)	1.168(4), 1.164(5), 1.168(5)	N/A
L ^{CF₃,Cl} (tris, 7)	1.952(2), 1.846(2), 1.843(2)	1.166(3), 1.169(3), 1.169(3)	0.25, 0.63
L ^{Me,iPr} (bis, ref 20)	1.817(1), 1.821(1)	1.222(9), 1.153(9)	N/A
L ^{CF₃,Cl} (bis, 8)	1.988(6)	1.158(8)	0.64, 2.36