Electronic Structure of Open-Shell, First-Row Transition Metal Complexes for C–H Functionalization

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Accessibility
Electronic Structure of Open-Shell, First-Row Transition Metal Complexes for C–H Functionalization

A dissertation presented

by

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Electronic Structure of Open-Shell, First-Row Transition Metal Complexes
for C–H Functionalization

Abstract

The electronic and steric factors that enable the isolation of open-shell iron
dipyrromethene compounds containing ligand-centered radicals were explored. In addition to
isolating these complexes, the relationship between their electronic structure and functional
reactivity was investigated. In particular, upon addition of several different diazoalkane
substrates to FeI-supported dipyrromethene complexes, a series of iron-diazoalkane adducts were
isolated. While the coordination geometry of the diazoalkane ligand varied, one electron
reduction of the diazoalkane upon binding was universally observed, as supported by X-ray
crystallography, EPR spectroscopy, DFT calculations, and reactivity trends.

In contrast, reaction between a sterically accessible FeII dipyrromethene compound and
diphenyldiazomethane does not yield the corresponding diazoalkane adduct. Instead, the metal
center promotes dinitrogen extrusion to furnish the respective four-coordinate iron-carbene,
(1BuL)FeCl(CPh2) (1BuL = 1,9-di-tert-butyl-5-(2,6-dichlorophenyl)-dipyrromethene). X-ray
crystallography, DFT calculations, 57Fe Mössbauer, EPR, and X-ray absorption spectroscopies
support the assignment of this species as an intermediate FeII/FeIII complex, featuring some small
amount of carbene-radical character, consistent with its observed singlet- and radical-type
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carbene ligand. The corresponding reduced species, (1BuL)Fe(CPh2)(solv), are best described as
high-spin FeII complexes antiferromagnetically coupled to carbene-centered ligand radicals. In
line with this assignment, these species undergo hydrogen atom abstraction from hydroxyl-2-azaadamantane.

As shown with diazoalkanes and carbenes, open-shell iron dipyrrin complexes can promote electron transfer from the metal center to redox-active ligands upon coordination. The reactivity of these transiently generated ligand-centered radicals was further explored. Of note, addition of long-chain α-diazo-β-ketoesters to a catalytic amount of \((\text{Bu}L)\text{FeCl} (\text{Et}_2\text{O})\) furnished a variety of substituted 2-alkylidene-tetrahydrofurans in modest yields. While mechanistic studies are still underway, a bidentate radical coordinated to the metal center through two oxygen atoms from the diazoester substrate is proposed as the reactive intermediate.
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## List of Acronyms, Symbols, and Units

- radical
- $^{13}\text{C}$ carbon-13
- $^{19}\text{F}$ fluorine
- $^{57}\text{Fe}$ iron
- $^{1}\text{H}$ proton
- Å angstrom, $10^{-10}$ meters
- avg average
- BDE bond dissociation energy
- br broad
- BS broke symmetry
- CHN% combustion or elemental analysis
- cm$^{-1}$ wavenumbers or inverse centimeters
- $D$ axial zero field splitting parameter
- d doublet in NMR
- DFT density functional theory
- $E$ rhombic zero field splitting parameter
- $e^{-}$ electron
- EPR electron paramagnetic resonance
- ESI$^+$ positive ion electron spray ionization
- eV electron volts
- F/T freeze/thaw
- G gauss
- $g$ Landé g-factor
- g grams
- h hours
- $H$ Hamiltonian operator
- $H$ magnetic field
- HAA hydrogen atom abstraction
- HOMO highest occupied molecular orbital
- HRMS high-resolution mass spectrometry
- IR infrared spectroscopy
- $J$ coupling constant
- K kelvin
- kcal kilocalorie or 1000 calories
- KIE kinetic isotope effect
- LC/MS liquid chromatography/mass spectrometry
- LUMO lowest unoccupied molecular orbital
- M molar, moles per liter
- m multiplet in NMR
- $m$- meta position on an aryl ring, indicating 1,3 relationship
- mg miligrams or $10^{-3}$ grams
- mm millimeters or $10^{-3}$ meters
- $m/z$ mass to charge ratio
- MHz megahertz, 106 Hertz or $10^6$ s$^{-1}$
mmol millimole, $10^{-3}$ moles
mV millivolt, $10^{-3}$ volts
nb non-bonding orbital
nm nanometer, $10^{-9}$ meters
NMR nuclear magnetic resonance
$\sigma$- ortho position on an aryl ring, indicating a 1,2 relationship
Oe oersted
$p$- para position on an aryl ring, indicating a 1,4 relationship
ppm parts per million
q quartet in NMR
RT room temperature
s singlet in NMR
$S$ spin
$S$ spin operator
sec or s seconds
SQUID superconducting quantum interference device
T tesla
t triplet in NMR
T temperature
UV-Vis ultraviolet-visible absorption spectroscopy
VT variable temperature
XANES X-ray absorption near edge spectroscopy
$\delta$ isomer shift for $^{57}$Fe Mössbauer in $\text{mm/s}$
$\delta$ delta, chemical shift in ppm
$\Delta E_Q$ quadrupole splitting for $^{57}$Fe Mössbauer in $\text{mm/s}$
$\eta^n$ eta, hapticity or number, n, of atoms in a polydentate ligand bound to a metal
$\lambda$ lambda, wavelength in nm
$\rho$ density
$\mu_B$ Bohr magnetron, $9.274 \times 10^{-21}$ erg/G
$\nu$ frequency
$\chi$ magnetic susceptibility
$\chi_M$ molar magnetic susceptibility in $\text{cm}^3/\text{mol}$
$\sigma$ sigma bond
$\pi$ pi bond
Chapter 1

Controlling the Electronic Structure of Metal-Ligand Multiple Bonds for C–H Functionalization

1.1 C–H Bond Functionalization

The development and application of complex organic molecules and natural products as pharmaceuticals and new materials can be hindered due to the economic cost associated with precious metal catalysis and waste generation associated with inefficient, multi-step organic syntheses. Key transformations to target in order to streamline synthetic protocols are reactions that selectively form new bonds between carbon and oxygen, nitrogen, sulfur, or another carbon from unactivated C–H bonds. Direct C–H functionalization is challenging due to the relative inertness of aliphatic C–H bonds (BDE 95–105 kcal/mol). Synthetic protocols that target these types of transformations are often unselective between similar C–H bonds or require harsh reaction conditions, such as high temperatures or strong oxidants. Transition metal catalysts capable of inserting these types of functionalities selectively into unactivated C–H bonds demonstrate the potential to simplify the syntheses of pharmaceuticals and natural products.

Metal complexes perform C–H functionalization through processes including oxidative addition/reductive elimination, sigma-bond metathesis, concerted metalation-deprotonation, and


direct insertion.\(^5\) In the Betley Group, we are particularly interested in engineering transition metal complexes containing metal-ligand multiple bonds capable of oxidative group transfer to unreactive substrates. To target reactive complexes, our group utilizes weak-field ligands, resulting in minimal metal-ligand anti-bonding orbital destabilization, generating complexes with high-spin electronic configurations.\(^6\)

**Scheme 1.1.** Mechanism by which Cytochrome P450 performs hydrogen atom abstraction/radical recombination.\(^7\)

One example of nature utilizing highly reactive metal-ligand multiple bonds to functionalize C–H bonds is cytochrome P450. Cytochrome P450 is a heme-based monooxygenase enzyme that selectively hydroxylates hydrocarbons. As shown in Scheme 1.1, the active site of the enzyme reacts with molecular oxygen to generate a high-valent Fe\(^{IV}\) oxo species known as Compound I. The reactivity of this intermediate is attributed to its electronic structure. Two unpaired electrons populate \(\pi^*\) Fe–O anti-bonding molecular orbitals, thus

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weakening the Fe–O bond and engendering radical character at the multiply bonded fragment (Figure 1.1). This highly reactive intermediate is then poised to perform hydrogen-atom abstraction, followed by radical recombination to afford the hydroxylated hydrocarbon products (Scheme 1.1).7

Cytochrome P450 has been engineered to support other types of catalytic reactivity as well.8 For instance, Arnold and co-workers showed that heme proteins can be modified via site-directed mutagenesis to react with push/pull diazo compounds to perform carbene transfer into olefins, alkynes, B–H bonds, N–H bonds, and Si–H bonds (Scheme 1.2).9 The reactive iron carbene intermediate invoked in these transformations is best described as an $S = 0$ complex bearing a singlet-type carbene ligand, as deduced from crystallography, $^{57}$Fe Mössbauer spectroscopy, and computations.10

Figure 1.1. Molecular orbital diagram for the reactive intermediate for Cytochrome P450 (Compound I).7


To develop synthetic catalysts that mimic the reactivity of Cytochrome P450 and its engineered variants, we must develop a systematic understanding of the relationship between electronic structure and function. In particular, we are interested in studying how selection of metal and ligand environment can promote specific electronic states to affect desired transformations. Understanding the structure of reactive intermediates can drive the rational design of catalysts for desirable reactions, such as C–H functionalization.

We employ weak-field and bulky dipyrrin ligands to support the synthesis and isolation of high-spin metal complexes featuring metal-ligand multiple bonds. We have previously reported two isolable high-spin iron nitrenoid complexes. The first complex, \((^A\text{L})\text{FeCl}(^N\text{N}(C_6H_4-p^t\text{Bu}))\), was isolated via aryl azide addition to \((^A\text{L})\text{FeCl}\). The resulting product is best described as a high-spin Fe\textsuperscript{III} anti-ferromagnetically coupled to a nitrenoid nitrogen-based radical and is corroborated by single-crystal X-ray diffraction, X-ray absorption spectroscopy, magnetometry,
$^{57}$Fe Mössbauer spectroscopy, and computations. This iron iminyl complex is highly reactive, demonstrated by the amination of toluene at room temperature (Scheme 1.3).\(^6\)

Reduction of ($^{\text{ArL}}$)FeCl($^{\text{N(C}_6\text{H}_4-p^t\text{Bu})}$) with KCl result in precipitation of graphite and KCl to furnish the respective three-coordinate complex, ($^{\text{ArL}}$)Fe($^{\text{N(C}_6\text{H}_4-p^t\text{Bu})}$). This imido species is best described as a high-spin Fe$^{\text{III}}$ complex with a closed-shell imide ligand. Noteworthy, ($^{\text{ArL}}$)Fe($^{\text{N(C}_6\text{H}_4-p^t\text{Bu})}$) required elevated temperatures to aminate toluene, albeit in diminished yields (Scheme 1.3). These results together demonstrate the relationship between electronic structure and reactivity. In the case of the iron-iminyl complex, the ability of the imido fragment to support a ligand-centered radical was crucial in governing group transfer processes into C–H bonds under mild conditions.\(^6\)

**Scheme 1.3.** Isolation and reactivity of the iron imido (($^{\text{ArL}}$)Fe($^{\text{N(C}_6\text{H}_4-p^t\text{Bu})}$)) and iminyl (($^{\text{ArL}}$)FeCl($^{\text{N(C}_6\text{H}_4-p^t\text{Bu})}$)) complexes from the Betley Group.\(^6\)
Following the isolation of Fe imido and iminyl complexes, we extended the use of the dipyrrin ligand platform to isolate cobalt\textsuperscript{11} and several other iron nitrenoid complexes.\textsuperscript{12} With these results in hand, we were interested in targeting the synthesis of related metal complexes featuring metal-ligand multiple bonds, including metal-carbene species.

1.2. Metal Carbene Complexes

1.2.1 Electronic Structure of Metal Carbene Complexes

Traditionally, two descriptions best describe the nature of the metal-carbon multiple bond. Schrock-type alkylidenes (M=CR\textsubscript{2}, R = alkyl or H) are derived from a triplet carbene fragment, which forms two covalent bonds with two unpaired electrons from the metal center. Once bound to the metal center, the carbene-derived highest occupied molecular orbital (HOMO) renders the species nucleophilic (Figure 1.2). Schrock-type alkylidenes are generally found in highly oxidized early transition metal complexes. Fischer-type carbenes (M=CR'(OR), R = aryl or alkyl), however, are derived from heteroatom stabilized carbene fragments. In this case, the singlet-derived carbene donates two electrons into an empty metal-based molecular orbital and accepts two electrons from the metal center via \(\pi\)-back donation. The lowest unoccupied molecular orbital (LUMO) is carbene-based, and the resulting complex behaves as an electrophile (Figure 1.2).\textsuperscript{13}


\textsuperscript{13} Crabtree, R. H. The Organometallic Chemistry of the Transition Metals. 5 ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, \textbf{2009}; pgs 296-360.
Intermediate between that of Schrock-type and Fischer-type carbenes is an electronic structure depiction that invokes significant radical-character onto the carbene fragment. In the case of these carbene radicals, there is partial occupation of the metal-carbene $\pi^*$ anti-bonding molecular orbital (Figure 1.3). The presence of unpaired electron density on the carbene fragment weakens the M–C bond and promotes unique, radical-type reactivity.

### 1.2.2 Synthesis of Metal Carbene Complexes

Several synthetic routes exist to access transition metal carbene complexes. For example, Schrock-type alkylidenes are generally synthesized via alpha-abstraction from a metal-dialkyl intermediate (Scheme 1.4).  

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Another common route towards accessing transition metal carbene complexes is via dinitrogen extrusion from diazoalkane substrates. For example, dirhodium carbene compounds, which are highly reactive and used in a variety of catalytic applications, are generated upon reaction between a dirhodium tetracarboxylate salt and a diazoalkane moiety.

Diazoalkane adducts, however, can coordinate to the transition metal in a geometry not conducive towards dinitrogen expulsion. Diazoalkanes can serve as redox-active ligands and may coordinate the metal side-on or via the terminal nitrogen atom. The bond metrics within the diazoalkane ligand fragment indicate its degree of reduction. For example, diazoalkane ligands produce dative or covalent bonds with the metal center. In redox innocent instances, the ligand adopts a linear conformation with M–N–N and N–N–C angles equal to 180°. Upon coordination to the metal center, diazoalkane ligands can also be doubly reduced, resulting in N–N–C or M–N–N bond angles equal to 120°.


There is also evidence for the existence of diazoalkane ligand radicals. These diazo ligands are reduced by one electron upon metal coordination and adopt unique conformations (Figure 1.4). The M–N–N and N–N–C bond angles are intermediate between that of linear and trigonal planar. To design catalytic systems capable of dinitrogen extrusion from diazoalkanes and subsequent carbene transfer into organic substrates, it is important to develop an understanding of how binding motifs and electronic structure of diazoalkane ligands are influenced by both metal identify and ligand environment.

1.2.3 Reactivity of Transition Metal Carbene Complexes

The electronic structure of the carbene ligand influences the propensity for group transfer from metal carbene complexes. Schrock-type alkylidenes are nucleophilic and best known for their olefin metathesis reactivity. In this reaction, a [2+2] cycloaddition between a transition metal alkylidene and an alkene forms a metallacyclobutane intermediate. This intermediate subsequently decomposes to generate a new alkene product (Scheme 1.5). The discovery of catalysts for olefin metathesis, as well as the

elucidation of their mechanism, was ultimately awarded a Nobel Prize in Chemistry in 2005. Catalysts for this transformation are often based on molybdenum, tungsten, or ruthenium. Translating this reactivity to iron or other first row transition metals would have significant impact by reducing the costs associated with catalyst development.

Electrophilic, Fischer-type carbene complexes, however, are prone to singlet-type carbene transfer reactions, including C–H insertion and cyclopropanation. The most utilized systems to date displaying this type of reactivity are those comprised of dirhodium coordinated by various carboxylate ligands. These dirhodium(II) complexes decompose donor/acceptor diazo compounds and subsequently transfer the carbene fragment into a wide range of C–H bonds with high diastereo- and enantioselectivity to form new C–C bonds. Intramolecular protocols have also been developed. Dirhodium(II) catalysts can convert long-chain diazo compounds containing weak C–H bonds into a variety of carbocyclic structures (Scheme 1.6). Common diazo substrates for these metal-catalyzed cyclization reactions are either α-diazoketones or α-diazo-β-ketoesters.

Carbene radicals behave quite differently from either Fischer-type or Schrock-type...

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carbene complexes. The first example of a carbene radical was described in 1976, where Casey and co-workers reported the EPR spectrum of the one-electron reduced (phenylmethoxycarbene)pentacarbonyl chromium complex.\textsuperscript{21} The existence of carbene radicals has been further supported by their reactivity. For example, de Bruin and coworkers reported the Co\textsuperscript{II}-porphyrin catalyzed cyclopropanation of electron-deficient olefins. The reaction between this cobalt catalyst with diazoesters resulted in the transient formation of a cobalt-carbene complex in which the multiply-bonded ligand was best described as a one-electron, reduced Fischer-type carbene. The presence of a ligand-centered radical gave rise to its unique reactivity with electron-deficient substrates. Most cyclopropanation reactions proceed \textit{via} traditional, electrophilic Fischer-carbene complexes, which react poorly with electron-deficient olefins.\textsuperscript{22}

Evidence for the existence of these carbene radicals comes not only from their reactivity with olefins, but also from X-ray crystallographic studies. Reaction of a Co\textsuperscript{II} porphyrin complex with ethyl styryldiazoacetate resulted in the synthesis of a Co\textsuperscript{III} carbene radical, where the radical resided on the terminal, gamma carbon. This species subsequently dimerized \textit{via} C–C coupling (Scheme 1.7).\textsuperscript{23}

\begin{itemize}
\end{itemize}
More recently, Groysman and co-workers have reported the isolation and structural characterization of a high-valent cobalt carbene complex. Reaction between a cobalt bis-alkoxide (OR = OC\textsubscript{6}Bu\textsubscript{2}Ph) starting material and diphenyldiazomethane (N\textsubscript{2}CPh\textsubscript{2}) yielded the first crystallographically characterized example of a cobalt carbene complex in a weak-field ligand environment. Solution magnetic measurements, EPR spectroscopy, and computations best describe this species as a high-valent Co\textsuperscript{IV} complex bound to a terminal carbene ligand containing some non-negligible amount of radical character.\textsuperscript{24}

Given the unique reactivity attributed to carbene radical species, we sought to target their synthesis and isolation so that we may form a better understanding of how their electronic structure dictates reactivity. As previously discussed, the dipyrrin ligand employed has been successful in isolating iron nitrenoid radical species.\textsuperscript{6} We wanted to investigate if this ligand platform could also support the isolation of other types of ligand radicals. In particular, we were

interested in targeting complexes comprised of iron and other first-row transition metals. If metal compounds are to impact industrial level organic syntheses, the catalysts must be cheap, synthetically accessible, and selective. The use of iron and other earth abundant transition metals would significantly reduce the costs associated with the production of these types of catalysts.

1.2.4. Iron Carbene Complexes

There are several examples of iron carbene complexes, most of which are low-spin diamagnetic species (Figure 1.5). The reactivity of these complexes was generally limited to cyclopropanation. There are, however, two examples of open-shell compounds reported by the Holland and Chirik groups. Using a variety of spectroscopic methods, the example from the Chirik Group (Figure 1.5 (h)) was best described as an open-shell FeII complex anti-ferromagnetically coupled to both diphenyl carbene and bis(amino)pyridine ligand-centered radicals. This particular example, however, displayed minimal reactivity, limited to group transfer of the carbene fragment into carbon monoxide and aryl azides. We were, therefore, interested in targeting open-shell iron carbene complexes with enhanced reactivity that could potentially be used for C–H functionalization chemistry.


Figure 1.5. Previous examples of isolated and crystallographically characterized iron carbene complexes.²⁵,²⁶,²⁷
Deng and co-workers have reported a reactive, open-shell “masked” iron alkylidene, which reacted with olefins to yield cyclopropanated products (Scheme 1.8). Reaction between \((p\text{-tolyl})\text{diazomethane}\) with the (amido-phosphine-amido)Fe\textsuperscript{II} starting material furnished an open-shell iron complex \((S = 2)\) bound to a phosphorus ylide ligand. While there was no direct observation of an iron carbene intermediate, the resulting reactivity from this ylide complex suggested that an iron carbene radical species may have been generated.\(^{28}\)

**1.3 Studying the Relationship Between Electronic Structure and Reactivity for Iron Dipyrrin Complexes**

The electronic structure similarities between \((^{\text{Ar}}\text{L})\text{FeCl}(\text{N}(\text{C}_6\text{H}_4-\text{p}^3\text{Bu}))\)^\textsuperscript{6} and the reactive intermediate (compound I) in Cytochrome P450\(^{7}\) highlight the significance of an open-shell electronic configuration in promoting hydrogen atom abstraction and radical recombination as a means of performing C–H functionalization. We sought to target the synthesis of other types of open-shell metal complexes containing ligand radicals, specifically iron diazoalkane and carbene species. In addition to isolating and characterizing these complexes, we were also interested in studying their resulting reactivity.

Before we can study the electronic structure and reactivity of open-shell iron carbene complexes, we must first develop an understanding of the behavior of their reduced and protonated derivatives. **Chapter 2** describes the synthesis and electronic structure of iron(II) dipyrrin mono-alkyl species. These complexes are best described as high-spin ($S = 2$) though display perturbed isomer shift values in their $^{57}$Fe Mössbauer spectra. Multiple synthetic attempts towards an iron di-alkyl species were also explored. We were not able to isolate an open-shell iron di-alkyl species. Instead, we observe that the transiently generated four-coordinate Fe$^{III}$ species containing alkyl ligands decomposed \textit{via} homolytic cleavage of an Fe–C bond with expulsion of alkyl radicals (Scheme 1.9).
With a firm understanding of the behavior of our iron dipyrrin complexes containing carbon-based ligands, we sought to explore the ability of these complexes to promote dinitrogen extrusion from diazoalkanes as a route towards carbene formation. In particular, we were interested in understanding how specific coordination modes and electronic structures were necessary for dinitrogen expulsion. Chapter 3 describes the synthesis of a variety of diazoalkane compounds and their resulting reactivity with several different dipyrrin iron starting materials. Several adducts were isolated in which the diazoalkane ligand coordinates the metal center terminally ($^{\text{Ar}L}$)Fe(N$_2$CPh$_2$), side-on ($^{\text{Ar}L}$)Fe(N$_2$CHAR), or in a chelated manner ($^{\text{tr}L}$)Fe(CH$_3$OC$_6$H$_4$CN$_2$CO$_2$CH$_3$) (Figure 1.6) ($^{\text{Ar}L}$ = 1,9-(2,4,6-Ph$_3$C$_6$H$_2$)$_2$-5-mesityldipyrromethene; $^{\text{tr}L}$ = 1,9-(C$_6$H$_5$)$_3$-5-mesityldipyrromethene). Regardless of the coordination mode, the diazo fragments in each compound are reduced by one electron and are best described as radical anions anti-ferromagnetically coupled to an Fe$^{\text{II}}$ center. X-ray crystallography, EPR spectroscopy, DFT calculations, and reactivity trends support the existence of these diazoalkane ligand-centered radicals. Anti-ferromagnetic coupling to the high-spin ferric center stabilizes electron transfer from the metal center to the diazoalkane ligands upon binding.
By a combination of increasing the steric bulk of the diazoalkane precursor and decreasing the steric bulk around the metal center, the reaction between (tBu)LFeCl(Et₂O) and N₂CPh₂ furnished the respective carbene complex, (tBu)LFeCl(CPh₂) (tBuL = 1,9-di-tert-butyl-5-(2,6-dichlorophenyl)-dipyrromethene), as described in Chapter 4. Using a variety of spectroscopic and computational methods, this species is best described as an intermediate FeII/FeIII with some small amount of radical character on the carbene ligand. This species performed reactivity consistent with that of a singlet-carbene, including cycloproponation. Reduction of (tBu)LFeCl(CPh₂) with KC₈ resulted in the formation of a highly reactive three-coordinate carbene complex, (tBu)LFe(CPh₂). The solvent-adducts of this reduced complex, (tBu)LFe(CPh₂)(pyr) and (tBu)LFe(CPh₂)(Et₂O), were amenable for X-ray crystallography, DFT calculations, ⁵⁷Fe Mössbauer spectroscopy, electron paramagnetic resonance, and X-ray absorption spectroscopies. These reduced species are best described as high-spin FeII complexes anti-ferromagnetically coupled to a carbene ligand radical. These species performed hydrogen-atom abstraction from the O–H bond of hydroxyl-2-azaadamantane (Figure 1.7).
Figure 1.8 Reduction of (pyrL)CoCl, followed by addition of N2CPh2 furnishes (pyrL**)Co(pyr).

We sought to extend the use of the dipyrrin ligand platform to attempt to isolate other first-row transition metal compounds containing metal-carbon multiple bonds. As discussed in Chapter 5, deprotonation with LiN(Si(CH3)3)2 followed by metallation with CoCl2 of a pyridine-substituted dipyrrin ligand platform (pyrL) (pyrL = 1,9-(C6H4N)2-5-(C6F5)dipyrromethene) furnished the respective five-coordinate CoII complex, (pyrL)CoCl. Reduction of (pyrL)CoCl with KC8 in the presence of excess pyridine provided the one-electron reduced (pyrL)Co(pyr). Reaction between (pyrL)CoCl and ArCHN2 (Ar = (2,4,6-triphenyl)phenyl) resulted in a highly reactive compound, which rapidly decomposed via multiple carbene insertions into the dipyrrin ligand. Similar results were observed in the reaction between (pyrL)Co(pyr) and N2CPh2, though the diphenyl-carbene functionalized the dipyrrin ligand in a distinct manner, presumably due to differences in the steric of the diazoalkane precursor (Figure 1.8). One possible mechanism that can be used to describe the observed insertion reactivity is via cobalt-mediated dinitrogen extrusion from the diazoalkane precursor to form a high-valent cobalt carbene complex. This transiently generated cobalt compound then undergoes carbene transfer into the dipyrrin ligand, poising it to react with another diazoalkane equivalent.
Given the ability of our open-shell iron dipyrrin complexes to promote electron transfer to coordinated diazoalkane and carbene ligands, we sought to further explore how the presence of these ligand centered radicals influences reactivity. As discussed in Chapter 6, we explored the catalytic reactivity of \((^{tBu}L)FeCl(Et_2O)\) with a variety of long-chain \(\alpha\)-diazo-\(\beta\)-ketoesters compounds. Instead of forming new C–C bonds via singlet carbene insertion analogous to \([Rh_2]\) catalysis,\(^{20}\) we alternatively made a variety of substituted tetrahydrofurans via C–O bond formation (Scheme 1.10). While the mechanism is not fully understood, we believe that the reactive intermediate may be a radical chelate where two oxygen atoms from the diazoalkane substrate coordinate to the iron center.

Scheme 1.10. Reactivity of \((^{tBu}L)FeCl(Et_2O)\) with \(\alpha\)-diazo-\(\beta\)-ketoesters compounds.
Chapter 2

Electronic Structure and Reactivity of High-Spin Iron Dipyrrin Alkyl Complexes

2.1. Introduction

Organometallic alkyl complexes serve as intermediates in a variety of transition metal catalyzed transformations, including hydrogenation, cross-coupling, hydroformylation, and olefin polymerization.\(^1\) Wilkinson and Piper reported the first example of an iron alkyl complex in 1956.\(^2\) Since then, many synthetic routes towards the preparation of iron alkyl complexes spanning a range of ligands, geometries, and oxidation and spin states have been reported.\(^3\) Iron alkyl complexes serve as intermediates in several different C–C bond forming reactions. For example, in the 1990s Brookhart and Bennet showed that bis(imino)pyridine Fe\(^{II}\) halide complexes could catalyze the polymerization of ethylene in the presence of methylaluminoxane.\(^4\) Chirik and others further went on to demonstrate that open-shell iron-alkyl complexes were catalytically competent intermediates for this ethylene oligomerization reactivity.\(^5\)

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In the 1970s, Kochi and co-workers reported the ability of simple iron salts to catalyze the coupling of Grignard reagents with organic halides to form new and stereoselective C–C bonds. In the years following this discovery, many synthetic protocols and methodologies were developed for iron-catalyzed cross-coupling reactions. More recently, Neidig and colleagues have contributed mechanistic insight into these types of reactions. Using a variety of spectroscopic techniques, they revealed that several different types of organoiron complexes could serve as active catalysts for iron-based C–C coupling reactions. In particular, an $S = 1$ Fe$^{II}$ bis-aryl species was shown to react with alkyl halides to transiently generate a highly reactive Fe$^{III}$ bis-aryl/halide species which decomposes via homolysis of the Fe-aryl bond. The organic C–C coupled products then combine via radical-recombination (Scheme 2.1).

As previously established within the Betley Group, the use of a sterically-hindered

![Scheme 2.1 Proposed mechanism for Fe-catalyzed Kumada cross coupling](image)
dipyrromethene ligand with two flanking (1,3,5-triphenyl)phenyl units led to the isolation of low-coordinate, high-spin iron complexes featuring highly reactive metal-ligand multiple bonds. We were interested in extending the use of this ligand platform to synthesize other types of reactive-iron containing species, including those with alkyl ligands. In this chapter, we describe the synthesis of high-spin, ferrous alkyl complexes and our attempts to isolate Fe\textsuperscript{III} alkyl complexes that could serve as precursors for an iron-alkylidene.

2.2. Synthesis and Electronic Structure of Iron Dipyrrin Alkyl Complexes

Stirring a just-thawed benzene solution containing (\(^{\text{ArL}}\)FeCl (1) (\(^{\text{ArL}} = 1,9-(2,4,6-\text{Ph}_3\text{C}_6\text{H}_2)_2\)-5-mesityldipyrromethene), synthesized according to established procedures,\textsuperscript{10} with either LiCH\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3}, Mg(CH\textsubscript{2}Ph)\textsubscript{2}, or LiCH\textsubscript{3} at room temperature for one hour resulted in complete consumption of the starting material and generation of new species with uniquely shifted paramagnetic \(^1\text{H}\) NMR spectra. Each reaction mixture was filtered through Celite to remove LiCl or MgCl\textsubscript{2} and the benzene lyophilized to give red-pink solids as the corresponding alkyl complexes: (\(^{\text{ArL}}\)Fe(CH\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3}) (2), (\(^{\text{ArL}}\)Fe(CH\textsubscript{2}Ph) (3), and (\(^{\text{ArL}}\)Fe(CH\textsubscript{3}) (4) (Scheme 2.2).

**Scheme 2.2.** Synthesis of (\(^{\text{ArL}}\)Fe-alkyl complexes.

The solid-state structures of 2 and 4 were verified using X-ray crystallography and feature Fe–C bond lengths of 2.12(2) Å and 2.037(10) Å, respectively (Figure 2.1). These Fe–C bond lengths are consistent with that of other open-shell iron alkyl complexes reported by the Holland and Chirik groups. Compound 4 proved to be significantly more difficult to crystallize due to its instability in solution. Within several hours at –35 °C, 4 decomposed into ((^3)L)Fe(OH))2, presumably via reaction with trace water present in solvents.13


Figure 2.1. Solid-state molecular structures of $(^{\text{Ar}}L)\text{Fe}(\text{CH}_2\text{Si(CH}_3)_3)$ (2) (a) and $(^{\text{Ar}}L)\text{Fe}(\text{CH}_2\text{Ph})$ (3) (b) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, silicon = pink.

The $^{57}$Fe Mössbauer spectra for these alkyl complexes displayed similar isomer shift and quadrupole splitting values (2: $\delta = 0.42$ mm/sec, $|\Delta E_Q| = 1.18$ mm/sec. 3: $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 0.98$ mm/sec. 4: $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 1.27$ mm/sec) (Figure 2.2). The quadrupole splitting values are consistent with that of a low-coordinate iron complex. The isomer shift values, however, are much lower than what would be expected for that of high-spin ($S = 2$) Fe$^{II}$ complexes. For example, 1 (Fe$^{II}$; $S = 2$) has an isomer shift value of 0.68 mm/sec. The measured isomer shift values for 2, 3, and 4, however, are consistent with those of other high-spin Fe$^{II}$ alkyl complexes synthesized by the Holland and Chirik groups. Holland and colleagues reported a three-coordinate Fe$^{II}$ compound supported by a $\beta$-diketiminate ligand with a terminally-bound methyl group that displayed an isomer shift value of 0.48 mm/sec. Evans
method\textsuperscript{14} confirmed the spin state \((S = 2)\) for this iron-methyl complex. The low isomer shift values observed for \(S = 2\) Fe\textsuperscript{II} alkyl complexes can be attributed to alkyl ligands contributing to a greater electron density at iron, compared to other sigma-donating ligands.\textsuperscript{15}

\textbf{Figure 2.2.} Zero-field \(^{57}\text{Fe}\) Mössbauer spectrum of \((^\text{Ar}L)\text{Fe(CH\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3}})\text{ (2) (a),} (^\text{Ar}L)\text{Fe(CH\textsubscript{2}Ph) (3) (b), and} (^\text{Ar}L)\text{Fe(CH\textsubscript{3}) (4) (c).} \text{ Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature:} (2): \(\delta = 0.42\ \text{mm/sec,} |\Delta E_Q| = 1.18\ \text{mm/sec.} (3): \delta = 0.46\ \text{mm/sec,} |\Delta E_Q| = 0.98\ \text{mm/sec.} (4): \delta = 0.46\ \text{mm/sec,} |\Delta E_Q| = 1.27\ \text{mm/sec).}

To verify the spin states for these dipyrrin Fe\textsuperscript{II} mono-alkyl species, the room-temperature solution magnetic moment was measured by using the method of Evans.\textsuperscript{14} For 3, the magnetic moment was determined to be 4.5(9) \(\mu_B\), consistent with an \(S = 2\), Fe\textsuperscript{II} formulation.

The electronic structures of 2 and 3 were further probed using DFT calculations. An unrestricted, single point calculation at the B3LYP level on the crystallographic coordinates for both 2 and 3 supports the assignment of these species as high-spin \((S = 2)\) Fe\textsuperscript{II} complexes (Figures 2.3 and 2.4). The calculated \(^{57}\text{Fe}\) Mössbauer parameters are in good agreement with the experimental data.


Figure 2.3. Molecular orbital diagram for ($^{14}$L)Fe(CH$_3$Si(CH$_3$)$_3$)$_2$ (2) (isovalue = 0.05), derived from the quintet solution. Quasi-restricted orbitals depicted. $^{57}$Fe Mössbauer parameters calculated via DFT: $\delta = 0.57$ mm/sec; $|\Delta E_Q| = 0.78$ mm/sec.
Figure 2.4. Molecular orbital diagram for ($^4$L)Fe(CH$_2$Ph) (3) (isovalue = 0.05), derived from the quintet solution. Quasi-restricted orbitals depicted. $^{57}$Fe Mössbauer parameters calculated via DFT: $\delta = 0.55$ mm/sec; $|\Delta E_Q| = 0.57$ mm/sec.

2.3. Attempts to Isolate a Four-Coordinate Fe-Alkyl Species

With the three-coordinate iron alkyl complexes in hand, we sought to determine if we could generate a ferric organometallic complex. Mindiola and coworkers had established that early transition metal alkyl complexes could be converted to alkylidene and alkylidyne species...
by oxidation and subsequent deprotonation.\textsuperscript{16} Thus, we attempted a variety of synthetic routes aimed at targeting an oxidized, four-coordinate iron dipyrrin complex containing an alkyl ligand. As had been previously described by our group, the addition of excess \(^{n}\text{Bu}_4\text{NCI} \) to \((^{\text{ArL}}\text{FeCl})\) (1) furnished \([^{\text{ArL}}\text{FeCl}_2][^{n}\text{Bu}_4\text{N}]\) (5), which could be oxidized to the ferric species \((^{\text{ArL}}\text{FeCl}_2\) (6) upon reaction with \([\text{Cp}_2\text{Fe}][\text{PF}_6]\).\textsuperscript{17} The addition of a variety of alkylating agents (e.g., alkyl lithium or dialkyl magnesium reagents) with either of the ferrous (5) or ferric dichloride (6) starting materials in thawing solutions of THF led to the near quantitative isolation of the respective three-coordinate Fe\textsuperscript{II} alkyl complexes (Scheme 2.3). The results of these reactions were confirmed by \(^1\text{H} \) NMR spectroscopy. In the case where we perform the reactions starting with ferrous dichloride 5, presumably the first alkyl equivalent metathesized, followed by loss of \(^{n}\text{Bu}_4\text{NCI}.\) To rule out the possibility that an equivalent of alkylating agent could deprotonate the ammonium cation, we changed the countercation in 5 for tetraphenylphosphonium, but obtained similar results. Using ferric dichloride 6 as a starting material, we presume that one equivalent of alkylating agent is consumed in reducing the ferric starting material. Using less reducing alkylating agents (i.e., Zn(CH\textsubscript{3})\textsubscript{2}, Al(CH\textsubscript{3})\textsubscript{3}), surprisingly, yielded similar results, potentially suggesting at an inherent instability of the ferric alkyl complexes.


Scheme 2.3. Results of the reactions between \([\text{(ArL)FeCl}_2][\text{"Bu}_4\text{N}^+]\) (5) or \((\text{ArL})\text{FeCl}_2\) (6) with alkyl lithium or alkyl magnesium reagents.

To address the potential instability of the alkyl ferric species, we explored the generation of four-coordinate, mixed alkyl/halide complexes. An attractive route to these types of complexes is via oxidative addition of alkyl halides. As previously synthesized within our group, reduction of 1 with KC\(_8\) resulted in the preparation of \((\text{ArL})\text{Fe}\) (7), an \(\text{Fe}^1\) species where the iron forms an \(\eta^6\)-interaction with one of the arene rings of the dipyrrin ligand.\(^{18}\) Addition of one equivalent of either methyl iodide or benzyl bromide to a frozen benzene solution of 7 resulted in the near-quantitative synthesis of the respective \((\text{ArL})\text{FeI}\) (8) and \((\text{ArL})\text{FeBr}\) (9) upon thawing. One potential mechanism that could account for the formation of \(\text{Fe}^\text{II}\) halide products would involve reductive cleavage of the \(R\text{−}X\) bond by \(\text{Fe}^1\), followed by dimerization of the carboradical byproducts (Scheme 2.4). Compounds 8 and 9 were assigned based on X-ray crystallography and \(^1\text{H}\) NMR spectroscopy, respectively.

Scheme 2.4. Results of the reaction between \((\text{ArL})\text{Fe}\) (7) with alkyl halide reagents.

The aforementioned evidence suggests that a four-coordinate Fe$^{\text{III}}$ complex containing an alkyl ligand may not be a stable, isolatable species on our ligand platform. To test our hypothesis, we examined oxidation of the iron-benzyl complex $3$ with a fluorinated benzyl bromide. Stirring a benzene solution of $3$ with one equivalent of 4-fluorobenzyl bromide at room temperature for one hour furnished the bromide adduct, ($^{\text{Ar}}L$)FeBr ($9$). The organic products from this reaction were a mixture of three bibenzyl derivatives (Scheme 2.5): 1,2-diphenylethane, 1-fluoro-4-phenylethylbenzene, and 1,2-bis(4-fluorophenyl)ethane, as confirmed by $^1$H and $^{19}$F NMR spectroscopy.$^{19}$ We propose that an Fe$^{\text{III}}$ halide/alkyl complex was generated, followed by homolytic cleavage of the iron-benzyl bond, which recombined to form the organic products, similar to what is observed in iron-catalyzed Kumada cross-coupling reactions.$^{20}$ We, therefore, conclude that an Fe$^{\text{III}}$ dialkyl complex on our ligand platform is not stable.


**Scheme 2.5.** Results of the reaction between \((^{3}Ar)\Fe(CH_2Ph)\) (3) with 4-fluorobenzyl bromide.

\[
\begin{align*}
\text{(3)} & \xrightarrow{\text{Br-PhF, C_6H_6, 1 h RT}} \text{(9)} + \\
\text{Br-PhF} & \xrightarrow{\text{C_6H_6, 1 h RT}} \\
\end{align*}
\]

2.4 Conclusions

In this work, we were able to demonstrate the ability of the dipyrrin ligand to support the isolation of open-shell iron complexes containing alkyl ligands. While the isomer shift values measured in the \(^{57}\Fe\) Mössbauer spectra were unusual, subsequent computations and magnetic susceptibility measurements supported the spin-state assignment of these alkyl complexes as high-spin \((S = 2)\). Despite numerous efforts to isolate a more oxidized iron alkyl complex, we observed that transiently generated \(\text{Fe}^{\text{III}}\) dipyrrin alkyl complexes decompose rapidly via expulsion of \(\text{R}\). Subsequent efforts towards the generation of an iron alkylidene will focus on oxidative group transfer from ylide or diazoalkane precursors.
2.5. Experimental

2.5.1 General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported.\(^\text{10}\) \((\text{ArL})\text{FeCl}, \)(\(\text{ArL}\))\(_\text{Fe}, \)(\(\text{ArL}\))\(_\text{FeCl_2}\)[\(\text{nBu}_4\text{N}\)], \(^\text{17}\) and \((\text{ArL})\text{FeCl_2}\)\(^\text{17}\) were synthesized according to previous methods. All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, dichloromethane, hexanes, pentane, pyridine, toluene, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-\(d\) was purchased from Cambridge Isotope Labs and used as received. Benzene-\(d_6\) was purchased from Cambridge Isotope Labs and was degassed and stored over 4 Å molecular sieves prior to use. 4-Fluorobenzyl bromide, LiCH\(_2\)Si(CH\(_3\))\(_3\), and LiCH\(_3\) were purchased from Aldrich. Mg(CH\(_2\)Ph)\(_2\)(thf)\(_2\) was synthesized according to literature methods.\(^\text{21}\) Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 µ (AIC, Framingham, MA) was used as received.

2.5.2 Characterization and Physical Measurements

\(^1\text{H}\) spectra were recorded on Varian Unity/Inova 400, 500, or 600 MHz- spectrometers. \(^1\text{H}\) NMR chemical shifts are reported relative to SiMe\(_4\) using the chemical shift of residual solvent peaks as reference. \(^19\text{F}\) NMR chemical shifts are reported to an external standard of trifluorotoluene. Zero-field \(^{57}\text{Fe}\) Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN) at 90 K. Isomer shifts are quoted relative to Fe foil at 21. Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-González, D.; Parkin, A.; Parsons, S. Chem. Eur. J. 2003, 9, 4820-4828.
room temperature. Data was analyzed and simulated with Igor Pro 6 software (WaveMetrics, Portland, OR) using Lorentzian fitting functions. Samples were prepared by suspending 25-50 mg of compound in Paratone oil and immobilizing by rapid freezing in liquid nitrogen. For compounds that decomposed in the presence of Paratone oil, samples were measured as frozen solutions in benzene.

### 2.5.3 Synthesis

\((\text{ArL})\text{Fe(CH}_2\text{Si(CH}_3\text{)})_3 \) (2): A just-thawed benzene solution (2 mL) containing \((\text{ArL})\text{FeCl} \) (80.0 mg, 0.083 mmol) was added to a frozen benzene solution (2 mL) containing \(\text{LiCH}_2\text{Si(CH}_3\text{)}_3 \) (9.4 mg, 0.10 mmol). The reaction mixture was warmed to room temperature and stirred for a total of one hour before being filtered through a pad of celite. The solvent was lyophilized to yield a red-pink powder (75.8 mg, 90%). Crystals suitable for X-ray diffraction were grown from a solution of concentrated \(\text{Et}_2\text{O} \) at \(-35^\circ\text{C}\).\(^{11}\) H NMR (600 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) (ppm) 70.14 (s), 52.72 (s), 24.05 (s), 19.55 (s), 11.66 (s), 10.48 (s), 10.25 (s), 9.40 (s), 7.73 (s), 7.57 (s), 6.82 (s), 6.29 (s), 5.82 (s), 2.23 (s), \(-11.04\) (s), \(-16.63\) (s), \(-34.67\) (s). Zero-field \(^{57}\text{Fe Mössbauer}\) (90K) \(\delta = 0.42\) mm/s, \(|\Delta E_Q| = 1.18\) mm/s.
Figure 2.5. $^1$H NMR spectrum for ($^\text{Ar}$L)Fe(CH$_2$Si(CH$_3$)$_3$) (2) collected in C$_6$D$_6$. 

![H NMR spectrum](image)
Figure 2.6. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{\text{Al}}$L)Fe(CH$_2$Si(CH$_3$)$_3$) (2). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: $\delta = 0.42$ mm/sec, $|\Delta E_Q| = 1.18$ mm/sec. Parameters calculated via single point DFT: $\delta = 0.57$ mm/sec, $|\Delta E_Q| = 0.78$ mm/sec.
Figure 2.7. Solid-state molecular structure for \(^{13}L\)Fe(CH\(_2\)Si(CH\(_3\))\(_3\) \((2)\) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, silicon = pink.
(\textsuperscript{ArL})\text{Fe(CH}_{2}\text{Ph}) (3): A just-thawed benzene solution (2 mL) containing (\textsuperscript{ArL})\text{FeCl} (100.0 mg, 0.10 mmol) was added to a frozen benzene solution (2 mL) containing Mg(CH\textsubscript{2}Ph\textsubscript{2}) (10.8 mg, 0.05 mmol). The reaction mixture was stirred at room temperature for one hour, filtered through a pad of celite, and the solvent lyophilized to give a red-pink powder (83.0 mg, 42\%). Crystals suitable for X-ray diffraction were grown from a 1:3 mixture of toluene:hexanes at \(-35^\circ\text{C}\). \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) (ppm) 74.89 (s), 58.01 (s), 33.33 (s), 25.44 (s), 20.50 (s), 12.06 (s), 10.90 (s), 9.57 (s), 8.85 (s), 3.25 (s), 2.10 (s), 1.08 (s), \(-13.93\) (s), \(-20.63\) (s), \(-39.18\) (s). Zero-field \textsuperscript{57}Fe Mössbauer (90K) \(\delta = 0.46\) mm/s, \(|\Delta E_Q| = 0.98\) mm/s.
Figure 2.8. $^1$H NMR spectrum for ($^\text{Ar}$L)Fe(CH$_2$Ph) (3) collected in C$_6$D$_6$. 
Figure 2.9. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{35}$L)Fe(CH$_2$Ph) (3). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 0.98$ mm/sec. Parameters calculated via single point DFT: $\delta = 0.55$ mm/sec, $|\Delta E_Q| = 0.57$ mm/sec.
Figure 2.10. Solid-state molecular structure for (\(^{\Lambda}\)L)Fe(CH\(_2\)Ph) (3) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray.
$^{(\text{ArL})\text{Fe} (\text{CH}_3)}$ (4): A just-thawed benzene solution (2 mL) containing $^{(\text{ArL})\text{FeCl}}$ (50.0 mg, 0.052 mmol) was added to a frozen benzene solution (2 mL) containing solid LiCH$_3$ (23.8 mg, 0.052 mmol) and stirred for one hour. The mixture was filtered through celite and the benzene lyophilized to give a pink-red powder (38.9 mg, 80%). $^1$H NMR (600 MHz, C$_6$D$_6$): $\delta$ (ppm) 75.69 (s), 56.86 (s), 27.79 (s), 21.36 (s), 14.09 (s), 12.26 (s), 11.29 (s), 10.41 (s), 9.57 (s), 2.06 (s), $-14.81$ (s), $-21.06$ (s), $-40.92$ (bs). Zero-field $^{57}$Fe Mössbauer (90K) $\delta = 0.46$ mm/s, $|\Delta E_0| = 1.27$ mm/s.
Figure 2.11. $^1$H NMR spectrum for ($^{\text{Ar}}$L)Fe(CH$_3$)$_2$ (4) collected in C$_6$D$_6$. 
Figure 2.12. Zero-field $^{57}$Fe Mössbauer spectrum of $(^1$H$)Fe(CH_3)_2$ (4). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 1.27$ mm/sec.
Attempts to isolate a four-coordinate Fe-alkyl species

Reactivity of [(^Ar)L]FeCl_2[^Bu_4N/Ph_4P] (5) and [(^Ar)L]FeCl_2 (6) with either alkyl lithium or dialkyl magnesium reagents. A just-thawed THF solution (2 mL) containing the desired alkyl lithium (1 eq.)/dialkyl magnesium (0.5 eq) was added dropwise to a frozen THF solution (2 mL) containing either 5 or 6 (1 eq.). Immediately upon warming to room temperature, the solvent was removed \textit{in vacuo}. The red residue was re-dissolved in C_6D_6 and characterized by ^1H NMR spectroscopy. Selected ^1H NMR and ^57Fe Mössbauer spectra are presented below.
For the reaction of 5 ("Bu₄N counterion) with 0.5 eq. of Mg(CH₃)₂, ¹H and ⁵⁷Fe Mössbauer spectroscopy data were in good agreement with the authentically prepared (ArL)Fe(CH₃) (4) (Figures 2.13 and 2.14).

Figure 2.13. ¹H NMR spectrum for (ArL)Fe(CH₃) (4) (black, bottom) compared to that of the reaction between [(ArL)FeCl₂]["Bu₄N] (5) and 0.5 eq. Mg(CH₃)₂ (red, top). NMRs taken in C₆D₆.
Figure 2.14. Zero-field $^{57}$Fe Mössbauer spectrum for the reaction between [($^{Ar}$L)FeCl$_2$]$^{n}$Bu$_4$N] (5) and 0.5 eq. Mg(CH$_3$)$_2$. Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 1.00$ mm/sec. $^{57}$Fe Mössbauer parameters for ($^{Ar}$L)Fe(CH$_3$) (3): $\delta = 0.46$ mm/sec, $|\Delta E_Q| = 1.27$ mm/sec.
For the reaction of 6 with 0.5 eq. of Mg(CH₃)₂, ¹H NMR spectroscopy data was in good agreement with the authentically prepared (Ar⁺L)Fe(CH₃) (4) (Figure 2.15).

**Figure 2.15.** ¹H NMR spectrum for (Ar⁺L)Fe(CH₃) (4) (black, bottom) compared to that of the reaction between (Ar⁺L)FeCl₂ (6) and 0.5 eq. Mg(CH₃)₂ (red, top). NMRs taken in C₆D₆.
For the reaction of 5 (Ph₄P counterion) with 0.5 eq. of Mg(CH₃)$_2$, $^1$H NMR spectroscopy data was in good agreement with the authentically prepared ($^{^6}$L)Fe(CH₃)$_2$ (4) (Figure 2.16).

**Figure 2.16.** $^1$H NMR spectrum for ($^{^6}$L)Fe(CH₃) (4) (black, bottom) compared to that of the reaction between [($^{^6}$L)FeCl$_2$][PPh$_4$] (5) and 0.5 eq. Mg(CH₃)$_2$ (red, top). NMRs taken in C$_6$D$_6$. 
Reactivity of ($^{\Delta}L$)$_2$Fe (7) with alkyl halide reagents. A just-thawed benzene solution (2 mL) containing the desired alkyl halide (1 eq.) was added dropwise to a frozen benzene solution (2 mL) containing 7 (1 eq.). Immediately upon warming to room temperature, the reaction mixture was characterized by $^1$H NMR spectroscopy. Selected $^1$H NMR spectroscopy data are presented below.
For the reaction of 7 with 1.0 eq. of CH\textsubscript{3}I, a new paramagnetic $^1$H spectrum was generated (Figure 2.17). $^1$H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ (ppm) 85.59 (s), 37.27 (s), 22.56 (s), 15.05 (s), 11.20 (s), 9.75 (2), 9.47 (s), 7.19 (s), 4.70 (s), 1.61 (s), 1.16 (s), 0.48 (s), −11.42 (s), –16.18 (s), −17.64 (s). The product of this reaction mixture was crystallized from a 1:3 mixture of toluene:pentane at −35 °C. The solid-state molecular structure for the product of this reaction mixture was (\textsuperscript{Ar}L)FeI (8) (Figure 2.18).

\hspace{1cm}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_17.png}
\caption{$^1$H NMR spectrum for the reaction of (\textsuperscript{Ar}L)Fe (7) with 1.0 eq. of CH\textsubscript{3}I (red, top) compared to that of (\textsuperscript{Ar}L)FeCl (1) (black, bottom). NMRs taken in C\textsubscript{6}D\textsubscript{6}.}
\end{figure}
Figure 2.18. Solid-state molecular structure for ($^4$L)FeI (8) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, iodine = green.
For the reaction of 7 with 1.0 eq. of benzyl bromide, a new paramagnetic $^1$H spectrum was observed (Figure 2.19). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ (ppm) 75.62 (s), 53.91 (s), 19.35 (s), 18.84 (s), 18.43 (s), 14.94 (s), 13.55 (s), 11.71 (s), 7.55 (s), 6.33 (s), -9.90 (s), -14.43 (s), -23.43 (s). The positions of the peaks in the $^1$H NMR spectrum were similar to that of (ArL)FeCl (Figure 2.19), suggesting that we were indeed making (ArL)FeBr (9).

![Figure 2.19](image-url)  
**Figure 2.19.** $^1$H NMR spectrum for the reaction of (ArL)Fe (7) with 1.0 eq. of benzyl bromide (red, top) compared to that of (ArL)FeCl (1) (black, bottom). NMRs taken in C$_6$D$_6$. 
Reactivity of \( ^\text{ArL} \)Fe(CH\(_2\)Ph) (3) with 1-(bromomethyl)-4-fluorobenzene. A benzene solution (2 mL) containing 4-fluorobenzyl bromide (0.22 mL, 0.011 mmol) was added to benzene solution containing \((^\text{ArL})\)Fe(CH\(_2\)Ph) (10.0 mg, 0.011 mmol) dropwise. The reaction mixture was allowed to stir at room temperature for one hour. Analysis and identity of the products were assessed using \(^1\)H and \(^{19}\)F NMR spectroscopy. For \((^\text{ArL})\)FeBr (9): \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\) (ppm) 71.12, 49.76, 24.60, 15.31, 14.85, 14.32, 13.79, 11.76, 11.19, 9.86, 6.10, 5.78, 3.89, 2.25, 1.19, –12.01, –16.54, –25.92. For 1-fluoro-4-phenylethylbenzene: \(^{19}\)F NMR (470 MHz, C\(_6\)D\(_6\)) \(\delta\) (ppm) –117.27. For 1,2-bis(4-fluorophenyl)ethane: \(^{19}\)F NMR (470 MHz, C\(_6\)D\(_6\)) \(\delta\) (ppm) –117.04.
Figure 2.20. $^1$H NMR spectrum for ($^{Ar}$L)Fe(Br) (9) (black, bottom) compared to that of ($^{Ar}$L)FeCl (1) (top, red). NMRs collected in C$_6$D$_6$. 
Figure 2.21. $^{19}$F NMR spectrum for the reaction mixture of $(^\text{Ar}L)\text{Fe}(\text{CH}_2\text{Ph})$ (3) with 4-fluorobenzyl bromide. The peak at $-113.13$ corresponds to unreacted 4-fluorobenzyl bromide.
2.5.4. X-Ray Diffraction Techniques

Structures of 2, 3, and 8 were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone oil. Structures were collected at 100 K. Data was collected as a series of ϕ and/or ω scans.

Data was integrated using SAINT\textsuperscript{22} and scaled with either a numerical or multi-scan absorption correction using SADABS.\textsuperscript{22} The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELX-2014 and refined against $F^2$ on all data by full matrix least squares with SHELX-2014.\textsuperscript{23} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

$(\text{ArL})\text{Fe(CH}_2\text{Si(CH}_3\text{)}_3)$ (2): The structure was solved in the monoclinic space group C2/c. The intensity of the data was weak because the crystal is micro-sized and poorly diffracting. The dipyrrin ligand exhibited disorder and was modeled using similarity restraints and constraints.

$(\text{ArL})\text{Fe(CH}_2\text{Ph})$ (3): The structure was solved in the triclinic space group P-1. Due to high disorder of a toluene molecule, an acceptable model could not be refined. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically...
significant features of the structure.

(\textsuperscript{Ar\textprime}L)FeI (8): The structure was solved in the monoclinic space group P2\textsubscript{1}/c. The crystal is a non-meroherdral twin, but we have refined the structure by using reflections in hkl4 format. The dipyrrin ligand exhibited disorder and was modeled using similarity restraints and constraints.
Table 2.1. X-ray diffraction experimental details.\(^a\)

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</tbody>
</table>

\(^a\) \(R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|, wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}\)
### 2.5.5. Computational Methods

Computations were carried out utilizing the ORCA 4.0\textsuperscript{24} program package. The B3LYP\textsuperscript{25} functional was used with the def2-TZVP (Fe, N, Cl) and def2-SV(P) (C, H) basis sets.\textsuperscript{26} For single point calculations and property calculations the def2-TZVP/J (Fe, N, Cl) and def2-SVP/J (C, H) auxiliary basis sets\textsuperscript{27} were employed to utilize the RIJCOSX\textsuperscript{28} approximation for accelerating the calculation. For the calculation of the Mössbauer parameters the basis set at Fe was expanded to the CP(PPP) basis.\textsuperscript{29} All geometries were taken from X-ray structures.

Mössbauer parameters were obtained from additional single-point calculations, following the method described by F. Neese.\textsuperscript{30} Quadrupole splitting values ($\Delta E_Q$) were calculated from electric field gradient (Equation 1):

$$\Delta E_Q = \frac{1}{2} eQ \sqrt{1 + \frac{1}{3} \eta^2}$$

**Equation 2.1.** Calculation of quadrupole splitting.

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The nuclear quadrupole moment $Q(^{57}\text{Fe})$ was taken to be 0.16 barn.\textsuperscript{30} The principal tensor components of the EFG are $V_{xx}$, $V_{yy}$, and $V_{zz}$, from which the symmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be defined chosen such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

Isomer shift values ($\delta$) were calculated from the electron density at the nucleus $\rho_0$, using a linear equation ($\delta = a(\rho_0 - C) + b$, with constraints determined by fitting the calculated densities to experimental isomer shifts for a series of iron dipyrrromethane complexes synthesized in the lab. For this series of compounds, the parameters were determined to be $C = 11580$ au\textsuperscript{3}, $a = -0.355$ au\textsuperscript{3}mms\textsuperscript{-1}, and $b = 1.418$ mm. The basis sets and functional described above were used for all structures. X-ray coordinates were used, and spin-states were assigned based on experimental $^{57}\text{Fe}$ Mössbauer data.
Chapter 3

Diazoalkane Ligand Radicals Supported by High-Spin Iron Complexes

3.1 Introduction

Transition metal complexes containing diazoalkane ligands display a wide range of coordination modes, electronic structures, and reactivity profiles.\(^1\) Typically, concomitant loss of dinitrogen upon ligation of the diazoalkane motif to a metal complex affords the corresponding organometallic carbene complex. These metal-supported carbene species may subsequently transfer the multiply bonded substituent to organic substrates to perform catalytic or stoichiometric transformations such as olefin metathesis, cyclopropanation, and C–H functionalization.\(^2\) The coordination mode of the diazoalkane moiety to the metal center influences the propensity to extrude N\(_2\). In particular, certain binding geometries disfavor N\(_2\) loss and carbene formation.\(^3,4\)

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Diazooalkane ligands can be redox active and can bind transition metals as neutral ligands (e.g., $M^n(N_2CR_2)$), singly-reduced (e.g., $M^{n+1}(N_2CR_2)$), or doubly reduced adducts (e.g., $M^{n+2}(N_2CR_2)^2$). Diazooalkanes may bind the metal end-on via the terminal nitrogen (Figure 3.1, I–IV) or side-on via the N=N or N=C $\pi$ bond (Figure 3.1, V–VI). For example, neutral diazoalkanes typically bind linearly with M–N–N and N–N–C angles equal to 180° and act as two electron donors to the transition metal (Figure 3.1, I). Singly-reduced diazoalkane ligands feature unique bond metrics with M–N–N and N–N–C bond angles intermediate between linear and trigonal planar (Figure 3.1, II). Upon two-electron reduction, diazoalkanes feature short M–N bond lengths (1.6–1.8 Å) consistent with metal-imido ligation when terminally ligated, elongated N–N bond lengths, and $\angle$N–N–C or M–N–N bond angles equal to 120° (Figure 3.1, III–VI).

Figure 3.1 Binding motifs of neutral (I), one electron reduced (II), and two electron reduced (III, IV, V) diazoalkane ligands.

One method used to promote the formation of reactive metal-ligand multiple bonds is through the use of weak-field ligands, which engenders high-spin electronic configurations.

resulting in population of metal-ligand anti-bonding molecular orbitals. Our group has shown how the electronic structure of high-spin imido and iminyl complexes affords both inter- and intramolecular C–H bond amination reactivity. We were interested in extending the use of these design principles to other types of metal-ligand interactions susceptible to metal-ligand multiple bond formation (e.g., M–carbene or diazoalkane adducts). Herein we investigate the electronic structure and binding modes of diazoalkane ligands with iron dipyrrin complexes. We examine how the metal-ligand geometries are impacted by the steric and electronic properties of both the metal center and the diazoalkane ligand. Three examples of dipyrrin-supported, high-spin iron aryl-diazo adducts featuring varying geometries are presented, noting differences in the resulting reactivity profiles despite maintaining similar electronic structures.

3.2 Results and Discussion

3.2.1 Synthesis and Metalation of a Triphenylmethyl Substituted Dipyrrin Ligand

The geometry and diazoalkane substituents have a significant impact on the diazoalkane adduct’s propensity to release dinitrogen. The substituents bound to the diazo-bearing carbon of the diazoalkane influence the properties and reactivity of the resulting adducts to transition metals. We, therefore, wanted to study how changing these substituents influences diazoalkane coordination, the diazoalkane redox state, and the resulting adduct reactivity. We were also particular interested in analyzing how changes in the steric profile of the dipyrrin metal complex impacts the resulting reactivity with the selected diazoalkane.

Our group has previously reported the synthesis and metalation of a sterically hindered (2,4,6-triphenyl)phenyl substituted dipyrrin scaffold \((\text{Ar}_L \text{H})\) \((\text{Ar}_L = 1,9-(2,4,6-\text{Ph}_3\text{C}_6\text{H}_2)_{3}-5\text{-mesityldipyrromethene})\).\(^5\) Metalation of the deprotonated ligand \((\text{Ar}_L\text{Li})\) with \(\text{FeCl}_2\) in refluxing toluene furnishes the three-coordinate \((\text{Ar}_L)\text{FeCl}\), which can be reduced with one equivalent of potassium graphite \((\text{KC}_8)\) to afford the monovalent synthon \((\text{Ar}_L)\text{Fe}\) \((1)\).\(^5,6\) We have recently made an additional sterically hindered dipyrrin ligand flanked by triphenylmethyl (trityl) substituents.\(^7\) Preparation of this trityl-supported ligand proceeds analogously to other sterically encumbered dipyrrin platforms.\(^5\) Condensation of 2-trityl-1\(H\)-pyrrole\(^8\) with mesitaldehyde dimethyl acetal\(^9\) afforded the corresponding dipyrromethane, which was followed by subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to yield the trityl-substituted dipyrrin ligand, \((\text{trt}_L)\text{H}\) \((\text{trt}_L = 1,9-(\text{C}_6\text{H}_3)_{3}-5\text{-mesityldipyrromethene})\) in 40% overall yield following purification. Metallation of \((\text{trt}_L)\text{H}\) proceeded via deprotonation in benzene with phenyl lithium \((\text{PhLi})\) to afford \((\text{trt}_L)\text{Li}\), followed by addition of \(\text{FeCl}_2\) in THF at room temperature to yield \((\text{trt}_L)\text{FeCl}\) \((2)\) (Scheme 3.1) in 52% yield.\(^7\)


\(^{7}\) Hennessy, E. T. and Betley, T. A. Unpublished results.


Scheme 3.1. Synthesis of (\textsuperscript{t}tL)H and (\textsuperscript{t}tL)FeCl (2).

The solid-state molecular structure of 2 revealed\textsuperscript{7} that the geometry about iron is pseudo-tetrahedral with the metal forming an $\eta^1$-interaction (Fe–C 2.426(8) Å) with one of the phenyl rings from the dipyrrin trityl substituent. The Fe–Cl (2.238(2) Å) bond is perpendicular to that of the dipyrrin ligand plane (N\textsubscript{dipyrrin}–Fe–Cl: 108.59(9)°, (Figure 3.2). This geometry about iron is distinct from that found in the analogous (\textsuperscript{A}rL)FeCl, which is trigonal planar with an Fe–Cl bond length of 2.154(2) Å.\textsuperscript{5} The differences in the coordination environment about the iron center for 2 and (\textsuperscript{A}rL)FeCl suggest that each complex may react with and bind diazoalkane substrates differently. The $^{57}$Fe Mössbauer parameters for 2 ($\delta = 0.91$ mm/sec; $|\Delta E_Q| = 2.3$ mm/sec) are consistent with a high-spin, low-coordinate Fe$^{II}$ species. These values are similar to those found for (\textsuperscript{A}rL)FeCl ($\delta = 0.68$ mm/sec; $|\Delta E_Q| = 0.68$ mm/sec) (Figure 3.2).\textsuperscript{5} The differences in the quadrupole splitting values for 2 and (\textsuperscript{A}rL)FeCl are attributed to differences in the coordination number and geometry about the iron center.
Compound 2 can be reduced by adding it as a frozen solution in THF to a frozen THF solution containing one equivalent of potassium graphite (KC₈), resulting in a rapid color change from bright red to maroon with precipitation of graphite and KCl. Filtering the reaction mixture through Celite, followed by evaporation of the solvent furnished (trtL)Fe(thf) (3) as a red-colored solid (Scheme 3.2). Analysis of the solid-state molecular structure of 3 revealed an η² interaction between the iron and one of the phenyl substituents of the ligand (Figure 3.3). The coordination mode about iron for 3 is distinct from that found in the analogous (ArL)Fe (1). For 1, the iron center forms an η⁶ interaction with one of the arene rings of the ligand, again suggesting that 1 and 3 may interact with substrates differently.
Scheme 3.2. Synthesis of ([L]Fe(thf)) (3).

While thf-adduct 3 displayed no resonances in the $^1$H NMR spectrum, the frozen toluene EPR spectrum at 77 K contained a rhombic signal ($g_{\text{eff}} = 2.23, 2.03, 1.98$) supportive of an $S = \frac{1}{2}$ spin state (Figure 3.3) (fit with EasySpin). The $S = \frac{1}{2}$ spin state was further corroborated by density functional theory (DFT) calculations. We performed unrestricted, single-point calculations using the crystallographic coordinates obtained for 3 with a doublet configuration. The calculated $^{57}\text{Fe}$ Mössbauer parameters ($\delta = 0.74 \text{ mm/sec}; |\Delta E_Q| = 1.01 \text{ mm/sec}$) match well with the experimental data ($\delta = 0.68 \text{ mm/sec}; |\Delta E_Q| = 0.73 \text{ mm/sec}$) (Figure 3.3). The assignment of 3 as a low-spin Fe$^I$ is analogous to that of our previously reported solvent-free, Fe$^I$ dipyrrin complex 1.\textsuperscript{6}

Figure 3.3. (a) Solid-state molecular structure for $^3$LFe(thf) (3) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red. (b) Zero-field $^{57}$Fe Mössbauer spectrum of $(^3L)$Fe(thf) (3). Isomer shift and quadrupole splitting values are reported relative to Fe foil at room temperature ($\delta = 0.68$ mm/sec, $|\Delta E_Q| = 0.73$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.74$ mm/sec, $|\Delta E_Q| = 1.01$ mm/sec. (c) Frozen toluene EPR spectrum of $(^3L)$Fe(thf) (3) (red line) at 77 K. The black line represents a fit using EasySpin$^{10}$ with $g = 2.23, 2.03, 1.98$ and $S = \frac{1}{2}$.

3.2.2 Synthesis and Characterization of Iron-Diazo Adducts

We began our investigation studying the reactivity of a stabilized, push-pull diazo compound that contains both electron-donating aryl and electron-withdrawing ester substituents. Push-pull diazoesters are easy to synthesize due to their stability and have been used as precursors to isolate highly reactive metal carbene complexes.$^{11}$ Addition of a thawing benzene solution containing 3 to a frozen benzene solution containing one equivalent of methyl $\alpha$-diazo-4-methoxyphenylacetate (CH$_3$OC$_6$H$_4$CN$_2$CO$_2$CH$_3$) (Scheme 3.3) resulted in a color change from deep red to orange-red. The reaction mixture was stirred at room temperature for 30 minutes, which furnished a new product, characterized by a unique paramagnetic $^1$H NMR spectrum and a

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single quadrupole doublet in the $^{57}$Fe Mössbauer spectrum ($\delta = 0.82$ mm/sec; $|\Delta E_Q| = 1.61$ mm/sec) (Figure 3.4). This isomer shift value is consistent with that of a high-spin Fe$^{II}$ complex.$^5$

**Scheme 3.3.** Synthesis of (L)$\text{Fe(}\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CO}_2\text{CH}_3\text{)}$ (4).

The product of this reaction mixture was crystalized from a 1:3 mixture of toluene:hexanes at –35°C. The solid-state molecule structure obtained the 1:1 adduct for (L)$\text{Fe(}\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CO}_2\text{CH}_3\text{)}$ (4), where the diazoester is chelated to the metal center in a bidentate manner (Fe–N$_{\text{diazo}}$, 1.854(1) Å; Fe–O$_{\text{diazo}}$, 1.905(3) Å; Figure 3.4). The N–N (1.219(5) Å), N–C (1.375(5) Å), and C–O (1.278(5) Å) bond lengths of the bound diazoalkane ligand are slightly elongated compared to those found in a similar unbound alpha-carbonyl diazoester (N–N: 1.1224(15) Å, N–C: 1.3229(16) Å, and C–O: 1.2104(16) Å).$^{12}$ The overall spin-state for 4 was ascertained by EPR spectroscopy, displaying a rhombic signal ($g_{\text{eff}} = 6.11, 1.62, 1.26$) in frozen toluene at 2.8 K, consistent with an $S = \frac{3}{2}$ spin state (Figure 3.4).

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Figure 3.4. (a) Solid-state molecular structure for (RtL)Fe(CH₃OC₆H₄CN₂CO₂CH₃) (4) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red. (b) Zero-field $^{57}$Fe Mössbauer spectrum of (RtL)Fe(CH₃OC₆H₄CN₂CO₂CH₃) (4). Isomer shift and quadrupole splitting values are reported relative to Fe foil at room temperature ($\delta = 0.82$ mm/sec, $|\Delta E_Q| = 1.61$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.88$ mm/sec, $|\Delta E_Q| = 1.67$ mm/sec. (c) Frozen toluene EPR spectrum of (RtL)Fe(CH₃OC₆H₄CN₂CO₂CH₃) (4) (red line) at 2.8 K. The minor signal at $g = 2$ corresponds to a trace organic radical impurity. The black line represents a fit using EasySpin$^{10}$ with $g = 2.19, 1.81, 1.79$ and $S = \frac{3}{2}$.

We sought to investigate the reactivity of diphenyldiazomethane (N₂CPh₂) as a relatively stabilized diazoalkane reagent, though more reactive than the diazoesters. As will be discussed in Chapter 4, reaction between (BuL)FeCl(Et₂O) ((BuL = 1,9-di-tert-butyl-5-(2,6-dichlorophenyl)-dipyrromethene)) with one equivalent of N₂CPh₂ furnished the respective carbene complex, (BuL)FeCl(CPh₂).$^{13}$ We were interested in investigating if increasing the steric bulk of the dipyrromethene ligand from tert-butyl to (2,4,6-triphenyl)phenyl would prevent carbene formation and lead to the isolation of a metal diazoalkane adduct. For example, Chirik and coworkers have reported that changing the substituents on a series of bis(imino)pyridine iron complexes from methyl/ethyl to isopropyl impacts the propensity of N₂ loss from N₂CPh₂ upon coordination to the metal center.$^{3}$

$^{13}$ Wrobel, A. T. and Betley, T. A. Manuscript in preparation.
Scheme 3.4. Synthesis of ($^{Ar}$L)Fe(N$_2$CPh$_2$) (5).

Addition of a thawing benzene solution containing 1 to a thawing benzene solution of a stoichiometric amount of N$_2$CPh$_2$ (Scheme 3.4) resulted in a rapid color change from dark purple to pink. After stirring for two hours at room temperature, this reaction cleanly generated a new product, which was crystallized from a 1:3 mixture of toluene:pentane at −35 °C. The solid-state molecular structure revealed a terminally-bound diazo adduct ($^{Ar}$L)Fe(N$_2$CPh$_2$) (5) (Figure 3.5), with an Fe–N$_{diazo}$ bond distance of 1.758(2) Å, well within the bond distances invoked for metal-ligand multiple bonding in related Fe$^{III}$ imido and iminyl complexes (Fe–N: 1.708(4)–1.768(2) Å).$^{5,6,14}$ The N–N and N–C bond lengths of the diazo ligand are 1.272(2) Å and 1.310(1) Å and the Fe–N–N and N–N–C bond angles are 161.7(3)°, and 133.72(12)°, respectively. The spin state for 5 was ascertained from the EPR spectrum (Figure 3.5), which displayed a rhombic signal (g$_{eff}$ = 5.45, 4.24, 1.99) in frozen toluene at 2.8 K, consistent with an overall S = $^{3/2}$ spin state (Figure 3.5). The isomer shift ($\delta$) and quadrupole splitting ($|\Delta E_{Ql}|$) values found in the $^{57}$Fe Mössbauer spectrum of 0.60 and 1.37 mm/sec, respectively, are indicative of a low-coordinate, high-spin Fe$^{II}$ (Figure 3.5).$^{5}$

Figure 3.5. (a) Solid-state molecular structure for \((^{\text{Ar}}L)\text{Fe(N}_2\text{CPh}_2\text{)}\) (5) with thermal ellipsoids at 50\% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray. (b) Zero-field \(^{57}\text{Fe}\) Mössbauer spectrum of \((^{\text{Ar}}L)\text{Fe(N}_2\text{CPh}_2\text{)}\) (5). Isomer shift and quadrupole splitting values are reported relative to Fe foil at room temperature \((\delta = 0.67 \text{ mm/sec}, |\Delta E_Q| = 1.44 \text{ mm/sec})\). Parameters calculated via single point DFT: \(\delta = 0.67 \text{ mm/sec}, |\Delta E_Q| = 1.24 \text{ mm/sec}\). (c) Frozen toluene EPR spectrum of \((^{\text{Ar}}L)\text{Fe(N}_2\text{CPh}_2\text{)}\) (5) (black line) at 2.8 K. The red line represents a fit using EasySpin\(^{10}\) with \(g = 2.30, 2.30, 1.99\) and \(S = 3/2\).

In addition to the disubstituted diazoester and stabilized diazoalkane molecules described, we were also interested in investigating the reactivity of highly reactive mono-substituted diazoalkanes of the form \(\text{N}_2\text{CHR}\). Alkyl- and aryl-substituted diazomethane compounds can be difficult to synthesize due to their high toxicity and low stability.\(^{15}\) To circumvent problems associated with diazoalkane purification and storage, several groups have developed continuous flow methods for the \textit{in situ} generation of unstabilized alkyl- and aryl-substituted diazomethane reagents. These transiently generated species can then be used immediately as carbene transfer reagents. Unfortunately, the diazoalkane molecules synthesized using this methodology are not isolable, therefore limiting their use in synthetic organometallic chemistry.\(^{16}\)


To isolate stable aryl-substituted diazomethane molecules, we chose an easily modifiable synthetic route that generates products requiring minimal purification to prevent decomposition during work-up (Scheme 3.5). Following analogous protocols\textsuperscript{15,17} the desired aromatic aldehyde was converted to the respective hydrazone via condensation with hydrazine monohydrate in refluxing ethanol. Oxidation of the colorless arylhydrazone intermediate with yellow mercury oxide in diethyl ether at room temperature resulted in a rapid color change to dark orange. Upon completion, as determined by TLC analysis, the reaction mixture was filtered through Celite and the desired aryldiazomethane product was recrystallized from a concentrated solution of diethyl ether at \(-35^\circ\text{C}\) (Scheme 3.5).

Following this procedure (Scheme 3.5), we have been able to synthesize and isolate a variety of aryl-substituted diazomethane compounds that are stable as solids and can be stored at \(-35^\circ\text{C}\) for up to several months. We note that while (3,5-di-tert-butylbenzylidene)- and (2,4,6-trimethyl-benzylidene)-diazomethane could be synthesized cleanly, decomposition within a few hours at \(-35^\circ\text{C}\) was observed in both solution and in the solid state.

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**Scheme 3.5.** Synthesis of mono-substituted diazoalkanes.

Addition of a just-thawed benzene solution containing (Λ')Fe (1) to a frozen solution containing one equivalent of ArCHN₂ (Ar = (2,4,6-triphenyl)phenyl)) (Scheme 3.6) resulted in a color change from dark purple to pink. A new paramagnetic \(^1\)H NMR spectrum with complete consumption of starting material was observed after 30 minutes. Single crystals suitable for X-ray diffraction were obtained from a 1:3 mixture of toluene:hexanes at −35°C. The solid-state molecular structure revealed the side-bound diazoalkane complex (Λ')Fe(ArCHN₂) (6) with Fe–N bond lengths of 1.921(2) Å and 1.839(2) Å (Figure 3.6). The shorter Fe–N bond length can be assigned as a Fe–N single bond and is consistent with the Fe–N bond lengths present in previously reported iron dipyrrin anilide complexes.\(^5\) The elongated Fe–N bond length found in 6, however, is more in line with that of a dative interaction and is similar to the Fe–N bond lengths found in reported iron dipyrrin aniline complexes.\(^5\)
Scheme 3.6. Synthesis of (LFe(N₂CHAr) (6).

The overall spin state for 6 was determined to be $S = \frac{3}{2}$ based on EPR spectroscopy. The EPR spectrum at 2.8 K displayed a rhombic signal with $g_{\text{eff}} = 5.44, 4.27, \text{ and } 1.99$, which could be fit as an $S = \frac{3}{2}$ signal (Figure 3.6). Additionally, the $^{57}\text{Fe Mössbauer}$ spectrum for 6 is consistent with that of a high-spin Fe$^{II}$ complex (Figure 3.6). Together with the other two diazoalkane adducts, the results presented here demonstrate the ability of the dipyrrin ligand platform to support the isolation of high-spin iron complexes with diazoalkane adducts. Changes in the steric profile of the diazoalkane molecule resulted in differences in coordination modes to the metal center. Regardless of the coordination geometry of the diazoalkane ligand, complexes 4, 5, and 6 displayed similar $^{57}\text{Fe Mössbauer}$ and EPR spectra, suggesting common oxidation levels and spin states for the iron center.
Figure 3.6. (a) Solid-state molecular structure for \((^{\text{Ar}}L){\text{Fe}}(\text{ArCHN}_2)\)\(^6\) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray. (b) Zero-field \(^{57}\text{Fe}\) Mössbauer spectrum of \((^{\text{Ar}}L){\text{Fe}}(\text{ArCHN}_2)\)\(^6\). Isomer shift and quadrupole splitting values are reported relative to Fe foil at room temperature (\(\delta = 0.63 \text{ mm/sec}, |\Delta E_Q| = 1.17 \text{ mm/sec}\)). Parameters calculated via single point DFT: \(\delta = 0.70 \text{ mm/sec}, |\Delta E_Q| = 1.14 \text{ mm/sec}\). (c) Frozen toluene EPR spectrum of \((^{\text{Ar}}L){\text{Fe}}(\text{ArCHN}_2)\)\(^6\) (red line) at 2.8 K. The black line represents a fit using EasySpin\(^10\) with \(g = 2.25, 1.94, 2.10\) and \(S = \frac{3}{2}\).

3.2.3 Electronic Structure and DFT of Iron-Diazoalkane Adducts

As outlined in the introduction, transition metal binding of diazoalkanes can occur via simple dative donation (e.g., Lewis acid/base pair), or with concomitant electron transfer (either with one or two-electron transfer possible) (Figure 3.1). Examination of the bond metrics present in the diazoalkane ligands for 4, 5, and 6 suggests reduction by one electron upon coordination to the metal center. Our group, the Holland group, and the Meyer group have previously reported the synthesis of either an iron-, cobalt-, or uranium-supported complex\(^18\) bound to a diphenyldiazoalkane ligand.\(^4\) Using a variety of spectroscopic techniques, the diazoalkane ligand in each example was assigned as a one electron reduced radical anion.\(^4,18\) The diazoalkane ligand

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fragments in these previously reported complexes adopt a unique geometry. For example, the N–N and N–C bond lengths range from 1.216(2)–1.338(5) Å and 1.310(1)–1.333(6) Å, respectively. These N–N and N–C bond lengths are intermediate between that of a single or a double bond (N–N: 1.425 Å; N=N: 1.240 Å; N–C: 1.499 Å, N=C: 1.279 Å). The bond metrics found within the diazoalkane ligands for 4, 5, and 6 match well with those previously reported as radical anions (Figure 3.7).

Figure 3.7. Selected bond metrics for metal complexes containing radical diazoalkane ligands.\textsuperscript{4,18}

The electronic structure of each iron diazoalkane adduct was also investigated using the spectroscopy obtained and single-point DFT calculations using the crystallographic coordinates for 4, 5, and 6 at the B3LYP/Def2-SV(P) level. \textsuperscript{57}Fe Mössbauer spectroscopy corroborates a ferrous oxidation state assignment for 4, 5, and 6 and EPR spectroscopy support a quartet ($S =$
configuration. The quartet electronic configuration for 4, 5, and 6 is consistent with a high-spin Fe$^{II}$ anti-ferromagnetically coupled to a diazoalkane ligand radical. Broken-symmetry BS(4,1) calculations revealed large anti-ferromagnetic exchange coupling constants for 4 (−1390 cm$^{-1}$), 5 (−1193 cm$^{-1}$), and 6 (−2453 cm$^{-1}$). The spin density plots (Figure 3.8) for each complex revealed that the α/β spin pair in each complex is localized in a molecular orbital that forms via π-back donation between the Fe and the N$_2$ fragment of the diazoalkane ligand. Additionally, we calculated the $^{57}$Fe Mössbauer parameters for each complex using the BS(4,1) solution and the experimental data is in good agreement with the calculated parameters.

Figure 3.8. Spin density (α–β) plots calculated for (a) 4, (b) 5, and (c) 6 from the BS(4,1) solution, showing the antiferromagnetic coupling between the high-spin Fe$^{II}$ and the diazoalkane ligand radical. Isovalue = 0.005.

The weak-field dipyrrin ligand results in compressing the Fe 3$d$-based molecular orbitals, promoting high-spin electronic configurations. Anti-ferromagnetic coupling to the high-spin ferric center stabilizes electron transfer from the metal center to the diazoalkane ligands upon binding.$^{4,5}$ We have previously observed similar electronic structures in a series of high-spin iron
iminyl complexes, where the iron center is anti-ferromagnetically coupled to an imido-based ligand radical. Intramolecular electron transfer from a metal center to a ligand has been observed in several paramagnetic metal complexes. For example, de Bruin, Zhang, and co-workers have reported the existence of open-shell cobalt porphyrin complexes containing redox non-innocent carbene ligands, which are reduced by one electron upon coordination to the metal center. The reactivity demonstrated by paramagnetic transition metal porphyrin complexes was generalizable and led to the detection of cobalt complexes bound to imido-centered radicals, presumably formed via a similar mechanism.


3.2.2 Reactivity of Iron-Diazo Adducts

Scheme 3.7. Reactivity of $^{\text{Hth}}$Fe(CH$_3$OC$_6$H$_4$CN$_2$CO$_2$CH$_3$) (4) with cyclohexadiene to generate $^{\text{Hth}}$Fe(CH$_3$OC$_6$H$_4$CHN$_2$CO$_2$CH$_3$) (7).

The presence of a diazoalkane ligand-centered radical in 4 was further corroborated by its H-atom abstraction reactivity. Complex 4 aromatized cyclohexadiene (1,4-CHD) (BDE = 76.0 kcal/mol) to benzene at room temperature (Scheme 3.7). Complex 4 was consumed over the span of four hours in neat 1,4-CHD, yielding a distinct paramagnetic species as ascertained by both $^1$H NMR and $^{57}$Fe Mössbauer spectroscopy. A unique quadrupole doublet in the $^{57}$Fe Mössbauer spectrum with parameters ($\delta = 0.87$ mm/sec; $|\Delta E_Q| = 1.92$ mm/sec) similar to that of 4, suggests a similar oxidation state and coordination environment around the metal center (Figure 3.9).

The product, $^{\text{Hth}}$Fe(CH$_3$OC$_6$H$_4$CHN$_2$CO$_2$CH$_3$) (7) was crystallized from a 1:3 mixture of toluene:hexanes at –35°C. The solid-state molecular structure revealed H-atom transfer to the terminal nitrogen of the chelated diazoalkane ligand with the hydrogen atom resolved in the difference map. Following H-atom abstraction, the Fe–N, Fe–O, and N–N bond lengths for 7 are

1.981(3) Å, 1.917(5) Å, and 1.308(4) Å (Figure 3.9), respectively. These bond lengths are significantly elongated when compared to the analogous bonds present in 4 (Fe–N: 1.854(1) Å; Fe–O: 1.905(3) Å; N–N: 1.219(5) Å). In particular, the N–N bond length present in the diazoalkane fragment for 7 is approaching that of a single bond, whereas the N–N bond length present in 4 is closer to that of a double bond. These bond metrics found within the diazoalkane ligand in 7 are comparable to that of a similarly synthesized iridium complex bearing a chelated, protonated diazoalkane ligand.23

Figure 3.9. (a) Solid-state molecular structure for (\(\text{trt}L\))Fe(CH\(_3\)OC\(_6\)H\(_4\)CHN\(_2\)CO\(_2\)CH\(_3\)) (7) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity, except for relevant \(N\)-protonated hydrogen. Solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red, hydrogen = white. (b) Zero-field \(^{57}\text{Fe}\) Mössbauer spectrum of (\(\text{trt}L\))Fe(CH\(_3\)OC\(_6\)H\(_4\)CHN\(_2\)CO\(_2\)CH\(_3\)) (7). Isomer shift and quadrupole splitting values are reported relative to Fe foil at room temperature (\(\delta = 0.87\) mm/sec, \(|\Delta E_Q| = 1.92\) mm/sec). Parameters calculated via single point DFT: \(\delta = 0.95\) mm/sec, \(|\Delta E_Q| = 1.75\) mm/sec. (c) Spin density (\(\alpha–\beta\)) plot calculated for 7 from the quartet solution. Isovalue = 0.005.

The assignment of 7 containing a high-spin Fe\(^{II}\) center was corroborated by DFT calculations. The results of the unrestricted, single point calculation for 7 in the quartet state gave

calculated $^{57}$Fe Mössbauer parameters ($\delta = 0.95$ mm/sec; $|DE_Q| = 1.75$ mm/sec) that are in good agreement with the experimental data. The spin density plot for 7 (Figure 3.9) revealed no significant spin density located on the diazoalkane fragment, supporting the assignment of 7 as a high-spin Fe$^{II}$ coordinated to both an anionic dipyrpin ligand and an anionic diazoester ligand.

**Scheme 3.8.** Reactivity of ($^{\text{ArL}}$)Fe(N$_2$CPh$_2$) (5) upon heating to 80°C.

While 5 does not react cleanly with any substrates containing weak C–H bonds (e.g., 1,4-cyclohexadiene or 9,10-dihydroanthracene), 5 affords a new paramagnetic species upon prolonged heating in benzene (80°C, 24 h), contrasting the thermal stability of 4 (Scheme 3.8). The thermolysis product of 5 is characterized by a unique quadrupole doublet in the $^{57}$Fe Mössbauer spectrum (Figure 3.10). The resulting product, confirmed by single crystal X-ray diffraction, is a three-coordinate Fe$^{II}$ ketimide adduct ($^{\text{ArL}}$)Fe(NCPh$_2$) (8) (Figure 3.10).
A similar transformation was recently reported by Holland and co-workers, where a β-diketiminate Co\textsuperscript{II} ketimide complex was synthesized via thermolysis at 80°C in benzene of the corresponding Co\textsuperscript{II} diazoalkane radical anion. In this example, it was proposed that the diazoalkane ligand reversibly binds the metal center. Free diazoalkane in solution can then couple at 80°C to generate benzophenone azine, which can then react with the metal complex via reductive N–N bond cleavage.\textsuperscript{4} In our case, we independently synthesized 8 by heating a benzene solution of 1 containing one equivalent of benzophenone azine to 80°C for 12 hours, as evidenced by \textsuperscript{1}H NMR spectroscopy, lending support to this mechanistic proposal (Scheme 3.8).

**Figure 3.10.** (a) Solid-state molecular structure for (\textsuperscript{Ar}L)Fe(NCPh\textsubscript{2}) (8) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray. (b) Zero-field $^{57}$Fe Mössbauer spectrum of (\textsuperscript{Ar}L)Fe(NCPh\textsubscript{2}) (8). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.77$ mm/sec, $|\Delta E_Q| = 1.68$ mm/sec).

Finally, the side-bound diazoalkane adduct 6 is highly reactive. While 4 and 5 cleanly convert to new species upon reaction with substrates containing weak C–H bonds or upon heating, 6 decomposes to a variety of unidentifiable species under similar reaction conditions. In particular, after heating 6 to 80°C for 24 hours, we observe the presence of the respective diaryl
ethene by GCMS, presumably formed via dimerization of two carbene fragments. These results suggest we may be accessing a carbene intermediate which is too reactive to isolate.\textsuperscript{24}

While species 4, 5, and 6 have similar electronic structures, they each display unique reactivity profiles that match the stability of the diazoalkane precursor. Complex 4, which contains a chelated, push-pull diazoester ligand is stable in solution at elevated temperatures. In contrast, complexes 5 and 6, which contain no stabilizing heteroatoms, decompose upon heating. The observed trend in reactivity mimics that of organometallic carbene complexes. For example, N-heterocyclic carbene ligands, which contain two nitrogen atoms bound to the carbene carbon, function as unreactive spectator ligands. Fischer-type carbene ligands, which contain one heteroatom bound to the carbene carbon, are more reactive and undergo transfer into olefins to make cyclopropanes. Carbene ligands that contain no heteroatom stabilizing groups are even more reactive and undergo transformations such as olefin metathesis.\textsuperscript{2}

\subsection*{3.3 Conclusions}

By using a variety of substituted diazoalkane complexes, we demonstrate that differences in the steric bulk provide distinct coordination geometries upon binding to the metal center. Regardless of the coordination mode, the diazoalkanes function as redox-active ligands and were subsequently reduced by one electron upon binding, as ascertained by single crystal X-ray diffraction, \textsuperscript{57}Fe Mössbauer spectroscopy, EPR spectroscopy, and DFT calculations. The presence of a one-electron reduced diazoalkane ligand was further corroborated by its ability to perform radical hydrogen atom abstraction from 1,4-cyclohexadiene. Furthermore, the reactivity of the iron diazoalkane complexes mimicked the stability of the diazoalkane ligand. These results

demonstrate that the interaction between a metal center and a diazoalkane moiety is impacted by
the steric properties and stability of the diazoalkane ligand and may subsequently influence the
ability of the metal center to promote dinitrogen extrusion and carbene formation.
3.4 Experimental Procedures

3.4.1 General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported. All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, dichloromethane, hexanes, pentane, pyridine, toluene, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-$d$ was purchased from Cambridge Isotope Labs and used as received. Benzene-$d_6$ was purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use. Reagents 1,4-cyclohexadiene, trityl chloride, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, hydrazine monohydrate, yellow mercury (II) oxide, 2-naphthaldehyde, mesitaldehyde, 3,5-di-tert-butylbenzaldehyde, 3,5-dimethoxybenzaldehyde, lithium bis(trimethylsilyl) amide, lithium diisopropylamide, potassium bis(trimethylsilyly) amide, and benzophenone azine were purchased from Aldrich. Aluminum trichloride was purchased from Alfa Aesar. Pyrrole and pyridinium $p$-toluenesulfonate was purchased from Oakwood Chemical. All C–H substrates were dried over calcium hydride and distilled under nitrogen or vacuum or re-crystallized from hexanes. Anhydrous iron dichloride was purchased from Strem and used as received. Reagents 2,4,6-triphenylbenzaldehyde, potassium graphite, $a$-diazo-4-}


methoxyphenylacetate, \(^{27}\) phenyllithium, \(^{28}\) and diphenyldiazomethane\(^{17}\) were synthesized following literature procedures.

Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

\(^1\)H NMR spectra were recorded on Varian Unity/Inova 400, 500, or 600 MHz-spectrometers. \(^1\)H NMR chemical shifts are reported relative to SiMe\(_4\) using the chemical shift of residual solvent peaks as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent GC/MS 5975 Turbo system. High-resolution mass spectrometry was performed on a Bruker microTOFII ESI LCMS or Bruker Maxis Impact LC-q-TOF Mass Spectrometer. Elemental analyses (% CHN) were obtained on a PerkinElmer 2400 Series II CHNS/O Analyzer. Infrared spectra were collected for a sample in C\(_6\)H\(_6\) (~5 mg per mL) deposited onto a KBr plate on a Varian 1000 FT-IR spectrometer.

Zero-field \(^{57}\)Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN) at 90 K. Isomer shifts are quoted relative to Fe foil at room temperature. Data was analyzed and simulated with Igor Pro 6 software (WaveMetrics, Portland, OR) using Lorentzian fitting functions. Samples were prepared by suspending 25-50 mg of compound in Paratone oil and immobilizing by rapid freezing in liquid nitrogen. For compounds that decomposed in the presence of Paratone oil, samples were measured as frozen solutions in benzene. EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra were measured as frozen toluene glasses at a microwave power of 0.6325–

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2 mW. Spectral simulations incorporating spin state and rhombicity were performed using EasySpin.\textsuperscript{10}

3.4.2 Syntheses

Diazoo Synthesis

\[
\text{R} - \overset{\text{NH}_2}{\text{C}} - \overset{\text{H}}{\text{H}} + \text{H}_2\text{N}_2\text{H}_2\cdot\text{H}_2\text{O} \rightarrow \text{R} - \overset{\text{N}_2}{\text{C}} - \overset{\text{H}}{\text{H}}
\]

General Procedure for Diazo Synthesis:\textsuperscript{29} Hydrazine monohydrate (33 equiv.) was added to an ethanol solution (20 mL) containing the respective benzaldehyde (1 equiv.). After heating the reaction mixture to reflux overnight, water (30 mL) was added and the product extracted using ethyl acetate (3 x 20 mL). The organic fractions were dried with sodium sulfate and the solvent removed in vacuo to give the respective hydrazone intermediate as a white solid. The hydrazone (1 equiv.) was then suspended in diethyl ether (20 mL) and yellow mercury oxide (1.5 equiv.), Na\textsubscript{2}SO\textsubscript{4} (1.25 equiv.), and a saturated solution of KOH in EtOH (1.0 equiv. KOH) were added. The reaction mixture was stirred for 30 minutes to overnight before being filtered through a pad of celite. The solvent was removed in vacuo to give orange oils. The respective diazo products were re-crystalized from a concentrated solution of diethyl ether at \(-35^\circ\text{C}\) to give orange to pink crystals.

**Characterization of Hydrazone Products**

(2,4,6-triphenylbenzylidene)hydrazine: Reaction run on 1.49 mmol scale; Yield: 96%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 5.16 (bs, 2H), 7.33-7.38 (m), 7.41-7.50 (m), 7.55 (s, 1H), 7.58 (s, 1H), 7.65-7.67 (m). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 142.55, 141.88, 141.64, 140.55, 140.18, 130.24, 129.82, 129.54, 128.85, 128.50, 128.04, 127.67, 127.56, 127.37, 127.14, 126.88, 125.19. HRMS (ESI+) m/z Calc. 349.1705 [C$_{25}$H$_{20}$N$_2$+H]$^+$, Found 349.1735 [M+H]$^+$.

(2-naphylmethyl)hydrazine: Reaction run on 12.80 mmol scale; Yield: 99%. Characterization data is consistent with literature values.$^{30}$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 4.76 (s, 1H), 5.62 (bs, 2H), 7.43-7.45 (m, 2H), 7.80-7.92 (m, 5H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 143.31, 133.64, 133.33, 132.82, 128.41, 128.08, 127.81, 126.68, 126.37, 126.30, 122.87.

(3,5-dimethoxybenzylidene)hydrazine: Reaction run on 6.01 mmol scale; Yield: 65%. Characterization data is consistent with literature values.$^{31}$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 3.80 (s, 6H), 5.53 (bs, 2H), 6.42 (s, 1H), 6.71 (s, 2H), 7.68 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 160.90, 142.85, 137.17, 103.96, 101.37, 55.37.

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(3,5-di-tert-butybenzylidene)hydrazine: Reaction run on 0.92 mmol scale; Yield 53%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 1.32 (s, 18H), 5.47 (bs, 2H), 7.38 (m, 3H), 7.77 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 151.04, 144.05, 134.29, 123.13, 120.60, 34.86, 31.41. HRMS (ESI+) m/z Calc. 233.2017 [C$_{15}$H$_{24}$N$_2$+H]$^+$, Found 233.2007 [M+H]$^+$.

(2,4,6-trimethylbenzylidene)hydrazine: Reaction run on 2.02 mmol scale; Yield: 72%. Characterization data is consistent with literature values. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 2.26 (s, 3H), 2.37 (s, 6H), 5.49 (bs, 2H), 6.85 (s, 2H), 8.04 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 145.00, 139.58, 131.27, 131.17, 23.02.

Characterization of Diazo Products

(2,4,6-triphenylbenzylidene)diazomethane: Reaction run on 0.57 mmol scale. Yield: 65%. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ (ppm): 4.45 (s, 1H), 7.06-7.18 (m), 7.25-7.28 (m), 7.35-7.38 (m). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 140.93, 140.15, 138.05, 136.72, 129.41, 128.80, 128.42, 127.42, 127.21, 126.71, 125.18, 124.74, 45.54. IR (thin film): $\nu$ (cm$^{-1}$): 4058, 3092, 3072, 3037, 2962, 2905, 2062 (N–N stretch), 1957, 1813, 1480, 1412, 1260, 1034, 798, 674. This compound fragmented with loss of N$_2$ in the MS. HRMS (ESI+) m/z Calc 319.1487 [C$_{25}$H$_{18}$+H]$^+$, Found 319.1484 [M+H]$^+$.

(2-naphylmethyl)diazomethane: Reaction run on 2.90 mmol scale; Yield: 58%. Characterization data is consistent with literature values.\(^{33}\) \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \(\delta\) (ppm): 4.22 (s, 1H), 6.67 (dd, \(J = 8.4\) Hz, 2.4 Hz, 1H), 6.97 (s, 1H), 7.19 (td, \(J = 8.7\) Hz, 1.7 Hz, 1H), 7.41 (t, \(J = 8.6\) Hz, 3H), 7.51 (d, \(J = 10.2\) Hz, 1H). IR (thin film): \(\nu\) (cm\(^{-1}\)): 2963, 2905, 2500, 2059 (N–N stretch), 1946, 1412, 1260, 1091, 1018, 800.

(3,5-dimethoxybenzylidene)diazomethane: Reaction run on 0.46 mmol scale; Yield: 42%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 3.77 (s, 6H), 4.89 (s, 1H), 6.08 (d, \(J = 2.2\) Hz, 2H), 6.17 (t, \(J = 2.2\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 163.45, 134.15, 101.55, 98.43, 57.29, 49.89. IR (thin film): \(\nu\) (cm\(^{-1}\)): 4090, 3082, 2962, 2906, 2839, 2060 (N–N stretch), 1592, 1460, 1260, 1020, 800, 681. This compound fragmented with loss of N\(_2\) in the MS. HRMS (ESI+) m/z Calc 151.0759 [C\(_9\)H\(_{11}\)O\(_2\)+H]\(^+\), Found 151.0760 [M+H]\(^+\).

(3,5-di-tert-butybenzylidene)diazomethane: Reaction run on 0.48 mmol scale; Yield: 35%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 1.30 (s, 18H), 4.93 (s, 1H), 6.74 (d, \(J = 1.4\) Hz, 2H), 7.11 (t, \(J = 1.4\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 151.64, 128.35, 118.70, 115.75, 34.87, 31.48, 31.34. IR (thin film): \(\nu\) (cm\(^{-1}\)): 3189, 3036, 2963, 2054 (N–N stretch), 2013, 1957, 1811, 1594, 1478, 1362, 1248, 1202, 1036, 860, 676. This compound fragmented with loss of N\(_2\) in the MS. HRMS (ESI+) m/z Calc 203.1780 [C\(_{15}\)H\(_{22}\)+H]\(^+\), Found 203.1777 [M+H]\(^+\).

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(2,4,6-trimethylbenzylidene)diazomethane: Reaction run on 0.62 mmol scale; Yield: 52%. Characterization data is consistent with literature values.\(^\text{34}\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 2.23 (s, 6H), 2.26 (s, 3H), 4.78 (s, 1H), 6.87 (s, 2H).

**Ligand Synthesis**

![Ligand Synthesis Diagram]

In a 1 L round bottom flask, pyrrole (30.7 g, 0.46 mol) and aluminum trichloride (32.2 g, 0.24 mol) were suspended in CH\(_2\)Cl\(_2\) (175 mL) and cooled to −78°C. A solution of trityl chloride (33.4 g, 0.12 mol) in CH\(_2\)Cl\(_2\) (200 mL) was added dropwise over the course of 3 h during which time the reaction mixture changed color to mustard yellow. Upon addition of trityl chloride, the reaction mixture was allowed to stir for an additional 30 minutes at −78°C before being quenched with a saturated aqueous solution of NaHCO\(_3\) (150 mL). The reaction mixture was filtered through celite and the layers separated. The organic layer was washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* to give a brown powder, which was triturated with hexanes (3 x 30 mL) and methanol (3 x 30 mL) to give a white solid (12.9 g, 35% yield). Characterization data matches that of previously synthesized material.\(^8\) \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 6.02 (m, 1H), 6.16 (q, \(J = 2.3\) Hz, 1H), 6.73 (m, 1H), 7.12-7.15 (m), 7.22-7.29 (m), 7.70 (bs, 1H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 146.13, 136.69, 130.33, 130.14, 127.65, 126.46, 117.29, 110.30, 107.65, 60.41.

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In an oven-dried 1 L storage flask, mesitaldehyde dimethyl acetal (4.40 g, 22.6 mmol), synthesized as previously reported, 9 2-trityl-1H-pyrrole (7.0 g, 22.6 mmol) and pyridinium p-toluenesulfonate (PPTS) (567 mg, 2.26 mmol) were suspended in anhydrous CH₂Cl₂ (150 mL). The reaction mixture was heated to reflux overnight before being filtered through an alumina plug. The plug was washed with CH₂Cl₂ until the eluent turned colorless. The solvent was removed in vacuo to give a yellow-brown solid that was used without further purification. The crude yellow-brown solid was dissolved in CH₂Cl₂ (150 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.60 g, 11.45 mmol) was added in one portion. The mixture was stirred for one hour before being filtered through a plug of alumina. The plug was washed using a 10:1 mixture of hexanes:ethyl acetate until the eluent turned colorless. The solvent was removed under reduced pressure and the red-brown solid was triturated with hexanes to give the product as a dark red solid (3.34 g, 40%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 2.10 (s, 6H), 2.32 (s, 3H), 5.97 (d, J = 3.5 Hz, 2H), 6.13 (d, J = 3.5 Hz, 2H), 6.88 (s, 2H), 7.06-7.11 (m, 30H), 11.50 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 161.06, 145.64, 140.53, 137.81, 137.05, 136.84, 133.92, 130.34, 130.13, 127.58, 126.29, 120.53, 62.13, 31.60, 22.66, 21.12, 20.00, 14.13. Anal. Calc. for C₅₆H₄₆N₂: C 90.04, H 6.21, N 3.75; Found C 89.64, H 6.56, N 3.83.
Metal Complex Syntheses and Characterization Data

\((^\text{trt} \text{L})\text{FeCl} (2)\): To a frozen benzene suspension (4 mL) of PhLi (112 mg, 1.34 mmol), a just-thawed benzene solution (10 mL) containing \((^\text{trt} \text{L})\text{H} (1.00 \text{ g}, 1.34 \text{ mmol})\) was added. The reaction mixture stirred at room temperature overnight. The dark brown solution was lyophilized to give \((^\text{trt} \text{L})\text{Li}\) as a brown powder (1.00 g, 99%), which was used without further purification. A THF solution (10 mL) containing \((^\text{trt} \text{L})\text{Li} (1.00 \text{ g}, 1.32 \text{ mmol})\) was added to a THF solution (4 mL) containing FeCl\(_2\) (168 mg, 1.34 mmol). The reaction mixture was stirred overnight at room temperature during which time the solution changed color from brown to dark red. The reaction mixture was then filtered through celite and the solvent removed \textit{in vacuo}. The red solid was re-dissolved in benzene, filtered through celite, and lyophilized. The resulting powder was washed with Et\(_2\)O to give dark red crystals of 2 (580 mg, 52%). Crystals suitable for X-ray diffraction were grown from a solution of Et\(_2\)O at \(-35^\circ\text{C}\). \(^1\text{H NMR}\) (500 MHz, C\(_6\)D\(_6\)): \(\delta\) (ppm) 60.77 (s), 44.79 (bs), 11.94 (s), 2.10 (s), –1.49 (s), –9.69 (s), –28.96 (s). Anal. Calc. for C\(_{56}\)H\(_{45}\)ClFeN\(_2\): C 80.33, H 5.42, N 3.35; Found C 80.70, H 5.95, N 3.34. Zero-field \(^{57}\text{Fe Mössbauer}\) (90 K) \(\delta = 0.91 \text{ mm/s, } |\Delta E_G| = 2.3 \text{ mm/s.}\)
Figure 3.11. $^1$H NMR spectrum for ($^{1}$L)FeCl (2) collected in C$_6$D$_6$. 
Figure 3.12. Zero-field $^{57}$Fe Mössbauer spectrum of (6L)FeCl (2). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.91$ mm/sec, $|\Delta E_Q| = 2.3$ mm/sec).
Figure 3.13. Solid-state molecular structure for ($^{1}$L)FeCl (2) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green.
(trtL)Fe(thf) (3): A just-thawed THF solution (6 mL) containing (trtL)FeCl (2) (130 mg, 0.15 mmol) was added to a frozen THF solution (2 mL) of KC₈ (42 mg, 0.30 mmol). The reaction mixture was stirred for 30 minutes at room temperature during which time the solution changed color from dark red to maroon. The reaction was filtered through Celite and the solvent removed \textit{in vacuo}. The solid was re-dissolved in hexanes, filtered through Celite, and the solvent removed \textit{in vacuo} to give 3 (28.0 mg, 23\%) as a red powder. Crystals suitable for X-ray diffraction were grown from a 1:3 mixture of toluene:hexanes at −35°C. $^1$H NMR (500 MHz, C₆D₆): δ (ppm) 15.76 (bs), 12.34 (s), 0.25 (s). EPR (toluene, 77 K): $g_{\text{eff}} = 2.23, 2.03, 1.98$. Anal. Calc. for C₆₀H₅₃FeN₂O·C₄H₈O: C 81.25, H 6.50, N 2.96; Found C 80.82, H 6.03, N 3.08. Zero-field $^{57}$Fe Mössbauer (90 K) δ = 0.68 mm/s, $|\Delta E_p| = 0.73$ mm/s.
Figure 3.14. Zero-field $^5\gamma$Fe Mössbauer spectrum of ($^{1}L$)Fe(thf) (3). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.68 \text{ mm/sec}, |\Delta E_Q| = 0.73 \text{ mm/sec}$). Parameters calculated via single point DFT: $\delta = 0.74 \text{ mm/sec}, |\Delta E_Q| = 1.01 \text{ mm/sec}$. 
Figure 3.15. Frozen toluene EPR spectrum of \((^{13}L)\text{Fe(thf)}\) (3) (red line) at 77 K. The black line represents a fit using EasySpin\textsuperscript{10} with $g = 2.23, 2.03, 1.98$ and $S = \frac{1}{2}$. 
Figure 3.16. Solid-state molecular structure for (...)Fe(thf) (3) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red.
(trtL)Fe(CH$_3$OC$_6$H$_4$CN$_2$CO$_2$CH$_3$) (4): A just-thawed benzene solution (2 mL) containing α-diazo-4-methoxyphenylacetate (9.5 mg, 0.046 mmol) was added to a frozen benzene solution (2 mL) containing (trtL)Fe(thf) (3) (40.0 mg, 0.046 mmol). Upon thawing, the reaction mixture was stirred for 30 minutes accompanied by a color change from red to orange-red. The solvent was lyophilized and the product washed with hexanes (10 mL) to give 4 as a red solid (28.0 mg, 60%). Crystals suitable for analysis by X-ray diffraction were grown from a 1:3 mixture of toluene:hexanes at −35°C. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ (ppm) 54.58 (s), 20.47 (bs), 16.80 (s), 11.95 (s), 10.64 (s), 9.67 (s), 6.16 (s), 5.17 (s), 3.31 (s), 3.20 (s), 2.75 (s), −6.80 (bs), −8.67 (s), −9.78 (s), −20.58 (s). EPR (toluene, 2.8 K): $g_{\text{eff}} = 6.11, 1.62, 1.26$. IR (thin film): $\nu$ (cm$^{-1}$): 2962, 2083, 1559, 1540, 1260, 1091, 1019, 798. Anal. Calc. for C$_{66}$H$_{55}$FeN$_4$O$_3$: C 77.69, H 6.05, N 5.18; Found C 76.41, H 5.18, N 4.98. Zero-field $^{57}$Fe Mössbauer (90 K) $\delta = 0.82$ mm/s, $|\Delta E_Q| = 1.61$ mm/s.
Figure 3.17. $^1$H NMR spectrum for $(^{1H}L)\text{Fe(CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CO}_2\text{CH}_3) \ (4)$ collected in $\text{C}_6\text{D}_6$. 
Figure 3.18. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{{\text{tr}}}$L)Fe(CH$_3$OC$_6$H$_4$CN$_2$CO$_2$CH$_3$) (4). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.82$ mm/sec, $|\Delta E_Q| = 1.61$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.88$ mm/sec, $|\Delta E_Q| = 1.67$ mm/sec.
Figure 3.19. Frozen toluene EPR spectrum of \((^{1}L)Fe(CH_{3}OC_{6}H_{4}CN_{2}CO_{2}CH_{3})\) (4) (red line) at 2.8 K. The minor signal at \(g = 2\) corresponds to a trace organic radical impurity. The black line represents a fit using EasySpin\textsuperscript{10} with \(g = 2.19, 1.81, 1.79\) and \(S = \frac{3}{2}\).
Figure 3.20. Solid-state molecular structure for \((^{67}\text{L})\text{Fe}(\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CO}_2\text{CH}_3)\) (4) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red.
(\textsuperscript{A}L)Fe(N\textsubscript{2}CPh\textsubscript{2}) (5): A just-thawed benzene solution (2 mL) containing N\textsubscript{2}CPh\textsubscript{2} (10.5 mg, 0.054 mmol) was added to a frozen benzene solution (10 mL) of (\textsuperscript{A}L)Fe (1) (50 mg, 0.054 mmol). The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 2 hours, during which time the color changed from dark purple to pink-red. The solution was filtered through Celite and the solvent was removed \textit{in vacuo}. The solid pink-red powder was washed with 10 mL hexanes and the solid pink precipitate was collected (19 mg, 31\%). Crystals suitable X-ray diffraction were grown from a solution of toluene layered with pentane at –35°C. \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) 57.33 (s), 43.04 (s), 29.76 (s), 24.03 (s), 21.46 (s), 19.27 (br. s), 11.21 (s), 10.30 (s), 9.76 (s), 9.27 (s), 7.02 (s), 5.80 (br. s), 2.11 (s), 0.88 (s), –11.56 (s), –12.75 (s), –22.86 (br. s), –64.29 (br. s), –81.48 (br. s). IR (thin film): \(\nu\) (cm\(^{-1}\)): 2963, 2906, 2038, 1948, 1413, 1091, 1028, 863, 798, 698. Anal. Calc. for C\textsubscript{79}H\textsubscript{59}FeN\textsubscript{4}·C\textsubscript{7}H\textsubscript{8}: C 85.2, H 5.57, N 4.62; Found C 85.47, H 5.85, N 5.00. EPR (toluene, 2.8 K): \(g_{\text{eff}} = 5.45, 4.24, 1.99\). Zero-field \textsuperscript{57}Fe Mössbauer (90 K) \(\delta = 0.67\) mm/s, \(|\Delta E_Q| = 1.44\) mm/s.
**Figure 3.21.** $^1$H NMR spectrum for ($^{Ar}L$)Fe(N$_2$CPh$_2$) (5) collected in C$_6$D$_6$. 
Figure 3.22. Zero-field $^{57}\text{Fe}$ Mössbauer spectrum of ($^\text{Ar}$L)Fe(N$_2$CPh$_2$) (5). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.67$ mm/sec, $|\Delta E_Q| = 1.24$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.67$ mm/sec, $|\Delta E_Q| = 1.44$ mm/sec.
Figure 3.23. Frozen toluene EPR spectrum of (ArL)Fe(N$_2$CPh$_2$) (5) (black line) at 2.8 K. The red line represents a fit using EasySpin$^\text{10}$ with $g = 2.30, 2.30, 1.99$ and $S = \frac{3}{2}$. 
Figure 3.24. Solid-state molecular structure for \((\text{ArL})\text{Fe(N}_2\text{CPh}_2)\) (5) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray.
(\(\text{Ar}L\))Fe(N\(_2\)CH\(\text{Ar}\)) (6): A just-thawed benzene solution (2 mL) containing N\(_2\)CH\(\text{Ar}\) (18.7 mg, 0.054 mmol) was added to a frozen benzene solution (10 mL) of (\(\text{Ar}L\))Fe (1) (50.0 mg, 0.054 mmol). The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 30 minutes, during which time the color changed from dark purple to pink-red. The solution was filtered through Celite and the solvent was removed in vacuo to give a solid, pink-red powder (41.2 mg, 60%). Crystals suitable X-ray diffraction were grown from a solution of toluene layered with hexanes at –35°C. \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \(\delta\) 46.21 (s), 30.79 (s), 28.82 (s), 22.31 (s), 15.97 (s), 13.62 (s), 11.81 (s), 10.14 (s), 9.40 (s), 6.55 (s), 2.44 (s), –12.42 (s), –21.49 (s), –32.14 (s). EPR (toluene, 2.8 K): \(g_{\text{eff}}\) = 5.44, 4.27, 1.99. Anal. Calc. for C\(_{91}\)H\(_{68}\)FeN\(_4\)C\(_6\)H\(_{14}\): C 85.76, H 6.01, N 4.12; Found C 85.03, H 5.85, N 3.28. IR (thin film): \(\nu\) (cm\(^{-1}\)): 2963, 2906, 2662, 2279, \(\mathbf{1946}\), 1596, 1534, 1492, 1251, 1032, 803, 699. Zero-field \(^{57}\)Fe Mössbauer (90 K) \(\delta\) = 0.63 mm/s, \(|\Delta E_Q|\) = 1.17 mm/s.
Figure 3.25. $^1$H NMR spectrum for ($^{Ar}$L)Fe(N$_2$CHAr) (6) collected in C$_6$D$_6$. 
Figure 3.26. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{3}$Li)Fe(N$_2$CHAr) (6). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.63$ mm/sec, $|\Delta E_Q| = 1.17$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.70$ mm/sec, $|\Delta E_Q| = 1.14$ mm/sec.
Figure 3.27. Frozen toluene EPR spectrum of ($^{6}$L)Fe(N$_2$CHAr) (6) (red line) at 2.8 K. The black line represents a fit using EasySpin$^{10}$ with $g = 2.25$, 1.94, 2.10 and $S = \frac{3}{2}$. 
Figure 3.28. Solid-state molecular structure for (\textsuperscript{\textit{Ar}}L)Fe(N\textsubscript{2}CH\textit{Ar}) (6) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted and solvent molecules for clarity. Iron = orange, nitrogen = blue, carbon = gray.
(\textsuperscript{trt}L)Fe(CH\textsubscript{3}OC\textsubscript{6}H\textsubscript{4}CHN\textsubscript{2}CO\textsubscript{2}CH\textsubscript{3}) (7): (\textsuperscript{trt}L)Fe(CH\textsubscript{3}OC\textsubscript{6}H\textsubscript{4}CN\textsubscript{2}CO\textsubscript{2}CH\textsubscript{3}) (4) (29 mg, 0.029 mmol) was stirred in neat 1,4-cyclohexadiene (2 mL) at room temperature for 4 hours. Upon complete consumption of (\textsuperscript{trt}L)Fe(CH\textsubscript{3}OC\textsubscript{6}H\textsubscript{4}CN\textsubscript{2}CO\textsubscript{2}CH\textsubscript{3}) (4), the solvent was removed \textit{in vacuo} to give a dark, red solid (28 mg, 96%). Crystals suitable for analysis by X-ray diffraction were grown from a 1:3 mixture of toluene:pentane at $-35\,^\circ C$. $^1$H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): $\delta$ (ppm) 49.73 (s), 48.04 (s), 31.18 (bs), 27.10 (s), 20.98 (s), 20.01 (s), 14.57 (s), 11.05 (s), 3.61 (s), 2.89 (s), 2.14 (s), $-13.32$ (s), $-20.55$ (s). Anal. Calc. for C\textsubscript{66}H\textsubscript{56}FeN\textsubscript{4}O\textsubscript{3}: C 79.62, H 5.86, N 5.09; Found C 79.29, H 5.39, N 4.34. Zero-field $^{57}$Fe Mössbauer (90 K) $\delta = 0.87$ mm/s, $|\Delta E_Q| = 1.92$ mm/s.
Figure 3.29. $^1$H NMR spectrum for ($^{\text{213}}$L)Fe(CH$_3$OC$_6$H$_4$CHN$_2$CO$_2$CH$_3$) (7) collected in C$_6$D$_6$. 
Figure 3.30. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{1}$H)$\text{Fe}$(CH$_3$OC$_6$H$_4$CHN$_2$CO$_2$CH$_3$) (7). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature ($\delta = 0.87$ mm/sec, $|\Delta E_Q| = 1.92$ mm/sec). Parameters calculated via single point DFT: $\delta = 0.95$ mm/sec, $|\Delta E_Q| = 1.75$ mm/sec.
**Figure 3.31.** Solid-state molecular structure for \((^{1}L)\text{Fe(OC}_{6}H_{4}\text{CHN}_{2}\text{CO}_{2}\text{CH}_{3})\) (7) with thermal ellipsoids at 50% probability level. Only relevant hydrogen atoms are shown. Solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, oxygen = red.
(ArL)Fe(NCPh$_2$) (8): A benzene solution (2 mL) containing (ArL)Fe(N$_2$CPh$_2$) (5) (19 mg, 0.017 mmol) was added to a J. Young NMR tube. The pink-red solution was heated to 80 °C for 24 hours. The solution was filtered through Celite and the solvent was removed in vacuo. The solid pink-red powder was washed with 10 mL hexanes and the solid pink precipitate was collected (10 mg, 53%). Crystals suitable for X-ray diffraction were grown from a solution of toluene layered with pentane at –35 °C. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 84.73 (br. s), 53.80 (br. s), 49.73 (br. s), 47.39 (s), 34.02 (s), 18.70 (s), 15.55 (s), 14.58 (s), 12.81 (s), 2.11 (s), –1.46 (br. s), –18.80 (s), –20.49 (s), –29.33 (s), –60.07 (br. s). Anal. Calc. for C$_{79}$H$_{59}$FeN$_3$: C 85.78, H 5.38, N 3.80; Found C 85.36, H 5.63, N 3.97. Zero-field $^{57}$Fe Mössbauer (90 K) $\delta$ = 0.77 mm/s, $|\Delta E_Q|$ = 1.68 mm/s.
(ArL)Fe(NCPh₂) (8): A benzene solution (1 mL) containing (ArL)Fe (1) (50 mg, 0.054 mmol) was added to a J. Young NMR tube holding a benzene solution (1 mL) of benzophenone azine (9.6 mg, 0.027 mmol). The purple solution was heated to 80°C for 12 hours during which time the solution turned pink-red. The solid, pink precipitate was collected upon lyophilization of the benzene and subsequently washed with 10 mL hexanes to yield the product as a pink solid (17.3 mg, 29%). ¹H NMR (500 MHz, C₆D₆): δ 84.73 (br. s), 53.80 (br. s), 49.73 (br. s), 47.39 (s), 34.02 (s), 18.70 (s), 15.55 (s), 14.58 (s), 12.81 (s), 2.11 (s), –1.46 (br. s), –18.80 (s), –20.49 (s), –29.33 (s), –60.07 (br. s).
Figure 3.32. $^1$H NMR spectrum for $(^{Ar}L)Fe(NCPh_2)$ (8) collected in $C_6D_6$. 
Figure 3.33. Zero-field $^{57}$Fe Mössbauer spectrum of (ArL)Fe(NCPh$_2$) (8). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: $\delta = 0.77$ mm/s, $|\Delta E_Q| = 1.68$ mm/s.
Figure 3.34. Solid-state molecular structure for ($^6_{6}L$)Fe(NCPh$_2$) (8) with thermal ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray.
3.4.3. X-Ray Diffraction Techniques

Structures of 2, 3, 4, 5, 6, 7, and 8 were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans.

Data was integrated using SAINT and scaled with either a numerical or multi-scan absorption correction using SADABS. The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELX-2014 and refined against F² on all data by full matrix least squares with SHELX-2014. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

(\(\text{trt}L\))FeCl (2): The structure was solved in the triclinic space group P-1 with two molecules per unit cell. The crystal is a non-merohedral twin, but we have refined the structure by using reflections in hkl4 format that is created by Cell_Now/Twinabs. Additionally, the structure contained large, solvent accessible voids, which could not be located and were instead squeezed out using a solvent mask.

(\(\text{trt}L\))Fe(thf) (3): The structure was solved in the monoclinic space group C2/c. The structure exhibited a high amount of disorder in several places and was modeled using similarity

35. APEX2 Software Suite; Bruker AXS: Madison, WI, 2014.

restraints and constraints. Additionally, a highly disordered hexane solvent molecule was present that could not be refined. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically significant features of the structure.

\((^{\text{trt}}L)\text{Fe}(\text{CH}_3\text{OC}_6\text{H}_4\text{CN}_2\text{CO}_2\text{CH}_3)\) (4): The structure was solved in the triclinic space group P-1. The diazo ligand exhibited disorder and was modeled using similarity restraints and constraints.

\((^{\text{Ar}}L)\text{Fe}(\text{N}_2\text{CPh}_2)\) (5): The structure was solved in the monoclinic space group P2_1/n. One of the phenyl rings of the ligand exhibited disorder and was modeled using similarity restraints and constraints. The structure contained large, solvent accessible voids, which could not be located and were instead squeezed out using a solvent mask.

\((^{\text{Ar}}L)\text{Fe}(\text{QCHN}_2)\) (6): The structure was solved in the triclinic space group P-1 with two molecules per unit cell. The structure contained multiple disordered toluene molecules, which were modeled using similarity constraints and restraints. Additionally, the structure contained large, solvent accessible voids, which could not be located and were instead squeezed out using a solvent mask.

\((^{\text{trt}}L)\text{Fe}(\text{CH}_3\text{OC}_6\text{H}_4\text{CHN}_2\text{CO}_2\text{CH}_3)\) (7): The structure was solved in the triclinic space group P-1. Two toluene solvent molecules exhibited disorder and were modeled using similarity restraints and constraints.

\((^{\text{Ar}}L)\text{Fe}(\text{NCPh}_2)\) (8): The structure was solved in the triclinic space group P-1. Due to high disorder of a toluene molecule, an acceptable model could not be refined. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically significant features of the structure. Additionally, the intensity of the data is weak because the crystal is micro-size and poorly diffracting.
Table 3.1. X-ray diffraction experimental details.$^a$

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$^a$ R1 = $\Sigma |F_o| - |F_c| / |\Sigma F_o|$, wR2 = $\{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$
Table 3.2. X-ray diffraction experimental details continued.\textsuperscript{a}

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<td>25465</td>
<td>34886</td>
</tr>
<tr>
<td>Completeness to 2(\Theta)</td>
<td>99.82%</td>
<td>99.80%</td>
<td>99.60%</td>
<td>99.96%</td>
</tr>
<tr>
<td>GOF on (F^2)</td>
<td>1.037</td>
<td>1.031</td>
<td>0.962</td>
<td>0.713</td>
</tr>
<tr>
<td>(R_1, wR^2) ([I &gt; 2\sigma(I)])</td>
<td>0.0707, 0.1674</td>
<td>0.0547, 0.1376</td>
<td>0.0676, 0.1828</td>
<td>0.0825, 0.713</td>
</tr>
<tr>
<td>(R_1, wR^2) ([all data])</td>
<td>0.1404, 0.1947</td>
<td>0.0984, 0.1579</td>
<td>0.1003, 0.2025</td>
<td>0.1521, 0.713</td>
</tr>
</tbody>
</table>

\[a\] \(R_1 = \Sigma |F_o - |F_c| | \Sigma |F_o| , wR^2 = \{ \Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)] \}^{1/2}\]
3.4.4. Computational Methods

Computations were carried out utilizing the ORCA 2.9\textsuperscript{37} program package. The B3LYP\textsuperscript{38} functional was used with the def2-TZVP (Fe, N, Cl) and def2-SV(P) (C, H) basis sets.\textsuperscript{39} For single point calculations and property calculations the def2-TZVP/J (Fe, N, Cl) and def2-SVP/J (C, H) auxiliary basis sets\textsuperscript{40} were employed to utilize the RIJCOSX\textsuperscript{41} approximation for accelerating the calculation. For the calculation of the Mössbauer parameters the basis set at Fe was expanded to the CP(PPP) basis.\textsuperscript{42} All geometries were taken from X-ray structures.

Mössbauer. Mössbauer parameters were obtained from additional single-point calculations, following the method described by F. Neese.\textsuperscript{43} Quadrupole splitting values (\(\Delta E_Q\)) were calculated from electric field gradient (Equation 1):

\begin{equation}
\Delta E_Q = \frac{e q}{\gamma} \frac{G}{r^3}
\end{equation}

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\end{itemize}
\[ \Delta E_Q = \frac{1}{2} e Q V_{zz} \sqrt{1 + \frac{1}{3} \eta^2} \]

**Equation 1.** Calculation of quadrupole splitting.

The nuclear quadrupole moment \(Q(^{57}\text{Fe})\) was taken to be 0.16 barn.\(^{43}\) The principal tensor components of the EFG are \(V_{xx}, V_{yy},\) and \(V_{zz},\) from which the symmetry parameter \(\eta = (V_{xx} - V_{yy})/V_{zz}\) can be defined chosen such that \(|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|.|\)

Isomer shift values (\(\delta\)) were calculated from the electron density at the nucleus \(\rho_0\), using a linear equation \((\delta = a(\rho_0 - C) + b,\) with constraints determined by fitting the calculated densities to experimental isomer shifts for a series of iron dipyrromethane complexes synthesized in the lab.\(^{5}\) For this series of compounds, the parameters were determined to be \(C = 11580\) au\(^3\), \(a = -0.355\) au\(^3\) mms\(^{-1}\), and \(b = 1.418\) mm. The basis sets and functional described above were used for all structures. X-ray coordinates were used, and spin-states were assigned based on experimental Mössbauer data.

**Broken Symmetry Solutions.** A broken symmetry solution was used to model with antiferromagnetically coupled Fe\(^{\text{III}}\) and Fe\(^{\text{II}}\) carbene radicals, and the Fe\(^{\text{II}}\) diazo radical. The broken symmetry notation BS\((m,n)\)\(^{44}\) refers to a system with \((m+n)\) unpaired electrons, and a net spin of \((m+n)/2\) (if antiferromagnetically coupled). One fragment will bear \(m\) \(\alpha\) spin electrons and the other fragment \(n\) \(\beta\) spin electrons.

**Figure 3.35.** Molecular Orbital Diagram for (\(^{15}\)L)Fe(CH\(_3\)OC\(_6\)H\(_5\)CN\(_2\)CO\(_2\)CH\(_3\)) (4) (isovalue 0.05), derived from the BS (4, 1) solution. Unrestricted corresponding orbitals for the spin-coupled pair (262\(\alpha\), 262\(\beta\)) and quasi-restricted orbitals (263\(\alpha\)–265\(\alpha\)).
Figure 3.36. Molecular Orbital Diagram for ($^\text{Ar}$L)Fe(N$_2$CPh$_2$)$_2$ (5) (isovalue 0.03), derived from the BS(4, 1) solution. Unrestricted corresponding orbitals for the spin-coupled pair (291$\alpha$, 291$\beta$) and quasi-restricted orbitals (290$\alpha$, 292$\alpha$, 292$\alpha$, and 294$\alpha$).
Figure 3.37. Molecular Orbital Diagram for ($^{A_{L}}$L)Fe(N$_{2}$CHAr) (6) (isovalue 0.05), derived from the BS(4, 1) solution. Unrestricted corresponding orbitals for the spin-coupled pair ($331\alpha$, $331\beta$) and quasi-restricted orbitals ($332\alpha$–$334\alpha$).
Figure 3.38. Molecular Orbital Diagram for $[^1\text{H}]\text{Fe}(\text{CH}_3\text{OC}_6\text{H}_4\text{CHN}_2\text{CO}_2\text{CH}_3)$ (7) (isovalue 0.05), derived from the quintet solution. Quasi-restricted orbitals (261$\alpha$–266$\alpha$).
3.4.5. NMRs of Diazo Molecules

Figure 3.39. $^1$H NMR spectrum for (2,4,6-triphenylbenzylidene)diazomethane collected in CDCl$_3$. The peaks at 1.21 and 3.48 ppm correspond to residual solvent.
Figure 3.40. $^{13}$C NMR spectrum for (2,4,6-triphenylbenzyldene)diazomethane collected in CDCl$_3$. Peaks at 18.4 and 58.5 ppm correspond to residual solvent.
Figure 3.41. $^1$H NMR spectrum for (2-naphylmethyl)diazomethane collected in CDCl$_3$. 
Figure 3.42. $^1$H NMR spectrum for (2,4,6-trimethylbenzylidene)diazomethane collected in CDCl$_3$. 
Figure 3.43. $^1$H NMR spectrum for (3,5-dimethoxybenzylidene)diazomethane collected in CDCl$_3$. The peaks at 1.21, 1.56, and 3.48 ppm correspond to residual solvent.
Figure 3.44. $^{13}$C NMR spectrum for (3,5-dimethoxybenzylidene)diazomethane collected in CDCl$_3$. 
Chapter 4

Iron Stabilized High Spin Carbenes¹

4.1 Introduction

Transition metal complexes bearing metal-ligand multiple bonds are often implicated as intermediates capable of inserting heteroatom functionalities into unreactive C–H bonds. The reactivity of the multiply-bonded substituent and its propensity for group transfer is influenced by the electronic structure of the transition metal center.² Two metal-carbene binding motifs have traditionally been used to describe the nature of the metal-carbon multiple bond. In the case of Schrock-type alkylidenes, a triplet carbene binds as a dianionic ligand, forming two covalent bonds (σ+π) with the metal center, resulting in a nucleophilic carbene. Fisher-type carbenes are neutral donors, where the singlet carbene datively adds to the metal center and is stabilized by metal π-back donation or stabilization from α-heteroatom π-donation into the empty carbene p orbital. The lowest unoccupied molecular orbital is carbene-based, rendering the fragment

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electrophilic. Tuning the electronic structure of metal carbene complexes is a key factor in determining the propensity for \([\text{CR}_2]\) transfer to form new C–C bonds via processes, such as olefin metathesis\(^4\) or C–H insertion.\(^5\)

Intermediate between the dianionic, Schrock-type alkylidenes and neutral Fischer-type carbenes is an electronic structure depiction that invokes significant radical character on the multiply bonded carbon functionality. Upon reduction of Fischer-type carbenes (or potentially the oxidation of an alkylidene), the added electron populates a carbene-based molecular orbital, giving rise to unpaired electron density localized on the carbene fragment.\(^6\)

In 1976, Casey and co-workers reported the EPR spectrum of the one-electron reduced (phenylmethoxycarbene)penta-carbonylchromium, which supports the existence of a carbon-centered radical.\(^7\) Carbene radicals can also be synthesized from dinitrogen extrusion from diazoalkanes by paramagnetic metal complexes.\(^6\) The Groysman group reported a cobalt-bound diphenyl carbene ligand, which by DFT was suggested to possess significant electron density on the carbene-carbon.\(^8\) Similarly, the Chirik group has isolated an open-shell Fe\(^{II}\) complex anti-

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ferromagnetically coupled to both diphenyl carbene and bis(amino)pyridine ligand-centered radicals to give an overall $S = 1$ complex.\textsuperscript{9} While these isolated examples have displayed limited or no reactivity, it is proposed that carbene radicals may demonstrate distinct, potentially ambiphilic, reactivity, including radical-type C–C bond formation and C–H functionalization.\textsuperscript{6} For example, the cobalt-catalyzed cyclopropanation of electron-deficient olefins with diazo reagents is proposed to proceed via an open-shell Co\textsuperscript{III} carbene radical intermediate.\textsuperscript{10}

Our group has previously shown that using weak field, sterically hindered dipyrrin ligands facilitates the isolation of reactive metal-ligand multiple bonds in high-spin electronic configurations. Using these ligand platforms, we have isolated several examples of high-spin iron iminyl complexes competent for catalytic nitrene insertion into C–H bonds, where an $S = \frac{5}{2}$ Fe\textsuperscript{III} is anti-ferromagnetically coupled to an $S = \frac{1}{2}$ N\textsubscript{iminyl}-based radical.\textsuperscript{11} We were thus interested in investigating whether the observed electronic structure and reactivity for the iron iminyl complexes could be translated to other types of metal-ligand multiple bonds, including iron carbenes. Herein we report the synthesis and characterization of two high-spin iron carbene complexes in different oxidation states. Changing the complexes’ oxidation state results in enhancing the carbene radical character and changes in the observed reactivity along the iron-

\begin{itemize}
\end{itemize}
4.2 Results and Discussion

4.2.1 Synthesis of Iron Carbenes

Scheme 4.1. Synthesis of \((\text{Bu}_L)\text{FeCl(CPh}_2\) (2).

Addition of a thawing benzene solution containing \([\text{Bu}_L\text{FeCl}](1) (\text{Bu}_L = 1,9\text{-di-}

\text{tert-butyl-5-(2,6-dichlorophenyl)-dipyrromethene}) to a frozen solution containing two equivalents of \(\text{N}_2\text{CPh}_2\) in benzene at \(-196^\circ\text{C}\) resulted in a color change from bright red to maroon upon warming to room temperature (Scheme 4.1). \(^1\text{H NMR analysis of the reaction mixture revealed a new paramagnetically-shifted spectrum and the consumption of 1. Following isolation, the product was crystallized from a 1:3 mixture of toluene:pentane at \(-35^\circ\text{C}\), yielding dark maroon crystals suitable for X-ray diffraction analysis. The solid state molecular structure revealed the reaction product to be the four-coordinate, iron carbene adduct \((\text{Bu}_L)\text{FeCl(CPh}_2\) (2) (Figure 4.1). The sum of the bond angles about the carbene carbon [359.9(3)°] indicate sp\(^2\)-hybridization, supporting the assignment of this ligand as a carbene instead of as an alkyl moiety. The solid-state molecular structure displays an Fe–C\(_\text{carbene}\) bond distance of 1.962(4) Å. The Fe–C\(_\text{carbene}\) bond distance is significantly elongated compared to previously isolated low-spin iron carbene complexes, which have Fe–C bond distances ranging

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carbene bond.
from 1.69–1.88 Å. The elongated Fe–C<sub>carbene</sub> bond length is, however, in line with recently isolated high-spin, open-shell iron carbene complexes reported by the Holland and Chirik groups, which display Fe–C bond distances of 1.973(6), 1.956(6), and 1.936(2) Å, respectively.

**Figure 4.1.** Solid-state molecular structure of (tBuL)FeCl(CPh₂) (1) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green.


Scheme 4.2. Synthesis of \((^{\text{Bu}}\text{L})\text{Fe(CPh}_2\text{)}\) (3), \((^{\text{Bu}}\text{L})\text{Fe(CPh}_2\text{)}\text{(Et}_2\text{O)}\) (4), and \((^{\text{Bu}}\text{L})\text{Fe(CPh}_2\text{)(pyr)}\) (5).

Addition of a thawing benzene solution containing 2 to a frozen solution of potassium graphite (KC₈) in benzene resulted in a color change from maroon to dark red upon thawing to room temperature, yielding a new paramagnetic species as ascertained by ¹H NMR spectroscopy (Scheme 4.2). Complex 2 can be regenerated by addition of a thawing benzene solution of trityl chloride (1 equiv) to a frozen benzene solution containing the reduction product. Thus, the reduction product is proposed to be the three-coordinate carbene adduct \((^{\text{Bu}}\text{L})\text{Fe(CPh}_2\text{)}\) (3).

Single crystals of 3 suitable for X-ray diffraction analysis could not be obtained, rather the solvato adducts of 3 \((^{\text{Bu}}\text{L})\text{Fe(CPh}_2\text{)(L)}\), L: Et₂O (4), pyr (5)) could be crystallized and structurally characterized. The solvato adducts of 3 could be generated by addition of the corresponding solvent to 3 in benzene followed by crystallization at −35°C in diethyl ether. Dissolution of crystals of 4 in C₆D₆ revealed only the presence of 3 by ¹H NMR spectroscopy, suggesting weak and reversible coordination of the solvent. Conversely, the pyridine in 5 remains bound in C₆D₆ solution and is stable to vacuum. The solid-state molecular structures for 4 and 5 are provided in Figure 4.2. The solid-state molecular structure of 4 and 5 are comparable, featuring Fe–C_carbene bond lengths of 1.977(2) and 1.959(5) Å, respectively, very similar to the Fe–C bond distance of 2. The sum of the bond angles about the carbene carbon (359.9(2)°, 4;
359.4(8)°, (5) are indicative of an sp²-hybridized carbon.

**Figure 4.2.** Solid-state molecular structures of (⁻BuL)FeCl(CPh₂)(Et₂O) (4) (a) and (⁻BuL)FeCl(CPh₂)(pyr) (5) (b) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, oxygen = red.

**Scheme 4.3.** Synthesis of (⁻BuL)Fe(CH₂Ph) (6) and (⁻BuL)FeCl(CH₂PPh₃) (7).

We have also synthesized two reference molecules to serve as authentic dipyrrin ferrous compounds bound to carbon-based ligands. The first, (⁻BuL)Fe(CH₂Ph) (6), was synthesized via
metathesis between \((\text{Bu}_L)\text{FeCl(Et}_2\text{O})\) and 0.5 equivalents of dibenzyl magnesium \((\text{Mg(CH}_2\text{Ph})_2(\text{thf})_2)\) in a thawing solution of benzene (Scheme 4.3). The second, \((\text{Bu}_L)\text{FeCl(CH}_2\text{PPh}_3)\) (7), was prepared upon addition of one equivalent of methylenetriphenylphosphane \((\text{CH}_2\text{PPh}_3)\) to \((\text{Bu}_L)\text{FeCl(ET}_2\text{O})\) (Scheme 4.3). The solid-state molecular structures for 6 and 7 each display elongated Fe–C bond lengths of 2.048(4) Å and 2.142(6) Å, respectively (Figure 4.3). Of particular note, the C–P bond in the phosphorus ylide ligand of 7 has a length of 1.749(6) Å. The phosphorus ylide bound to 7, therefore, serves as a neutral, singlet-type ligand.

Figure 4.3. Solid-state molecular structures of \((\text{Bu}_L)\text{Fe(CH}_2\text{Ph})\) (6) (a) and \((\text{Bu}_L)\text{FeCl(CH}_2\text{PPh}_3)\) (7) (b) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, phosphorus = pink.

4.2.2 Mössbauer Spectroscopy and Magnetometry on Carbene Adducts 2, 3, and 5

To assess the oxidation levels of carbene adducts 2, 3, and 5, we acquired the zero-field, \(^{57}\text{Fe Mössbauer}\) spectra at 90 K for each complex (Figure 4.4). The spectral data for the
complexes are best modeled with the following parameters for isomer shift, δ (mm/s), and quadrupole splitting, $|\Delta E_Q| (\text{mm/s}): 0.31, 2.75 (2); 0.42, 1.24 (3); \text{and} 0.68, 2.63 (5)$. The isomer shift and quadrupole splitting data for the four-coordinate carbene adducts 2 and 5 are consistent with other four-coordinate iron dipyrrin complexes synthesized within our group.\textsuperscript{11} Although structural confirmation of the solvent-free 3 was not possible, the Mössbauer spectrum, especially the smaller observed quadrupole splitting, is consistent with other three-coordinate, iron dipyrrin complexes bearing metal-ligand multiple bonds\textsuperscript{14} or π-basic ligands.\textsuperscript{15}


Figure 4.4. Zero-field $^{57}$Fe Mössbauer spectrum of ((Bu)L)FeCl(CPh$_2$) (2) (a), ((Bu)L)Fe(CPh$_2$) (3) (b), ((Bu)L)Fe(CPh$_2$)(pyr) (5) (c), ((Bu)L)Fe(CH$_2$Ph) (6) (d), and ((Bu)L)FeCl(CH$_2$PPh$_3$) (7) (e). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature: (2): $\delta = 0.31$ mm/sec, $|\Delta E_Q| = 2.75$ mm/sec. 3: $\delta = 0.42$ mm/sec, $|\Delta E_Q| = 1.24$ mm/sec. 5: $\delta = 0.68$ mm/sec, $|\Delta E_Q| = 2.63$ mm/sec. 6: $\delta = 0.54$ mm/sec, $|\Delta E_Q| = 0.85$ mm/sec. 7: $\delta = 0.87$ mm/sec, $|\Delta E_Q| = 2.47$ mm/sec.

Qualitatively, the carbene adducts 3 and 5 have higher isomer shift values than the oxidized precursor 2. The isomer shift of 2, however, is largely consistent with the previously reported iminyl radical adducts ((Ar)L)FeCl(NAr), 0.28 mm/s; ((Ar)L)FeCl(NAd), 0.26 mm/s; ((Bu)L)FeCl(NAr), 0.37 mm/s) and terminal imido complexes ((Ar)L)Fe(NAd), 0.37 mm/s; ((Ar)L)Fe(NAr), 0.44 mm/s), which have all been ascribed to a ferric oxidation level. However, a direct comparison between the imido/iminyl isomer shift values with those of the carbene adducts is not straightforward as Fe$^{II}$ complexes bearing alkyl ligands exhibit lower isomer shift...
values. Indeed, the Mössbauer spectrum of 6 features a lower isomer shift and smaller quadrupole splitting \( [\delta, |A_{\text{Q}}| (\text{mm/s}): 0.54, 0.85] \) than other ferrous complexes supported by the dipyrrin platform. Additionally, the isomer shift for 7 is shifted to a higher value than that for carbene complexes 2, 3, and 5 and suggests that the carbene ligands are not best described as neutral, singlet-type ligands.

To further probe the electronic structure of 2, the magnetic behavior was investigated via SQUID magnetometry. Variable temperature (VT) magnetic susceptibility measurements on 2 give a \( \chi T \) of 2.7 cm\(^3\)K/mol, consistent with an \( S = 2 \) state. Magnetization measurements collected at 1, 3, and 7 T, which were fit using the program PHI,\(^{17}\) give the following parameters: \( g = 1.92, D = -5.29 \) cm\(^{-1}\), and \( |E/D| = 0.317 \) (Figure 4.5). An \( S = 2 \) state can be arrived at by either a high-spin \( (S = 2) \) Fe\(^{\text{II}}\) bound to a singlet carbene, or a high-spin \( (S = \frac{5}{2}) \) Fe\(^{\text{III}}\) antiferromagnetically coupled to a carbene radical \( (S = \frac{1}{2}) \).

The low temperature (2.8 K) EPR spectrum of 5 is best modeled with an \( S = \frac{3}{2} \) configuration. The quartet configuration can result from a singlet carbene bound to a high spin \( (S = \frac{3}{2}) \) Fe\(^{\text{III}}\) center, or via a high-spin \( (S = 2) \) Fe\(^{\text{II}}\) antiferromagnetically coupled to a carbene radical \( (S = -\frac{1}{2}) \) (Figure 4.5).

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Figure 4.5. Variable temperature susceptibility data for 2: $\chi T = 2.7 \text{ cm}^3\text{K/mol}$; (inset) Reduced magnetization collected at 1, 3, and 7 T: $g = 1.92$, $D = -5.29 \text{ cm}^{-1}$, and $|E/D| = 0.317$. (b) Frozen toluene X-band EPR spectrum at 2.8 K of 5 (black trace). EPR fit (red trace) represents simulation with EasySpin\textsuperscript{18} using $g = 2.40$, 2.00, 1.80 and $S = \frac{3}{2}$.

4.2.3 Fe K- and L-edge X-Ray Absorption Near Edge Spectroscopy (XANES)

To further examine the metal oxidation level, samples of carbene adducts 2, 3, and 5 and the authentic ferrous 6 were investigated by X-ray absorption near edge spectroscopy (XANES). The maxima of the resolved pre-edge features, which represents the Fe 1s $\rightarrow$ 3d transition, for 3 (7112.7 eV), 5 (7112.6 eV), and 6 (7112.8 eV), as well as the respective rising edge positions, suggest carbene adducts 3 and 5 and benzyl complex 6 possess Fe in a common oxidation state. The pre-edge features present in 2 (7113.3 eV and 7114.2 eV) are shifted to slightly higher energies and suggest a more oxidized Fe center (Figure 4.6). Taken together, we propose that 3 and 5 are comprised of a ferrous center antiferromagnetically coupled to a carbene radical, while the data suggests 2 has an intermediate Fe$^{II}$/Fe$^{III}$ ground state that is expected to contain only a small amount of radical carbene character. Fe L$_{2,3}$-Edge spectra, seen in Figure 4.6, were also collected in order to support our oxidation state assignments. The position of the L$_3$-edge

maxima occurs at 707.7 eV in the spectra for all species (2, 3, 5, and 6), suggesting a common ferrous oxidation state.

Figure 4.6. (a) Overlaid Fe K-edge XANES with inset Fe (1s→3d) pre-edge features for (tBu)LFeCl(CPh2) (2, black), (tBu)LFe(CPh2) (3, blue), (tBu)LFe(CPh2)(pyr) (5, red), and (tBu)LFe(CH2Ph) (6, green). (b) Fe L-edge absorption spectra of compounds 2 (black), 3 (blue), 5 (red), and 6 (green). In comparing the spectra of the bona fide FeII species, (tBu)LFe(CH2Ph) (6) to that of compounds 2, 3, and 5, only minor changes in intensity are observed. The main L3 peaks for all complexes occur at the same energy, 707.7 eV, within experimental error suggesting a common effective nuclear charge at the metal center. The combined Fe K-edge, Fe-L edge, and computational data suggest that complexes 3 and 5 share a common oxidation state of FeII with that of 6, while complex 2 contains an intermediate FeII/FeIII state.

4.2.4 Electronic Structure of Iron Carbenes by DFT

To resolve the ambiguity in the electronic structure of 2, calculations at the B3LYP level for both the quintet and the BS(5,1) states were performed. A geometry optimization of 2 using the BP86 functional was carried out to produce coordinates from which to carry out these electronic structure calculations. The geometry-optimized structure of 2 closely reproduces the crystallographically determined bond lengths: Fe–C_carbene: 1.953 Å, Fe–Cl: 2.268 Å, Fe–N_pyrrole: 2.049 Å, 2.031 Å. Additionally, we have noted that for our dipyrrin complexes that converge to a broken symmetry solution, the corresponding orbital overlap for the α/β electron pair is generally less than 80%.11,15 For 2 in the BS(5,1) state, the α and β electron pair is located in the iron-
carbene $\pi$ molecular orbital with an orbital overlap of 83.1%, suggesting some spin polarization.\textsuperscript{19}

\textbf{Figure 4.7}. Spin density ($\alpha$–$\beta$) plots calculated for (a) 2 from the quintet solution and (b) 5 from the BS(4,1) solution, showing the antiferromagnetic coupling between the high-spin Fe$^{\text{II}}$ and the carbene radical ($J = -559.52$ cm$^{-1}$). The spin density plot for 7 (c) was calculated from the quintet state.

The spin density plot ($\alpha$–$\beta$) for 2 is provided in Figure 4.7, which reveals some partial $\beta$-spin delocalization onto the carbene C. The DFT calculation results corroborate the oxidation state assignment for Fe in 2 as intermediate Fe$^{\text{II}}$/Fe$^{\text{III}}$, consistent with the Mössbauer (predicted $\delta = 0.36$ mm/sec; $|\Delta E_Q| = 2.96$ mm/sec) and XANES results (calculated transition energy 7112.9 and 7113.7 eV upon application of the global energy correlation (Figure 4.8)). For the pyridine adduct 5, we calculated both the quartet and the broken symmetry BS(4,1) states at the B3LYP level using BP86 geometry-optimized coordinates. The results of the geometry optimized structure for 5 match well with the experimentally derived bond lengths and angles: Fe–C$_{\text{carbene}}$: 2.013 Å, Fe–N$_{\text{pyridine}}$: 2.108 Å, Fe–N$_{\text{pyrrole}}$: 2.083 Å, 2.095 Å. Additionally, in the BS(4,1) state, the $\alpha$ and $\beta$ electron pair is located in an iron-carbene $\pi$ molecular orbital with a corresponding orbital overlap of 45.7%, suggesting significant localized orbital character.\textsuperscript{19} The spin density plot ($\alpha$–$\beta$) for 5 is provided in Figure 4.7, which reveals a substantial amount of spin

delocalization onto the carbene fragment. We therefore propose that the electronic structure that best describes both 5 and, by extension 3, is a high-spin ($S = 2$) \( \text{Fe}^{\text{II}} \) antiferromagnetically coupled to a carbene-based ($S = 1/2$) radical. The calculated \( ^{57}\text{Fe} \) Mössbauer parameters ($\delta = 0.60 \text{ mm/sec}$ and $|\Delta E_Q| = 2.77 \text{ mm/sec}$), as well as the XANES results (Figure 4.8), for the BS(4,1) state are in good agreement with the experimental data.

The assignment of 7 as a high-spin \( \text{Fe}^{\text{II}} \) was corroborated by unrestricted, single point calculations in the quintet state that provided calculated \( ^{57}\text{Fe} \) Mössbauer parameters ($\delta = 0.87 \text{ mm/sec}$; $|\Delta E_Q| = 3.03 \text{ mm/sec}$) that match well with the experimental data. The spin density plot for 7 (Figure 4.7) reveals no significant spin density located on the phosphorus ylide ligand.

![Figure 4.8](image.png)

**Figure 4.8** (a) Fe K-edge absorption spectra of \((^\text{Bu}L)\text{FeCl(CPh}_2\) (2) (black) overlaid with the B3LYP calculated spectra (grey). (b) Fe K-edge absorption spectra of \((^\text{Bu}L)\text{Fe(CPh}_2\)(pyr) (5) (red) overlaid with the B3LYP calculated spectra (grey).

### 4.2.5 Reactivity of Iron Carbenes

Heating a benzene solution of 2 to 60°C for 6 hours results in complete consumption of 2 and re-generation of 1 as observed by \(^1\text{H} \) NMR (Scheme 4.4). The organic product is confirmed
by both $^1$H NMR spectroscopy and GC-MS to be tetraphenylethylene, consistent with carbene expulsion and dimerization, typical for Fisher carbenes. Stirring a solution of 2 in neat styrene at room temperature overnight results in the formation of 1 concomitantly with the cyclopropanation\textsuperscript{20} of styrene (59\%) as observed by $^1$H NMR. Furthermore, stirring a solution of 2 in neat 1,4-cyclohexadiene (CHD) for 30 minutes at room temperature furnishes 1 and the product of carbene C–H bond insertion (45\%), not H-atom abstraction, of CHD, similar to [Rh\textsubscript{2}] carbene transfer reactivity.\textsuperscript{21}

**Scheme 4.4.** Reactivity of (tBu\textsubscript{L})FeCl(CPh\textsubscript{2}) (2).

While carbene adduct 2 does not H-atom abstract from CHD, complex 2 does hydrogen atom abstract (HAA) from hydroxy-2-azaadamantane. Stirring a benzene solution of 2 containing one equivalent of hydroxy-2-azaadamantane for 5 minutes at room temperature


generates 2-azaadamantane-N-oxyl, confirmed via EPR spectroscopy (Scheme 4.4). No evidence of HAA is observed, however, upon reaction with toluene, cyclohexene, 9,10-dihydroanthracene, fluorene, or 2,4,6-tri-tert-butyl-phenol. Similarly, we observe no reaction between 2 and a variety of radical traps, including 2,4,6-tri-tert-butyl-phenoxy, triphenylmethyl radical, or TEMPO. The reactivity presented supports the results of the DFT calculations in assigning the oxidation state at Fe for 2 to be intermediate on the Fe$^{II}$/Fe$^{III}$ continuum with some spin delocalization onto the carbene ligand: 2 displays typical Fischer carbene transfer chemistry, but can also engage in H-atom abstraction from weak O–H bonds.

**Scheme 4.5.** Reactivity of ($^{t}$Bu$L$)Fe(CPh$_2$)(pyr) (5) with AdNOH.

Reduction of 2 to 3 or 5 leads to full reduction of the carbene moiety, suggesting an Fe$^{II}$(CPh$_2$) formulation. 5 does not exhibit any reactivity representative of Fisher-type carbenes. 5 is stable in both C$_6$H$_6$ at 80°C and styrene at 80°C and does not show significant decomposition in contrast to 2 (vide supra). Pyridine adduct 5, however, does display radical-like reactivity by performing HAA from hydroxyl-2-azaadamantane at room temperature as evidenced by the formation of 2-azaadamantane-N-oxyl in the EPR spectrum of the reaction mixture (Scheme 4.5). No evidence of HAA at room temperature or upon heating to 80°C is observed, however, upon reaction of 5 with toluene, 9,10-dihydroanthracene, or 2,4,6-tri-tert-butyl-phenol. Similarly, we observe no reaction between 5 and a variety of radical traps,
including 2,4,6-tri-tert-butyl-phenoxy, triphenylmethyl radical, or TEMPO.

4.3 Conclusions

In conclusion, we have isolated two iron carbenes in a weak-field ligand environment. Diphenyldiazoalkane undergoes dinitrogen extrusion upon reaction with the ferrous dipyrrin complex to afford an intermediate ferrous/ferric carbene adduct. One electron reduction of the carbene adduct leads not to an iron-centered reduction, but rather the carbene is fully reduced to a carbenyl radical anion, coupling to the high-spin ferrous center. The electronic structures of these complexes were determined using Mössbauer, EPR, and X-ray absorption spectroscopy, SQUID magnetometry, DFT calculations, X-ray crystallography, analysis of their respective reactivity, and comparison to authentically prepared dipyrrin ferrous compounds bound to carbon-based ligands.
4.4 Experimental

4.4.1 Characterization and Physical Measurements

$^1$H NMR spectra were recorded on Varian Unity/Inova 400, 500, or 600 MHz spectrometers. $^1$H NMR chemical shifts are reported relative to SiMe$_4$ using the chemical shift of residual solvent peaks as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent GC/MS 5975 Turbo system. High-resolution mass spectrometry was performed on a Bruker microTOFII ESI LCMS or Bruker Maxis Impact LC-q-TOF Mass Spectrometer. Elemental analyses (% CHN) were obtained on a PerkinElmer 2400 Series II CHNS/O Analyzer.

Zero-field $^{57}$Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN) at 90 K. Isomer shifts are quoted relative to Fe foil at room temperature. Data was analyzed and simulated with Igor Pro 6 software (WaveMetrics, Portland, OR) using Lorentzian fitting functions. Samples were prepared by suspending 25-50 mg of compound in Paratone oil and immobilizing by rapid freezing in liquid nitrogen. For compounds that decomposed in the presence of Paratone oil, samples were measured as frozen solutions in benzene. EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra were measured as frozen toluene glasses at a microwave power of 0.6325–2 mW. Spectral simulations were performed using the program EasySpin.$^{18}$ Magnetic data were collected using a Quantum Design MPMS-5S SQUID magnetometer. Measurements were obtained for finely ground microcrystalline powders restrained in a frozen eicosane matrix within polycarbonate capsules. Samples were prepared under a dry nitrogen atmosphere by packing the powder in a gelcap and adding warm liquid eicosane, which formed a solid wax upon cooling. Dc susceptibility measurements were collected in the temperature range 5-300 K under a dc field
of 5000 or 10000 Oe. Dc magnetization measurements were obtained in the temperature range 1.8–10 K under dc fields of 1, 4, and 7 T. The susceptibility data was corrected for contributions from the sample holder and eicosane, as well as the core diamagnetism of the sample using Pascal’s constants. The reduced magnetization data were fit using PHI.\textsuperscript{17}

4.4.2 General Procedures

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported.\textsuperscript{25} All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antichamber prior to use in the drybox. Benzene, diethyl ether, dichloromethane, hexanes, pentane, pyridine, toluene, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-\textit{d} was purchased from Cambridge Isotope Labs and used as received. Benzene-\textit{d}_6 was purchased from Cambridge Isotope Labs and was degassed and stored over 4 Å molecular sieves prior to use. 1,4-cyclohexadiene, styrene, cyclohexene, 2,4,6-tri-\textit{tert}-butylphenol, trityl chloride, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), fluorene, 9,10-dihydroanthracene, benzophenone azine, and samarium(III) trifluoromethanesulfonate were purchased from Aldrich. Tris(pentafluorophenyl)borane was purchased from Alfa Aesar. 2-azaadamantane-N-oxyl was purchased from Santa Cruz Biotechnology. 2-hydroxy-2-azaadamantane was purchased from TCI. All C-H substrates were dried over calcium hydride and distilled under nitrogen or vacuum or recrystallized from hexanes. Iron dichloride was purchased from Strem and used as received. Diphenyldiazomethane,\textsuperscript{22} potassium graphite,\textsuperscript{23} Gomberg’s dimer,\textsuperscript{24} 2,4,6-tri-\textit{tert}-butylphenoxyl


radical,\textsuperscript{25} Mg(CH\textsubscript{2}Ph\textsubscript{2})(thf)\textsubscript{2},\textsuperscript{26} and methylene-triphenylphosphane\textsuperscript{27} were synthesized following literature procedures. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150°C prior to use in a drybox. Silica gel 32-63 µ (AIC, Framingham, MA) was used as received.

4.4.3 Metal Complex Syntheses

\((^\text{tBu}L)\text{FeCl(CPh}_2\text{)} (2):\) A thawing benzene solution (2 mL) containing \([^\text{tBu}L]\text{FeCl}\] \textsubscript{2} (1) (52.5 mg, 0.065 mmol), synthesized as previously reported,\textsuperscript{11} was added to a frozen benzene solution (10 mL) at −196°C of N\textsubscript{2}C\textsubscript{6}H\textsubscript{6} (25.2 mg, 0.13 mmol). The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 30 minutes, during which time the color changed from bright red to maroon. The benzene was lyophilized and the product was crystallized from a solution of toluene layered with pentane at −35°C to afford dark, maroon crystals of 2 (42.7 mg, 53%). \(^1\text{H} \text{NMR (600 MHz, C}_6\text{D}_6\text{): } \delta \text{ (ppm) 119.13 (br. s), 70.37 (br. s), 24.}

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28.26 (br. s), 22.37 (br. s), 6.36 (br. s), –19.74 (br. s). Anal. Calc. for C\textsubscript{36}H\textsubscript{35}Cl\textsubscript{3}FeN\textsubscript{2}: C 65.73, H 5.36, N 4.26; Found C 65.55, H 5.40, N 4.22. Zero-field \textsuperscript{57}Fe Mössbauer (90 K) $\delta = 0.31$ mm/s, $|\Delta E_Q| = 2.75$ mm/s. $\mu_{\text{eff}}$ (295 K, SQUID) 4.5 $\mu_B$. 

Figure 4.9. $^1$H NMR spectrum for ($^{\text{Bu}}$L)FeCl(CPh$_2$) (2) collected in C$_6$D$_6$. 
Figure 4.10. Zero-field $^{57}$Fe Mössbauer spectrum of $^{(\text{BuL})}\text{FeCl}(\text{CPh}_2)$ (2). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature. Parameters calculated via DFT: $\delta = 0.36$ mm/sec, $|\Delta E_Q| = 2.96$ mm/sec.
Figure 4.11. Magnetization data for ($^1$Bu-L)FeCl(CPh$_2$) (2). Magnetization versus field collected at 100 K – linear plot reflects the sample is free from ferromagnetic impurities. Linear fit correlation coefficient $R^2 = 0.9998$. 
Figure 4.12. Variable temperature susceptibility data for 2: $\chi T = 2.7 \text{ cm}^3\text{K/mol}$; (inset) Reduced magnetization collected at 1, 3, and 7 T: $g = 1.92$, $D = -5.29 \text{ cm}^{-1}$, and $|E/D| = 0.317$. 
Figure 4.13. Solid-state molecular structure of $^{\text{Bu}}L\text{FeCl(CPh}_2\text{)}$ (1) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green.
(\textsuperscript{t}Bu\textsubscript{L})Fe(CPh\textsubscript{2}) (3): A just-thawed benzene solution (2 mL) containing (\textsuperscript{t}Bu\textsubscript{L})FeCl(CPh\textsubscript{2}) (2) (53.1 mg, 0.081 mmol) was added to a frozen benzene solution (2 mL) of potassium graphite (15.3 mg, 0.081 mmol). The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 30 minutes, during which time the color changed from dark maroon to bright red. The solution was filtered through a glass fiber and the solvent was removed \textit{in vacuo} to afford (\textsuperscript{t}Bu\textsubscript{L})Fe(CPh\textsubscript{2}) (3) (45.2 mg, 89\%). \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): δ (ppm) 186.21 (s), 138.64 (br. s), 42.18 (s), 6.14 (s), 4.91 (s), 3.65 (s), 1.13 (s), −6.73 (s), −8.92 (s), −59.36 (s). Anal. Calc. for C\textsubscript{36}H\textsubscript{35}Cl\textsubscript{2}FeN\textsubscript{2}: C 69.47, H 5.67, 4.50; Found C 68.55, H 5.69, N 4.11. EPR (toluene, 2.8 K): g\textsubscript{eff} = 5.69, 2.54, 2.13. Zero-field \textsuperscript{57}Fe Mössbauer (90 K) δ = 0.42 mm/s, |ΔE\textsubscript{Q}| = 1.24 mm/s.
Figure 4.14. $^1$H NMR spectrum for (Bu)LFe(CPh$_2$) (3) collected in C$_6$D$_6$. 
Figure 4.15. Zero-field $^{57}$Fe Mössbauer spectrum of $^{(tBu)}_{L}$Fe(CPh$_2$) (3). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature. Parameters calculated via DFT: $\delta = 0.41$ mm/sec, $|\Delta E_Q| = 0.75$ mm/sec.
Figure 4.16. Frozen toluene EPR spectrum of $^{1}$BuLFe(CPh$_2$)$_2$ (3) (black line) at 2.8 K. The minor signal at $g = 2$ corresponds to a trace organic radical impurity. The red line represents a fit using EasySpin$^{18}$ with $g = 2.40, 2.00, 1.80$ and $S = \frac{3}{2}$.
(\textsuperscript{t}BuL)Fe(CPh\textsubscript{2})(L) (L: Et\textsubscript{2}O (4); pyridine (5)): Several drops of either Et\textsubscript{2}O or pyridine were added to a benzene solution (2 mL) containing (\textsuperscript{t}BuL)Fe(CPh\textsubscript{2}) (3) (45.2 mg, 0.073 mmol) and stirred at room temperature for 1 hour, during which time the color changed from bright red to dark orange. The solvent was removed \textit{in vacuo} and the product dissolved in minimal Et\textsubscript{2}O to afford crystals at \(-35^\circ\text{C}\) of either 4 or 5 (50.0 mg, 98%) suitable for X-ray diffraction. \textsuperscript{1}H NMR for 5 (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta\) (ppm) 50.03 (s), 28.47 (s), 21.29 (s), 16.72 (s), 14.43 (s), 13.35 (s), 9.71 (s), 9.04 (s), 7.70 (s), 4.94 (s), 3.26 (s), \(-3.29\) (s), \(-7.35\) (br. s). Anal. Calc. for C\textsubscript{41}H\textsubscript{40}Cl\textsubscript{2}FeN\textsubscript{3} (5): C 70.20, H 5.75, N 5.99; Found C 70.76, H 5.78, N 5.68. EPR (toluene, 2.8 K) for 5: \(g\text{eff} = 6.20, 3.26, 1.78\). Zero-field \textsuperscript{57}Fe Mössbauer (90 K) for 5: \(\delta = 0.68\) mm/s, \(|\Delta E_{Q}| = 2.63\) mm/s.
Figure 4.17. $^1$H NMR spectrum for ($^{^{13}}$Bu)LFe(CPh$_2$)(pyr) (5) collected in C$_6$D$_6$. 
Figure 4.18. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{13}$Bu)LFe(CPh$_2$)(pyr) (5). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature. Parameters calculated via DFT: $\delta = 0.60$ mm/sec, $|\Delta E_Q| = 2.77$ mm/sec.
Figure 4.19. Frozen toluene X-band EPR spectrum at 2.8 K of 5 (black trace). EPR fit (red trace) represents simulation with EasySpin\textsuperscript{18} using \( g = 2.40, 2.00, 1.80 \) and \( S = \frac{3}{2} \).
Figure 4.20. Solid-state molecular structures of \((^{\text{Ia}}L)\text{FeCl}(\text{CPh}_2)(\text{Et}_2\text{O})\) (4) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, oxygen = red.
Figure 4.21. Solid-state molecular structures of (tBuL)FeCl(CPh₂)(pyr) (5) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green.
(tBuL)Fe(CH2Ph) (6): A thawing benzene solution (2 mL) containing Mg(CH2Ph)2(thf)2 (7.9 mg, 0.038 mmol) was added to a frozen benzene solution (2 mL) containing (tBuL)FeCl(Et2O) (43 mg, 0.076 mmol), synthesized as previously reported. The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 30 minutes. The reaction mixture was filtered through celite and the benzene lyophilized to give the product, (tBuL)Fe(CH2Ph) (6), as a dark red solid (25 mg, 60%). Crystals suitable for X-ray diffraction were grown from a solution of toluene layered with pentane at −35°C. 1H NMR (500 MHz, C6D6): δ (ppm) 72.96 (s), 28.96, 9.55 (br. s), 6.03 (s), 4.54 (s), −6.77 (br. s), −7.46 (br. s), −48.23 (br. s), −52.75 (s). Anal. Calc. for C30H32Cl2FeN2: C 65.83, H 5.89, N 5.12; Found C 65.67, H 6.07, N 5.8. Zero-field 57Fe Mössbauer (90 K) δ = 0.54 mm/sec, |ΔEq| = 0.85 mm/s.
Figure 4.22. $^1$H NMR spectrum for ($^t$BuL)Fe(CH$_2$Ph) (6) collected in C$_6$D$_6$. 
Figure 4.23. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{t}$BuL)Fe(CH$_2$Ph) (6). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature. Parameters calculated via DFT: $\delta = 0.48$ mm/sec, $|\Delta E_Q| = 1.41$ mm/sec.
Figure 4.24. Solid-state molecular structures of \((^{\text{Bu}}\text{L})\text{Fe(CH}_2\text{Ph})\) (6) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green.
\((^{\text{BuL}})\text{FeCl(CH}_2\text{PPh}_3)\) (7): A thawing benzene solution (2 mL) containing \(\text{Ph}_3\text{PCH}_2\) (29.0 mg, 0.11 mmol) was added to a frozen benzene solution (2 mL) containing \((^{\text{BuL}})\text{FeCl}(\text{Et}_2\text{O})\) (50 mg, 0.11 mmol), synthesized as previously reported.\(^{11}\) The reaction mixture was warmed to room temperature and allowed to stir at this temperature for 30 minutes. The reaction mixture was filtered through celite and the benzene lyophilized. The product, \((^{\text{BuL}})\text{FeCl(CH}_2\text{PPh}_3)\) (7), was crystallized from a 1:3 mixture of toluene:hexanes at \(-35^\circ\text{C}\) (17.5 mg, 22%). \(^1\text{H} NMR (500 MHz, C}_6\text{D}_6): \delta \text{ (ppm)} \ 49.84 \text{ (s)}, 21.60 \text{ (s)}, 11.10 \text{ (s)}, 10.42 \text{ (s)}, 9.68 \text{ (s)}, 6.96 \text{ (s)}, 5.37 \text{ (s)}, 2.07 \text{ (s)}, 1.24 \text{ (s)}, -8.11 \text{ (s)}. \text{Anal. Calc. for C}\_42\text{H}\_41\text{Cl}_2\text{FePN}_2\cdot\text{C}_5\text{H}_{12}: \text{C} 67.27, \text{H} 5.84, \text{N} 3.34; \text{Found C} 66.69, \text{H} 5.84, \text{N} 3.13. \text{Zero-field } ^{57}\text{Fe Mössbauer (90 K)} \delta = 0.87 \text{ mm/sec, } |\Delta E_Q| = 2.47 \text{ mm/s.}
Figure 4.25. $^1$H NMR spectrum for ($^{t}$Bu)FeCl(CH$_2$PPh$_3$) (7) collected in C$_6$D$_6$. 
Figure 4.26. Zero-field $^{57}$Fe Mössbauer spectrum of ($^{\text{Bu}}L$)FeCl(CH$_2$PPh$_3$) (7). Isomer shift and quadrupole splitting are reported relative to Fe foil at room temperature. Parameters calculated via DFT: $\delta = 0.73$ mm/sec, $|\Delta E_Q| = 3.03$ mm/sec.
Figure 4.27. Solid-state molecular structures of ($^{\text{Bu}}$L)FeCl(CH$_2$PPh$_3$) (7) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Iron = orange, nitrogen = blue, carbon = gray, chlorine = green, phosphorus = pink.
Reactions of \((^t\text{Bu}L)\text{FeCl(CPh}_2\) \((2)\).

*Reactivity upon heating.*

A solution of \(2\) in \(C_6D_6\) (2 mL) was heated in a J. Young NMR tube at 60°C for 6 hours. Generation of \(1\) was confirmed by \(^1H\) NMR spectroscopy, which showed complete consumption of \(2\) and new resonances consistent with that of \(1\).\(^{11}\) The solution was filtered through a plug of silica gel, eluting with additional benzene to remove paramagnetic materials. Formation of tetraphenylethylene was confirmed via \(^1H\) NMR spectroscopy and GC-MS. Spectral data were consistent with previously reported characterization of the product.\(^{28}\)

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Figure 4.28. $^1$H NMR spectrum for the reaction of ($\text{Bu}_L$)FeCl(CPh)$_2$ (2) upon heating to 60°C in C$_6$D$_6$. 2 is shown in red. The reaction mixture after 6 hours is shown in green. [(BuL)FeCl]$_2$ (1) is shown in blue.
Reaction with 1,4-cyclohexadiene.

A solution of 2 in neat 1,4-cyclohexadiene (2 mL) was stirred for 30 minutes at room temperature. The solution was removed in vacuo and the products dissolved in C₆D₆. Generation of 1 was confirmed by ¹H NMR spectroscopy, which showed complete consumption of 2 and new resonances consistent with that of 1. The solution was filtered through a plug of silica gel eluting with additional benzene to remove paramagnetic materials. Formation of the 3-benzhydrolycyclohexa-1,4-diene (44%) was confirmed via ¹H NMR spectroscopy and GC-MS. Yield is reported by integration versus the internal standard ferrocene. Spectral data were consistent with previously reported characterization of the product.²⁹

Figure 4.29. $^1$H NMR spectrum for the reaction of ($^{t}{\text{Bu}}$L)FeCl(CPh$_2$) (2) upon stirring in neat 1,4-cyclohexadiene at room temperature. NMRs taken in C$_6$D$_6$. 2 is shown in red. The reaction mixture after 20 minutes is shown in green. [(tBuL)FeCl]$_2$ (1) is shown in blue.
Figure 4.30. $^1$H NMR spectrum for the reaction of ($^{2}$BuL)FeCl(CPh$_2$)$_2$ upon stirring in neat 1,4-cyclohexadiene at room temperature after filtering through SiO$_2$ to remove paramagnetic impurities. NMR taken in C$_6$D$_6$ reveals formation of 3-benzhydrylcyclohexa-1,4-diene. Peaks labeled with a star correspond to ($^{2}$BuL)H.
**Reaction with styrene.**

A solution of 2 in neat styrene (2 mL) was stirred at room temperature for 12 hours. The solution was removed *in vacuo* and the products dissolved in C$_6$D$_6$. Generation of 1 was confirmed by $^1$H NMR spectroscopy, which showed complete consumption of 2 and new resonances consistent with that of 1. The solution was filtered through a plug of silica gel eluting with additional benzene to remove paramagnetic materials. Formation of the functionalized styrene (59%) was confirmed *via* $^1$H NMR spectroscopy and GC-MS. Yield is reported by integration versus the internal standard ferrocene. Spectral data were consistent with previously reported characterization of the product.³⁰

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Figure 4.31. $^1$H NMR spectrum for the reaction of ($^{tBu}$L)FeCl(CPh$_2$) (2) upon stirring in neat styrene to room temperature. NMRs taken in C$_6$D$_6$. 2 is shown in red. The reaction mixture after 12 hours is shown in green. [($^{tBu}$L)FeCl]$_2$ (1) is shown in blue.
Figure 4.32. $^1$H NMR spectrum for the reaction of ((Bu)L)FeCl(CPh$_2$)$_2$ (2) upon stirring in neat styrene at room temperature after filtering through SiO$_2$ to remove paramagnetic impurities. NMR taken in C$_6$D$_6$ reveals formation of the functionalized styrene. The peak at ~1.2 ppm corresponds to free ligand. The broad resonances at ~1.3–2.4 ppm are assigned as polymerized styrene. The peak at ~4 ppm corresponds to the ferrocene reference. The peaks at ~5.0 and 5.6 ppm correspond to unreacted styrene.
Reaction with 2-hydroxy-2-azaadamantane.

A just-thawed benzene solution (2 mL) of 2 (20.0 mg, 0.019 mmol) was added to a frozen benzene solution (2 mL) containing 2-hydroxy-2-azaadamantane (5.90 mg, 0.019 mmol). The reaction mixture was warmed to room temperature and stirred for 30 minutes. Consumption of 2 was observed via $^1$H NMR spectroscopy and formation of 2-azaadamantane-$N$-oxyl was confirmed via EPR spectroscopy by comparison to an authentic sample.

**Figure 4.33.** $^1$H NMR spectrum for the reaction of ($^{18}$BuL)FeCl(CPh$_2$) (2) (red) with 2-hydroxy-2-azaadamantane. The reaction mixture after 30 minutes is shown in green.
Figure 4.34. Frozen toluene EPR spectrum at 77 K of the reaction between \((\text{dbu-L})\text{FeCl(CPh}_2\text{)}\) (2) and 2-hydroxy-2-azaadamantane revealing formation of 2-azaadamantane-N-oxyl (left). Frozen toluene EPR spectrum at 77 K of 2-azaadamantane-N-oxyl (right).

Figure 4.35. Frozen toluene EPR spectrum at 77 K of the reaction between \((\text{dbu-L})\text{FeCl(CPh}_2\text{)}\) (2) and 2-hydroxy-2-azaadamantane revealing formation of 2-azaadamantane-N-oxyl (left): \(g_{\text{eff}} = 2.02, 2.00, 1.98\). Frozen toluene EPR spectrum at 77 K of 2-azaadamantane-N-oxyl (right): \(g_{\text{eff}} = 2.02, 2.00, 1.98\).
Reactions of \((t^{Bu}_L)LFe(CPh_2)\) (3) and \((t^{Bu}_L)LFe(CPh_2)(pyr)\) (5).

**Reaction with trityl chloride.**

A just-thawed benzene solution (2 mL) of 3 (35 mg, 0.067 mmol) was added to a frozen benzene solution (2 mL) containing trityl chloride (18.6 mg, 0.067 mmol). The reaction mixture was warmed to room temperature and stirred for 5 minutes. Consumption of 3 and formation of 2 was observed via \(^1\)H NMR spectroscopy.
Figure 4.36. $^1$H NMR spectrum for the reaction of ($^{t}$BuL)Fe(CPh$_2$)$_2$ (3) (green) upon reaction with one equivalent of trityl chloride to re-generate ($^{t}$BuL)FeCl(CPh$_2$)$_2$ (2). The reaction mixture after 5 minutes is shown in blue. 2 is shown in red.

Reaction with 2-hydroxy-2-azaadamantane.

A just-thawed benzene solution (2 mL) of 5 (10.0 mg, 0.031 mmol) was added to a frozen benzene solution (2 mL) containing 2-hydroxy-2-azaadamantane (5.90 mg, 0.031 mmol). The reaction mixture was warmed to room temperature and stirred for 30 minutes. Consumption of 5 was observed via $^1$H NMR spectroscopy and formation of 2-azaadamantane-$N$-oxyl was confirmed via EPR spectroscopy by comparison to an authentic sample.
**Figure 4.37.** Frozen toluene EPR spectrum at 77 K of the reaction between $\left(\text{^tBuL}\right)\text{Fe(CPh}_2\text{)(pyr)}$ (5) and 2-hydroxy-2-azaadamantane revealing formation of 2-azaadamantane-N-oxyl (left). Frozen toluene EPR spectrum at 77 K of 2-azaadamantane-N-oxyl (right).

**Figure 4.38.** Frozen toluene EPR spectrum at 77 K of the reaction between $\left(\text{^tBuL}\right)\text{Fe(CPh}_2\text{)(pyr)}$ (5) and 2-hydroxy-2-azaadamantane revealing formation of 2-azaadamantane-N-oxyl (left): $g_{\text{eff}} = 2.02, 2.00, 1.98$. Frozen toluene EPR spectrum at 77 K of 2-azaadamantane-N-oxyl (right): $g_{\text{eff}} = 2.02, 2.00, 1.98$. 
4.4.4 XAS Data Collection

All data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 500 mA. All samples were prepared in an inert-atmosphere glovebox and were measured as solids. For Fe K-edge measurements, samples were ground with BN to a final concentration of 10 weight % Fe, pressed into 1 mm aluminum spacers and sealed with 37 µm Kapton tape. For Fe L-edge measurements, samples were ground to a fine powder and spread in a thin layer on carbon tape affixed to an Al sample rod.

Fe K-edge measurements were collected using beam line 9-3. Samples were maintained at 10 K in a liquid He cryostat during data collection. Spectra were collected in transmission mode, with X-rays detected by ionization chambers immediately downstream and upstream of the sample. A Fe foil and a third ionization chamber upstream of the sample were used for internal energy calibration, setting the first inflection point of the Fe foil scan to 7112.0 eV. Data were collected from 6800.0 to 7488.0 eV. Three scans of each sample were collected and averaged. Spectra were processed using Sixpack and Igor Pro. The region below 7050 eV was used to fit a linear background, while the region above 7130 eV was flattened with a piecewise spline and set to an average intensity of 1.

Fe L_{2,3}-edge XAS measurements were collected on the 31-pole wiggler beam line 10-1 with a 1000 lines/mm spherical grating monochromator and 20 µm entrance and exit slits. Data were measured by monitoring the change in sample current through detection of the total electron yield (TEY). The drain current was normalized to incident photon flux with a gold-grid reference monitor. Incident beam energy was calibrated by comparison of the Fe metal L_3 edge at 706.8 eV in a reference sample placed upstream of the sample chamber. Samples were maintained at room temperature under an ultra-high vacuum (10^{-9} Torr) during collection. Four scans were measured.
and averaged for each compound. Processing was done using PyMCA. Background subtraction was achieved by fitting a line to the pre-edge region and subtracting from the entire spectrum. The post edge region was fit to a flattened polynomial and normalized to 1.0. The edge jumps at \( L_3 \) and \( L_2 \) were subtracted using a statistics-sensitive non-linear iterative peak-clipping (SNIP) algorithm as implemented in PyMCA. Data were processed with Igor 6.37.

**DFT Calculations for XAS Data Collection.** Density Functional Theory (DFT) calculations were performed with version 3.03 of the ORCA software package.\(^{31}\) Fe K-edge XAS spectra were calculated using TDDFT. Spectra of 2, 3, 5, and 6 were calculated from coordinates taken from a BP86 geometry optimization. Single-point energies were calculated by using the \( \omega \)-B97X functional.\(^{32}\) Calculations with hybrid functionals used the RIJCOSX algorithm to speed the calculation of Hartree–Fock exchange.\(^{33}\) The CP(PPP) basis set was used for Fe with a special integration accuracy (ORCA Grid7).\(^{34}\) The scalar relativistically recontracted def2-TZVP(-f)-ZORA basis set\(^{35}\) with ORCA Grid4 was used for all other atoms. Calculations included the zeroth-order regular approximation (ZORA)\(^{36}\) for relativistic effects as implemented by van

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Wüllen.\textsuperscript{37} Solvation was modeled with COSMO in an infinite dielectric.\textsuperscript{38} A broken symmetry surface was used to optimize 2 [(BS) (5,1)], 3 [(BS) (4,1)], and 5 [(BS) (4,1)], structures that all converged as antiferromagnetically-coupled configurations.

\textbf{Figure 4.39.} (a) Overlaid Fe K-edge XANES with inset Fe (1s→3d) pre-edge features for (\textsuperscript{t}BuL)FeCl(CPh\textsubscript{2}) (2, (black), (\textsuperscript{t}BuL)Fe(CPh\textsubscript{2}) (3, blue), (\textsuperscript{t}BuL)Fe(CPh\textsubscript{2})(pyr) (5, red), and (\textsuperscript{t}BuL)Fe(CH\textsubscript{2}Ph) (6, green). (b) Fe L-edge absorption spectra of compounds 2 (black), 3 (blue), 5 (red), and 6 (green). In comparing the spectra of the bona fide Fe\textsuperscript{II} species, (\textsuperscript{t}BuL)Fe(CH\textsubscript{2}Ph) (6) to that of compounds 2, 3, and 5, only minor changes in intensity are observed. The main L\textsubscript{3} peaks for all complexes occur at the same energy, 707.7 eV, within experimental error suggesting a common effective nuclear charge at the metal center. The combined Fe K-edge, Fe-L edge, and computational data suggest that complexes 3 and 5 share a common oxidation state of Fe\textsuperscript{II} with that of 6, while complex 2 contains an intermediate Fe\textsuperscript{II}/Fe\textsuperscript{III} state.


Figure 4.40. Correlation of experimental Fe K-edge XAS pre-edge peak energies for compounds 2, 3, 5, and 6. Energies calculated by B3LYP/def2-TZVP-ZORA.

Figure 4.41. Fe K-edge absorption spectra of ($^3$BuL)FeCl(CPh$_2$) (2) (black) overlaid with the B3LYP calculated spectra (grey).
Figure 4.42. Fe K-edge absorption spectra of $^{(tBu)}L$Fe(CPh$_2$) (3) (blue) overlaid with the B3LYP calculated spectra (grey).

Figure 4.43. Fe K-edge absorption spectra of $^{(thi)}L$Fe(CPh$_2$)(pyr) (5) (red) overlaid with the B3LYP calculated spectra (grey).
Figure 4.44. Fe K-edge absorption spectra of (tBuL)Fe(CH$_2$Ph) (6) (green) overlaid with the B3LYP calculated spectra (grey).

Figure 4.45. Fe L-edge absorption spectra of compounds 2 (black), 3 (blue), 5 (red), and 6 (green). In comparing the spectra of the bona fide Fe$^{II}$ species, (tBuL)Fe(CH$_2$Ph) (6) to that of compounds 2, 3, and 5, only minor changes in intensity are observed. The main L$_3$ peaks for all complexes occur at the same energy, 707.7 eV, within experimental error suggesting a common effective nuclear charge at the metal center. The combined Fe K-edge, Fe-L edge, and computational data suggest that complexes 3 and 5 share a common oxidation state of Fe$^{II}$ with that of 6, while complex 2 contains an intermediate Fe$^{II}$/Fe$^{III}$ state.
4.4.5 X-Ray Diffraction Techniques

Structures of 2, 4, 5, 6, and 7 were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Ka (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of ϕ and/or ω scans.

Data was integrated using SAIN1 and scaled with either a numerical or multi-scan absorption correction using SADABS. The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELX-2014 and refined against F² on all data by full matrix least squares with SHELX-2014. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

\((t\text{-BuL})\text{FeCl(CPh}_2\text{)} (2)\): The structure was solved in the monoclinic space group C2/c. The presence of a strongly disordered toluene molecule prevented refinement of an acceptable model. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically significant features of the structure.

\((t\text{-BuL})\text{Fe(CPh}_2\text{)(Et}_2\text{O)} (4)\): The structure was solved in the monoclinic space group P2₁/n.

\((t\text{-BuL})\text{Fe(CPh}_2\text{)(Pyr)} (5)\): The structure was solved in the monoclinic space group P2₁/c.

The crystal is a non-merohedral twin, but we have refined the structure by using


reflections in hkl4 format that is created by Cell_Now/Twinabs.

\((^{tBu}L)Fe(CH_2Ph)\) (6): The structure is solved in the triclinic space group P-1 with two molecules per unit cell. The crystal is a non-merohedral twin, but we have refined the structure by using reflections in hkl5 format that is created by CrysAlis Pro.\(^{41}\)

\((^{tBu}L)FeCl(CH_2PPh_3)\) (7): The structure is solved in the triclinic space group P-1. Disordered solvent could not be located in the Fourier map and was squeezed out by using Platon/SQUEEZE, which did not seriously affect the chemically significant features of the structure.

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Table 4.1. X-ray diffraction experimental details. a

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[a] \( R1 = \Sigma|F_o - IF_c|/\Sigma|F_o|, \) \( wR² = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} \)
4.4.6 Computational Methods

Computations were carried out utilizing the ORCA 4.0\textsuperscript{42} program package. Coordinates were taken from a BP86 geometry optimization. For compound 7, the crystallographic coordinates were used. The B3LYP functional was used.\textsuperscript{43} Calculations with hybrid functionals used the RIJCOSX algorithm to speed the calculation of Hartree–Fock exchange.\textsuperscript{33} The CP(PPP) basis set was used for Fe with a special integration accuracy (ORCA Grid7).\textsuperscript{34} The scalar relativistically recontracted def2-TZVP(-f)-ZORA basis set\textsuperscript{35} with ORCA Grid4 was used for all other atoms. Calculations included the zeroth-order regular approximation (ZORA)\textsuperscript{36} for relativistic effects as implemented by van Wüllen.\textsuperscript{37} Solvation was modeled with COSMO in an infinite dielectric.\textsuperscript{38} A broken symmetry surface was used to optimize 2 [(BS) (5,1)], 3 [(BS) (4,1)], and 5 [(BS) (4,1)], structures that all converged as antiferromagnetically-coupled configurations.

Mössbauer. Mössbauer parameters were obtained from additional calculations using geometry optimized coordinates, following the method described by F. Neese.\textsuperscript{44} Quadrupole splitting values ($\Delta E_Q$) were calculated from electric field gradient (Equation 1):

\[
\Delta E_Q = \frac{1}{2} eQV_{zz} \sqrt{1 + \frac{1}{3} \eta^2}
\]


\textsuperscript{42} Neese, F. WIREs Comput. Mol. Sci. 2018, 8:e1327.


The nuclear quadrupole moment $Q^{\text{57} \text{Fe}}$ was taken to be 0.16 barn.\textsuperscript{44} The principal tensor components of the EFG are $V_{xx}$, $V_{yy}$, and $V_{zz}$, from which the symmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be defined chosen such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

Isomer shift values ($\delta$) were calculated from the electron density at the nucleus $\rho_0$, using a linear equation $\delta = a(\rho_0 - C) + b$, with constraints determined by fitting the calculated densities to experimental isomer shifts for a series of iron dipyrromethane complexes synthesized in the lab. For this series of compounds, the parameters were determined to be $C = 14774$ au\textsuperscript{3}, $a = -0.259$ au\textsuperscript{3}mms\textsuperscript{-1}, and $b = 0.837$ mm. The basis sets and functional described above were used for all structures.

**Broken Symmetry Solutions.** A broken symmetry solution was used to model with antiferromagnetically coupled Fe\textsuperscript{III} and Fe\textsuperscript{II} carbene radicals. The broken symmetry notation BS$(m,n)$\textsuperscript{45} refers to a system with $(m+n)$ unpaired electrons, and a net spin of $(m+n)/2$ (if antiferromagnetically coupled). One fragment will bear $m$ $\alpha$ spin electrons and the other fragment $n$ $\beta$ spin electrons.

Figure 4.46. Molecular Orbital Diagram for (\textsuperscript{tBu}L)FeCl(CPh\textsubscript{2}) (2) (isovalue 0.05), derived from the quintet solution. Quasi-restricted orbitals (168–173\(\alpha\)).
Figure 4.47. Molecular Orbital Diagram for (tBuL)FeCl(CPh\textsubscript{2}) (2) (isovalue 0.05), derived from the BS(4, 1) solution. Unrestricted corresponding orbitals for the spin-coupled pair (168\(\alpha\), 168\(\beta\)) and quasi-restricted orbitals (169\(\alpha\)–173\(\alpha\)).
Figure 4.48. Molecular Orbital Diagram for (BuL)Fe(CPh$_2$)(pyr) (5) (isovalue 0.05), derived from the BS(4,1) solution. Unrestricted corresponding orbitals for the spin-coupled pair (181$\alpha$, 181$\beta$) and quasi-restricted orbitals (180 and 182$\alpha$–185$\alpha$).
Figure 4.49. Molecular Orbital Diagram for ($^{t}$Bu)LFe(CH$_2$Ph) (6) (iso-value 0.05), derived from the quintet solution. Quasi-restricted orbitals (141$\alpha$–144$\alpha$).
**Figure 4.50.** Molecular Orbital Diagram for \((^\text{Bu}_L)^{\text{FeCl(CH}_2\text{PPh}_3)}\) (7) (isovalue 0.05), derived from the quintet solution. Quasi-restricted orbitals (148α–201α).
Geometry Optimized Coordinates for compounds 2, 3, 5, and 6.

These coordinates were used for the TDDFT calculations for calculating the XAS spectra.

**Table 4.2.** Optimized cartesian coordinates for \((^{\text{tBu}}\text{L})\text{FeCl(CPh}_2\text{)}\) (2).

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Chapter 5

Carbene transfer from Cobalt dipyrrin complexes

5.1 Introduction

In the 1970s, the ability of Co$^{II}$ compounds to catalyze the reaction between diazoalkanes and olefins to generate cyclopropanated products was reported. To date, Co$^{II}$ porphyrin complexes are the most effective cobalt-based catalysts for cyclopropanation, promoting high reactivity, stereocontrol, and reactivity with electron-deficient olefins. Zhang, de Bruin, and co-workers have recently shown via EPR, LC-MS, and DFT calculations that the reactive intermediate observed from addition of a diazoester to a Co$^{II}$ porphyrin is a Co$^{III}$-bound radicaloid carbene ligand. Though this intermediate has yet to be isolated, evidence for the existence of radical density on the carbene fragment was inferred based on its resulting reactivity. In particular, addition of ethyl styryldiazoacetate to a Co$^{II}$ porphyrin complex was shown to transiently generate a Co$^{III}$ carbene radical, which rapidly dimerized via C–C coupling to bridge two Co$^{III}$ centers. While one example of a cobalt carbene radical has been structurally characterized, the low-spin ($S = \frac{1}{2}$) species displayed minimal reactivity with olefins; after

1. The work presented in this Chapter was done in collaboration with Jessica J. Kim (Harvard University, B.S. Chemistry, 2019).


prolonged heating with a stoichiometric amount of styrene, only 15% conversion to the respective cycloproponated product was observed.\textsuperscript{5}

The presence of a carbene-centered radical is central in promoting the metalloradical cycloproponation of electron-deficient olefins.\textsuperscript{4} Most cyclopropanation reactions proceed \textit{via} the generation of Fischer-type carbene intermediates, which are electrophilic and react poorly with electron-deficient substrates.\textsuperscript{6} We were, therefore, interested in targeting the synthesis of a reactive, high-spin cobalt carbene complex. In the Betley group, we employ a dipyrrin ligand platform as a porphyrin analog to aid in the isolation of highly reactive compounds featuring metal-ligand multiple bonds, including iron imido and iminyl complexes.\textsuperscript{7} As discussed in Chapter 4,\textsuperscript{8} we extended the use of this ligand platform to isolate iron carbene complexes, where the carbene ligand contained a non-negligible amount of spin density. Herein we report the synthesis of a pyridine-supported dipyrrin ligand and its subsequent metalation with cobalt dichloride. Upon reaction of these cobalt complexes with several different diazoalkane substrates, we observe multiple carbene insertions into the dipyrrin ligand, presumably mediated by a high-valent Co(CR₂) complex.


\textsuperscript{8} Wrobel, A. T.; Lukens, J. T.; Lancaster, K. M.; Betley, T. A. \textit{Manuscript in preparation.}
5.2. Synthesis and Metalation of a Pyridine-Supported Dipyrrin Ligand Platform

Our group has shown that modulating the flanking substituents on dipyrrin ligands impacts the ability to isolate reactive complexes containing metal-ligand multiple bonds. For example, the use of a mesityl-substituted dipyrrin ligand \((\text{MesL})\mathrm{H}\) \((\text{MesL} = 1,5,9\text{-trimesityldipyrromethene})\) proved to be a liability. Reaction between \((\text{MesL})\text{FeCl(thf)}\) and a variety of azide reagents \((\text{RN}_3)\) resulted in the rapid insertion of the nitrene fragment into the benzylic C–H bond from the mesityl group on the dipyrrin ligand. The intramolecular amination reaction proceeded presumably \textit{via} a high-valent iron nitrenoid species.\(^9\) To remove weak and activatable C–H bonds, we showed that exchanging the mesityl groups for bulky \((2,4,6\text{-triphenyl})\text{phenyl groups supported the isolation and crystallographic characterization of high-spin iron imido and iminyl complexes.}\(^7\) Very recently, our group has reported the cobalt-catalyzed intramolecular C–H amination of substituted aliphatic azides. The reactive cobalt imido intermediate reversibly binds pyridine, preventing undesirable side reactions and enhancing reactivity.\(^10\) We were, therefore, interested in investigating the ability of pyridine-substituted dipyrrin ligands to support metal complexes containing multiply bonded ligands.

Incorporating pyridine directly into the dipyrrromethene ligand proceeded \textit{via} condensation of \(2(2\text{-pyrrolyl})\text{pyridine with pentafluorobenzaldehyde. Oxidation of the crude dipyrrromethane with 2,3\text{-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) furnished the respective pyridine-substituted dipyrrin ligand (pyrL)H (pyrL} = 1,9-\text{(C}_6\text{H}_4\text{N})_2\text{-5-}}


(C₆F₅)dipyrromethene) in 88% yield (Scheme 5.1).¹¹

Scheme 5.1. Synthesis and metalation of (pyrL)H.

Metalation of (pyrL)H proceeded via deprotonation with lithium bis(trimethylsilyl)amide (LiN(Si(CH₃)₃)₂), followed by addition of cobalt dichloride (CoCl₂) in thawing THF solutions to yield (pyrL)CoCl (1) as a dark, blue solid in 90% yield (Scheme 5.1). The solid-state molecular structure for 1 revealed a square pyramidal geometry about the cobalt center with a Co–Cl bond length of 2.312(3) Å (Figure 5.1).¹² While the ¹H NMR spectrum for 1 contains no discernable features, the ¹⁹F NMR spectrum contains three sharp, diagnostic resonances (¹⁹F NMR δ: −143.56, −155.29, and −163.76 ppm).


¹² Baek, Y. and Betley, T. A. Unpublished Results.
Scheme 5.2. Reduction of \((\text{PyrL})\text{CoCl} \ (1)\) with \(\text{KC8}\) to furnish \((\text{PyrL})\text{Co(pyr)} \ (2)\).

Addition of \(1\) as a thawing solution in THF containing one drop of pyridine to a frozen solution containing one equivalent of potassium graphite \((\text{KC8})\) resulted in a color change from deep blue to dark purple upon warming to room temperature. Following filtration to remove potassium chloride \((\text{KCl})\) and graphite, the respective one-electron reduced species \((\text{PyrL})\text{Co(pyr)} \ (2)\) was isolated in 60% yield (Scheme 5.2). The \(^{19}\text{F} \) NMR spectrum for \(2\) contains three, sharp resonances \(\left( ^{19}\text{F} \text{ NMR } \delta: \ -139.07, \ -159.35, \ \text{and} \ -164.78 \ \text{ppm} \right)\). Compound \(2\) was crystallized from a concentrated solution of THF at room temperature and the solid-state molecular structure was determined by X-ray diffraction analysis. Complex \(2\) adopts a similar geometry to that of \(1\), with the additional pyridine molecule located perpendicular to the dipyrrin plane \((\angle 102.3(3)^\circ)\) (Figure 5.1).
5.3. Attempts to Isolate a Cobalt Carbene Complex

Using a smaller tert-butyl-substituted dpyrrin ligand, we have shown that the reaction between \((^t\text{Bu}L)\text{FeCl(Et}_2\text{O})\) \((^t\text{Bu}L = 1,9\text{-di-tert-butyl-5-(2,6-dichlorophenyl)-dipyrromethene})\) and diphenyldiazomethane \((\text{N}_2\text{CPh}_2)\) generates the respective four-coordinate carbene complex, \((^t\text{Bu}L)\text{FeCl(CPh}_2)\). We, therefore, began probing the reactivity of 1 with various aryldiazomethanes. Addition of a thawing THF solution of 1 to a frozen THF solution containing two equivalents of \((2,4,6\text{-triphenylbenzylidene})\text{diazomethane (ArCHN}_2)\) resulted in a dramatic color change from dark blue to bright red upon thawing (Scheme 5.3). Analysis of the reaction mixture by \(^{19}\text{F NMR} \) spectroscopy reveals five unique resonances, corresponding to each fluorine atom present in the ligand \(\delta: -109.80, -131.23,\)
–147.62, –153.08, and –156.88 ppm). The presence of five resonances contrasts the three resonances observed in the $^{19}$F NMR spectrum for 1 and suggests desymmetrization of the ligand. Addition of less than two equivalents of ArCHN$_2$ resulted in incomplete consumption of 1 as ascertained by $^{19}$F NMR spectroscopy.

**Scheme 5.3.** Reaction between ($^{3}$pyrL)CoCl (1) and ArCHN$_2$ (Ar = (2,4,6-triphenyl)phenyl).

The identity of the product of the reaction between 1 and ArCHN$_2$ was determined by single crystal X-ray diffraction. The solid-state molecular structure revealed decomposition of the dipyrrin ligand by insertion of multiple carbene equivalents to generate ($^{3}$pyrL*)CoCl (3) (Figure 5.2). One carbene fragment expands one of the pyrrole subunits into a six-membered ring and the other carbene equivalent inserts between the expanded pyrrole and the pyridine-flanking unit of the dipyrrin ligand.
Figure 5.2. Solid-state molecular structure of \((5\text{yL}^\ddagger)\text{CoCl} (3)\) (a) with thermal ellipsoids at the 20% probability level, along with the truncated solid-state molecular structure of \((5\text{yL}^\ddagger)\text{CoCl} (3)\) (b) with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, chlorine = green, fluorine = yellow-green.

Given the highly reactive nature of the intermediate formed in the reaction between \(1\) and \(\text{ArCHN}_2\), which rapidly decomposed via carbene transfer into the dipyrrin ligand, we attempted to isolate this intermediate using a more stabilized diazoalkane. Addition of \(1\) to a frozen THF solution containing two equivalents of \(\text{N}_2\text{CPh}_2\) resulted in rapid consumption of \(1\) upon warming to room temperature. Although we observed no color change, we did observe five, new unique resonances in the \(^{19}\text{F}\) NMR spectrum (\(^{19}\text{F}\) NMR \(\delta\): –136.08, –144.43, –155.14, –160.96, and –162.97 ppm). Similar to the previously described reaction, addition of less than two equivalents of \(\text{N}_2\text{CPh}_2\) resulted in incomplete consumption of \(1\). The desymmetrization of the ligand, as implied by \(^{19}\text{F}\) NMR spectroscopy, suggests that the product of this reaction similarly decomposed via carbene insertion into the dipyrrin ligand, though we were not able to obtain crystals suitable for analysis by X-ray diffraction.
Scheme 5.4. Synthesis of \((^{\text{pyr}}L^{**})\text{Co(pyr)} \) (4).

Reduction of the product of the reaction between 1 and \(\text{N}_2\text{CPh}_2\) with one equivalent of \(\text{KC}_8\) in a thawing solution of THF containing one drop of pyridine resulted in a rapid color change to dark green and the generation of a new \(^{19}\text{F} \) NMR spectrum with five resonances (\(^{19}\text{F} \) NMR \(\delta\): –133.87, –138.75, –155.16, –160.87, and –161.83 ppm). A compound with the same \(^{19}\text{F} \) NMR spectrum can be synthesized upon addition of two equivalents of \(\text{N}_2\text{CPh}_2\) to the \(\text{Co}^1 \) synthon 2 (Scheme 5.4). Single crystals suitable for analysis by X-ray diffraction were grown from a concentrated solvent mixture containing THF, Et\(_2\)O, and hexanes. The solid-state molecular structure revealed, again, that two carbene equivalents inserted into the dipyrrin ligand to generate \((^{\text{pyr}}L^{**})\text{Co(pyr)} \) (5) (Figure 5.3). In this case, however, the carbene equivalents functionalize the dipyrrin ligand in a manner distinct from that of 4. For 5, both [CPh\(_2\)] fragments insert into one of the pyrrole units.
**Figure 5.3.** Solid-state molecular structure of (pyrL**)Co(pyr) (4) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, fluorine = yellow-green.

**5.3. Proposed Mechanism for the Observed Carbene Insertion Reactivity**

To arrive at compounds 3 and 4, we propose the following mechanistic possibility: dinitrogen extrusion from the diazoalkane molecules results in the generation of a high-valent cobalt carbene complex, which then rapidly undergoes carbene transfer into the dipyrrin ligand, poising it to react with another diazoalkane equivalent. Unfortunately, the build-up of any cobalt carbene intermediate was not observed by NMR spectroscopy.

We propose that the differences in the pattern of insertion between ArCHN$_2$ and N$_2$CPh$_2$ arise due to differences in the steric bulk of the diazoalkanes. The proposed mechanism for carbene insertion into the dipyrrin ligand is shown in Scheme 5.5. For both diazoalkane substrates, the first carbene transfer is proposed to expand the pyrrole ring following
cyclopropanation of the pyrrolic subunit. Diphenyldiazoalkane (N₂CPh₂) contains two phenyl groups bound to the carbene carbon, leading to a more sterically hindered ligand compared to ArCHN₂ and, therefore, undergoes insertion into the more sterically accessible expanded pyrrole ring (Scheme 5.5, carbene transfer path #1). For the mono-substituted aryldiazomethane (ArCHN₂), the second carbene equivalent inserts into the sterically-hindered bond bridging the ring-expanded pyrrole and the pyridine unit, giving rise to the observed product 4 (Scheme 5.5, carbene transfer path #2).

Scheme 5.5. Proposed mechanism for the synthesis of compounds 3 and 4.

5.4 Conclusions

The foregoing results describe the synthesis and metalation with CoCl₂ of a pyridine-substituted dipyrrin ligand. Reaction between either a Co⁺ or a Co⁰ complex with aryldiazoalkane
substrates transiently generates a highly-reactive cobalt carbene species, which rapidly decomposes via multiple intramolecular carbene insertion into the dipyrrin framework. For less sterically encumbered diazoalkane substrates, two sequential pyrrole cyclopropanations result in multiple carbene insertions into the dipyrrin. While the more sterically encumbered diphenyldiazomethane addition to the Co platform induces carbene insertion into the pyrrole subunit, followed by insertion into the C–C bond connecting the pyrrole and pyridine groups.
5.5 Experimental Procedures

5.5.1 General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, dichloromethane, hexanes, pentane, pyridine, toluene, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-\textit{d} was purchased from Cambridge Isotope Labs and used as received. Benzene-\textit{d}_6 was purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use.

Reagents 2-bromopyridine, trifluoroacetic acid, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and lithium bis(trimethylsilyl)amide were purchased from Aldrich. Lithium bis(trimethylsilyl)amide was re-crystallized prior to use from a concentrated solution of pentane at −35°C. (N-boc-2-pyrrole)boronic acid was purchased from Frontier Scientific. Pentafluorobenzaldehyde was purchased from Matrix Scientific. Anhydrous cobalt dichloride and tetrakis(triphenylphosphine)palladium(0) were purchased from Strem. Reagents potassium graphite\textsuperscript{13} (2,4,6-triphenylbenzylidene)diazomethane,\textsuperscript{14} and diphenyldiazomethane\textsuperscript{15} were synthesized following literature procedures. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.


\textsuperscript{14} See Chapter 3.

\textsuperscript{15} Miller, J. B. \textit{J. Org. Chem.} 1959, 24, 560-561.
$^1$H, $^{19}$F, and $^{13}$C NMR spectra were recorded on Varian Mercury 400 MHz or Varian Unity/Inova 500 MHz spectrometers. $^1$H chemical shifts are reported relative to SiMe$_4$ using the chemical shift of residual solvent peaks as reference. $^{19}$F chemical shifts are reported relative to an external standard of trifluorotoluene. Mass spectrometry was performed on an Agilent 6210 TOF LC/MS with a dual nebulizer ESI source.

5.5.2 Synthesis

![Chemical Reaction Diagram]

2-(2-pyrrolyl)pyridine. Procedure was adapted following a literature protocol.$^{11}$ In a 1 L round bottom pressure vessel, (N-boc-2-pyrrole)boronic acid (8.22 g, 39.0 mmol), 2-bromopyridine (3.7 mL, 39.0 mmol), tetrakis(triphenylphosphine)palladium(0) (2.06 g, 1.95 mmol) were suspended in THF (250 mL). Potassium carbonate (17.0 g, 123 mmol) was added as a solution in water (50 mL). The mixture was stirred vigorously, under static vacuum, and heated to 100 ºC for 5 days. The aqueous layer was separated from the organic phase, which was washed with brine (3 x 200 mL), and dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure to yield (2-(N-Boc-1H-pyrrole-2-yl)pyridine), which was used without further purification. To remove the tert-butyloxycarbonyl (Boc) protecting group, the crude (2-(N-Boc-1H-pyrrole-2-yl)pyridine) was suspended in CH$_2$Cl$_2$ (250 mL) and aqueous 3 M HCl (72 mL) was added dropwise. The reaction mixture was stirred vigorously for 48 hours at room temperature. Occasionally, dH$_2$O was added to resolubilize excess product that had precipitated out of solution. The reaction mixture was filtered twice through a Büchner funnel fitted with filter paper. The filtrate was basified with a saturated solution of NaHCO$_3$ to pH 8.5. The solution was extracted with CH$_2$Cl$_2$ and the combined organic layers dried with sodium sulfate. Removal of
solvent *in vacuo* gave 2-(2-pyrrolyl)pyridine as a white solid (4.7 g, 83%). Characterization data matches that of previously reported material.\textsuperscript{11} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ (ppm): 10.01 (br. s, 1H), 8.47 (d, J = 4.0 Hz, 1H), 7.63 (m, 1H), 7.56 (m, 1H), 7.04 (m, 1H), 6.90 (m, 1H), 6.73 (m, 1H), 6.31 (q, J = 2.6 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ (ppm): 150.50, 148.54, 136.69, 120.45, 120.17, 118.29, 110.22, 107.44.

(\textsuperscript{pyrL})H. Procedure was adapted following a literature protocol.\textsuperscript{11} In a 500 mL pressure vessel, 2-(2-pyrrolyl)pyridine (2.2 g, 15.2 mmol), pentafluorobenzaldehyde (2.1 g, 10.6 mmol), and trifluoroacetic acid (3.5 mL, 45.7 mmol) were dissolved in dichloroethane (45 mL). The reaction mixture was stirred, under static vacuum, at 90°C for 3 days. Upon cooling to room temperature, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.1 g, 9.5 mmol) was added in one portion. After stirring at room temperature for 5 days, the reaction mixture was basified with a saturated solution of NaHCO\textsubscript{3} to pH = 8.5. The layers were separated and the aqueous phase extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic layers were washed with water, brine, dried with Na\textsubscript{2}SO\textsubscript{4}, and filtered through a plug of neutral alumina. The alumina was washed with CH\textsubscript{2}Cl\textsubscript{2} until the eluent turned colorless. The solvent was removed under reduced pressure to yield (\textsuperscript{pyrL})H as a dark red powder (3.1 g, 88%). Characterization data matches that of previously reported material.\textsuperscript{11} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ (ppm): 13.71 (br. s, 1H), 8.72 (dt, J = 4.8, 0.7 Hz, 3H), 8.19 (m, 3H), 7.82 (td, J = 7.7, 1.8 Hz, 3H), 7.29 (m, 3H), 7.10 (d, J = 4.3 Hz, 2H), 6.59 (d, J = 4.3 Hz, 3H).
$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ (ppm): –137.96, –152.28, –160.83. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 150.48, 149.56, 148.57, 141.71, 136.38, 136.24, 127.63, 123.12, 121.17, 120.42, 117.81, 117.69, 107.25.

$\text{(pyrL)CoCl} \ (1)$. A THF solution (5 mL) containing lithium bis(trimethylsilyl)amide (108 mg, 0.65 mmol) was added dropwise to a frozen THF solution (5 mL) containing ($\text{pyrL} \text{H}$) (300 mg, 0.65 mmol). The reaction mixture was warmed to room temperature and allowed to stir at that temperature for 30 minutes during which time the solution changed color from deep red to dark purple. The reaction mixture containing ($\text{pyrL} \text{Li}$) was re-frozen and added as a just-thawed solution to a frozen THF solution (5 mL) containing CoCl$_2$ (93 mg, 0.71 mmol). The reaction mixture was stirred at room temperature overnight, during which time a color change to dark blue was observed. The solution was filtered through Celite and the solvent was removed in vacuo to give a blue solid, which was washed with hexanes to give 1 (324 mg, 90%). Crystals suitable for analysis by X-ray diffraction were grown from a concentrated solution of THF at room temperature. $^{19}$F NMR (470 MHz, THF) $\delta$ (ppm): –143.56, –155.29, –163.76. This compound fragmented with loss of Cl in the MS. HRMS (ESI+) m/z Calc. 522.0314 [C$_{25}$H$_{12}$CoF$_5$N$_4$]$^+$, Found 522.0376 [M]$^+$. 
Figure 5.4. $^{19}$F NMR spectrum for ($^{3}$PyL)CoCl (1) collected in THF.
Figure 5.5. Solid-state molecular structure of \((\text{PyL})\text{CoCl} \ (1)\) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, chlorine = green, fluorine = yellow-green.
(pyrL)Co(py) (2). A just-thawed THF solution (5 mL) with one drop of pyridine containing (pyrL)CoCl (150 mg, 0.27 mmol) was added to a frozen THF solution (5 mL) containing KC₈ (36 mg, 0.27 mmol). The reaction mixture was warmed to room temperature and stirred for 30 minutes during which time the color changed from deep blue to dark purple. The mixture was filtered through Celite and the THF removed in vacuo gave 2 as a dark purple solid (84.4 mg, 60%). Crystals suitable for analysis by X-ray diffraction were grown from a 1:3 mixture of toluene:hexanes at −35 °C. ¹⁹F-NMR (470 MHz, THF) δ (ppm): −139.07, −159.35, −164.78. This compound fragmented with loss of pyridine in the MS. HRMS (ESI+) m/z Calc. 522.0314 [C₂₅H₁₂CoF₅N₄]⁺, Found 522.0305 [M]⁺.
Figure 5.6. $^{19}\text{F}$ NMR spectrum for ($^{3\text{pyr}}$L)Co(pyr) (2) collected in THF.
Figure 5.7. Solid-state molecular structure of \((\text{PyL})\text{Co(pyr)}\) (2) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, fluorine = yellow-green.
(PyrL*)CoCl (3). A just-thawed THF (2 mL) solution containing (PyrL)CoCl (1) (10 mg, 0.018 mmol) was added to a frozen THF solution (2 mL) containing ArCHN₂ (12.4 mg, 0.036 mmol). The reaction mixture was warmed to room temperature upon which a rapid color change from dark blue to red was observed. After stirring for 30 minutes, the solvent was removed in vacuo to give a dark brown solid. The product (3), as confirmed by X-ray diffraction analysis, was crystallized from a concentrated solution containing THF, Et₂O, and pentane at −35 °C. ¹H NMR (500 MHz, C₆D₆) δ (ppm): 120.21 (s), 91.95 (s), 65.51 (s), 49.54 (s), 40.77 (s), 36.97 (s), 35.38 (s), 22.01 (s), 21.56 (s), 21.31 (s), 21.11 (s), 20.04 (s), 18.98 (s), 18.20 (s), −1.94 (s), −3.34 (s), −3.96 (s), −6.31 (s), −6.70 (s), −10.50 (s), −15.70 (s), −19.85 (s), −21.93 (s). ¹⁹F NMR (470 MHz, C₆D₆) δ (ppm): −109.80, −131.23, −147.62, −153.08, −156.88. This compound fragments with loss of Cl in the MS. HRMS (ESI+) m/z Calc. 1158.3131 [C₇₅H₄₈CoF₅N₄]⁺, Found 1158.3035 [M]⁺.
Figure 5.8. $^1$H NMR spectrum for $(\text{pyr}^*\text{L}^*)\text{CoCl}$ (3) collected in THF.
Figure 5.9. $^{19}$F NMR spectrum for ($^{p}$N$_2$L$_2$)CoCl (3) collected in THF.
Figure 5.10. Solid-state molecular structure of (PY3L*)CoCl (3) with thermal ellipsoids at the 20% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, chlorine = green, fluorine = yellow-green.
Figure 5.11. Truncated Solid-state molecular structure of \((\text{pyr}^* \text{L}^*)\text{CoCl} (3)\) with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, chlorine = green, fluorine = yellow-green.
A just-thawed THF solution (2 mL) containing (pyrL)**Co(pyr) (2) (10 mg, 0.018 mmol) was added to a frozen THF solution (2 mL) containing N$_2$CPh$_2$ (7.4 mg, 0.036 mmol). After stirring for 30 minutes, the reaction mixture changed color from deep purple to dark green. The solvent was removed in vacuo to give a dark green solid. Crystals suitable for analysis by X-ray diffraction were grown from a concentrated solution of THF, Et$_2$O, and hexanes solution at −35 °C. $^{19}$F NMR (470 MHz, THF) $\delta$ (ppm): −133.87, −138.75, −155.16, −160.87, −161.83.
Figure 5.12. $^{19}$F NMR spectrum for (pyrL**)Co(pyr) (4) collected in THF.
Figure 5.13. Solid-state molecular structure of \((\text{pyr}^*\text{L}^{**})\text{Co(pyr)}\) (4) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. Cobalt = aquamarine, nitrogen = blue, carbon = gray, fluorine = yellow-green.
5.5.2 X-ray Diffraction Techniques

Structures of \((\text{pyr}L)\text{CoCl} (1)\), \((\text{pyr}L)\text{Co(pyr)} (2)\), \((\text{pyr}L^*)\text{CoCl} (3)\), and \((\text{pyr}L^{**})\text{Co(pyr)} (4)\) were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans.

Data was integrated using SAINT\(^{16}\) and scaled with either a numerical or multi-scan absorption correction using SADABS.\(^{16}\) The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELX-2014 and refined against \(F^2\) on all data by full matrix least squares with SHELX-2014.\(^{17}\) All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

\((\text{pyr}L)\text{CoCl} (1)\): The structure was solved in the triclinic space group P-1. The structure contained large, solvent accessible voids, which could not be located. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically significant features of the structure.

\((\text{pyr}L)\text{Co(pyr)} (2)\): The structure was solved in the monoclinic space group Cc with two molecules per unit cell.

---


(**pyrL**)CoCl (3): The structure was solved in the tetragonal space group I41/a. The structure contained large, solvent accessible voids, which could not be located. Instead, a solvent mask was implemented in the Olex2 software, which did not seriously affect the chemically significant features of the structure.

(**pyrL**)Co(pyr) (4): The structure was solved in the monoclinic space group P21/c.

Table 5.1. X-ray diffraction experimental details.\(^a\)

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<th>Moiety Formula</th>
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<th>(<strong>pyrL</strong>)Co(pyr) (2)</th>
<th>(<strong>pyrL</strong>)CoCl (3)</th>
<th>(<strong>pyrL</strong>)Co(pyr) (4)</th>
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<td>C(<em>{30})H(</em>{18})CoF(_5)N(_5)</td>
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<td>P21/c (4)</td>
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<tr>
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<td>0.1007, 0.1998</td>
<td>0.0687, 0.1573</td>
</tr>
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\(^a\) R\(_1\) = Σ|\(F_o\) - \(|F_c|\)\|/Σ|\(F_o\)\|, wR\(_2\) = \{\Σ[w(\(F_o^2 - F_c^2\))^2]/\Σ[w(\(F_c^2\)]\}^{1/2}
Chapter 6

Synthesis of 2-Alkylidene-tetrahydrofurans Mediated by a High-Spin Iron Complex

6.1 Introduction

Direct functionalization of unactivated C–H bonds is an effective strategy for the construction of new carbon-heteroatom bonds in organic molecules. In particular, transition metals capable of inserting these types of functionalities through the generation of a reactive intermediate show promise in streamlining synthetic protocols. For example, dirhodium(II) [Rh2] complexes catalyze a wide range of organic C–C bond forming transformations via transient formation of an electrophilic carbene intermediate. While the reactivity of dirhodium-based catalysts with diazoalkane substrates has been widely developed and utilized, it may be of interest to explore other catalytic systems based on other metals with altered electronic properties, such as iron and other first row transition metals.

Our group has previously reported the iron-catalyzed intramolecular C–H amination of aliphatic azides to generate N-heterocycles. The reactive intermediate is a high-spin dipyrrin-supported iron iminyl complex, competent for hydrogen atom abstraction (HAA), followed by radical recombination. We wanted to investigate the ability of metal complexes supported by

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1. The work presented in this chapter was done in collaboration with Jessica J. Kim, Yuyang Dong, and Jake Essman.


this ligand platform to catalyze other types of organic transformations. In particular, we were interested in examining the reactivity of diazoketone substrates containing weak and accessible C–H bonds with a dipyrrin-supported high-spin Fe\textsuperscript{II} complex \((\text{^tBuL})\text{FeCl(}\text{Et}_2\text{O) } (1) \text{ (}^\text{tBuL} = 1,9\text{-di-}^\text{t}^\text{t}\text{er}-\text{butyl-5-} (2,6\text{-dichlorophenyl})\text{-dipyrromethene}).\) Unexpectedly, addition of these diazoalkane substrates to 1 does not catalyze C–C bond formation to furnish the respective carbocyclic products akin to [Rh\textsubscript{2}] catalysis (Scheme 6.1).\textsuperscript{3} Instead, we observe the synthesis of substituted 2-alkylidene-tetrahydrofurans via formation of new C–O bonds (Scheme 6.1). While [Rh\textsubscript{2}] catalysts have shown the ability to synthesize oxygen-atom heterocycles from diazoketone compounds, the cyclization is distinct from what we observe with the dipyrrin-supported iron catalysis. In the case of [Rh\textsubscript{2}], the carbene intermediate undergoes intramolecular insertion into an O–H bond (Scheme 6.1).\textsuperscript{6}

**Scheme 6.1.** Example of the reactivity observed upon addition of \(\alpha\)-diazo-\(\beta\)-ketoesters to a catalytic amount of \((\text{^tBuL})\text{FeCl(}\text{Et}_2\text{O) } (1)\) compared to [Rh\textsubscript{2}] catalysis. For [Rh\textsubscript{2}] catalysis, when \(Y = H\), the carbene undergoes insertion into a C–H bond. When \(Y = \text{OH}\), the carbene undergoes insertion into the O–H bond.

\[ \text{R} \begin{array}{c} \text{H} \\ \text{C} \\ \text{O} \\ \text{H} \\ \text{C} \\ \text{O} \end{array} \xrightarrow{[\text{Rh}\textsubscript{2}]} \text{R} \begin{array}{c} \text{H} \\ \text{Y} \\ \text{C} \\ \text{O} \\ \text{H} \end{array} \]


The observed products, 2-alkylidene-tetrahydrofurans, are important building blocks for the synthesis of nactins, a class of macrotetrolide antibiotics. While transition metal-promoted methodologies exist for the synthesis of this class of cyclic ketals, these protocols rely on the use of precious metals, such as palladium, platinum, rhodium, and ruthenium. Here, we report the synthesis of a variety of substituted 2-alkylidene-tetrahydrofurans via iron-catalyzed dinitrogen extrusion from diazoketone substrates.

6.2 Catalysis Optimization and Substrate Scope

Scheme 6.2. Synthesis of diazoalkane substrates (3a–3j).

We began our investigation studying the reactivity of a synthetically accessible class of α-diazo-β-ketoesters and α-diazo-β-ketones. These diazoalkane substrates (3a–3k) were readily


synthesized upon diazo transfer to the respective β-ketoester or diketone starting material (Scheme 6.2). Upon heating a benzene solution to 80°C containing 1 and 5 equivalents of diazooester 3a, we observe complete consumption of 3a and generation of a single new product (4a) after 12 hours, as evidenced by 1H (Figure 6.1) and 13C NMR spectroscopy. Atom connectivity of the catalysis product (4a) was further verified using 1H (Figure 6.1), 13C, COSY, and HSQC NMR spectroscopy, mass spectrometry, and X-ray crystallography (Figure 6.2).

Figure 6.1. (a) 1H NMR of diazoester 3a (black). (b) After heating of 5 equivalents of 3a with catalyst 1 in C6H6 for 12 h, the reaction mixture was filtered through silica and eluted with a 50:50 mixture of hexanes:EtOAc to remove paramagnetic impurities and 1H NMR taken of the crude reaction mixture (red). (c) The isolated and crystallized product 4a (blue). NMRs taken in CDCl3.

Figure 6.2. Solid-state molecular structure of product 4a with thermal ellipsoids at the 50% probability level. Solvent molecules omitted for clarity. Carbon = gray, oxygen = red, hydrogen = white.

Table 6.1. Results of catalysis optimization.

<table>
<thead>
<tr>
<th>Catalyst [Fe]</th>
<th>Catalyst Loading (%)</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Product Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>12</td>
<td>80</td>
<td>63</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>12</td>
<td>25</td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>12</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>12</td>
<td>80</td>
<td>47</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>20</td>
<td>12</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>(³⁶⁶)LFe(thf)</td>
<td>20</td>
<td>12</td>
<td>80</td>
<td>0</td>
</tr>
</tbody>
</table>

*NMR yield using an internal standard of ferrocene.

Heating the reaction mixture to lower temperatures or using lower catalyst loadings resulted in incomplete consumption of the diazoester starting material (Table 6.1). Additionally, we screened the reactivity of substrate 3a with a variety of iron containing compounds as potential catalysts (Table 6.1). Using simple iron salts (i.e., FeCl₂) did not furnish the respective cyclized product, suggesting the significance of a dipyrrin-supported complex in affecting this
transformation. Removing the bound Et₂O molecule or providing a more labile anion through the use of [(tBu)LFeCl]₂ and (tBu)LFe(BF₄)(thf), respectively, resulted in the desired product formation in isolated yields comparable to the use of catalyst 1.

The use of low-spin Fe¹ complexes supported by bulky dipyrromethene ligands, (ArL)Fe¹⁺⁺⁶⁺ (ArL = 1,9-(2,4,6-Ph₃C₆H₂)₂-5-mesityldipyrromethene) and (trtL)Fe(thf) (trtL = 1,9-C(C₆H₅)₃-5-mesityldipyrromethene),¹⁷ did not result in any substrate turnover. We do, however, observe a new, paramagnetically-shifted ¹H NMR spectrum upon substrate addition to both (ArL)Fe and (trtL)Fe(thf), suggesting diazoester coordination to the metal center. The newly generated diazoester adducts are stable to prolonged heating and are not catalytically competent intermediates. Previous results have shown that coordination of diazoalkanes to (ArL)Fe and (trtL)Fe(thf) generates stable species in which the diazoalkane coordinates the metal center in a geometry not conducive towards dinitrogen loss.¹⁸ In contrast, addition of diphenyldiazomethane (N₂CPh₂) to 1 furnishes the carbene adduct upon dinitrogen extrusion.¹⁹

The dipyrrin-iron catalyzed conversion of substrates 3a–3j to the respective substituted 2-

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15. Wrobel, A. T.; Betley, T. A. Unpublished results. (tBu)LFe(BF₄)(thf)₂ can be synthesized upon addition of a just-thawed THF solution containing (tBu)LFeCl(Et₂O) to a frozen THF solution containing 1 eq. of AgBF₄. Stirring for 30 minutes at room temperature, followed by filtration through a pad of celite furnishes (tBu)LFe(BF₄)(thf)₂, which was crystallized from a 1:3 mixture of THF:Et₂O at −35 °C. ¹H NMR (CD₂Cl₂) δ (ppm): 57.73 (s), 52.27 (s), 28.18 (s), 21.90 (s), 13.26 (s), 10.09 (br. s) 4.74 (s), 3.36 (s), 2.71 (s).


alkylidene-tetrahydrofurans is generalizable and a variety of products (4a–4j) were isolated in modest to good yields (Table 6.2).

**Table 6.2.** Catalytic synthesis of 2-alkylidene-tetrahydrofurans.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%)*</th>
<th>Product</th>
<th>Yield (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>59 ± 6</td>
<td>4g</td>
<td>63 ± 12</td>
</tr>
<tr>
<td>4b</td>
<td>73 ± 6</td>
<td>4h</td>
<td>68 ± 6</td>
</tr>
<tr>
<td>4c</td>
<td>39 ± 12</td>
<td>4i</td>
<td>41 ± 13</td>
</tr>
<tr>
<td>4d</td>
<td>61 ± 3</td>
<td>4j</td>
<td>57 ± 12</td>
</tr>
<tr>
<td>4e</td>
<td>85 ± 6</td>
<td>4k</td>
<td>71 ± 9</td>
</tr>
<tr>
<td>4f</td>
<td>53 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Isolated yield averaged over three runs.

While we are able to synthesize a variety of products using the methodology presented above from substrates containing secondary, allylic, and benzylic C–H bonds, we cannot activate primary C–H bonds even under stoichiometric conditions. Furthermore, addition of terminal α-diazoketones (5a and 5b) to 1 resulted in the generation of carbene-coupled products, including dimers and short-chain oligomers (Scheme 6.3), suggesting that the ketoester motif is essential
for synthesis of substituted tetrahydrofurans using this methodology. Transition metal catalyzed oligomerization of \( \alpha \)-carbonyl diazo compounds is well documented and has been reported for several metals, including palladium,\textsuperscript{20} rhodium,\textsuperscript{21} and copper.\textsuperscript{22} Finally, while catalyst 1 can tolerate esters, other functional groups, such as nitriles or indoles, result in catalyst deactivation.

**Scheme 6.3.** Reactivity of \( \alpha \)-diazo ketones with catalyst 1.

We also screened a series of substrates in which the targeted C–H bond is located within the ester group (6–10) (Figure 6.3). These substrates were not competent for cyclization.

**Figure 6.3.** Diazoester substrates screened that are not competent for cyclization.


6.3 Potential Mechanisms to Afford the Corresponding Substituted 2-Alkyldene-Tetrahydrofurans

There are several potential mechanisms that could explain the observed reactivity of α-diazo-β-ketoester substrates with catalyst 1. The first possibility involves metal-mediated dinitrogen extrusion from the diazoester substrate to transiently generate an Fe\textsuperscript{III} carbene radical (1-a) as shown in Scheme 6.4. The generated carbene radical could be stabilized by coupling to the high-spin ferric center akin to the stabilization observed in the related carbene adduct (\textsuperscript{tBu}L)FeCl(CPh\textsubscript{2}),\textsuperscript{19} or via conjugation to the O heteroatoms from the keto and ester functionalities. The carbene-centered radical could then undergo hydrogen-atom abstraction to form the an Fe\textsuperscript{III} alkyl and corresponding carboradical intermediate (1-b). Instead of radical recombination to form a new C–C bond, one of the ketones on the bound diazoester traps the newly generated carboradical to generate a new C–O bond. Homolytic Fe–C bond cleavage from the ferric alkyl (1-c) quenches the carboradical and affords the 2-alkylidene-tetrahydrofuran product. This proposed mechanism seems unlikely for several reasons. First, as previously shown in our group, dipyrrin-supported Fe\textsuperscript{III} alkyl species rapidly decompose via homolysis of the iron-alkyl bond.\textsuperscript{23} Additionally, if the carbene undergoes hydrogen atom abstraction, we would expect rapid radical recombination to generate a carbocyclic product, analogous to the synthesis of N-heterocycles previously reported by our group.\textsuperscript{4}

Scheme 6.4. Proposed mechanism in which the reactive intermediate is a high-spin Fe$^{III}$ carbene radical.

A second possible mechanism is related to the Bamford-Stevens reaction whereby tosylhydrazones are converted to alkenes upon treatment with strong base.\(^{24}\) While no bases are added to the reaction under discussion, a strong diketo-supported carbene could be generated as an intermediate. As opposed to binding of the α-diazo-β-ketoester substrate via a carbene interaction as illustrated in Scheme 6.4, the substrate could bind via chelation between the keto and ester functionalities, illustrated as 2-a in Scheme 6.5. Dinitrogen loss from the distal-to-iron diazo functionality affords a carbene intermediate 2-b that could be stabilized by conjugation to the keto and ester moieties. Carbene deprotonation of the internal alkyl group could generate the zwitterionic carbanion and carbocationic units (2-c), the latter of which could be stabilized by the two adjoining keto and ester groups. The final step necessary to furnish the 2-alkylidene-tetrahydrofuran would be C–O formation via carbanion attack on the keto group, quenching the zwitterionic intermediate. While the iron center in 1 is indeed Lewis acidic, which could

accommodate binding of the diazoalkane substrate, it is as of yet unclear how this would promote dinitrogen expulsion without redox-promotion from the iron center. Substitution of the iron in 1 with a suitable redox-innocent Lewis acid should be able to promote the reaction if this mechanism is operative. While FeCl₂ was not suitable to facilitate the reaction, screening the cyclization reaction with Zn²⁺ or Mg²⁺ dipyrrin adducts are critical control experiments to do. Furthermore, the carbene 2-b generated might be anticipated to induce direct C–H bond insertion as opposed to acting like a based in Scheme 6.5. However, the α-diazo-β-ketoester substrate binding invoked in Scheme 6.5 might play an essential role in a redox-mediated mechanism considered next.

**Scheme 6.5.** Proposed mechanism in which the reactive intermediate is a distally-stabilized carbene by a Lewis-acidic iron center.

A third potential mechanism invokes chelation of the α-diazo-β-ketoester substrate to 1 via the ketone and terminal ester (3-a, Scheme 6.6). Reduction of the bound α-diazo-β-ketoester substrate reduces the ketone, induces alkene formation via double bond migration with concomitant expulsion of dinitrogen. Expulsion of dinitrogen leaves an O₂-ligated Fe⁰ vinylic
radical (3-b). The vinylic radical 3-b can undergo H-atom abstraction to afford the corresponding carboradical 3-c which can undergo radical recombination with the anionic O-moiety remaining, yielding the corresponding substituted 2-alkylidene-tetrahydrofurans. The mechanism outlined in Scheme 6.6 is consistent with our observations for diazoalkanes to undergo single electron reduction when bound to dipyrrin supported iron complexes, as well as the propensity for the high-spin ferric stabilized radical intermediates to undergo H-atom abstraction reactivity.\textsuperscript{14,16,18,19} Furthermore, the proposed mechanism seems is consistent with the observation that terminal $\alpha$-diazoketones do not undergo cyclization. Additionally, the exclusive generation of cyclized products in which the oxygen atoms derived from the ketones of the substrate are arranged in a \textit{cis} orientation about the alkene suggests that the metal center may play an active role in dictating the geometry of the final product.
Scheme 6.6. Proposed mechanism in which the reactive intermediate is a dipyrrin-iron supported radical chelate.

To support the mechanism proposal outlined in Scheme 6.6, we would like to obtain data to provide insight into the nature of the critical intermediates. Several attempts were made to isolate or observe reactive intermediates to no avail. We synthesized dimethyl 2-diazomalonate and diacetyldiazomethane as substrates that do not contain weak and accessible C–H bonds. While stoichiometric addition of these substrates to 1 did results in small changes in the $^1$H NMR spectrum, attempts to crystallize the products of these reaction mixtures only yielded crystals of 1. These results suggest that the α-diazo-β-ketoester substrate may only transiently associate with the metal complex. If the vinylic radical 3-b is a viable intermediate, we would anticipate an observable kinetic isotope effect to be present for the H-atom abstraction step if dinitrogen loss is not rate-limiting. Mono-deuteration of the α-diazo-β-ketoester substrate will provide information regarding if H-atom abstraction features in the rate determining step of the reaction. Lastly, if the generated carboradical 3-c has an appreciable lifetime, intercepting the radical intermediate might be kinetically feasible with a variety of radical traps (e.g., TEMPO, haloform, Me$_3$NO).
6.4 Conclusions and Future Work

Herein we report the unique transformation of $\alpha$-diazo-$\beta$-ketoesters and $\alpha$-diazo-$\beta$-ketones to substituted 2-alkylidene-tetrahydrofurans catalyzed by a high-spin Fe$^{II}$ dipyrrin complex. Future work will include further studies to help determine the reaction mechanism. In particular, we are interested in elucidating the active species responsible for cyclization. Moving towards more sterically encumbered dipyrrin ligands may facilitate isolation of a reactive intermediate. Additionally, kinetics studies are underway so that we may gain further insight into this transformation. Measuring the kinetic isotope effect (KIE) by comparison of the rate of reaction of a proteo- versus deutero- substrate will provide information on the rate-determining step. Finally, we are interested in improving the catalytic efficiency and expanding the scope of diazoester substrates. We will explore the impact of metal identity, as well as several other dipyrrromethene ligands, on substrate tolerance and turnover.
6.5 Experimental Procedures

6.5.1 General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. Ligand and ligand precursors were synthesized as previously reported. All glassware was oven dried for a minimum of 1 hour and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, dichloromethane, hexanes, pentane, pyridine, toluene, and tetrahydrofuran were dried over 4 Å molecular sieves (Strem) prior to use. Chloroform-\(d\) was purchased from Cambridge Isotope Labs and used as received. Benzene-\(d_6\) was purchased from Cambridge Isotope Labs and was degassed and stored over 4 Å molecular sieves prior to use.

Ethyl diazoacetate, potassium monomethyl malonate, magnesium chloride, carbonyl diimidazole, 4-(4-methoxyphenyl)butyric acid, 4-(4-bromophenyl)butanoic acid, 4-(phenyl)butyric acid, para-acetamidobenzenesulfonyl azide, triethylamine, cyclohexanol, bromoacetyl bromide, N,N’-bis(p-toluenesulfonyl)hydrazine, diethyl malonate, 1,8-diazabicyclo[5.4.0]undec-7-ene, 2,2-dimethyl-1,3-dioxane-4,6-dione, 2,2,2-trifluoroethanol, bromobenzene, 4-ethoxy-4-oxobutylzinc bromide, LiN(Si(CH\(_3\))\(_3\))\(_2\), 4-cyclohexylbutanoic acid, pyridine, isobutyl phenyl acetate, tosyl azide, 2,4-octanedione, cyclohexanecarbonylic acid, 4-(2-thienyl)butyric acid, indol-3-butyric acid, 5-hexenoic acid, propyl 3-oxobutanoate, methylacetoacetate, 2-phenylethanol, 2,4-dimethylpentan-3-ol, 2,2,6-trimethyl-4H-1,3-dion-4-one, dicyclohexyl methanol, adamant-1-ol, and potassium tert-butoxide were purchased from Aldrich. 4-(p-tolyl)butyric acid, 4-(4-fluorophenyl) butyric acid, and 2,4-nonanenedione were

purchased from Alfa Aesar. Iron dichloride and Pd(OAc)$_2$ were purchased from Strem and used as received. 10% Palladium on carbon was purchased from Oakwood. Imidazole sulfonyl azide$^{26}$ was synthesized according to literature protocols. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150°C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

6.5.2 Characterization and Physical Measurements

$^1$H spectra were recorded on Varian Unity/Inova 400, 500, or 600 MHz- spectrometers. $^1$H NMR chemical shifts are reported relative to SiMe$_4$ using the chemical shift of residual solvent peaks as reference. High-resolution mass spectrometry was performed on a Bruker microTOFII ESI LCMS or Bruker Maxis Impact LC-q-TOF Mass Spectrometer. Elemental analyses (% CHN) were obtained on a PerkinElmer 2400 Series II CHNS/O Analyzer.

6.5.3 Synthesis of diazoketone compounds

General procedure for the synthesis of β-ketoester compounds.

![Diagram](image.png)

Procedure was adapted following a previous literature report.$^{27}$ Potassium monomethyl malonate (1.5 eq) and MgCl$_2$ (1 eq) were dissolved in anhydrous THF (25 mL). The suspension was stirred at 65°C for 3 hours, cooled to room temperature, and stirred for an additional 1 hour. Separately, the butyric acid (1 eq) and carbonyl diimidazole (1.1 eq) were dissolved in anhydrous


THF (10 mL) and stirred at 45°C for 1 hour. The acyl imidazole solution was then transferred via syringe to the magnesium malonate solution and stirred at room temperature overnight. A 1 M solution of HCl (5 mL) was added dropwise to the reaction mixture. The quenched reaction mixture was extracted into EtOAc (2 x 50 mL), washed with brine, dried with sodium sulfate, and concentrated under reduced pressure. The resulting oil was further purified by SiO₂ chromatography (10–20% EtOAc in Hexanes) to give the β-ketoesters as either yellow oils or white solids.

**methyl 3-oxo-6-phenylhexanoate (2a).** Characterization data is consistent with literature values.²⁷ Reaction was run on 6.8 mmol scale. Yield: 0.44 g, 28%. 

1H NMR (600 MHz, CDCl₃): δ (ppm): 7.28 (t, 2H, J = 7.6 Hz), 7.16–7.21 (m, 3H), 3.72 (s, 3H), 3.42 (s, 2H), 2.63 (t, 2H, J = 7.7 Hz), 2.54 (t, 2H, J = 7.3 Hz), 1.90–1.96 (m, 2H).

**methyl 3-oxo-6-(p-tolyl)hexanoate (2b).** Reaction was run on 13.5 mmol scale. Yield: 0.88 g, 28%. 

1H NMR (500 MHz, CDCl₃): δ (ppm): 7.04–7.10 (m, 4H), 3.73 (s, 3H), 3.42 (s, 2H), 2.59 (t, 2H, J = 7.8 Hz), 2.53 (t, 2H, J = 7.4 Hz), 2.33 (s, 3H), 1.91 (m, 2H). 


**methyl 6-(4-methoxyphenyl)-3-oxohexanoate (2c).** Reaction was run on 13.5 mmol scale. Yield: 0.21 g, 6%. 

1H NMR (500 MHz, CDCl₃): δ (ppm): 7.08 (d, 2H, J = 8.6 Hz), 6.82 (d, 2H, J = 8.6 Hz), 3.79 (s, 3H), 3.72 (s, 3H), 3.42 (s, 2H), 2.51 – 2.61 (m, 4H), 1.84 – 1.93 (m, 2H). 

13C NMR (125 MHz, CDCl₃): δ (ppm): 202.46, 167.67, 157.92, 133.36, 129.34, 113.83, 55.26, 52.32,
methyl 6-(4-fluorophenyl)-3-oxohexanoate (2d). Reaction was run on 2.7 mmol scale. Yield: 0.34 g, 52%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.11 (m, 2H), 6.96 (m, 2H), 3.73 (s, 3H), 3.42 (s, 2H), 2.60 (t, $J = 7.8$ Hz, 2H), 2.54 (t, $J = 7.3$ Hz, 2H), 1.91 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ (ppm): -118.39. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 202.25, 162.33, 160.39, 136.94, 129.72, 115.24, 52.35, 49.05, 42.00, 33.98, 24.96. HRMS (ESI+) m/z Calc 261.0897 [C$_{13}$H$_{15}$FO$_3$+Na]$^+$, Found 261.0894 [M+Na]$^+$.

methyl 6-(4-bromophenyl)-3-oxohexanoate (2e). Reaction was run on 4.1 mmol scale. Yield: 0.60 g, 49%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.40 (d, 2H, $J = 8.3$ Hz), 7.04 (d, 2H, $J = 8.3$ Hz), 3.73 (s, 3H), 3.42 (s, 2H), 2.52 – 2.62 (m, 4H), 1.87–1.94 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 202.23, 167.57, 140.29, 131.46, 130.19, 119.77, 52.37, 49.03, 41.94, 34.16, 24.62. HRMS (ESI+) m/z Calc 321.0102 [C$_{13}$H$_{15}$BrO$_3$+Na]$^+$, Found 321.0108 [M+Na]$^+$.

methyl 6-cyclohexyl-3-oxohexanoate (2f). Reaction was run on 5.9 mmol scale. Yield: 0.13 g, 10%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 3.73 (s, 3H), 3.44 (s, 2H), 2.50 (t, $J = 7.6$ Hz, 2H), 1.58–1.70 (m, 7H), 1.11–1.28 (m, 8H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 202.86, 167.69, 52.31, 49.00, 43.37, 37.42, 36.73, 33.19, 26.62, 26.31, 20.84. HRMS (ESI+) m/z Calc 228.1676 [C$_{13}$H$_{22}$O$_3$+H]$^+$, Found 228.1684 [M+H]$^+$.

methyl 3-oxo-6-(thiophen-2-yl)hexanoate (2g). Reaction was run on 6.7 mmol scale. Yield: 0.46 g, 30%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm): 7.12 (d, $J = 5.1$ Hz, 1H), 6.91 (m, 1H), 6.78 (m, 2H), 3.72 (s, 3H), 3.43 (s, 2H), 2.86 (t, 278
\( J = 7.1 \text{ Hz, 2H}, 2.59 \) (t, \( J = 7.1 \text{ Hz, 2H}), 1.98 \) (m, 2H). \(^{13}\text{C} \text{ NMR} (125 \text{ MHz, CDCl}_3): \delta \) (ppm): 202.14, 167.53, 144.04, 126.85, 124.60, 123.29, 52.34, 49.04, 41.77, 28.78, 25.15. HRMS (ESI+) m/z Calc 251.0537 \([\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}+\text{Na}]^+\), Found 251.0548 \([\text{M}+\text{Na}]^+\).

**Methyl 3-oxooocyte-7-enoate (2h).** Reaction was run on 8.7 mmol scale. Yield: 0.32 g, 21%. \(^1\text{H} \text{ NMR} (500 \text{ MHz, CDCl}_3): \delta \) (ppm): 5.76 (m, 1H), 4.99 (t, \( J = 11.5 \text{ Hz, 2H}), 3.75 \) (s, 3H), 3.44 (s, 2H), 2.54 (t, \( J = 7.0 \text{ Hz, 2H}), 2.07 \) (m, 2H), 1.69 (m, 2H). \(^{13}\text{C} \text{ NMR} (125 \text{ MHz, CDCl}_3): \delta \) (ppm): 202.49, 167.62, 137.69, 115.43, 52.32, 49.08, 42.12, 32.81, 22.41. HRMS (ESI+) m/z Calc 171.1021 \([\text{C}_9\text{H}_{14}\text{O}_3\text{+H}]^+\), Found 171.0981 \([\text{M}+\text{H}]^+\).

**Methyl 6-(1H-indol-2-yl)-3-oxohexanoate.** Reaction was run on 4.9 mmol scale. Yield: 0.33 g, 26%. \(^1\text{H} \text{ NMR} (500 \text{ MHz, CDCl}_3): \delta \) (ppm): 7.95 (br. s, 1H), 7.60 (d, \( J = 8.0 \text{ Hz, 1H}), 7.37 \) (d, \( J = 8.1 \text{ Hz, 1H}), 7.19 \) (t, \( J = 7.5 \text{ Hz, 1H}), 7.11 \) (t, \( J = 7.1 \text{ Hz, 1H}), 6.99 \) (s, 1H), 3.71 (s, 3H), 3.41 (s, 2H), 2.80 (t, \( J = 7.4 \text{ Hz, 2H}), 2.60 \) (t, \( J = 7.3 \text{ Hz, 2H}), 2.03 \) (m, 2H). \(^{13}\text{C} \text{ NMR} (125 \text{ MHz, CDCl}_3): \delta \) (ppm): 175.42, 168.94, 158.29, 147.11, 138.79, 124.95, 119.67, 119.38, 112.02, 108.83, 51.66, 35.64, 24.40, 22.11.

**General procedure for the synthesis of \( \alpha\)-diazo-\( \beta\)-ketoester compounds.**

\[
\begin{align*}
\text{RCH}_{\text{2}}\text{C(=O)}_{\text{2}} & \quad \xrightarrow{p\text{ABS}, \text{Et}_3\text{N}} \quad \text{RCH}_{\text{2}}\text{C(=O)}_{\text{2}}\text{N}_2
\end{align*}
\]

Procedure was adapted following a previous literature report.\(^27\) The respective \( \beta\)-ketoester (1 eq) and \textit{para}-acetamidobenzenesulfonyl azide (1.5 eq) were dissolved in CH\(_2\)Cl\(_2\) (20 mL) and cooled to 0°C. Triethylamine (1.8 eq) was added \textit{via} syringe and the reaction mixture was stirred...
at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with CH$_2$Cl$_2$ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO$_2$ chromatography (10–20% EtOAc in Hexanes) to give the diazo products as yellow oils or white solids.

**methyl 2-diazo-3-oxo-6-phenylhexanoate (3a).** Characterization data is consistent with literature values.$^{27}$ Reaction was run on 3.5 mmol scale. Yield: 0.58 g, 75%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.27 – 7.30 (m, 2H), 7.18 – 7.20 (m, 3H), 3.82 (s, 3H), 2.88 (t, $J = 7.3$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 1.92 – 2.00 (m, 2H).

**methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (3b).** Reaction was run on 3.75 mmol scale. Yield: 0.43 g, 43%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.08 (m, 4H), 3.82 (s, 3H), 2.86–2.89 (m, 2H), 2.61–2.65 (m, 2H), 2.31 (s, 3H), 1.92-1.97 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 194.48, 163.72, 140.50, 137.27, 130.96, 130.30, 54.09, 41.60, 36.73, 27.96, 22.94. IR (thin film): $\nu$ (cm$^{-1}$): 2959, 2134, 1729, 1516, 1399, 1260, 1127, 1069, 780. HRMS (ESI+) m/z Calc 283.1059 [C$_{14}$H$_{16}$N$_2$O$_3$+Na]$^+$, Found 283.1052 [M+Na]$^+$.

**methyl 2-diazo-3-oxo-6-(4-methoxyphenyl)hexanoate (3c).** Reaction was run on 0.80 mmol scale. Yield: 88 mg, 38%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.12 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.88 (t, $J = 7.3$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 1.92–1.98 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 192.55, 161.77, 157.84, 133.73, 129.37, 113.76, 55.25, 52.15, 39.59, 34.32, 26.14. IR (thin film): $\nu$ (cm$^{-1}$): 4057, 3092, 3037,
methyl 2-diazo-3-oxo-6-(4-fluorophenyl)hexanoate (3d).

Reaction was run on 1.68 mmol scale. Yield: 0.27 g, 61%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.14 (t, \(J = 8.6\) Hz, 2H), 6.96 (t, \(J = 7.5\) Hz, 2H), 2.86 (t, \(J = 7.8\) Hz, 2H), 2.69 (t, \(J = 7.8\) Hz, 2H), 1.91–1.99 (m, 2H). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 192.36, 162.28, 161.74, 160.34, 137.24, 129.24, 115.14, 52.16, 39.44, 34.38, 25.96. \(^1^9\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) (ppm): −117.47 IR (thin film): \(\nu\) (cm\(^{-1}\)): 4059, 3093, 3073, 3039, 2963, 2905, 2662, 2500, 2325, 2135, 2051, 1956, 1730, 1481, 1412, 1260, 865. HRMS (ESI+) m/z Calc 287.0808 [C\(_{13}\)H\(_{13}\)FN\(_2\)O\(_3\)+Na]\(^+\), Found 287.0823 [M+Na]\(^+\).

methyl 2-diazo-3-oxo-6-(4-bromophenyl)hexanoate (3e).

Reaction was run on 2.0 mmol scale. Yield: 0.50 g, 80%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.39 (d, \(J = 8.2\) Hz, 2H), 7.06 (d, \(J = 8.1\) Hz, 2H), 3.82 (s, 3H), 2.85 (t, \(J = 7.2\) Hz, 2H), 2.62 (t, \(J = 7.7\) Hz, 2H), 1.91–1.97 (m, 2H). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 192.27, 161.73, 140.58, 131.39, 130.24, 119.67, 52.18, 39.40, 34.58, 25.64. IR (thin film): \(\nu\) (cm\(^{-1}\)): 3093, 3073, 2963, 2905, 2662, 2500, 2325, 2135, 1956, 1723, 1647, 1412, 1260, 1091, 1018, 790. HRMS (ESI+) m/z Calc 326.0213 [C\(_{13}\)H\(_{13}\)BrN\(_2\)O\(_3\)+H\(^+\)], Found 326.0217 [M+H\(^+\)].

methyl 6-cyclohexyl-2-diazo-3-oxohexanoate (3f). Reaction was run on 0.59 mmol scale. Yield: 87 mg, 59%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 3.84 (s, 3H), 2.82 (t, \(J = 7.5\) Hz, 2H), 1.63-1.75 (m, 10H), 1.69-1.28 (m, 5H). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 161.82, 109.99, 108.30, 52.12, 40.49, 37.46, 36.94, 33.24,
methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (3g). Reaction was run on 0.88 mmol scale. Yield 79 mg, 35%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.12 (d, \(J = 5.0\) Hz, 1H), 6.91 (t, \(J = 3.5\) Hz, 1H), 6.80 (d, \(J = 3.0\) Hz, 1H), 3.83 (s, 3H), 2.88-2.93 (m, 4H), 1.99-2.06 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 192.20, 161.75, 144.37, 127.74, 124.44, 123.16, 52.18, 39.35, 29.21, 26.17. IR (thin film): \(\nu\) (cm\(^{-1}\)): 4058, 3093, 3073, 3038, 2963, 2905, 2654, 2500, 2325, 2135, 1957, 1729, 1663, 1480, 1438, 1412, 702. HRMS (ESI+) m/z Calc. 276.0544 [C\(_{11}\)H\(_{13}\)N\(_2\)O\(_3\)S+Na\(^+\)], Found 276.0538 [M+Na\(^+\)].

Methyl 2-diazo-3-oxoeyt-7-enoate (3h). Reaction was run on 1.28 mmol scale. Yield 0.16 g, 68%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 5.79 (m, 1H), 4.97–5.06 (m, 2H), 3.83 (s, 3H), 2.86 (t, \(J = 7.5\) Hz, 2H), 2.12 (q, \(J = 5.5\) Hz, 2H), 1.74 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 192.65, 161.79, 137.92, 115.19, 52.14, 39.49, 33.11, 23.44. IR (thin film): \(\nu\) (cm\(^{-1}\)): 4058, 3093, 3073, 3038, 2963, 2905, 2654, 2500, 2325, 2135, 1957, 1729, 1663, 1480, 1438, 1412, 702. HRMS (ESI+) m/z Calc. 219.0746 [C\(_{9}\)H\(_{12}\)N\(_2\)O\(_3\)S+Na\(^+\)], Found 219.0744 [M+Na\(^+\)].

Methyl 2-diazo-6-(1H-indol-2-yl)-3-oxohexanoate. Reaction was run on 0.96 mmol scale. Yield 0.13 g, 47%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.93 (br. s, 1H), 7.63 (d, \(J = 7.9\) Hz, 1H), 7.34 (d, \(J = 8.1\) Hz, 1H), 7.18 (t, \(J = 9.1\) Hz, 1H), 7.11 (t, \(J = 7.1\) Hz, 1H), 7.02 (s, 1H), 3.80 (s, 3H), 2.94 (t, \(J = 7.4\) Hz, 2H), 2.83 (t, \(J = 7.6\) Hz, 2H), 2.07 (m, 2H). \(^{13}\)C NMR (125
MHz, CDCl₃): δ (ppm): 192.71, 161.81, 136.33, 127.48, 121.92, 121.36, 119.17, 118.98, 115.96, 110.99, 52.12, 39.98, 24.70, 24.61.

**Synthesis of potassium 3-oxo-3-(2,2,2-trifluoroethoxy)propanoate.**

![Chemical structure]

Procedure was adapted following a previous literature report.²⁸ 2,2-Dimethyl-1,3-dioxane-4,6-dione (1.5 g, 10.4 mmol) and 2,2,2-trifluoroethanol (1.5 mL, 20.8 mmol) were dissolved in anhydrous toluene (15 mL) and transferred to an oven-dried 50 mL pressure tube. The sealed reaction mixture was heated to 100 °C for 20 hours. The toluene was removed under reduced pressure to give the desired product as a white solid (1.80 g, 93%). Characterization data is consistent with literature values.²⁸ ¹H NMR (500 MHz, CDCl₃): δ (ppm): 3.54 (s, 2H), 4.56 (q, J = 7.4 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm): −73.77. The intermediate, 3-oxo-3-(2,2,2-trifluoroethoxy)propanoic acid (1.90 g, 10.2 mmol), was suspended in anhydrous THF (5 mL). KO'Bu (1.14 g, 10.2 mmol) was dissolved in anhydrous THF (10 mL) and added dropwise. The reaction mixture was stirred overnight at room temperature before evaporation of the solvent under reduced pressure. The resulting yellow-white solid was washed with Et₂O (3 x 20 mL) to give the product as a bright, white solid (1.54 g, 67%). ¹H NMR (500 MHz, CD₃OD): δ (ppm): 4.84 (s, 2H), 4.58 (q, J = 7.0 Hz, 2H). ¹⁹F NMR (470 MHz, CD₃OD): δ (ppm): −75.44. ¹³C NMR (125 MHz, CD₃OD): δ (ppm): 171.40, 167.79, 124.51, 59.95 (J = 145 Hz), 43.60. HRMS (ESI+) m/z Calc 262.9330 [C₅H₄F₃KO₄+K]⁺, Found 262.9333 [M+K]⁺.

Synthesis of 2,2,2-trifluoroethyl 2-diazo-3-oxo-6-phenylhexanoate (3i).

Procedure was adapted following a previous literature report. Potassium 6,6,6-trifluoro-3-oxohexanoate (160 mg, 0.71 mmol) and MgCl₂ (45 mg, 0.47 mmol) were dissolved in anhydrous THF (10 mL). The suspension was stirred at 65°C for 3 hours, cooled to room temperature, and stirred for an additional 1 hour. Separately, 4-(phenyl)butyric acid (77 mg, 0.47 mmol) and carbonyl diimidazole (85 mg, 0.52 mmol) were dissolved in anhydrous THF (5 mL) and stirred at 45°C for 1 hour. The acyl imidazole solution was then transferred via syringe to the magnesium hexanoate solution and stirred at room temperature overnight. A 1 M solution of HCl (5 mL) was added dropwise to the reaction mixture. The quenched reaction mixture was extracted into EtOAc (2 x 50 mL), washed with brine, dried with sodium sulfate, and concentrated under reduced pressure. The resulting oil was filtered through a plug of SiO₂ using a 9:1 mixture of hexanes:EtOAc to give 2,2,2-trifluoroethyl 3-oxo-6-phenylhexanoate as a crude, yellow oil that was used without further purification.

2,2,2-trifluoroethyl 3-oxo-6-phenylhexanoate (168 mg, 0.59 mmol) and para-acetamidobenzenesulfonyl azide (212 mg, 0.88 mmol) were dissolved in CH₂Cl₂ (10 mL) and cooled to 0°C. Triethylamine (0.42 mL, 1.05 mmol) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with DCM (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO₂ chromatography (10% EtOAc in Hexanes) to give the respective diazo product as a yellow oil (0.12 g, 92%). ^1H NMR
(500 MHz, CDCl₃): δ (ppm): 7.28 (m, 1H), 7.19 (m, 3H), 4.61 (q, J = 8.3 Hz, 2H), 2.86 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 7.9 Hz, 2H), 1.98 (m, 2H). ¹⁹F NMR (470 MHz, CDCl₃): δ (ppm): −74.80. ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 191.48, 159.58, 141.44, 128.47, 128.37, 125.98, 123.71, 121.50, 60.27, 39.72, 35.13, 25.72. IR (thin film): ν (cm⁻¹): 4058, 3092, 3072, 2963, 2905, 2654, 2325, 2140, 2051, 1958, 1813, 1734, 1669, 1480, 1412, 1262. HRMS (ESI+) m/z Calc 316.0982 [C₁₄H₁₃F₃N₂O₃+H]⁺, Found 316.0989 [M+H]⁺.

Synthesis of 3-diazononane-2,4-dione (3j), 3-diazooctane-2,4-dione (3k), and Propyl 2-diazo-3-oxobutanoate (7).

2,4-Nonanedione (1000 mg, 6.41 mmol) or 2,4-octanedione (500 mg, 3.5 mmol) or propyl 3-oxobutanoate (1000 mg, 6.93 mmol) and para-acetamidobenzenesulfonyl azide (1.5 eq.) were dissolved in CH₂Cl₂ (10 mL) and cooled to 0°C. Triethylamine (1.8 eq.) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with CH₂Cl₂ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO₂ chromatography (10% EtOAc in Hexanes) to give the respective diazo products as yellow oils.

3-diazononane-2,4-dione (3j). Reaction was run on 6.4 mmol scale. Yield: 0.25 g, 21%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 2.70 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.65 (m, 2H), 1.32 (m, 4H), 0.90 (t, J = 7.4 Hz, 2H).
Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 191.00, 109.99, 83.91, 40.55, 31.28, 28.67, 23.80, 22.41, 13.88. IR (thin film): $\nu$ (cm$^{-1}$): 3315, 2961, 2265, 2116, 1672, 1412, 1261, 1020, 800, 680. HRMS (ESI+) m/z Calc 205.0953 [C$_9$H$_{14}$N$_2$O$_2$+Na]$^+$, Found 205.0954 [M+Na]$^+$.

3-diazoctane-2,4-dione (3k). Reaction was run on 3.5 mmol scale.

Yield: 0.26 g, 43%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 2.70 (t, $J = 7.6$ Hz, 2H), 2.44 (s, 3H), 1.63 (m, 2H), 1.38 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 191.10, 188.56, 83.91, 40.31, 28.66, 26.18, 22.26, 13.81. IR (thin film): $\nu$ (cm$^{-1}$): 2961, 2905, 2499, 2114, 1943, 1677, 1413, 1260, 863. HRMS (ESI+) m/z Calc 191.0796 [C$_8$H$_{12}$N$_2$O$_2$+Na]$^+$, Found 191.0815 [M+Na]$^+$.

Propyl 2-diazo-3-oxobutanoate (7). Reaction was run on a 6.9 mmol scale. Yield: 0.60 g, 50%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 4.20 ($J = 6.5$ Hz, 2H), 2.48 (s, 3H), 1.72 (m, 2H), 0.97 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 190.21, 161.49, 66.95, 28.25, 22.05, 10.29. IR (thin film): $\nu$ (cm$^{-1}$): 4058, 3302, 3092, 3072, 2963, 2905, 2392, 2211, 2138, 1959, 1723, 1666, 1480, 1260, 802. HRMS (ESI+) m/z Calc 194.0612 [C$_7$H$_{10}$N$_2$O$_3$+Na]$^+$, Found 194.0621 [M+Na]$^+$.

Synthesis of diethyl 2-diazomalonate.

Procedure was adapted following a literature report.$^{29}$ Diethyl malonate (1000 mg, 6.24 mmol) and para-acetamidobensensulfonyl azide (2.25 g, 9.36 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL) and cooled to 0 °C. Triethylamine (0.63 mL, 11.2 mmol) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL)

was added and the reaction mixture extracted with CH$_2$Cl$_2$ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO$_2$ chromatography (10% EtOAc in Hexanes) to give the respective diazo product as a bright yellow oil (0.50 g, 43%). Characterization data matches literature values.$^{29}$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 4.31 (q, $J = 7.1$ Hz, 4H), 1.32 (t, $J = 7.1$ Hz, 6H).

**Synthesis of 2-diazo-3-oxo-6-phenylhexanenitrile.**

Procedure was adapted following a previous literature report.$^{27}$ Bromobenzene (500 mg, 3.18 mmol), Pd(OAc)$_2$ (72 mg, 0.32 mmol), SPhos (263 mg, 0.64 mmol) were dissolved in THF (10 mL). A 0.5 M solution of 4-ethoxy-4-oxobutylzinc bromide (7.63 mL, 3.82 mmol) was added dropwise and the reaction mixture heated to 50°C for two hours. After cooling to room temperature, a saturated solution containing NH$_4$Cl was added and the reaction mixture extracted with a 1:1 mixture of hexanes:EtOAc. (3 x 15 mL) The combined organic layers were washed with brine, dried using sodium sulfate, and the solvent removed under reduced pressure to give a yellow oil. The crude product was purified using SiO$_2$ chromatography (9:1 hexanes:EtOAc) to give the resulting ethyl 4-phenylbutanoate (250 mg, 61%). Characterization data matches that of previously reported material.$^{27}$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.27–7.30 (m, 2H), 7.18–7.21 (m, 3H), 4.15 (q, $J = 7.2$ Hz, 2H), 2.66 (t, $J = 7.8$ Hz, 2H), 2.32 (t, $J = 7.6$ Hz, 2H), 1.96 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 2H).
LiN(Si(CH₃)₃)₂ (478 mg, 2.86 mmol) was sealed in a flask under N₂ and cooled to –78°C. CH₃CN (0.18 mL, 3.38 mmol) was added and the reaction mixture stirred for 30 minutes. Ethyl 4-phenylbutanoate (250 mg, 1.30 mmol) was then added via syringe as a solution in THF (10 mL). After slowly warming the reaction mixture to room temperature over the course of two hours, a saturated solution containing NH₄Cl was added. The resulting mixture was extracted with EtOAc (3 x 15 mL) and the combined organic layers washed with brine and dried over sodium sulfate. The crude oil was further purified via SiO₂ chromatography (9:1 hexanes:EtOAc) to give 3-oxo-6-phenylhexanenitrile (120 mg, 33%). Characterization data matches that of previously reported.²⁷ ¹H NMR (600 MHz, CDCl₃): δ (ppm): 7.16–7.33 (m, 5H), 3.42 (s, 2H), 2.60–2.72 (m, 4H), 1.96–2.03 (m, 2H).

3-Oxo-6-phenylhexanenitrile (100 mg, 0.51 mmol) was dissolved in CH₃CN (5 mL) and transferred to a 20 mL vial. The HCl salt of imidazole sulfonyl azide²⁶ (95 mg, 0.55 mmol) and pyridine (0.21 mL, 2.55 mmol) were added and the reaction mixture heated to 35°C for 6 hours. The solvent was removed under reduced pressure and the crude product was purified using SiO₂ chromatography (9:1 hexanes:EtOAc) to give the product as a dark, yellow solid (60 mg, 53%). Characterization data matches literature values.²⁷ ¹H NMR (500 MHz, CDCl₃): δ (ppm): 7.30 (m, 2H), 7.19 (m, 3H), 2.62-2.70 (m, 4H), 2.03 (m, 2H).
Synthesis of isobutyl α-phenyl-α-diazoacetate (5b).

![Chemical Structure](image)

Procedure was adapted following a literature report. Isobutyl phenyl acetate (1.92 g, 10 mmol) and tosyl azide (29.8 mL, 15 mmol) (11% in toluene) were dissolved in CH$_3$CN (15 mL) and cooled to 0°C. Diazabicyclo[5.4.0]undec-7-ene (2.24 mL, 15 mmol) was added dropwise and the reaction mixture slowly warmed to room temperature overnight. A saturated solution containing NH$_4$Cl was added and the resulting solution was extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic fractions were washed with brine, dried using sodium sulfate, and concentrated under reduced pressure to give a crude, yellow oil. The product was further purified with SiO$_2$ chromatography (9:1 hexanes:EtOAc) to give isobutyl 2-diazo-2-phenylacetate as a yellow oil. Characterization data matches previously published material. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm): 7.47–7.50 (m, 2H), 7.38 (t, $J = 7.7$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 1H), 4.06 (d, $J = 6.6$ Hz, 2H), 2.00 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

Synthesis of Phenethyl 2-diazo-3-oxobutanoate (6).

![Chemical Structure](image)

Procedure was adapted following a literature report. Methylacetoacetate (950.5 mg, 8.19 mmol) and 2-phenylethanol (1.0 g, 8.19 mmol) were sealed in a 200 mL pressure vessel and

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heated to 110°C for 3 hours. The product, phenethyl 3-oxobutanoate, was purified using SiO₂ chromatography (80:20 Hexanes:EtOAc) and used without further purification.

Phenethyl 3-oxobutanoate (500 g, 2.4 mmol) and para-acetamidobenzenesulfonyl azide (864 mg, 3.6 mmol) were dissolved in CH₂Cl₂ (20 mL) and cooled to 0°C. Triethylamine (0.24 mL, 4.32 mmol) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with CH₂Cl₂ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO₂ chromatography (10–20% EtOAc in Hexanes) to give the diazo product as a white solid (141.5 mg, 25%). ¹H NMR (500 MHz, CDCl₃): δ (ppm): 7.30-7.34 (m, 2H), 7.20-7.24 (m, 3H), 4.45 (t, J = 7.0 Hz, 2H), 3.00 (t, J = 6.50 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 190.07, 161.30, 137.21, 128.83, 128.64, 126.82, 65.77, 35.16, 28.21. IR (thin film): ν (cm⁻¹): 4060, 3036, 2963, 2905, 2499, 2395, 2214, 2139, 1956, 1718, 1659, 1388, 1314, 1258, 1151, 1075, 1022, 800. HRMS (ESI+) m/z Calc 233.0921 [C₁₂H₁₂N₂O₃+H]⁺, Found 233.0924 [M+H]⁺.

Synthesis of 2,4-dimethylpentan-3-yl 2-diazo-3-oxobutanoate (8), cyclohexyl 2-diazo-3-oxobutanoate (9), and (1r,3r,5r,7r)-adamantan-2-yl 2-diazo-3-oxobutanoate (10).

Procedure was adapted following a literature protocol.³² The desired alcohol (1 eq) was added to 2,2,6-trimethyl-4H-1,3-dioxin-4-one (1 eq) and xylene (5 mL). The reaction mixture was heated to 140°C for 2 hours, followed by removal of the xylene under reduced pressure. The

crude residue was purified by SiO₂ chromatography using 9:1 Hexanes:EtOAc as eluent to give the desired β-ketoester intermediates. The β-ketoester intermediate (1 eq) and para-acetamidobenzenesulfonyl azide (1.5 eq.) were dissolved in CH₂Cl₂ (10 mL) and cooled to 0°C. Triethylamine (1.8 eq.) was added via syringe and the reaction mixture was stirred at room temperature overnight. A 2 M solution of NaOH (2 mL) was added and the reaction mixture extracted with CH₂Cl₂ (1 x 10 mL). The organic fractions were acidified to pH = 5 with acetic acid, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure. The yellow oil was purified by SiO₂ chromatography (10% EtOAc in Hexanes) to give the respective diazo products as white solids.

2,4-dimethylpentan-3-yl 2-diazo-3-oxobutanoate (8). Reaction run on 1.0 mmol scale. Yield: 0.12 g, 54%. Characterization data matches previously reported material. ³²¹H NMR (500 MHz, CDCl₃): δ (ppm): 4.70 (t, J = 6.1 Hz, 1H), 2.50 (s, 3H), 1.95 (m, 2H), 0.90 (m, 12H).

Cyclohexyl 2-diazo-3-oxobutanoate (9). Reaction run on 3.8 mmol scale. Yield: 0.25 g, 31%. Characterization data matches previously reported material. ³²¹H NMR (500 MHz, CDCl₃): δ (ppm): 4.92 (m, 1H), 2.47 (s, 3H), 1.89 (m, 2H), 1.74 (m, 2H), 1.27-1.55 (m, 6H).

(1r,3r,5r,7r)-adamantan-2-yl 2-diazo-3-oxobutanoate (10). Reaction run on 2.1 mmol scale. Yield: 0.14 g, 24%. Characterization data matches previously reported material. ³²¹H NMR (500 MHz, CDCl₃): δ (ppm): 2.20 (m, 4H), 2.16 (m, 10H).
6.5.4 Catalysis

\[
\begin{align*}
\text{(3)} & \quad \xrightarrow{\text{20 mol\% } [\text{Fe}]} \quad \xrightarrow{\text{C}_6\text{H}_6, 12 \text{ h} \quad 80 \degree \text{C}} \quad \xrightarrow{\text{(4)}} \\
\text{R} & \quad \text{N}_2 & \quad \text{Y} & \quad \text{R} & \quad \text{O} & \quad \text{Y}
\end{align*}
\]

In an inert atmosphere drybox, a benzene solution (1 mL) containing the desired diazo (5.0 eq) was added to a benzene solution (1 mL) containing \((^{\text{tBu}}L)\text{FeCl(ET}_2\text{O)}\) (1) (1.0 eq.). The resulting mixture was transferred to a J. Young tube and heated to 80\degree C for 12 hours. Organic products were isolated via SiO\textsubscript{2} gel chromatography, eluting with either a 9:1 or 8:2 mixture of hexanes:EtOAc. Fractions containing the desired product were combined and the solvent removed in vacuo. Reactions were run in triplicate and the average isolated yields are reported. Selected \(^1\text{H}\) NMR yields are reported using ferrocene as an internal standard. To measure the \(^1\text{H}\) NMR yield of the crude reaction mixture, the solution was filtered through a pad of SiO\textsubscript{2} and washed with a 50:50 mixture of hexanes:EtOAc to remove paramagnetic impurities. The combined solvent was removed in vacuo and the crude mixture re-dissolved in CDCl\textsubscript{3}.

**Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4a).**

Isolated Yield: 59 ± 6\%. \(^1\text{H}\) NMR yield: 63 ± 17\%. \(^1\text{H}\) NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm): 7.28–7.40 (m, 5H), 5.63 (t, \(J = 7.2\) Hz, 1H), 4.96 (s, 1H), 3.69 (s, 3H), 2.81 (m, 2H), 2.49 (m, 1H), 2.01 (m, 1H). \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3): \delta \text{ (ppm)}: 171.42, 166.24, 139.88, 128.57, 128.04, 125.38, 88.20, 86.69, 50.73, 32.06, 31.70. HRMS (ESI+) m/z Calc 241.0841 \([\text{C}_{13}\text{H}_{14}\text{O}_3+\text{Na}]^+\), Found 241.0850 \([\text{M+Na}]^+\).
Methyl (Z)-2-(5-(p-tolyl)dihydrofuran-2(3H)-ylidene)acetate (4b).

Yield: 73 ± 6%. \(^1\)H NMR yield: 78 ± 4%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.19 (m, 4H), 5.42 (s, 1H), 5.36 (t, \(J = 8.2\) Hz, 1H), 3.68 (s, 3H), 3.41 (m, 1H), 3.08 (m, 1H), 2.49 (m, 1H), 2.35 (s, 3H), 2.04 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 176.39, 169.04, 138.13, 136.70, 129.30, 125.65, 89.41, 84.76, 50.49, 32.29, 30.70, 21.14. HRMS (ESI\(^+\)) m/z Calc 255.0997 [C\(_{14}\)H\(_{16}\)O\(_3\)+Na]\(^+\), Found 255.1004 [M+Na]\(^+\).

Methyl (Z)-2-(5-(4-methoxyphenyl)dihydrofuran-2(3H)-ylidene)acetate (4c). Yield: 39 ± 12%. \(^1\)H NMR yield: 38 ± 12%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.25 (d, \(J = 8.5\) Hz, 2H), 6.92 (d, \(J = 8.5\) Hz, 2H), 5.42 (s, 1H), 5.35 (t, \(J = 7.5\) Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.08 (m, 1H), 2.44-2.64 (m, 2H), 2.02 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 169.07, 159.69, 131.57, 129.34, 127.22, 114.05, 89.39, 84.70, 55.33, 32.22, 30.84. HRMS (ESI\(^+\)) m/z Calc 269.1153 [C\(_{15}\)H\(_{18}\)O\(_3\)+Na]\(^+\), Found 269.1189 [M+Na]\(^+\).

Methyl (Z)-2-(5-(4-fluorophenyl)dihydrofuran-2(3H)-ylidene)acetate (4d). Yield: 61 ± 3%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.34 (t, \(J = 5.3\) Hz, 2H), 7.06 (t, \(J = 8.6\) Hz, 2H), 5.60 (t, \(J = 7.0\) Hz, 1H), 4.98 (s, 1H), 3.70 (s, 3H), 2.78–2.89 (m, 2H), 2.50 (m, 1H), 1.99 (m, 1H). \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) (ppm): -113.51. HRMS (ESI\(^+\)) m/z Calc 237.0921 [C\(_{13}\)H\(_{13}\)FO\(_3\)+H]\(^+\), Found 237.0914 [M+H]\(^+\).

Methyl (Z)-2-(5-(4-bromophenyl)dihydrofuran-2(3H)-ylidene)acetate (4e). Yield: 85 ± 6%. \(^1\)H NMR yield: 64 ± 10%.
NMR (500 MHz, CDCl₃): δ (ppm): 7.47 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.58 (t, J = 7.3 Hz, 1H), 4.96 (s, 1H), 3.69 (s, 3H), 2.80 (m, 2H), 2.48 (m, 1H), 1.95 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 170.94, 166.10, 138.95, 131.70, 127.07, 121.94, 88.54, 85.86, 50.74, 31.93, 31.65. HRMS (ESI+) m/z Calc 297.0121 [C₁₃H₁₃BrO₃+H]^+, Found 297.0127 [M+H]^+.

**Methyl (Z)-2-(5-cyclohexyldihydrofuran-2(3H)-ylidene)acetate (4f).**

Yield: 53 ± 5%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 4.81 (s, 1H), 4.24–2.29 (m, 1H), 3.60 (s, 3H), 2.65–2.74 (m, 4H), 2.03–2.09 (m, 3H), 1.64–1.77 (m, 6H), 1.20 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 172.20, 166.47, 91.11, 86.98, 50.56, 42.56, 32.44, 29.60, 26.28, 25.57. HRMS (ESI+) m/z Calc 225.1491 [C₁₃H₂₀O₃+H]^+, Found 225.1500 [M+H]^+.

**Methyl (Z)-2-(5-thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (4g).** Yield: 63 ± 12%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 7.06 (m, 1H), 7.00 (m, 1H), 6.96 (m, 2H), 5.62 (t, J = 7.1 Hz, 1H), 5.39 (s, 1H), 3.68 (s, 3H), 3.12 (m, 1H), 2.46 (m, 1H), 2.07 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 126.99, 126.01, 123.93, 89.97, 80.51, 63.39, 52.70, 50.75, 41.42, 38.59, 30.70. HRMS (ESI+) m/z Calc 225.0580 [C₁₁H₁₂O₃S+H]^+, Found 225.0584 [M+H]^+.

**Methyl (Z)-2-(5-vinyl)dihydrofuran-2(3H)-ylidene)acetate (4h).** Yield: 68 ± 6%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 5.91 (m, 1H), 5.37 (d, J = 16.5 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 5.04 (q, J = 6.5 Hz, 1H), 4.88 (s, 1H), 3.67 (s, 3H), 2.73 (m, 2H), 2.20 (m, 1H), 1.83 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 166.24, 135.63, 117.58, 87.98, 86.31, 52.52, 50.70, 38.45, 29.02. HRMS (ESI+) m/z Calc. 169.0864 [C₉H₁₂O₃+H]^+, Found 169.0865 [M+H]^+. 

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2,2,2-trifluoroethyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4i). Yield: 41 ± 13%. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm): 7.36 (m, 5H), 5.69 (t, $J$ = 7.0 Hz, 1H), 5.06 (s, 1H), 4.43-4.58 (m, 2H), 2.88 (m, 2H), 2.54 (m, 1H), 2.07 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ (ppm): 174.01, 163.62, 139.44, 128.64, 128.20, 125.33, 107.96, 87.27, 86.51, 59.55 (q, $J$ = 143.4 Hz), 32.46, 31.53. $^{19}$F NMR (470 MHz, CDCl$_3$): δ (ppm): −73.91. HRMS (ESI+) m/z Calc 287.0895 [C$_{14}$H$_{13}$F$_3$O$_3$+H]$^+$, Found 287.0911 [M+H]$^+$.

Methyl (Z)-2-(5-ethyldihydrofuran-2(3H)-ylidene)acetate (4j). Yield: 57 ± 12%. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm): 5.09 (s, 1H), 4.51 (m, 1H), 2.75 (m, 2H), 2.32 (s, 3H), 2.15 (m, 1H), 1.62–1.82 (m, 3H), 1.03 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ (ppm): 197.60, 176.72, 98.22, 85.36, 31.37, 31.14, 28.69, 27.89, 9.80. HRMS (ESI+) m/z Calc 179.0942 [C$_9$H$_{14}$O$_2$+Na]$^+$, Found 179.0945 [M+Na]$^+$.

Methyl (Z)-2-(5-methyldihydrofuran-2(3H)-ylidene)acetate (4k). Yield: 71 ± 9%. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm): 5.11 (s, 1H), 4.72 (m, 1H), 2.76 (t, $J$ = 7.0 Hz, 2H), 2.30 (s, 3H), 2.19 (m, 1H), 1.65 (m, 1H), 1.44 (d, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ (ppm): 197.66, 176.62, 98.33, 80.25, 33.22, 31.57, 30.95, 20.39. HRMS (ESI+) m/z Calc 141.0915 [C$_8$H$_{12}$O$_2$+H]$^+$, Found 141.0906 [M+H]$^+$.
Figure 6.4. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-phenylhexanoate (3a) in CDCl$_3$. 
Figure 6.5. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-phenylhexanoate (3a) in CDCl$_3$. 
Figure 6.6. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (3b) in CDCl$_3$. 
Figure 6.7. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-(p-tolyl)hexanoate (3b) in CDCl$_3$. 

![NMR spectrum image]
Figure 6.8. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-(4-methoxyphenyl)hexanoate (3c) in CDCl$_3$. 
Figure 6.9. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-(4-methoxyphenyl)hexanoate (3c) in CDCl$_3$. 

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The diagram shows the NMR spectrum with various chemical shifts indicated. The molecule structure is also depicted, showing the diazo group and the methoxyphenyl group attached to the hexanoate moiety.
Figure 6.10. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-(4-fluorophenyl)hexanoate (3d) in CDCl$_3$. 
Figure 6.11. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-(4-fluorophenyl)hexanoate (3d) in CDCl$_3$. 
Figure 6.12. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-(4-bromophenyl)hexanoate (3e) in CDCl$_3$. 
Figure 6.13. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-(4-bromophenyl)hexanoate (3e) in CDCl$_3$. 
Figure 6.14. $^1$H NMR spectrum of methyl 6-cyclohexyl-2-diazo-3-oxohexanoate (3f) in CDCl$_3$. 
Figure 6.15. $^{13}$C NMR spectrum of methyl 6-cyclohexyl-2-diazo-3-oxohexanoate (3f) in CDCl$_3$. 
Figure 6.16. $^1$H NMR spectrum of methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (3g) in CDCl$_3$. 
Figure 6.17. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxo-6-(thiophen-2-yl)hexanoate (3g) in CDCl$_3$. 
Figure 6.18. $^1$H NMR spectrum of methyl 2-diazo-3-oxoocy-7-enoate (3h) in CDCl$_3$. 
Figure 6.19. $^{13}$C NMR spectrum of methyl 2-diazo-3-oxooct-7-enoate (3h) in CDCl$_3$. 

![NMR spectrum of methyl 2-diazo-3-oxooct-7-enoate (3h) in CDCl$_3$.](image-url)
Figure 6.20. $^1$H NMR spectrum of 2,2,2-trifluoroethyl 2-diazo-3-oxo-6-phenylhexanoate (3i) in CDCl$_3$. 
Figure 6.21. $^{13}$C NMR spectrum of 2,2,2-trifluoroethyl 2-diazo-3-oxo-6-phenylhexanoate (3i) in CDCl$_3$. 
Figure 6.22. $^1$H NMR spectrum of 3-diaxononane-2,4-dione (3j) in CDCl$_3$. 
Figure 6.23. $^{13}$C NMR spectrum of 3-diaxonane-2,4-dione (3j) in CDCl$_3$. 
Figure 6.24. $^1$H NMR spectrum of 3-diazoctane-2,4-dione (3k) in CDCl$_3$. 
Figure 6.25. $^{13}$C NMR spectrum of 3-diazoctane-2,4-dione (3k) in CDCl$_3$. 
Figure 6.26. $^1$H NMR spectrum of phenethyl 2-diazo-3-oxobutanoate (6) in CDCl$_3$. 
Figure 6.27. $^{13}$C NMR spectrum of phenethyl 2-diazo-3-oxobutanoate (6) in CDCl₃.
Figure 6.28. $^1$H NMR spectrum of propyl 2-diazo-3-oxobutanoate (7) in CDCl$_3$. 
Figure 6.29. $^{13}$C NMR spectrum of propyl 2-diazo-3-oxobutanoate (7) in CDCl$_3$. 
Figure 6.30. $^1$H NMR spectrum of Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4a) in CDCl$_3$. 
Figure 6.31. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4a) in CDCl$_3$. 
Figure 6.32. COSY NMR spectrum of Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4a) in CDCl₃.
Figure 6.33. HSQC NMR spectrum of Methyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4a) in CDCl$_3$. 
Figure 6.34. $^1$H NMR spectrum of Methyl (Z)-2-(5-(p-tolyl)dihydrofuran-2(3H)-ylidene)acetate (4b) in CDCl$_3$. 
Figure 6.35. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-(p-tolyl)dihydrofuran-2(3H)-ylidene)acetate (4b) in CDCl$_3$. 
**Figure 6.36.** $^1$H NMR Methyl (Z)-2-(5-(4-methoxyphenyl)dihydrofuran-2(3H)-ylidene)acetate (4c) in CDCl$_3$. 
Figure 6.37. $^{13}$C NMR Methyl (Z)-2-(5-(4-methoxyphenyl)dihydrofuran-2(3H)-ylidene)acetate (4c) in CDCl$_3$. 
Figure 6.38. $^1$H NMR Methyl (Z)-2-(5-(4-fluorophenyl)dihydrofuran-2(3H)-ylidene)acetate (4d) in CDCl$_3$. 
**Figure 6.39.** $^{13}$C NMR Methyl (Z)-2-(5-(4-fluorophenyl)dihydrofuran-2(3H)-ylidene)acetate (4d) in CDCl$_3$. 
Figure 6.40. $^1$H NMR spectrum of Methyl (Z)-2-(5-(4-bromophenyl)dihydrofuran-2(3H)-ylidene)acetate (4e) in CDCl$_3$. 
Figure 6.41. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-(4-bromophenyl)dihydrofuran-2(3H)-ylidene)acetate (4e) in CDCl$_3$. 
Figure 6.42. $^1$H NMR spectrum of Methyl (Z)-2-(5-cyclohexyldihydrofuran-2(3H)-ylidene)acetate (4f) in CDCl$_3$. 
Figure 6.43. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-cyclohexyldihydrofuran-2(3H)-ylidene)acetate (4f) in CDCl$_3$. 

![C NMR spectrum of Methyl (Z)-2-(5-cyclohexyldihydrofuran-2(3H)-ylidene)acetate (4f) in CDCl$_3$.](image-url)
Figure 6.44. $^1$H NMR spectrum of Methyl (Z)-2-(5-thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (4g) in CDCl$_3$. 
Figure 6.45. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-thiophen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (4g) in CDCl$_3$. 
Figure 6.46. $^1$H NMR spectrum of Methyl (Z)-2-(5-vinylidihydrofuran-2(3H)-ylidene)acetate) (4h) in CDCl$_3$. 
Figure 6.47. $^{13}$C NMR spectrum of Methyl (Z)-2-(5-vinylhydrofuran-2(3H)-ylidene)acetate) (4h) in CDCl$_3$. The peaks at ~14, 21, 60, 31, and 171 ppm correspond to residual solvent.
Figure 6.48. $^1$H NMR spectrum of 2,2,2-trifluoroethyl (Z)-2-(5-phenyldihydrofuran-2(3H)-ylidene)acetate (4i) in CDCl$_3$. 
Figure 6.49. $^{13}$C NMR spectrum of 2,2,2-trifluoroethyl (Z)-2-(5-phenylhydrofuran-2(3H)-ylidene)acetate (4i) in CDCl$_3$. 

[Image of the NMR spectrum]
Figure 6.50. $^1$H NMR spectrum for Methyl (Z)-2-(5-ethyldihydrofuran-2(3H)-ylidene)acetate (4j) in CDCl$_3$. 
Figure 6.51. $^{13}$C NMR spectrum for Methyl (Z)-2-(5-ethyl-2(3H)-dihydrofuran-2(3H)-ylidene)acetate (4j) in CDCl$_3$. 
Figure 6.52. $^1$H NMR spectrum for Methyl (Z)-2-(5-methylenehydrofuran-2(3H)-ylidene)acetate (4k) in CDCl$_3$. 
Figure 6.53. $^{13}$C NMR spectrum for Methyl (Z)-2-(5-methyldihydrofuran-2(3H)-ylidene)acetate (4k) in CDCl$_3$. 
6.5.6 X-ray Diffraction Techniques

The structure of 4a was collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans.

Data was integrated using SAINT\textsuperscript{33} and scaled with either a numerical or multi-scan absorption correction using SADABS. The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELX-2014 and refined against \( F^2 \) on all data by full matrix least squares with SHELX-2014.\textsuperscript{34} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). The structure for 4a was solved in the monoclinic space group \( P2_1/c \). The structure was disordered and modeled using restraints and constraints.

\textsuperscript{33} APEX2 Software Suite; Bruker AXS: Madison, WI, 2014.

Table 6.3. X-ray diffraction experimental details.\textsuperscript{a}

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</tr>
<tr>
<td>GOF on (F^2)</td>
<td>1.153</td>
</tr>
<tr>
<td>R1, (wR2)\textsuperscript{a}</td>
<td>0.0856, 0.1685</td>
</tr>
<tr>
<td>[I &gt; 2(\sigma(I))]</td>
<td></td>
</tr>
<tr>
<td>R1, (wR2)\textsuperscript{a}</td>
<td>0.1330, 0.1871</td>
</tr>
<tr>
<td>[all data\textsuperscript{a}]</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} R1 = \(\Sigma|\text{I}_0 - \text{I}_c|/\Sigma|\text{I}_0|\), \(wR2 = \left\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\right\}^{1/2}\)