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Synthesis and Characterization of Pyridine Dipyrrolide Iron Complexes Relevant to Nitrene and Carbene Group Transfer

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SYNTHESIS AND CHARACTERIZATION OF PYRIDINE DIPYRROLIDE IRON
COMPLEXES RELEVANT TO NITRENE AND CARBENE GROUP TRANSFER

Brett M. Hakey

Dissertation submitted to the Eberly College of Arts and Sciences

at West Virginia University

In Partial Fulfillment of the Requirements for the Degree of

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Chemistry

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF PYRIDINE DIPYRROLIDE IRON COMPLEXES RELEVANT TO NITRENE AND CARBENE GROUP TRANSFER

Brett M. Hakey

The synthesis and electronic structures of the square-planar high-spin Fe^{II} complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ were investigated. Analysis of these compounds using a combination of ^1H NMR and ^{57}Fe Mössbauer spectroscopies, in conjunction with computational analysis, has resulted in a rationalization for their unusual electronic structures, which arise from the unique coordination environment enforced by the pyridine dipyrrolide chelate ligand.

The reactivity of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with organic azides has been probed and resulted in the isolation of an array of products that are consistent with the generation of reactive iron nitrene intermediates. Computational analysis has evidenced that the suspected iron nitrene species are intermediate-spin ferric ions engaged in antiferromagnetic coupling to iminyl radical ligands. Increasing the steric bulk of the nitrene source via the use of mesityl azide allowed for the spectroscopic observation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, which has been identified as a competent intermediate in nitrene transfer to a C-H bond of the pyridine dipyrrolide supporting ligand. In attempts to sequester intraligand C-H amination and leverage intermolecular reactivity, the new high-spin ferrous species $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ has been synthesized. $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ is also capable of generating nitrene adducts, as demonstrated by the isolation of diamagnetic $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ and paramagnetic $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ from its reaction with 1-adamantyl azide and mesityl azide, respectively. It is anticipated that these results will provide a foundation for future investigations of the efficacy of pyridine dipyrrolide iron complexes in nitrene group transfer reactions, which may find application in the construction of new carbon-nitrogen bonds from hydrocarbon substrates.

The reaction of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with diphenyldiazomethane has resulted in the isolation of an unprecedented paramagnetic square-planar iron carbene complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$. Physical characterization and computational analysis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ suggests an $S = 1$ ground state for the compound and an electronic structure which may be described as an intermediate-spin Fe^{III} ion engaged in antiferromagnetic coupling with a carbene radical ligand. The reactivity of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ with CO and isocyanides was explored and yielded the low-spin Fe^{II} carbene group transfer products $(\text{CPh}_2)^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CO})_2$ and $(\text{CPh}_2)^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph})_2$, arising from carbene insertion into an iron pyrrolide nitrogen bond.

BIOGRAPHICAL SKETCH

Brett Michael Hakey, the first of Michael Hakey and Betsy Isham's four children, was born on July 2nd, 1993, in Burlington, Vermont, on the shores of Lake Champlain. Owing to the great fortune of having a large extended family in Northeast Vermont, he grew up in the warm company of numerous family members, many with reputes as talented athletes, educators, and scientists, alike. He attended grade schools in Georgia, and Milton, Vermont. In 2007, Brett moved to neighboring Fairfax, a quiet farm town nestled in the shadows of Mount Mansfield and the surrounding Green Mountains. There, he attended high-school at Bellows Free Academy. During this time, Brett, and his younger siblings, Thomas, Jake, and Meghan, had the wonderful experience of living with their paternal grandparents, Mark and Louise Hakey. In 2011, after high-school graduation, Brett leapt at an opportunity to try his hand at college baseball, and headed south to West Virginia. Although baseball didn't quite work out, he studied chemistry while at West Virginia Wesleyan College. There, under the tutelage of Dr. Joanna Webb, he became interested in the application of late 3d transition metals in catalysis, and performed undergraduate research, with a focus on synthesizing cobalt pincer ligand complexes. Upon receiving his undergraduate degree in 2015, he took a graduate research position at West Virginia University, in the laboratory of newly minted Assistant Professor Carsten Milsmann. During his time in Morgantown, Brett had the great pleasure of exploring the synthesis, reactivity, and electronic structures of pyridine dipyrrolide iron compounds.

This dissertation is dedicated in loving memory of:

Charles, Doris, and Louise Hakey

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spectroscopy in support of my interest in understanding the electronic structures of the compounds I've synthesized. Without Jon's generous assistance and expertise, this work would not have been possible. With that being said, thanks are also extended to his supervisor, Professor Paul Chirik, who has graciously allowed access to his group's Mössbauer spectrometer.

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Thanks are also extended to the WVU Chemistry staff, Allen Burns, Randy Eaglen, Gregory Lusk, and Sherman Adams. I would especially like to thank Sherman for being a great friend during my time at WVU. Many hours were spent with him in his glassblowing shop hearing about his life experiences and discussing all things under the sun, with college football and politics being topics of special foci. I wish him the best in his retirement. I would also like to offer my thanks to Rebecca Secrist and Brenda Prentiss, who were always warm and supportive when logistical or administrative assistance was needed. Albert "JR" Taylor and Crys Povenski are also acknowledged, as they were not only patient and supportive supervisors during my time as a teaching assistant, but were also always willing to find time in their busy schedules to assist me in sending samples to our numerous collaborators.

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List of Chemical Abbreviations

Ad or ¹ Ad	1-adamantyl
Bn	benzyl
Cp	cyclopentadienyl
DCM	dichloromethane
dipp	2,6-diisopropylphenyl
Et	ethyl
Et ₂ O	diethylether
ⁱ Pr	isopropyl
L	ligand
LiHMDS	lithium bis(trimethylsilyl)amide
Me	methyl
Mes	mesityl or 2,4,6-trimethylphenyl
ⁿ Bu	<i>n</i> -butyl
PDI	pyridine diimine/ 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine
Ph	phenyl
py	pyridine
^t Bu	<i>tert</i> -butyl
thf or THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	toluene
Xyl	<i>meta</i> -xylyl or 2,6-dimethylphenyl

List of Acronyms, Symbols, and Units

•	radical
{ ¹ H}	proton decoupled
¹³ C	carbon-13
¹ H	proton
Å	angstrom, 10 ⁻¹⁰ meters
avg	average
br	broad
cm ⁻¹	wavenumbers or inverse centimeters
<i>D</i>	axial zero field splitting parameter
<i>d</i>	doublet resonance
<i>E</i>	rhombic zero field splitting parameter
e ⁻	electron
G	gauss
<i>g</i>	Landé <i>g</i> -factor (but may also refer to the anomalous gyromagnetic ratio, 2.0023)
<i>H</i>	Hamiltonian operator
<i>H</i>	magnetic field
HAA	hydrogen atom abstraction
HOMO	highest occupied molecular orbital
HRMS	High-resolution mass spectrometry
IR	infrared spectroscopy
<i>J</i>	coupling constant
<i>k</i>	Boltzmann constant, 0.695 cm ⁻¹ /K
K	kelvin
LUMO	lowest unoccupied molecular orbital
M	molar, moles per liter
m	multiplet in NMR
<i>m</i> -	<i>meta</i> position on an aryl ring, indicating a 1,3 relationship
<i>m/z</i>	mass to charge ratio
MHz	megahertz, 10 ⁶ Hertz or 10 ⁶ s ⁻¹
mmol	millimole, 10 ⁻³ moles
MO	molecular orbital
nb	non-bonding orbital
nm	nanometer, 10 ⁻⁹ meters
NMR	nuclear magnetic resonance
<i>o</i> -	<i>ortho</i> position on an aryl ring, indicating a 1,2 relationship
<i>p</i> -	<i>para</i> position on an aryl ring, indicating a 1,4 relationship
ppm	parts per million
q	quartet resonance
rt	room temperature
s	singlet resonance or second
<i>S</i>	spin
<i>S</i>	spin operator
T	tesla

t	triplet resonance
T or T	temperature
δ	delta, chemical shift in ppm or isomer shift for ^{57}Fe Mössbauer in mm/s
ΔE_Q	quadrupole splitting for ^{57}Fe Mössbauer in mm/s
η^n	eta, hapticity or the number, n , of contiguous atoms in a ligand bound to a metal
κ^n	kappa, denticity or the number, n , of atoms in a polydentate ligand bound to the metal
μ_B	Bohr magneton, 9.274×10^{-21} erg/G
μ_{eff}	mu effective, effective magnetic moment in Bohr magnetons
ν	frequency
χ	magnetic susceptibility
χ_M or χ_m	molar magnetic susceptibility in cm ³ /mol

CHAPTER I: IRON: THE NATURAL CHOICE FOR GROUP TRANSFER CHEMISTRY

1.1 Iron Coordination Chemistry

The chemistry of iron, the most abundant of the transition metal elements, has garnered longstanding attention owing to its diverse function in both anthropogenic and natural chemical processes. Particularly fascinating is the variety of electronic structures available to this particular element, which renders it inherently flexible in its application. Throughout decades of research, coordination complexes have been identified with iron centers spanning formal oxidation states from -2 to +6.^{1,2} This wealth of available oxidation states, coupled with the possibility for multiple spin-states to exist at each oxidation number obviates the fact that a myriad of potential electronic structures may be adopted by iron containing coordination compounds. Furthermore, by partnering the breadth of possible combinations of oxidation state and spin-state with the multitude of coordination geometries available to transition metal complexes, a seemingly limitless array of iron coordination compounds with disparate physical characteristics can be imagined. Accordingly, researchers have identified that by controlling the electronic structure of an iron complex via a well-defined ligand field may allow for the isolation of iron complexes well suited for use in catalysis,³ electron-transfer,^{4,5} magnetic materials,⁶ and photochemistry.⁷ Despite the intensive research and notable successes achieved within the context of synthetic inorganic and organometallic iron chemistry, the most elegant applications of this element are in biological systems. Prominent examples include iron's presence in active sites of enzymes which may engage small molecules substrates in both oxidative and reductive processes. Most notable are oxygenases, nitrogenases, and hydrogenases, examples of which are depicted in Figure 1.1.^{8,9}

Figure 1.1. Important biological structures containing iron. Heme unit in cytochrome P450 (top left), Heme b unit found in myoglobin (top right, note: histidine residue is truncated), FeMo cofactor of nitrogenase (middle), [FeFe] hydrogenase (bottom left), and [Fe₃S₄] cluster in *A. vinelandii* ferredoxin.

Moreover, the transport and storage of dioxygen via hemoglobin and myoglobin proteins and the electron transfer capabilities of iron-sulfur clusters are also critical for physiological function.^{8,9} Although the roles of these biological constructs are extremely diverse, one common theme that is critical for their successful operation is the redox flexibility available to the iron center(s). The seamless changes possible between formal oxidation states and accompanying spin-states of iron is what enables its utility in this variety of chemical processes. In consideration of this, it has become clear that the development of a thorough understanding of the electronic structures operative in these particular iron containing systems may offer tremendous promise for the

informed development of synthetic mimics with applications in fields such as catalysis and sustainable fuel production.^{10,11}

In this regard, a particularly striking example is considered within the context of a family of heme containing enzymes, the P450 monooxygenases. These enzymes are a fascinating example of how nature can leverage and exploit an iron containing complex to accomplish challenging chemical transformations under mild physiological conditions. Notably, the P450 family of enzymes are capable of leveraging highly-reactive iron-oxo intermediates towards the selective hydroxylation of inert C-H bonds. This process occurs via the capture and scission of molecular dioxygen at the iron center, forming an iron-oxo intermediate, referred to as Compound I. Compound I is highly reactive, and thus, capable of performing such a challenging reaction. Mechanistically, C-H hydroxylation is believed to occur via a stepwise process of hydrogen-atom abstraction to form an iron hydroxide intermediate. This is followed by radical recombination to form product, as depicted in Figure 1.2.^{8-10,12,13}

Figure 1.2. Proposed mechanism of C-H hydroxylation facilitated via P450.

Thorough studies on P-450 and model systems have elucidated the electronic structure of Compound I, which is characterized as containing a triplet ($S_{\text{Fe}} = 1$) formally Fe(IV) center engaged in antiferromagnetic coupling to a porphyrin radical cation. The overall $S = 1/2$ state has been corroborated via a combination of electron paramagnetic resonance and Mössbauer spectroscopies.^{12,14} An additional key characteristic of the electronic structure of Compound I is the presence of two unpaired electrons occupying Fe-O π^* antibonding orbitals (Figure 1.3).¹⁵ The occupation of orbitals of antibonding character significantly destabilizes the iron-oxo or “ferryl” unit. This destabilization, in combination with the presence of significant unpaired spin

density on the Fe-O bond vector renders Compound I poised to engage a C-H bond of a substrate molecule.

Figure 1.3. Simplified electronic structure of Compound I.

1.2 Biomimetic Iron Chemistry: Atom and Group Transfer Reactivity

Early researchers took notice of the remarkably reactivity of the P450 family of enzymes and sought to extend this reactivity to model systems. The development of biomimetic porphyrin complexes can be traced to the late 1970's when Groves and coworkers reported the application of (TPP)Fe(Cl) (TPP = meso-tetraphenylporphyrin) in the oxidation of cyclohexane to cyclohexanol using iodosobenzene as the oxygen atom source.¹⁶ Using the same catalyst system, olefins, such as cyclohexene could also be converted to the corresponding epoxide (Scheme 1.1). This work has spurred decades of research in the areas of biomimetic iron-porphyrin chemistries, which is now a mature field.^{10,17}

Scheme 1.1. Substrate dependent catalytic hydrocarbon oxidation with (TPP)Fe(Cl) and iodosobenzene.

Soon after, Breslow demonstrated the utility of (TPP)Fe(Cl) as an active catalyst in intramolecular nitrene transfer. Cyclic sulfonamides could be attained via the decomposition of the hypervalent iodine reagent 2,5-diisopropylbenzenesulfonylimidoiodobenzene as a model substrate (Scheme 1.2).¹⁸ In both cases, the formal insertion of an oxygen atom or an isoelectronic nitrene fragment (N-R) into a C-H bond are believed to operate via a mechanistic pathways akin to Compound I, with iron-oxo and nitrene complexes implicated as penultimate intermediates.

In consideration of the demonstration of these porphyrin complexes as efficient atom or group transfer catalysts, significant attention has recently been devoted to further developing nitrene group transfer with other iron catalyst systems. Synthetic researchers have identified the practicality of direct nitrene insertion into a C-H bond, or C-H amination, as an efficient means to access valuable amine containing structures, which are ubiquitous in pharmaceuticals and bioactive molecules.^{19,20} Iron catalyzed C-H amination offers tremendous promise, not only due to the ubiquity of iron, but also in part to iron's biocompatibility. Despite the attractiveness of base metal catalyzed direct C-H amination protocols, current practical synthetic methods employing small molecule catalysts are limited to systems containing scarce transition metals, such as rhodium and ruthenium. Despite the remarkable success and versatility of these noble

metal catalyst systems (vide infra), obvious questions surrounding their long-term sustainability exist.

1.3 Rhodium and Ruthenium Catalyzed Nitrene Group Transfer

Presently, one of the most popular systems employed for selective nitrene transfer to C-H bonds utilizes dirhodium complexes as catalysts. Ironically, dirhodium C-H amination chemistry finds its origins in the same report disclosing the successful utilization of the (TPP)Fe(Cl) as a nitrene group transfer catalyst. When evaluated under similar reaction conditions, Rh₂(OAc)₄ demonstrated superior catalytic activity and efficiency relative to (TPP)Fe(Cl), as exemplified by both higher yield and selectivity for the intramolecular C-H amination product (Scheme 1.2).¹⁸

Scheme 1.2. Catalytic intramolecular nitrene transfer with (TPP)Fe(Cl) or Rh₂(OAc)₄.

This initial discovery has resulted in the subsequent development of a remarkably successful field employing dirhodium tetracarboxylate catalysts in catalytic nitrene transfer reactions. In recent decades, a combination of mechanistic insight and elegant ligand design has led to the advent of modern dirhodium catalyst systems with practical applications in the synthesis of highly complex molecular architectures. To date, the most popular and well-studied dirhodium carboxylate catalyst is Rh₂(esp)₂ (where esp = α , α , α' , α' -tetramethyl-1,3-benzenedipropanoate) originally developed by Du Bois.^{21,22} In Rh₂(esp)₂ the esp ligands impart stability via the chelate effect, which in turn effects higher catalytic efficiencies under low loadings, as compared to

simpler dirhodium catalyst systems. An example is presented in Scheme 1.3, where an intramolecular C-H amination reaction can be performed using only 0.15 mol% of $\text{Rh}_2(\text{esp})_2$ as catalyst.

Scheme 1.3. Intramolecular C-H amination with $\text{Rh}_2(\text{esp})_2$ catalyst.

Further dirhodium catalyst elaboration has led to the discovery of asymmetric transformations, via informed ligand design. A noteworthy example is the intramolecular C-H amination of aryl substituted sulfamate esters where the carboxamidate catalyst $\text{Rh}_2(S\text{-nap})_4$ (*S*-nap = 4-Methyl-N-(2-oxopiperidin-3-yl)benzenesulfonamide) effects the enantioselective intramolecular C-H amination of sulfamate esters.²³

In regard to mechanistic considerations, it is widely agreed upon that a discrete Rh_2 nitrene intermediate is responsible for the observed reactivity (Figure 1.4). Generation of this nitrenoid species is typically accomplished *in situ* via the introduction of a hypervalent iodine reagent and oxidant, commonly MgO , to a nitrogen containing substrate. Suitable nitrene precursors include carbamates, sulfamates, and ureas, for example. This strategy bypasses the

direct isolation of the corresponding iminoiodinane nitrene precursors, which are generally challenging to manipulate and are potentially energetic materials.²²

Figure 1.4. Proposed mechanism of dirhodium catalyzed C-H amination. Note: R = solvent ligand and R' = the hydrocarbon skeleton of the sulfamate ester starting material.

Despite the agreement that Rh_2 C-H amination catalysis is facilitated by a Rh_2 -nitrenoid complex, the fleeting existence of such intermediates has complicated their characterization and study. Only recently has crystalline matrix isolation enabled the first X-ray crystallographically characterized example of a dirhodium nitrene complex, $\text{Rh}_2(\text{esp})_2(\text{N}^1\text{Ad})(^1\text{AdN}_3)$ (^1Ad = 1-adamantyl) (Scheme 1.4).²⁴ Generation of $\text{Rh}_2(\text{esp})_2(\text{N}^1\text{Ad})(^1\text{AdN}_3)$ was accomplished via irradiation of a single crystal of the bis-azido precursor $\text{Rh}_2(\text{esp})_2(^1\text{AdN}_3)_2$. In regard to electronic structure of this dirhodium nitrenoid, density functional theory studies favor a triplet ground state over a singlet for the truncated hypothetical nitrene model complex $\text{Rh}_2(\text{esp})_2(\text{N}^t\text{Bu})($

$^1\text{BuN}_3$). The electrophilic triplet nitrene is suggested to engage in two half order π bonds stemming from the overlap of Rh-Rh π^* orbitals with partially occupied orbitals of nitrene parentage.

Scheme 1.4. Photogeneration of a dirhodium nitrene complex.

Prior to this report, Berry and coworkers examined the mechanism of dirhodium catalyzed C-H amination.²⁵ In one aspect of this work, the electronic structures of $[\text{Rh}_2(\text{esp})_2]$ and $[\text{Rh}_2(\text{espn})_2]$ ($\text{espn} = \alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropanamidate) catalytic intermediates were interrogated theoretically. Results of this study suggest that $[\text{Rh}_2(\text{esp})_2]$ and $[\text{Rh}_2(\text{espn})_2]$ catalysts may proceed through a concerted insertion of the nitrene into the C-H bond, however, a stepwise mechanism involving radical intermediates was also identified. Currently, experimental evidence is available that is consistent with the concerted C-H insertion pathway, such as stereoretention in optically active substrates, radical clock experiments, and KIE studies.²² Despite mechanistic questions still existing within the context of dirhodium catalyzed C-H amination, it has become clear that this methodology is a powerful means to perform nitrene transfer to C-H bonds.

Complimentary to dirhodium systems are diruthenium C-H amination catalysts that have recently been developed. A noteworthy example is the diruthenium paddlewheel complex, tetrakis(2-oxy-pyridinato)diruthenium(II,III) chloride or $[\text{Ru}_2(\text{hp})_4(\text{Cl})]$, where evidence has been garnered from experimental and computational studies that suggests that this catalysts operates via a stepwise radical pathway, contrary to the asynchronous C-H insertion observed in Rh_2 systems.²⁶ The divergence in mechanistic pathways between Ru_2 and Rh_2 catalyst systems demonstrates the sensitivity of the electronic structure of the nitrene intermediate and its subsequent reactivity profile. An example that greatly exemplifies this dichotomy is found in allylic amination reactions of bis(homoallylic) sulfamate esters, where $[\text{Ru}_2(\text{hp})_4(\text{Cl})]$ is an efficient precursor for the generation of a catalyst with high chemoselectivity for allylic amination. Whereas under the same reaction conditions, $[\text{Rh}_2(\text{esp})_2]$ and the diruthenium analogue $[\text{Ru}_2(\text{esp})_2]$ show little or no preference between allylic amination and olefin aziridination (Figure 1.5).

Figure 1.5. Selectivity for allylic C-H amination vs. olefin aziridination in dirhodium and diruthenium catalyst systems.

Mononuclear ruthenium porphyrin complexes have also been extensively evaluated by Che, Gallo, and others as catalysts for the delivery of nitrene functionality to hydrocarbons.²⁷⁻³¹ Isolation of bis-imido Ru(VI) porphyrin complexes has been accomplished via the reaction of the corresponding Ru(II) porphyrin carbonyl complexes with iminodiodinanes or organic azides. (TPP)Ru(NAr)₂ (Ar = 3,5-(CF₃)₂C₆H₃) serves as a representative example of this class of compounds and has demonstrated activity in stoichiometric and catalytic allylic C-H amination of hydrocarbons (Scheme 1.5).

Scheme 1.5. Synthesis of (TPP)Ru(NAr)₂ and its stoichiometric and catalytic allylic C-H amination reactivity. Note: The TPP ligand is truncated via exclusion of the phenyl groups at the porphyrin meso positions.

An experimental mechanistic study of this system has suggested the likelihood of C-H abstraction from substrate in route to amidation product, while computational analysis has identified the subtle implications that the electronic structure of Ru imido species has on possible reaction manifolds.³¹ Results suggest that although these ruthenium complexes possess canonical dianionic closed shell imido ligands, intersystem crossing from the ground state singlet

electronic structure to a thermally accessible triplet state results in the observation of significant spin-density imparted onto both imido nitrogens. The accumulation of spin density on the imido nitrogens is believed to facilitate C-H functionalization via hydrogen atom abstraction from the substrate, followed by radical rebound to form the corresponding products. A second reaction manifold incorporating a mono-imido Ru(IV) carbonyl complex has also been identified. This intermediate is also proposed to undergo intersystem crossing to a triplet state and perform C-H amination. Both mechanistic possibilities are presented in Figure 1.6. The observation of open-shell electronic structures *in silico* in this system offers further evidence that the development of radical character at nitrene intermediates may be an important implication for the activation of C-H bonds in some contexts. In light of this discovery, researchers have sought to develop base metal systems which seek to incorporate this design principle.

Figure 1.6. Proposed mechanisms of ruthenium porphyrin catalyzed C-H amination. Note: The TPP ligand is truncated via exclusion of the phenyl groups.

1.4 Iron Mediated Nitrene Group Transfer

Despite the tremendous success that has been realized by rhodium and ruthenium catalyst systems in nitrene group transfer reactions, a recent focus has returned to the examination of systems incorporating earth abundant metals in analogous reactions. Base metals offer not only a cost effective alternative to noble transition metal catalysts, but are also attractive due to their benign nature. Furthermore, the compressed ligand fields of 3d metals relative to 4d congeners may even offer the promise of complimentary reaction mechanisms. Although historically nitrene group transfer reactions have been widely explored for copper and manganese,³² a recent renewed interest in the development of highly active and selective iron nitrene group transfer catalyst systems has resulted in intensive efforts in this area of research.

Drawing motivation from P450 enzymatic catalysis, Arnold, Fasan, and others have leveraged abiological heme and non-heme catalysts engineered via directed evolution in selective nitrene transfer.³³⁻⁴⁰ Although this approach is environmentally considerate, complementary is the design of well-defined molecular catalysts. In contrast to the inherent complexity associated with enzymatic structures, molecular systems offer the promise of tunable ligand fields where informed design and modulation of electronic and steric environments can be performed when necessitated by particular reaction manifolds. In consideration of this, White and coworkers have recently extended the use of polypyrrole macrocycles in nitrene transfer reactions from porphyrins to the closely related macrocyclic iron phthalocyaninato chloride complex, (Pc)Fe(Cl) (Scheme 1.6).⁴¹ This catalyst has demonstrated activity in the selective allylic amination of C-H bonds in the presence of iminoiodinane reagent PhI(OPiv)₂ as oxidant. Mechanistic studies suggest the canonical radical rebound mechanism is operative in this system, as nitrene insertion is highly favored over the competitive aziridination pathway.

Chemoselectivity for the C-H bond is consistent with a rapid radical rebound upon formation of an allylic radical following hydrogen atom abstraction from the in situ generated iron nitrene. Furthermore, the observation of configurational retention and the lack of olefin isomerization in the substrates is consistent with this mechanistic proposal.

Scheme 1.6. (Pc)Fe(Cl) catalyzed allylic C-H amination.

Recently, attention has also been devoted to the exploration of catalytic nitrene group transfer reactions within the context of non-heme iron systems. An exciting development reported by Van der Vlugt et al. describes an air-stable Fe^{III} C-H amination catalyst carrying a redox-active ligand, (NNO^{ISQ})Fe(Cl)₂.⁴² This complex is active in the direct intramolecular amination of C(sp³)-H bonds in aliphatic azides to form a variety of saturated N-heterocycles, such as pyrrolidines and piperidines with the highest TONs to date for this class of reactions. A variety of substrates, such as alkenyl, ethereal, and even carbonyl containing alkyl azides are amenable to the reaction. The direct C(sp³)-H amination of representative substrate 1-azido-4-phenylbutane to form the corresponding pyrrolidine product in moderate yield is depicted in Scheme 1.7. Although reactive intermediates have not yet been isolated within this system, mechanistic studies implicate a nitrenoid species. It is anticipated that the nitrenoid may either

undergo direct insertion into a C-H bond of the substrate to form the amine product or perform an H-atom abstraction followed by a radical rebound reminiscent of P450 chemistry.

Scheme 1.7. Iron catalyzed C-H amination of 1-azido-4-phenylbutane.

Similarly, Betley and coworkers have also reported a well-defined iron C-H amination catalyst utilizing dipyrromethenes as supporting ligands.^{43,44} In these protocols, bulky high-spin Fe^{II} dipyrromethene complexes, such as (^{Ad}L^{2,6-Cl₂Ph})Fe(Cl)(OEt₂) (where ^{Ad}L^{2,6-Cl₂Ph} = 1,9-di(1-adamantyl)-5-(2,6-dichloro)benzene-dipyrromethene), are capable of catalytically decomposing aliphatic azides to generate pyrrolidines. It is anticipated that nitrene intermediates are responsible for the intramolecular C-H amination reactivity. Notably, this system is able to generate valuable saturated N-heterocycle products with enantioselectivity (Scheme 1.8), a milestone for iron C-H amination catalysts.

Thorough mechanistic and electronic structure analysis of this system has allowed for elucidation of possible reaction pathways. It is suggested that the key penultimate intermediate is a high-spin Fe^{III} iminyl radical species. Despite the high reactivity of such complexes, careful selection of the ancillary ligand has allowed for their isolation and

crystallographically characterization, such as in the case of the $(^{\text{Ar}}\text{L})\text{Fe}(\text{NAr})(\text{Cl})$, (where $^{\text{Ar}}\text{L}$ = 1,9- Ar_2 -5-mesityl-dipyrromethene, and Ar = 2,4,6- $\text{Ph}_3\text{-C}_6\text{H}_2$) (Scheme 1.8).⁴⁵ Significant spin-density localized on the iron iminyl fragment of this and related compounds is considered a key characteristic of the electronic structure of this system which has direct implications for their efficacy in C-H amination catalysis of nitrene group transfer.

Scheme 1.8. Pyrrolidine synthesis via direct Fe catalyzed C-H amination (top) and isolation of an Fe^{III} iminyl radical intermediate (bottom). Note: Ad = 1-adamantyl, Ar = 2,4,6-triphenylbenzene, L = $\text{NPh-}p\text{-}^t\text{Bu}$.

Subsequent studies have allowed for further interrogation of the reaction mechanism, which is supported by the isolation and characterization of amine, amido, and terminal or

bridging imido/iminyl intermediates (Figure 1.7).⁴⁶ A mechanism has been proposed where upon addition of azide to the bridging dimeric Fe^{II} complex, [(^tBuL)FeCl]₂(μ-NC₆H₃-3,5-(CF₃)₂), a monomeric iminyl Fe^{III} iminyl radical species [(^tBuL)FeCl]₂(NC₆H₃-3,5-(CF₃)₂) is formed. [(^tBuL)FeCl]₂(NC₆H₃-3,5-(CF₃)₂) is proposed to exist in equilibria in solution with the structurally characterized dimeric form. C-H abstraction from substrate forms a monomeric Fe^{III} amido complex, which may recombine with an allylic radical to furnish the corresponding C-H amination product with concomitant formation of the high-spin ferrous starting material.

Figure 1.7. Proposed mechanism of allylic C-H amination of cyclohexene with dipyrromethene iron iminyl complexes. Note: Ar = C₆H₃-2,6-(Cl)₂, Ar' C₆H₃-3,5-(CF₃)₂, R = cyclohexene or the cyclohexenyl allylic radical.

Another ligand framework incorporating pyrrole moieties has recently been developed and utilized by Caulton, Mindiola, and others in the synthesis of the *cis*-divacant octahedral imido complex (^tBuPDP^tBu)Fe(N¹Ad).⁴⁷ Thorough spectroscopic and computational characterization of this complex has revealed a low-spin Fe^{IV} ground state (d⁴, S = 0) for the iron ion and a dianionic closed-shell imide ligand. In line with this assessment, (^tBuPDP^tBu)Fe(N¹Ad) was found to be unreactive towards C-H bonds, despite its high formal oxidation state.⁴⁸ In consideration that spin-density along a metal-imido or nitrene bonding interaction may promote C-H amination reactivity, the synthesis of the corresponding Co^{IV} (d⁵, S = 1/2) analogue, which was hypothesized to feature the additional d electron in a Co=N *π orbital of d_{yz} parentage (Scheme 1.9), was performed. Surprisingly, the reaction of the Co^{II} synthon (^tBuPDP^tBu)Co(OEt₂) with 1-adamantyl azide resulted in the isolation of a Co^{II} azido adduct, (^tBuPDP^tBu)Co(N₃¹Ad), instead of the anticipated imide (^tBuPDP^tBu)Co(N¹Ad). However, upon exposure to UV light, (^tBuPDP^tBu)Co(N₃¹Ad) underwent clean intramolecular C-H amination of a C-H bond of a proximal tert-butyl group of the supporting ligand, yielding the Co^{II} amine adduct Co(NH¹Ad^tBuPDP^tBu), as confirmed by X-ray crystallography (Scheme 1.9). Despite eluded direct observation, (^tBuPDP^tBu)Co(N¹Ad) has been implicated as the reactive intermediate responsible for this transformation.⁴⁸

Scheme 1.9. Reactivity of Fe and Co ($t\text{BuPDP}^{t\text{Bu}}$) complexes with 1-adamantyl azide.

In this dissertation, Chapter 2 discloses the development of the related $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand system and assessment of its Fe^{II} coordination chemistry. In contrast to $t\text{BuPDP}^{t\text{Bu}}$ Fe^{II} complexes, which are characterized by *cis*-divacant octahedral geometries, $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ has been found to

support unusual square-planar high-spin Fe^{II} complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})$ (where $\text{L} = \text{thf}$ or Et_2O). Chapter 3 describes the reactivity of these complexes with a variety of organic azides as nitrene sources. A diverse array of reaction outcomes has been documented depending on the identity of the azide employed, including the formation of a reactive iron nitrene intermediate, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. Paramagnetic $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ undergoes intramolecular nitrene group transfer to the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ supporting ligand, in stark contrast to $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{N}^1\text{Ad})$, which is unreactive to C-H bonds. Similarly, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})$ complexes also undergo analogous C-H amination chemistry when reacted with alkyl azides. A density functional theory study has illuminated a bias towards planar paramagnetic $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ iron nitrene adducts that have paramagnetic electronic structures and iminyl radical character.

The investigations presented in Chapter 4 seek to build on the aforementioned developments and describes the synthesis and characterization of a variety of new pyridine dipyrrolide ligands. It is anticipated that these complexes may find utility in stabilizing new iron imide or iminyl complexes in various coordination geometries or ultimately finding utility in productive nitrene group transfer chemistry. Chapter 5 discloses initial investigations of the reactivity of one of these complexes, $(^{\text{Cl}2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, with an array of organic azides. The synthesis and characterization of the iron imide and iminyl complexes $(^{2,6\text{-Cl}2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ and $(^{2,6\text{-Cl}2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ is presented. Furthermore, the electronic structures of these two complexes are interrogated via complementary density functional theory studies.

1.5 Iron Mediated Carbene Group Transfer

Similar to the generation of metallonitrenes in C-H amination, isoelectronic metallocarbene intermediates are utilized to effect the insertion of the carbene (CR_2) functionality into C-X or C-H bonds (where $\text{X} = \text{O}, \text{N}$, etc.). These transformations offer

significant appeal as the construction of new carbon-heteroelement or -carbon bonds allow for the rapid diversification of small molecules in one step. Owing to this efficiency, transition metal catalyzed carbene insertion reactions have become routinely implemented in modern organic synthesis.⁴⁹ Despite the variety of late transition metals that effect catalytic C-H insertion, this reaction is still underdeveloped for iron, which is unexpected given iron's ability to effect analogous C-H hydroxylation and amination chemistries.⁵⁰⁻⁵² Despite the challenges that have accompanied the development of iron catalyzed C-H insertion chemistry, other reactions implicating iron carbene intermediates, such as cyclopropanation of olefins and the aforementioned class of C-X insertion reactions have been studied in recent decades.⁵³

Consistent with the successes that have been realized via the directed evolution of enzymatic catalysts for oxygen atom and nitrene transfer, carbene transfer reactions have also been extensively explored in recent years.⁵⁴⁻⁵⁷ In contrast to these systems, the first example of a discrete small molecule iron catalyst capable of promoting carbene group transfer reactions was reported in the early 1990's by Hossain.⁵⁸ The use of $[(\text{Cp})\text{Fe}(\text{CO})_2(\text{thf})][\text{BF}_4]$ in carbene group transfer catalysis came nearly 40 years after the first evidence of stoichiometric iron carbene group transfer from $(\text{Cp})\text{Fe}(\text{CO})_2(\text{CH}_2\text{OCH}_3)$ was disclosed by Jolly (Scheme 1.10).⁵⁹ In recent decades, widespread investigations of small molecule iron catalysts in carbene group transfer reactions have been conducted by a variety of groups, with important contributions in the area of iron porphyrin group transfer catalysis made by Woo and coworkers. A notable advance includes Woo's report of insertion into aliphatic C-H bonds using α -diazoesters and a simple $(\text{TPP})\text{Fe}(\text{Cl})$ catalyst (Scheme 1.10).^{60,61} Subsequently, iron porphyrin complexes have been deemed privileged carbene group transfer catalysts due to their high activity in both olefin cyclopropanation and C-H/X insertion reactions.^{62,63}

Cyclopropanation

C-H Insertion

Scheme 1.10. Iron catalyzed carbene group transfer reactions.

More recently, an intramolecular C-H alkylation of diazoesters has been developed by White (Scheme 1.11).⁶⁴ The combination of catalytic $\text{NaBAR}_4^{\text{F}}$ ($\text{NaBAR}_4^{\text{F}}$ = sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate) and macrocyclic iron phthalocyanine $(\text{Pc})\text{Fe}(\text{Cl})$ is key to the success of this transformation, generating a sufficiently electrophilic active species. Despite its similarity to $(\text{Pc})\text{Fe}(\text{Cl})$, $(\text{TPP})\text{Fe}(\text{Cl})$ was found to be inactive in this transformation, a result ascribed to the greater π -accepting capability of the phthalocyanine macrocycle. Notably, this transformation is amenable to a diverse array of functional groups on the sulfonate ester and even found utility in the synthesis of biologically relevant δ -tocopherol. Mechanistic studies have

implicated an iron carbene intermediate capable of C-H abstraction to form allylic or benzylic radicals, which are poised to undergo radical rebound to form the corresponding δ -sultone products. Interestingly, this proposed mechanism is similar to those previously discussed for iron oxo and nitrene intermediates that promote C-H hydroxylation and amination, respectively.

Scheme 1.11. $(\text{Pc})\text{Fe}(\text{Cl})$ catalyzed allylic C-H alkylation.

The application of iron pincer complexes in the catalytic cyclopropanation of olefins as well as in a diverse array of insertion chemistries has also been recently developed.⁶⁵ Employing $[(^i\text{PrPDI})\text{Fe}(\text{CH}_3\text{CN})_2][(\text{SbF}_6)_2]$ as a catalyst, Deng and coworkers have accomplished the cyclopropanation of cyclohexene was accomplished in good yield with high diastereometric ratio ($>20:1$) (Scheme 1.12). Additionally, it was found that the application of $(S)\text{-}^{\text{VME}}\text{PDI}$ as ligand, featuring an L-valine methyl ester chiral element rendered the cyclopropanation of styrene enantioselective, albeit with a moderate ee of 67% (Scheme 1.12). This exciting result demonstrates that further tuning of PDI ligand environments may allow for future development of protocols capable of generating enantiomerically pure cyclopropanes from the corresponding vinyl arene.

Scheme 1.12. Pyridine diimine iron complex catalyzed cyclopropanation of olefins.

Despite this array of catalytic methods operating via presumed iron carbene intermediates, isolated examples of iron carbene complexes are uncommon and are currently limited to a small number of supporting ligand systems.⁶⁶ The precedent of pyridine dipyrrolide iron nitrene complexes that promote C-H amination suggests that isoelectronic pyridine dipyrrolide iron carbene adducts are likely possible and may offer exciting reactivity profiles. Furthermore, the isolable nature of pyridine dipyrrolide iron nitrene complexes suggests that

carbene analogues may be synthetically accessible and amenable to study via spectroscopic methods to ascertain their electronic structures. In Chapter 6 of this dissertation, such a pyridine dipyrrolide iron carbene system is presented. Utilizing the high-spin Fe^{II} complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ as the starting material, an unprecedented square-planar iron carbene complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, has been isolated via reaction with diphenyldiazomethane as the carbene source. Physical characterization of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ is consistent with a $S = 1$ ground state and an electronic structure best described as an intermediate-spin Fe^{III} ion engaged in antiferromagnetically coupling to a monoanionic diphenylidene radical ligand. The preliminary reactivity of this compound has been explored and exhibits rich carbene group transfer chemistry.

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CHAPTER II: SYNTHESIS AND ELECTRONIC STRUCTURE OF SQUARE PLANAR HIGH-SPIN IRON(II) PYRIDINE DIPYRROLIDE COMPLEXES

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2.1 Abstract

Two square-planar high-spin Fe^{II} complexes bearing a dianionic pyridine dipyrrolide pincer ligand and a diethyl ether or tetrahydrofuran ligand were synthesized and structurally characterized, and their electronic structures were elucidated by a combined spectroscopic and computational approach. In contrast to previous examples, the $S = 2$ ground states of these square-planar Fe^{II} complexes do not require an overall anionic charge of the compounds or incorporation of alkali metal cations. The tetrahydrofuran complex exhibits an equilibrium between four- and five-coordinate species in solution, which was supported by ^1H NMR and ^{57}Fe Mössbauer spectroscopy and comparison to a structurally characterized five-coordinate pyridine dipyrrolide iron bis-pyridine adduct. A detailed computational analysis of the electronic structures of the four- and five-coordinate species via density functional theory provides insight

into the origins of the unusual ground state configurations for Fe^{II} in a square-planar ligand field and explains the associated characteristic spectroscopic parameters.

2.2 Introduction

The coordination chemistry of iron is characterized by a broad range of available oxidation states that can each exhibit several different spin states. This flexibility in electronic structure results in a large diversity of physical properties and reactivity among iron compounds. Whether in synthetic or biological systems, carefully controlling these attributes via a well-defined ligand environment, (i.e., coordination number, geometry, and ligand type), has been key to the development of iron complexes for various applications ranging from catalysis¹⁻⁴ and single-electron transfer⁵ to magnetic materials⁶⁻⁹ and photochemistry.¹⁰⁻¹²

Among the many possible permutations of coordination geometry, oxidation state, and spin state, square-planar Fe^{II} complexes with a high-spin ground state ($S = 2$) are rare. This can readily be explained by the strong destabilization of the $d_{x^2-y^2}$ orbital of the metal ion in a square-planar ligand field compared to the remaining four d orbitals, which typically gives rise to intermediate-spin configurations with an $S = 1$ ground state for d^6 systems such as Fe^{II} .¹³ Until recently, high spin ferrous ions in square-planar coordination environments were only known for the iron-silicate minerals gillespite¹⁴ and eudialyte¹⁵ and macrocyclic¹⁶ complexes in which the unusual electronic structure is likely enforced by the steric environment of the solid-state materials or the tetradentate macrocycle. Aside from a fundamental curiosity for unusual electronic structures, the renewed interest in molecular, square-planar high-spin Fe^{II} compounds over the past decade was fueled by the discovery of planar $\text{Fe}^{\text{II}}\text{O}_4$ sites ($S = 2$) in iron-oxide ceramics¹⁷⁻¹⁹ and the remarkable reactivity of iron zeolites exhibiting similar motifs.²⁰⁻²² In 2011,

Klüfers et al. described the first example of a molecular square-planar Fe^{II} compound with an $S = 2$ ground state using non-macrocyclic ligands (Figure 1).²³

Figure 2.1. Mononuclear square-planar high-spin Fe^{II} complexes featuring bidentate alkoxide or siloxide ligands.

On the basis of their report, Holland proposed several conditions that favor the high-spin state in a square planar ligand field through electronic rather than steric effects: (a) anionic ligands imposing an overall negative charge on the complex that prevents further ligand binding via electrostatic effects; (b) alkali metal binding to stabilize the negative charge; and (c) weak-field ligands that reduce the splitting between the $d_{x^2-y^2}$ orbital and the remaining d orbitals via weak σ -donation (reducing the energy of $d_{x^2-y^2}$) and strong π -donation (raising the energy of d_{xz} , d_{yz} , and d_{xy}).¹³ Following these design principles, several complexes carrying chelating alkoxide

or siloxide ligands have been reported by the groups of Doerrer and Limberg, respectively.²⁴⁻²⁶ Additionally, Veige and coworkers showed that the common FeO_4 motif can be expanded to an FeO_2NCl environment by replacing two alkoxide ligands with amide and chloride donors that retain the dianionic nature of the complex.^{27,28} Breaking with requirement (b), the groups of Doerrer²⁹ and Tamm³⁰ reported alkali metal-free examples.

Often overlooked early examples for compounds with square-planar high-spin Fe^{II} centers are bis(imino)pyridine iron halide complexes reported by Chirik and co-workers in 2005.³¹ However, structural confirmation for a distorted square-planar coordination environment in these compounds was only provided in 2013.³² In contrast to the previously mentioned examples, these compounds possess an overall $S = 3/2$ ground state due to strong magnetic exchange coupling between the high-spin Fe^{II} center and a bis(imino)pyridine ligand radical anion.³³ A similar electronic structure has been proposed for bis(imino)pyridine iron alkoxide and siloxide complexes.^{32,34} The $S = 2$ ground state of the central metal ion under a square-planar ligand field is remarkable considering the complexes defy all three conditions outlined by Klüfers and coworkers, given their neutral charge and the presence of a π -accepting pincer ligand. One important feature of the bis(imino)pyridine ligand is the reduced bite angle of the pincer that leads to an in-plane distortion from idealized square-planar geometry, which should stabilize the $d_{x^2-y^2}$ orbital. To address whether this distortion or the magnetic interaction between the ligand radical and the metal center is responsible for the high-spin square-planar ground state of the metal center, we sought to investigate a related pincer type ligand based on a pyridine dipyrrolate(PDP) backbone.³⁵ Recently, this strongly π -donating dianionic ligand framework has been successfully employed in both early and late transition metal coordination chemistry.³⁶⁻⁴¹

Chirik, 2006

Tamm, 2014

Veige, 2015

This work

Figure 2.2. Mononuclear square-planar high-spin Fe^{II} complexes featuring tridentate pincer ligands.

For iron in particular, Mindiola and co-workers have shown that careful control of the steric environment imposed by the PDP ligand can yield unusual coordination environments and electronic structures.^{42,43}

Herein, is reported the synthesis, characterization, and electronic structure determination of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ ($\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ = 2,6-bis(5-(2,4,6-trimethylphenyl)-3-phenyl-1H-pyrrol-2-yl)pyridine) as examples for neutral high-spin Fe^{II} complexes with a distorted square planar ligand environment. The unique steric and electronic characteristics of the PDP pincer ligand support an FeN_3O core with $S = 2$ ground state in the absence of alkoxide or siloxide ligands. The high-spin ground states for these complexes expand the available electronic structures in pyrrole-containing pincer ligands and are distinct from the intermediate-

spin configurations ($S = 1$) recently reported for square-planar Fe^{II} complexes with 2,5-bis(di-tert-butylphosphinomethyl)pyrrolide ligands.^{44,45}

2.3 Synthesis and Characterization of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ Complexes

The ligand precursor $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ was readily prepared following a synthetic route analogous to the one reported previously for $\text{H}_2^{\text{Me}}\text{PDP}^{\text{Ph}}$.³⁷ Starting from 2,6-pyridinedicarboxaldehyde and the chalcone derivative 1-(2,4,6-trimethylphenyl)-3-phenyl-2-propen-1-one, $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ was obtained on a multigram scale via a straightforward two-step, one-pot protocol. Several different strategies for the synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ complexes were explored. Following a procedure by Caulton, Mindiola, and co-workers,⁴² treatment of a diethyl ether solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ with a diethyl ether suspension of $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ (1 equiv) resulted in a gradual dissolution of the ligand precursor accompanied by a color change of the reaction mixture from yellow to red (Scheme 2.1). Recrystallization of the red crude material via slow diffusion of pentane into a concentrated toluene solution yielded a dark red-purple, crystalline product identified as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$. The relatively poor isolated yield (40%) can be attributed to the formation of $(\text{H}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2\text{Fe}$ as the major byproduct, which requires careful repeated recrystallization to obtain analytically pure $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$. The structure of the $(\text{H}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2\text{Fe}$ impurity was established by X-ray crystallography and features a four-coordinate, high-spin iron(II) center in a distorted tetrahedral coordination environment generated by the two singly deprotonated pincer ligands (Figure 2.3).

Figure 2.3. ORTEP of $\text{Fe}(\text{H}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2$ displayed at 30% probability ellipsoids. Hydrogen atoms (excluding pyrrole hydrogens) and pyrrole mesityl substituents (with exception of the *ipso* carbon) have been excluded for clarity.

A similar complex, $(\text{H}^{\text{tBu}}\text{PDP}^{\text{tBu}})_2\text{Fe}$, was reported by Caulton and co-workers using a tert-butyl substituted PDP derivative.³⁶ The ^1H NMR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ in benzene- d_6 is consistent with a C_{2v} symmetric species in solution. Ten broad resonances are observed between 112 and -11 ppm, indicative of a paramagnetic ground state. The absence of an 11th resonance expected for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ is likely due to significant broadening indistinguishable above the spectral baseline. The solid-state magnetic moment of $5.5 \mu_{\text{B}}$ is consistent with a d^6 high-spin Fe^{II} species. The deviation from the spin-only value of $4.9 \mu_{\text{B}}$ can be rationalized by contributions from unquenched orbital-angular momentum. Single crystals suitable for analysis by X-ray diffraction were obtained by cooling a concentrated diethyl ether solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ to -35°C . A representation of the molecular structure is shown in Figure 2.4, and important bond lengths and angles are summarized in Table 2.1.

Scheme 2.1. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$.

Figure 2.4. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized solvent have been excluded for clarity. The second symmetry generated position of the disordered diethyl ether ligand is not depicted.

The compound crystallizes in the tetragonal space group $P4_32_12$, and each $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ molecule lies on a crystallographic C_2 axis, that coincides with the $\text{Fe}(1)\text{--N}(2)$ bond vector and renders the two halves of the pincer equivalent by symmetry. The coordination environment around the iron center is best described as distorted square-planar. The major deviation from rigorously square-planar geometry arises from the small bite angles of the pincer ligand enforced by the PDP backbone, which result in a $\text{N}(1)\text{--Fe}(1)\text{--N}(1)'$ angle of

155.02(15)°. Furthermore, the diethyl ether ligand is lifted slightly out of the plane described by the iron center and the three N-donor atoms of the pincer, reflected in a N(2)–Fe(1)–O(1) angle of 160.54(15)°. However, the disorder of the Et₂O ligand over two symmetry-generated sites in conjunction with the C_{2v} symmetry observed in solution via ¹H NMR spectroscopy indicates the dynamic nature of this distortion and facile interconversion between linear and bent structures via a vibrational bending mode. In several previous reports on square-planar high-spin Fe^{II} complexes, the τ_4 value, first introduced by Houser et al.,⁴⁶ has been used as a convenient tool to quantify variations between square-planar ($\tau_4 = 0$) and tetrahedral geometries ($\tau_4 = 1$) for these systems.^{24,27,29} On the basis of this parameter, (MesPDP^{Ph})Fe(OEt₂) is severely distorted with a τ_4 value of 0.32. However, caution should be taken in reducing a complex issue such as the description of coordination geometry to a single parameter. More specifically, the τ_4 value must be critically evaluated in systems with chelating ligands and, if at all, should only be applied rigorously to systems with four independent ligands as originally defined. On the one hand, complexes with two bidentate ligands, as reported by Doerrer et al., can exhibit perfect values of $\tau_4 = 0$ despite clear deviations from square planar geometry indicated by bite angles of 84.30(4)°.^{24,29} Even significantly smaller bite angles for the bidentate ligands would yield $\tau_4 = 0$ as long as the complexes are planar. On the other hand, the minimum τ_4 value attainable for (MesPDP^{Ph})Fe(OEt₂), assuming a perfectly planar FeN₃O moiety with an N(2)–Fe(1)–O(1) angle of 180° and unchanged bond lengths from the X-ray diffraction analysis, is 0.10 due to the constraints imposed by the pincer backbone leading to an in-plane distortion. Both types of distortions should by no means be regarded as trending toward tetrahedral geometry. A more rigorous, quantitative approach to evaluating the structural features of four-coordinate transition metal complexes is provided by the continuous shape measures developed by Alvarez and co-

workers⁴⁷⁻⁴⁹ based on early work on symmetry analysis by Pinsky and Avnir.⁵⁰ This method offers a systematic way to measure the difference between an experimentally determined coordination environment and an idealized geometric shape such as a tetrahedron (T_d), a square (D_{4h}), or a seesaw (cis-divacant octahedron, $SS-C_{2v}$). Following this formalism, the geometries of all structurally characterized square-planar high-spin Fe^{II} complexes reported to date were analyzed, and the results are shown in Table 2.1. Within the framework of continuous shape measures, small values indicate close agreement with the idealized structure. For reference, a perfectly square-planar coordination environment exhibits deviation values of 0, 33.33, and 19.05 compared to square, tetrahedron, and seesaw, respectively. Deviations of 33.31, 0, and 9.78 are characteristic for tetrahedral coordination spheres, while values of 19.05, 9.79, and 0 are indicative of seesaw geometries. The outcome of the continuous shape measure analyses confirms that (^{Mes}PDP^{Ph})Fe(OEt₂) is best described as a distorted square planar complex with deviations of 2.16 (D_{4h}), 27.73 (T_d), and 14.96 ($SS-C_{2v}$).

Table 2.1 Geometry analysis of reported square-planar high-spin Fe^{II} complexes by continuous shape measures.

	square (D_{4h})	tetrahedron (T_d)	seesaw ^a (C_{2v})	ref
$\text{Li}_2[\text{FeL}_2] \cdot 4\text{H}_2\text{O}^b$	0.24	33.50	19.01	23
$(\text{Na}_2[\text{FeL}_2] \cdot 4\text{H}_2\text{O})^b$	0.23	33.48	19.18	23
$\text{Na}_2[\text{FeL}_2] \cdot 9\text{H}_2\text{O}^b$	1.55	23.50	12.47	23
$\{\text{K}(\text{dme})_2\}_2[\text{Fe}(\text{ddfp})]2^c$	0.34	33.56	19.29	24
$(\text{Me}_4\text{N})_2[\text{Fe}(\text{ddfp})]2^c$	0.47	33.65	19.38	29
$[(\text{TL}^{\text{tBu}})\text{Fe}(\text{OTf})]\text{OTf}^d$	1.78	27.21	14.87	30
$[\text{Li}(\text{thf})_2]_2[(\text{CF}_3\text{-ONO})\text{FeCl}]^e$	0.52	31.57	16.83	27
$[\text{Li}(\text{thf})_2]_2[\text{Fe}(\{\text{OSiPh}_2\}_2\text{O})_2]$	0.24	33.49	19.13	26
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$	2.16	27.73	14.96	<i>This work</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	3.43	22.11	11.27	<i>This work</i>

^aVacant Trigonal bipyramid. ^bL = meso-oxolane-3,4-diolate dianion. ^cddfp = perfluoropinacolate dianion.

^dTL^{tBu} = 2,6-bis[(1,3-di-tertbutylimidazolin-2-imino)methyl]pyridine.

^eH₃(CF₃-ONO) = 2,2'-(azanediylbis(2,1-phenylene))bis(1,1,1,3,3,3-hexafluoropropan-2-ol).

The relatively long metal-ligand bond distances (>2 Å) in (^{Mes}PDP^{Ph})Fe(OEt₂) are consistent with a high-spin Fe^{II} description but are shorter than typically observed for tetrahedral or octahedral complexes of the same spin state. To rule out a potential spin-crossover from high-spin at room temperature to intermediate-spin under crystallography conditions at 100 K, the zero-field ⁵⁷Fe Mössbauer spectrum of a solid sample of (^{Mes}PDP^{Ph})Fe(OEt₂) was recorded at 80 K (Figure 2.6). The large isomer shift, δ , of 0.87 mm s⁻¹ unambiguously confirms the high-spin Fe^{II} assignment at low temperature. The remarkably small quadrupole splitting, $|\Delta E_Q|$, of 0.50 mm s⁻¹ is unusual for a high-spin Fe^{II} species and supports a description as a square-planar complex with a doubly occupied d_{z²} orbital (*vide infra*). In this particular ground state configuration, the asymmetry in charge distribution caused by the additional electron in the d_{z²}

orbital is compensated by ligand field contributions from the four ligands in the xy-plane resulting in a near radially symmetric electric field gradient at the iron nucleus. Veige and co-workers have suggested that small values of $|\Delta E_Q|$ can be considered a fingerprint of square-planar high-spin Fe^{II} .^{27,28} This proposal was further supported by data from Limberg and co-workers and is consistent with earlier studies of the electronic structure of the iron sites in gillespite.^{51,52}

Inspired by the unusual electronic structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, the synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ complexes with other L-type ligands was investigated. Deprotonation of $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ with 2 equiv of LiHMDS in THF followed by slow addition to a slurry of FeCl_2 in the same solvent resulted in the formation of an orange-red solution. Addition of pentane and cooling to $-35\text{ }^\circ\text{C}$ yielded a microcrystalline, orange solid. Importantly, only trace amounts of $(\text{H}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2\text{Fe}$ were observed under these reaction conditions in THF, as confirmed by ^1H NMR analysis of the crude reaction mixture. Recrystallization via slow diffusion of pentane into a concentrated THF solution of the orange product at $-35\text{ }^\circ\text{C}$ yielded single crystals suitable for X-ray diffraction analysis, which allowed for identification of the compound as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$. A representation of the molecular structure is shown in Figure 2.5 and reveals a five-coordinate iron center with distorted square-pyramidal geometry. A THF ligand and the three nitrogen donors of the pincer ligand form the base of the square pyramid, while a chloro ligand is located in the apical position and forms a bridge to a $\text{Li}(\text{thf})_3$ unit. The three THF molecules coordinated to the lithium center were found to be heavily disordered in the crystal structure and were treated isotropically during structure refinement. On the basis of the overall neutral charge of the complex and the long iron–ligand bond distances, the complex contains a high-spin Fe^{II} center, which was confirmed by a room-temperature magnetic moment

of $5.4 \mu_B$ and solid state Mössbauer parameters of $\delta = 1.09 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 2.63 \text{ mm s}^{-1}$ (Figure 2.6).

Figure 2.5. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ displayed at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent molecules have been excluded for clarity. Note: only one occupancy of the disordered THF ligands is depicted.

Figure 2.6. Zero field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (left) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ (right) recorded at 80 K. White circles represent experimental data and the blue line represents the fit of the data. Note, the shoulder present in the spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ is attributed to the presence of a minor unknown iron containing impurity.

The ^1H NMR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ in benzene- d_6 exhibits 11 broad resonances between 115 and -15 ppm, which is inconsistent with the solid-state molecular structure. Assuming the connectivity established by X-ray diffraction, the highest possible symmetry for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ in solution should be C_s , which would result in at least 15 resonances assuming free rotation of the phenyl substituents in the back of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand. Additionally, precipitation of a white solid in conjunction with a color change to red in benzene compared to the orange color of the solid material suggested loss of LiCl and concurrent formation of a new, C_{2v} symmetric product consistent with the 11 resonances observed in solution. Due to the similarities of the chemical shifts in the spectrum compared to those recorded for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, the new species was tentatively assigned as the desired complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$. However, on further inspection, small, but significant, differences

between the two species are apparent and most clearly illustrated in the chemical shift of the para-pyridine protons. Despite the paramagnetic broadening of all resonances, which complicates the overall assignment of the spectra, these resonances are easily identified via integration. While the 4-pyridine resonance appears at 1.66 ppm for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ in benzene- d_6 , the position of the same proton in benzene- d_6 solutions of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ varied significantly from approximately -2 ppm to 3 ppm between different independently prepared samples.

Additional NMR studies revealed that the chemical shifts of the C_{2v} -symmetric product were highly sensitive to the addition of THF to the benzene- d_6 solution, indicating a rapid equilibrium between species with different numbers of THF ligands, most likely $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$. To further support this hypothesis, ^1H NMR data of the reaction product were recorded in THF- d_8 solution. The resonance for the 4-pyridine proton in the resulting spectrum is found at 20.32 ppm. This chemical shift is consistent with formation of a five-coordinate complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (*vide infra*). Importantly, this peak position downfield of the diamagnetic reference value of the 4-pyridine proton in $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ indicates a difference in the electronic structure of the product compared to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, for which the same proton resonance is shifted upfield. Altogether, the experimental data support a complex speciation for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ adducts in solution (Scheme 2.2). The initially formed contact ion pair $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ dissociates in THF solution, yielding the five coordinate complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and THF-solvated lithium chloride. This process is reversible and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$ selectively crystallizes upon addition of pentane. Upon dissolution of the contact ion pair in aromatic solvents, LiCl precipitates to yield the four-coordinate species $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, which is in rapid equilibrium with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ due to the presence of three additional equivalents of THF. To isolate the desired four-coordinate

(^{Mes}PDP^{Ph})Fe(thf) species on preparative scale, (^{Mes}PDP^{Ph})Fe(thf)(μ-Cl)Li(thf)₃ was dissolved and stirred in toluene, resulting in precipitation of lithium chloride and a color change from orange to red. Filtration, followed by removal of all volatiles, provided a red solid. This process was repeated several times to remove excess THF and push the equilibrium completely toward (^{Mes}PDP^{Ph})Fe(thf). The resulting solid exhibits Mössbauer parameters of $\delta = 0.78 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 0.48 \text{ mm s}^{-1}$ (Figure 2.13), which are consistent with the formation of the desired square-planar high-spin Fe^{II} complex (^{Mes}PDP^{Ph})Fe(thf). The ¹H NMR spectrum of the compound in benzene-*d*₆ and toluene-*d*₈ shows a substantially upfield-shifted resonance for the 4-pyridine proton at −5.98 ppm (Figure 2.7 and Figure 2.9).

Figure 2.7. Comparison of the ¹H NMR spectra of (^{Mes}PDP^{Ph})Fe(thf)₂ in THF-*d*₈ (top) and (^{Mes}PDP^{Ph})Fe(thf) in benzene-*d*₆ (bottom).

Single crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane into a concentrated fluorobenzene solution of the compound. A representation of the molecular structure is shown in Figure 2.8, and geometric parameters are summarized in Table 2.2. The compound crystallizes in the monoclinic space group $P2_1/n$. In contrast to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, the individual molecules do not lie on special positions in the unit cell. The molecular structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ is very similar to that of the Et_2O adduct, but exhibits a significantly shorter $\text{Fe}(1)\text{--O}(1)$ bond of $2.055(1)$ Å. The decrease in bond length by approximately 5 pm is consistent with the stronger σ -donor ability of the THF ligand compared to diethyl ether. A second difference can be seen in the $\text{N}(2)\text{--Fe}(1)\text{--O}(1)$ angle at $152.99(5)^\circ$, which indicates a slightly more pronounced distortion from square planarity for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$.

Figure 2.8. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized solvent have been excluded for clarity.

Figure 2.9. Variable temperature ^1H NMR data from 25 $^{\circ}\text{C}$ to -80 $^{\circ}\text{C}$ for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in toluene- d_8 at 400 MHz.

This is also reflected in the τ_4 value of 0.38 and deviations obtained via continuous shape measures analysis of 3.43 (square), 22.11 (tetrahedron), and 11.27 (seesaw).

With the clean four-coordinate complex in hand, the equilibrium between $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ in the presence of THF was studied via NMR titration experiments. Addition of exact amounts of rigorously dried THF was performed via vacuum transfer using a calibrated gas bulb to a solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in benzene- d_6 at room temperature, resulting in systematic shifts of the observed resonances. The resulting ^1H NMR spectra were recorded and the changes in chemical shifts were fit using the nonlinear least squares method to extract the stability constant, K , for the formation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ from $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and THF.

Assuming rapid ligand exchange on the NMR timescale, the following equation was used for the 1:1 complexation event:

$$\delta_{obs} = \left(\frac{\delta_5 - \delta_4}{2} \right) * \left\{ \left(\frac{[THF]_0}{[Fe_4]_0} \right) + 1 + \left(\frac{1}{K * [Fe_4]_0} \right) \right\} - \sqrt{\left\{ \left(\frac{[THF]_0}{[Fe_4]_0} \right) + 1 + \left(\frac{1}{K * [Fe_4]_0} \right) \right\}^2 - 4 * \left(\frac{[THF]_0}{[Fe_4]_0} \right) \right\} + \delta_4}$$

where δ_4 and δ_5 are the chemical shifts of $(^{Mes}PDP^{Ph})Fe(thf)$ and $(^{Mes}PDP^{Ph})Fe(thf)_2$, respectively, $[Fe_4]_0$ is the starting concentration of $(^{Mes}PDP^{Ph})Fe(thf)$, and $[THF]_0$ is the concentration of added THF. No resonances for free THF were observed, indicating that ligand exchange occurs rapidly on the NMR time scale. The most significant changes in chemical shift were observed for the 4-pyridine proton as well as the 3-pyridine and pyrrole protons (Figure 2.10). Assuming a simple 1:1 equilibrium, the data were readily fit using nonlinear least-squares methods, providing a stability constant of $26(2) \text{ L mol}^{-1}$ for $(^{Mes}PDP^{Ph})Fe(thf)_2$ at 298 K.⁵³⁻⁵⁵

Scheme 2.2. Synthesis of (^{Mes}PDP^{Ph})Fe(thf)(μ-Cl)Li(thf)₃, (^{Mes}PDP^{Ph})Fe(thf), and (^{Mes}PDP^{Ph})Fe(thf)₂.

Figure 2.10. Changes in selected chemical shifts with added THF. Conditions: $[(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})]_0 = 41.5 \text{ mM}$, benzene- d_6 , 298 K. The black lines were obtained via a nonlinear least-squares fit.

To further study the differences in electronic structure between four- and five coordinate complexes in the absence of structural data for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$, the synthesis of an isolable, exclusively five-coordinate complex was pursued employing pyridine as a neutral donor ligand. Addition of excess pyridine to solutions of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in benzene or toluene yielded $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$.

Figure 2.11. ^1H NMR spectra of a titration of THF against $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in benzene- d_6 at 298 K.

In a more synthetically convenient route, the five-coordinate complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ was also obtained following the reaction of $\text{Fe}(\text{Ns})_2(\text{py})_2$ ($\text{Ns} = \text{CH}_2\text{SiMe}_3$) with $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ (Scheme 2.3). The iron dialkyl starting material was prepared *in situ* as described by Campora and co-workers.⁵⁶ The molecular structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ was established by single-crystal X-ray diffraction following recrystallization via slow diffusion of Et_2O into a toluene solution of the compound at $-35\text{ }^\circ\text{C}$ (Figure 2.12 and Table 2.2). The complex is best described as distorted square-pyramidal with an iron center that is located only $0.21\text{ \AA}$ above the plane described by the four nitrogen atoms of the pincer ligand and the pyridine ligand in the basal position. The most significant distortion within the square base of the structure is again introduced by the small bite angles of the pincer ligand ($\text{N}(1)\text{--Fe}(1)\text{--N}(3) = 148.42(5)^\circ$). The Fe–N bond distances are

consistent with a high-spin Fe^{II} ground state ($S = 2$), which was confirmed by magnetic susceptibility measurements ($\mu_{\text{eff}} = 5.5 \mu_{\text{B}}$).

Scheme 2.3. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$.

Figure 2.12. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ depicted at 30% probability ellipsoids. Hydrogen atoms and cocrystallized solvent have been excluded for clarity.

The zero-field Mössbauer parameters of $\delta = 0.98 \text{ mm s}^{-1}$ and $|\Delta E_{\text{Q}}| = 2.92 \text{ mm s}^{-1}$ are further evidence for this electron configuration (Figure 2.14).

Figure 2.13. Zero-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ recorded at 80 K. White circles represent experimental data and the blue line represents the fit of the data.

The significantly increased quadrupole splitting compared to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ is more typical for high-spin Fe^{II} and consistent with a change in electronic structure between the two compounds. The addition of a fifth ligand along the z-axis of the square-pyramidal structure raises the energy of the d_{z^2} orbital (σ^*) and results in a configuration with a doubly occupied d_{xz} , d_{yz} , or d_{xy} orbital. A more detailed analysis of the electronic structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ is provided in a later section (*vide infra*). The similarity in the Mössbauer parameters between $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and the proposed five-coordinate THF adduct supports the characterization as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ in the absence of structural data. The ^1H NMR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ recorded in benzene- d_6 exhibits 12 paramagnetically broadened resonances between 104 and 0 ppm, suggesting fast interconversion between square-pyramidal and trigonal-bipyramidal structures on the NMR time scale and apparent C_{2v} symmetry in solution. The resonance for the

4-pyridine proton of the PDP pincer ligand is located at 21.54 ppm, further indicating a close similarity in electronic structure between $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$.

Table 2.2. Summary of structural metrics obtained via X-ray crystallography for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$.

	$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)^a$	$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$	$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3$	
Fe(1)–N(1)	2.069(3)	2.0596(14)	2.1126(13)	Fe(1)–N(1)	2.137(3)
Fe(1)–N(2)	2.066(4)	2.0693(13)	2.0968(13)	Fe(1)–N(2)	2.132(3)
Fe(1)–N(3)	2.069(3)	2.0419(14)	2.0863(13)	Fe(1)–N(3)	2.130(3)
Fe(1)–N(4)	-	-	2.1506(14)	Fe(1)–O(1)	2.142(3)
Fe(1)–N(5)	-	-	2.1649(14)	Fe(1)–Cl(1)	2.412(1)
Fe(1)–O(1)	2.100(5)	2.0550(12)	-	Cl(1)–Li(1)	2.256(10)
N(1)–Fe(1)–N(2)	77.51(8)	78.04(5)	76.59(5)	N(1)–Fe(1)–N(2)	75.81(11)
N(1)–Fe(1)–N(3)	155.02(2)	154.07(5)	148.42(5)	N(1)–Fe(1)–N(3)	147.95(12)
N(2)–Fe(1)–N(3)	77.51(8)	77.67(5)	76.28(5)	N(2)–Fe(1)–N(3)	76.39(11)
N(2)–Fe(1)–O(1)	160.54(15)	152.99(5)	-	N(2)–Fe(1)–O(1)	157.88(12)
N(2)–Fe(1)–N(4)	-	-	173.86(5)	N(2)–Fe(1)–Cl(1)	110.32(9)
N(2)–Fe(1)–N(5)	-	-	86.20(5)	-	-

^aA crystallographic two-fold axis renders N(1) and N(3) equivalent; the coordinates of the second pyrrolide nitrogen, N(3), were determined by the application of the symmetry relationship: $y \ x \ -z$, to N(1).

Figure 2.14. Zero-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ recorded at 80 K. White circles represent experimental data and the blue line represents the fit of the data.

With clear spectroscopic markers for four- and five-coordinate $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ complexes in hand, the electronic structures of all four compounds were investigated computationally by DFT. Considering that $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ do not follow two of the three proposed design principles for square-planar high-spin complexes, we were particularly interested in explaining the unusual spin-state/geometry combination. All calculations were performed at the B3LYP level using the crystallographically determined molecular structure as the starting point for geometry optimizations. For $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, three separate calculations representing high-spin ($S = 2$), intermediate-spin ($S = 1$), and low-spin ($S = 0$) configurations for the central Fe^{II} ion were conducted without truncation or imposing any symmetry constraints. All three approaches yielded close to perfectly planar, C_{2v} symmetric structures with $\text{N}(2)\text{--Fe}(1)\text{--O}(1)$ angles of approximately 178° and an iron center

located within 1 pm of the plane defined by the three N donor atoms of the pincer. Consistent with the experimentally determined $S = 2$ ground state, the high-spin calculation was found to be lowest in energy and accurately reproduced the metal–ligand and intraligand bond lengths. A slight overestimation of the Fe–N and Fe–O bond distances by up to 6 pm is typical for B3LYP calculations of coordination compounds.⁵⁷ A spin-density value of 3.78 on the iron center obtained via Mulliken population analysis is consistent with four unpaired electrons on the metal center and a high-spin Fe^{II} center.

Figure 2.15. Splitting diagram for the iron 3d orbitals in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ obtained via DFT calculations at the B3LYP level. The orbital energies were extracted by taking the average of the corresponding single-electron α - and β -spin orbital energies for each d orbital from the unrestricted Kohn–Sham solution.

Figure 2.16. Molecular orbital diagram depicting the metal d orbitals obtained via unrestricted DFT calculations at the B3LYP level.

The $S = 1$ solution representing an intermediate-spin configuration was found to be 4.3 kcal/mol higher in energy, while the closed shell $S = 0$ solution was even less favorable at 35.8 kcal/mol relative to the computed high-spin ground state. The small energy difference between high spin and intermediate spin is not surprising given the general favorability of $S = 1$ ground states for square-planar Fe^{II} complexes. It should be noted that small energy gaps (<10 kcal/mol) in spin-state comparisons by DFT should be treated with great caution due to the tendency of hybrid functionals to overestimate the stability of high-spin configurations.⁵⁸ Whenever possible, the results of such calculations should be calibrated against experimental parameters. For

(^{Mes}PDP^{Ph})Fe(OEt₂), the computed intermediate and low-spin structures exhibit significantly shortened metal–ligand bonds that are inconsistent with the experimental structure, which further supports the high-spin Fe^{II} assignment. The comparison of computed and experimental ⁵⁷Fe Mössbauer parameters has been established as a reliable tool to corroborate electronic structures obtained from DFT. Reassuringly, the calculated Mössbauer isomer shift and quadrupole splitting for the quintet ground state of (^{Mes}PDP^{Ph})Fe(OEt₂) are in excellent agreement with the experimental values (Table 2.3).

A closer inspection of the molecular orbital manifold for the high-spin solution revealed that (^{Mes}PDP^{Ph})Fe(OEt₂) contains a doubly occupied d_{z²} orbital while the remaining four d orbitals are singly occupied (Figures 2.15 and 2.16). This electron configuration is similar to the one reported for all previous examples of square-planar high-spin Fe^{II} compounds and has been identified as the cause for the exceptionally small quadrupole splitting observed by Mössbauer spectroscopy and reproduced in our calculations. At first glance, the lowest energy position for the d_{z²} orbital is surprising given its weakly σ-antibonding character (σ*) in square-planar geometry. For all previously reported complexes containing alkoxide or siloxide ligands, this is readily explained by the strong π-donation of the ligands both in- and out-of-plane which substantially destabilizes the d_{xz}, d_{yz}, and d_{xy} orbitals (π*). In contrast, π-donation in (^{Mes}PDP^{Ph})Fe(OEt₂) is restricted to the pyrrolide moieties, which can also confer amide character to the pyridine nitrogen via conjugation. Due to the orientation of the N-heterocycles in the PDP ligand, π-donation alone would only destabilize the out-of-plane d_{xz} and d_{yz} orbitals in perfectly square-planar geometry, as shown in the center-right diagram in Figure 2.17. The resulting d orbital splitting diagram features the nonbonding d_{xy} orbital as the lowest orbital, slightly below the weakly σ antibonding d_{z²} orbital. This orbital arrangement would likely favor an

intermediate-spin configuration due to the large energy gap between the second lowest d orbital (here d_{z^2}) and the $d_{x^2-y^2}$ orbital. This particular energy difference in comparison to the spin-pairing energy is the critical parameter that distinguishes intermediate-spin and high-spin configurations. The in-plane distortion of the square-planar ligand field imposed by the PDP ligand is the key feature that allows (^{Mes}PDP^{Ph})Fe(OEt₂) to adopt a high-spin state in the absence of in-plane π -donation. The slight off-axis positioning of the pyrrolide donors results in a stabilization of the $d_{x^2-y^2}$ orbital and an equivalent destabilization of the d_{xy} orbital, which is now weakly σ -antibonding (Figure 2.17). This effect leads to a significant decrease of the energy difference between the second lowest iron d orbital (now d_{xy}) and the $d_{x^2-y^2}$ orbital and favors the $S = 2$ ground state. We note that any in-plane deviation from ideal square-planar geometry as observed for FeO₄ cores with bidentate chelate ligands results in a similar stabilization of the $d_{x^2-y^2}$ orbital (Figure 2.17).

Figure 2.17. Qualitative d-orbital splitting diagrams for square-planar high-spin Fe^{II} complexes showing the effect of σ - and π -interactions for compounds with two bidentate bis(alkoxide) or bis(siloxide) ligands (left) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (right).

Computations for the THF adduct $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, assuming the experimentally established $S = 2$ ground state, yielded a nearly identical electronic structure to the one described for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$. The calculations accurately reproduced the geometric and Mössbauer spectroscopic parameters (Table 1.3). Notably, the slightly smaller $\text{N}(2)\text{--Fe}(1)\text{--O}(1)$ angle observed experimentally in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ compared to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and the characteristically small quadrupole splitting are mirrored by the calculations. The electronic

structures of the two five-coordinate complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ are very similar to each other, but distinct from those described for the four-coordinate species. For the pyridine adduct, the structural parameters are in good agreement with the experimental data and show a square-pyramidal coordination environment.

Figure 2.18. Qualitative d-orbital diagram for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ obtained from DFT calculations at the B3LYP level.

Exceptions are the values obtained for the Fe–N_{pyrrole} bond lengths, which are overestimated by more than 10 pm. Despite this unusually large discrepancy, the Mössbauer parameters calculated based on the obtained structure are in good agreement with the experimental values (Table 2.3). A qualitative MO diagram for (^{Mes}PDP^{Ph})Fe(py)₂ is shown in Figure 2.18 and clearly establishes that the doubly occupied metal d orbital is predominantly of d_{xz} character. In the absence of structural data for (^{Mes}PDP^{Ph})Fe(thf)₂, the DFT-predicted Mössbauer parameters are the only piece of data to calibrate the computational results against experiment. Their excellent agreement provides support for the obtained electronic structure with a doubly occupied d_{xz} orbital. A summary of the experimental and computed Mössbauer parameters are provided in Table 2.3.

Table 2.3. Experimental (in parentheses) and calculated Mössbauer parameters of (^{Mes}PDP^{Ph})Fe(L)_n complexes.

	δ / mms ⁻¹ (calc)	ΔE_Q / mms ⁻¹ (calc)	η^a (calc)
(^{Mes} PDP ^{Ph})Fe(OEt ₂)	0.87 (0.71)	0.50 ^b (-0.79)	0.95 ^c
(^{Mes} PDP ^{Ph})Fe(thf)	0.78 (0.67)	0.48 ^b (0.78)	0.72
(^{Mes} PDP ^{Ph})Fe(thf) ₂ ^d	1.09 (0.93)	2.76 ^b (2.90)	0.89 ^c
(^{Mes} PDP ^{Ph})Fe(py) ₂	0.98 (0.84)	2.92 ^b (3.15)	0.86 ^c
(^{Mes} PDP ^{Ph})Fe(thf)(μ-Cl)Li(thf) ₃	1.09 (0.94)	2.63 ^b (2.69)	0.80 ^c

^a Asymmetry parameter of the electronic field gradient. ^b Sign not determined experimentally.

^c Not determined experimentally. ^d Recorded in frozen THF solution.

One interesting feature of the optimized structure is the Fe–O bond for the apical THF ligand in the overall square-pyramidal molecule, which is significantly longer than the one predicted for the basal THF ligand and the Fe–N bonds for the pyridine ligands in (^{Mes}PDP^{Ph})Fe(py)₂. This elongation is indicative of a weaker Fe–O bond for this ligand and is consistent with the experimentally observed equilibrium between four- and five coordinate THF

adducts. Aside from the Mössbauer quadrupole splitting, the chemical shift of the 4-pyridine proton of the PDP ligand in ^1H NMR spectroscopy is the most sensitive reporter for the change in electronic structure between four- and five coordinate ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{L})_n$) complexes.

Considering that the electronic structures obtained via DFT reproduce the change in Mössbauer quadrupole splitting, we were interested to establish a qualitative connection between the observed NMR shifts and the ground-state configurations. The NMR shifts for nuclei in paramagnetic iron compounds are the result of three separate terms: diamagnetic or orbital contributions equivalent to shielding effects in diamagnetic systems; Fermi contact shifts due to interactions between the magnetic moment of the nucleus and the magnetic field arising from unpaired electron density at the site of the nucleus; and pseudo-contact shifts.⁵⁹⁻⁶² Previous studies have shown that the dominating term for most iron compounds is the Fermi contact shift that can be related to the spin density at the nucleus of interest.⁶² On the basis of this assumption, the spin densities on the 4-pyridine protons obtained via Mulliken population analysis were compared for the four ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{L})_n$) complexes described herein (Figure 2.19). As further reference points, the values for the meta-pyridine and the pyrrole protons were examined as well. These protons are expected to carry the largest amount of spin density due to their direct connectivity to the π system of the PDP backbone, which can directly interact with the SOMOs of the iron center, resulting in delocalization of unpaired electron density and large Fermi contact shifts. For the four-coordinate complexes, the 3-pyridine protons carry the largest amount of spin density, closely followed by the pyrrole protons. This is consistent with the significant downfield shifts observed for two resonances corresponding to two protons each in the ^1H NMR spectra of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{OEt}_2)$) (111.69 and 92.58 ppm) and ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$) (113.68 and 110.95 ppm). In contrast, the 4-pyridine proton carries negative spin density, which is due to spin polarization

effects from π -interactions between the metal d_{xz} SOMO and the pyridine π -system. As a result, the 4-pyridine proton is shifted upfield with respect to its diamagnetic reference value in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (1.66 ppm) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ (−5.98 ppm).

Figure 2.19. Mulliken spin populations for selected protons of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand in four- (left) and five-coordinate (right) $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ complexes. All values given in units of 10^{-3} .

The change in ground-state electronic structure for the five coordinate complexes is clearly reflected in the calculated spin density distributions. In contrast to the four-coordinate compounds, the 4-pyridine protons show positive values in these complexes consistent with the observed downfield shifts in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ (21.54 ppm) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (20.32 ppm). The change in sign can be directly correlated with the now doubly occupied d_{xz} orbital, which removes the spin-polarization mechanism for spin delocalization via the π system of the pyridine moiety. In addition, the positive spin density at meta-pyridine, and to a lesser extent at the pyrrole protons, is reduced compared to the four coordinate complexes and results in smaller downfield shifts for these signals in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ (87.89 and 77.20 ppm) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (90.85 and 67.16 ppm).

Table 2.4 Reported ^{57}Fe Mössbauer parameters for square-planar high-spin Fe^{II} complexes.

	δ / mms^{-1}	$ \Delta E_Q $ / mms^{-1}	Ref
Gillespite	0.66	0.56	51
$(^{i\text{Pr}}\text{PDI})\text{FeCl}^a$	0.77	0.73	32
$[\text{Li}(\text{thf})_2]_2[(\text{CF}_3\text{-ONO})\text{FeCl}]^b$	0.83	0.45	27
$[(\text{TL}^{\text{tBu}})\text{Fe}(\text{OTf})]\text{OTf}^c$	0.81	0.64	30
$[\text{Li}(\text{thf})_2]_2[\text{Fe}(\{\text{OSiPh}_2\}_2\text{O})_2]$	0.87	0.52	26
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$	0.87	0.50	<i>This work</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	0.78	0.48	<i>This work</i>

^a $(^{i\text{Pr}}\text{PDI}) = 2,6\text{-(2,6-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N=CMe)}_2\text{C}_5\text{H}_3\text{N}$.

^b $\text{H}_3(\text{CF}_3\text{-ONO}) = 2,2'\text{-(azanediylbis(2,1-phenylene))bis(1,1,1,3,3,3-hexafluoropropan-2-ol)}$.

^c $\text{TL}^{\text{tBu}} = 2,6\text{-bis[(1,3-di-tert-butylimidazolin-2-imino)methyl]pyridine}$.

2.4 Conclusion

In this study, the synthesis and characterization of two distorted square-planar high-spin Fe^{II} complexes, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, supported by a pyridine dipyrrolide pincer ligand is described. These complexes are the first examples for this rare spin state/oxidation state combination that are of neutral charge and do not contain anionic oxygen donor ligands. Consistent with previous reports, the unique electronic structures imposed by the unusual coordination environment for Fe^{II} ions with a quintet ground state are reflected in characteristic ^{57}Fe Mössbauer parameters with small quadrupole splitting (Table 1.4). In the presence of excess THF, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ establishes an equilibrium with the five-coordinate complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ as was elucidated by ^1H NMR spectroscopy. The resulting change in electronic structure from a configuration with a doubly occupied d_{z^2} orbital to a configuration with a doubly occupied d_{xz} orbital was established by DFT studies and tracked experimentally by Mössbauer and ^1H NMR spectroscopy. The stronger-field ligand pyridine resulted in formation

of the five coordinate complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, which does not undergo ligand loss in solution. With the addition of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ as examples for alkali metal-free, neutral, high-spin Fe^{II} complexes with distorted square-planar geometry, a revision of the conditions promoting this unusual spin state/geometry pairing that is consistent with all examples reported to date is proposed: (a) destabilization of the d_{xz} and d_{yz} orbitals via strong out-of-plane π -donation, (b) destabilization of the d_{xy} orbital via strong in-plane π -donation and/or σ -donation resulting from reduced bite angles of the chelating ligands, and (c) decreased destabilization of the $d_{x^2-y^2}$ orbital by weak σ -donating ligands and/or in-plane deviations from ideal square planar geometry. The three conditions outlined above compel $S = 2$ ground states with a doubly occupied d_z^2 orbital which disfavors additional ligand binding by reducing the Lewis acidic character of the metal center along the z-axis and gives rise to the characteristically small Mössbauer quadrupole splitting.

2.5 Experimental Procedures

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH_2 and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Deuterated benzene (benzene- d_6) and tetrahydrofuran (THF- d_8) for NMR spectroscopy were distilled from sodium metal and sodium benzophenone, respectively. 3-Phenyl-1-(2,4,6-trimethylphenyl)2-propen-1-

one,⁶³ 2,6-pyridinedicarboxaldehyde,⁶⁴ $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$,^{65,66} and $\text{Fe}(\text{Cl})_2(\text{py})_4$ ⁵⁶ were prepared following reported literature procedures.

Preparation of 2,6-Bis(5-(2,4,6-trimethylphenyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine, $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$.

A 500 mL Schlenk flask was charged with 2,6-pyridinedicarboxaldehyde (1.016 g, 7.52 mmol), 3-phenyl-1-(2,4,6-trimethylphenyl)-2-propen-1-one (3.86 g 15.4 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (1.52 g, 5.64 mmol), 20 mL of anhydrous absolute ethanol, and a magnetic stirrer. A jacketed condenser was attached to the flask, and the apparatus was degassed three times and filled with an atmosphere of argon. Under a heavy flow of argon, a solution of 900 mg of sodium tert-butoxide (543 mg, 5.63 mmol) in 10 mL of anhydrous ethanol was added via syringe, resulting in an immediate change in the color of the reaction mixture from yellow to dark brown. The solvent was brought to reflux and maintained at temperature for 24 h. The intermediate diketone was not isolated. The reaction mixture was cooled to room temperature, and NH_4OAc (5 g, 45.1 mmol) was added in air. The mixture was returned to reflux which was maintained for 72 h. Progress of the reaction was monitored via ^1H NMR spectroscopy by sampling small aliquots of the crude reaction mixture. The yellow solid which precipitated from the reaction mixture was isolated on a medium porosity glass frit, washed three times with 0 °C ethanol, and dried in vacuo. The yellow powder was then transferred to a flask and dried under high vacuum at 200 °C for 48 h to remove any trace solvent and water, as confirmed via ^1H NMR spectroscopy. Yield 2.4 g (4.01 mmol, 53%). ^1H NMR (400 MHz, benzene- d_6 ; δ , ppm) 11.51 (s, 2H, NH), 7.64 (d, J = 7.6 Hz, 4H, *ortho*-PhH), 7.39 (m, 6H, *meta*- and *para*-PhH), 6.78 (d, J = 8.0 Hz, 2H, 3-pyridineH), 6.57 (s, 2H, mesityl-*meta*H), 6.06 (t, J = 8.0 Hz, 1H, 4-pyridineH), 6.01 (s, 2H, pyrrole-H), 1.96 (s, 12H, mesityl-*ortho*-CH₃), 1.93 (s, 6H,

mesityl-*para*-CH₃). ¹³C NMR (101 MHz, benzene-*d*₆; δ, ppm): 150.42, 138.76, 138.62, 137.19, 136.53, 133.37, 130.03, 129.92, 128.82, 128.00, 127.45, 126.94, 125.67, 117.74, 112.58, 21.02, 20.52. HRMS (ESI) calcd for C₄₃H₃₉N₃⁺ [M + H]⁺ m/z 598.32222. Found 598.32301. Note, H₂^{Mes}PDP^{Ph} can exist in either monomeric or hydrogen bonded dimeric forms, depending on the nature of the solvent. In benzene-*d*₆ the major species in the ¹H NMR spectra is tentatively assigned as the hydrogen bonded dimer [H₂^{Mes}PDP^{Ph}]₂, whereas the minor species is assigned as monomeric H₂^{Mes}PDP^{Ph}. See Chapter 4 for details presented within the context of similar H₂^{Ar}PDP^{Ph} ligands.

Preparation of (MesPDP^{Ph})Fe(OEt₂).

Fe[N(SiMe₃)₂]₂ (100 mg, 0.27 mmol) was added to a 20 mL scintillation vial equipped with a magnetic stirrer and dissolved in 5 mL of diethyl ether. H₂^{Mes}PDP^{Ph} (159 mg, 0.27 mmol) was added to a separate vial and suspended in 5 mL of diethyl ether. The suspension of H₂^{Mes}PDP^{Ph} was added dropwise to the pale-green solution of Fe[N(SiMe₃)₂]₂. The resulting mixture was vigorously stirred for 24 h. The bright red insoluble crude product precipitated from solution and was isolated on a medium porosity glass frit and washed with excess pentane. The resulting powder was dissolved in the minimum amount of toluene, filtered into a separate 20 mL vial, and layered with excess pentane. Storage at −35 °C resulted in the formation of dark red-purple crystals. The product was washed with excess pentane and dried in vacuo. Yield 78 mg (0.11 mmol, 40%). $\mu_{\text{eff}} = 5.5 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ¹H NMR (400 MHz, benzene-*d*₆; δ, ppm; fwhm, Hz) 111.69 (s, 120 Hz, 2H, 3-pyridineH), 92.58 (s, 152 Hz, 2H, pyrrole-CH), 74.69 (s, 2423 Hz, 4H), 12.18 (s, 17 Hz, 4H), 9.32 (s, 56 Hz, 4H), 7.45 (s, 62 Hz, 4H), 5.12 (s, 18 Hz, 2H, *para*-PhH), 4.17 (s, 17 Hz, 6H, mesityl-*para*-CH₃), 1.66 (s, 19 Hz, 1H, 4-pyridineH), −10.38 (s, 405 Hz, 12H, mesityl-*ortho*-CH₃). Anal. Calcd for

(^{Mes}PDP^{Ph})Fe(OEt₂), C₄₇H₄₇FeN₃O: C, 77.78; H, 6.53; N, 5.79. Found: C, 77.92; H, 6.78; N, 5.57. Crystals suitable for X-ray diffraction were obtained from layering a concentrated toluene solution with excess pentane and storing the mixture at −35 °C.

Preparation of (^{Mes}PDP^{Ph})Fe(thf)(μ-Cl)Li(thf)₃.

A 20 mL scintillation vial equipped with a magnetic stirrer was charged with 500 mg (0.84 mmol) of H₂^{Mes}PDP^{Ph} and 10 mL of THF, resulting in a pale yellow solution. In a separate vial, 280 mg (167 mmol) of lithium bis(trimethylsilyl)amide (LiHMDS) was dissolved in THF. The solution of Li(HMDS) was added dropwise to the solution of H₂^{Mes}PDP^{Ph}, resulting in an immediate color change to a yellow/ orange luminescent solution. Ligand deprotonation was allowed to proceed for approximately 2 h to ensure complete conversion. After this time, 106 mg (0.84 mmol) of FeCl₂ and 8 mL of THF were added to a separate vial equipped with a magnetic stirrer, forming a pale brown suspension. To the stirring slurry of FeCl₂ was added the solution of deprotonated ligand, resulting in an immediate color change to orange/red. The reaction mixture was allowed to stir for 12h. The resulting solution was filtered through a pad of Celite supported on a glass wool plug into a separate vial and concentrated to approximately 5 mL. An excess of n-pentane was added to the vial and mixed with the THF solution. Storage of the THF/pentane solution at −35 °C for 12 h resulted in precipitation of the orange microcrystalline product, (^{Mes}PDP^{Ph})Fe(thf)(μ-Cl)Li(thf)₃. Yield: 518 mg (0.53 mmol, 63%). $\mu_{\text{eff}} = 5.4 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). Anal. Calcd for (^{Mes}PDP^{Ph})Fe(thf)(μ-Cl)Li(thf)₃, C₅₉H₆₉ClFeLiN₃O₄: C, 72.13; H, 7.08; N, 4.28. Found: C, 74.03; H, 6.15; N, 5.55. The results of the elemental analysis suggest that 3 equivalence of THF were lost during the drying of the sample under high vacuum. Considering that the THF molecules coordinated to the lithium cation are readily lost upon stirring the complex in pentane, this is a likely candidate for the

deviation from the theoretical CHN values. Anal. Calcd for $C_{47}H_{45}ClFeLiN_3O$: C, 73.68; H, 5.92; N, 5.48. Found: C, 74.03; H, 6.15; N, 5.55.

Preparation of $(^{Mes}PDP^{Ph})Fe(thf)$.

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 390 mg (0.397 mmol) of $(^{Mes}PDP^{Ph})Fe(thf)(\mu-Cl)Li(thf)_3$. Addition of 10 mL of a 1:1 mixture of toluene and pentane dissolved the material. Upon stirring, LiCl began to precipitate from solution. The suspension was filtered through a Celite pad supported by a glass wool plug to remove precipitated LiCl. The dark red filtrate was collected in a 50 mL round bottom flask, and the solvent was removed *in vacuo*. The aforementioned procedure was repeated with an additional 10 mL of a 1:1 mixture of toluene and pentane to further precipitate LiCl. To the resulting dark red solid, approximately 15 mL of toluene was added, and the dark red solution was filtered into a tared 20 mL scintillation vial. Removal of volatiles and subsequent trituration with pentane afforded 200 mg of a red solid identified as $(^{Mes}PDP^{Ph})Fe(thf)$. Yield: 200 mg (0.276 mmol, 70%). $\mu_{eff} = 5.2 \mu_B$ (295 K, magnetic susceptibility balance). 1H NMR (400 MHz, benzene- d_6 ; δ , ppm; fwhm, Hz): 113.68 (s, 78 Hz, 2H, 3-pyridineH), 110.95 (s, 142 Hz, 2H, pyrrole-CH), 25.67 (s, 135 Hz, 4H), 24.28 (s, 107 Hz, 4H), 13.05 (s, 16 Hz, 4H), 11.57 (s, 41 Hz, 4H), 8.29 (s, 44 Hz, 4H), 5.68 (s, 16 Hz, 2H, *para*-PhH), 4.42 (s, 11 Hz, 6H, mesityl-*ortho*-CH₃), -5.98 (s, 69 Hz, 1H, 4-pyridineH), -11.58 (s, 393 Hz, 12 H, mesityl-*ortho*-CH₃). Anal. Calcd for $(^{Mes}PDP^{Ph})Fe(thf)$, $C_{47}H_{45}FeN_3O$: C, 78.00; H, 6.27; N, 5.81. Found: C, 76.81; H, 6.19; N, 5.39. The deviation in the elemental analysis results from the expected values is likely due to incomplete removal of LiCl. Anal. Calcd for $(^{Mes}PDP^{Ph})Fe(thf) \cdot 0.3 LiCl$, $C_{47}H_{45}Cl_{0.3}FeLi_{0.3}N_3O$: C, 76.65; H, 6.16; N, 5.71. Recrystallization via slow diffusion of pentane into a concentrated

fluorobenzene solution at $-35\text{ }^{\circ}\text{C}$ provided dark red crystals of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ suitable for X-ray diffraction.

Preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$.

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 376 mg (0.520 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$. The solid was dissolved in approximately 3 mL of THF. 15 mL of pentane was added to the solution, and upon stirring, an abundant bright orange precipitate was observed. The mixture was stored at $-35\text{ }^{\circ}\text{C}$ overnight to induce complete precipitation. The resulting orange solid was isolated on a fine porosity frit and briefly dried in vacuo. Yield: 290 mg, 0.364 mmol, 70%. $\mu_{\text{eff}} = 5.4\text{ }\mu_{\text{B}}$. ^1H NMR (400 MHz, $\text{THF-}d_8$; δ , ppm; fwhm, Hz): 90.85 (s, 90 Hz, 2H, pyrrole-CH), 67.16 (s, 94 Hz, 2H, 3-pyridineH), 20.32 (s, 35 Hz, 1H, 4-pyridineH), 8.54 (s, 18 Hz, 4H), 7.45 (s, 34 Hz, 4H), 6.69 (s, 133 Hz, 12 H, mesityl-ortho-CH₃), 5.99 (s, 26 Hz, 4H), 5.73 (s, 18 Hz, 2H, para-PhH), 0.81 (s, 11 Hz, 6H, mesityl-para-CH₃). Resonances for the THF ligands were not detected due to rapid exchange with $\text{THF-}d_8$.

Preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$.

$\text{FeCl}_2(\text{py})_4$ (300 mg, 0.677 mmol) was suspended in 5 mL of pentane in a 20 mL scintillation vial equipped with a Teflon-coated stirrer. (Trimethylsilyl)methylolithium (NsLi) (127 mg, 1.35 mmol) was dissolved in 5 mL pentane in a separate vial. The solution of NsLi in pentane was added dropwise with stirring to the $\text{Fe}(\text{Cl})_2(\text{py})_4$ suspension, immediately generating a dark purple solution. After 2 h of stirring, the mixture was filtered through a plug of glass wool to remove precipitated LiCl and was concentrated in vacuo to approximately 2 mL. The dark purple solution was diluted with 8 mL of toluene. In a separate vial, $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ (405 mg, 0.677 mmol) was dissolved in 10 mL of toluene. The pale yellow ligand solution was added slowly dropwise to the solution containing the iron complex while vigorously stirring. Within minutes, a

color change to dark red/orange was observed. After 2 h of stirring, the crude reaction mixture was concentrated to dryness, leaving a bright orange powder. A minimum amount of toluene was used to dissolve the crude material, and the solution was filtered and layered with 10 mL of n-pentane. Red/orange plates of crystalline material precipitated from solution after storage at -35°C for 12 h. The mother liquor was decanted, and the product was transferred to a medium porosity glass frit where it was washed with 20 mL of cold pentane and dried under reduced pressure. Yield: 510 mg (0.630 mmol), 93%. Single crystals suitable for X-ray crystallography were obtained via slow diffusion of diethyl ether into a concentrated toluene solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ at -35°C . $\mu_{\text{eff}} = 5.5 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ^1H NMR (400 MHz, benzene- d_6 ; δ , ppm; fwhm, Hz) 103.96 (s, 1386 Hz, 2H), 87.89 (s, 111 Hz, 2H), 77.20 (s, 115 Hz, 2H), 36.56 (s, 121 Hz, 4H), 21.54 (s, 64 Hz, 1H, PDP-4-pyridineH), 9.73 (s, 15 Hz, 4H), 7.37 (s, 37 Hz, 4H), 6.58 (s, 32 Hz, 6H), 4.86 (s, 15 Hz, 2H), 1.91 (s, 9 Hz, 6H, mesityl-*para*- CH_3), 0.80 (s, 187 Hz, 12H, mesityl-*ortho*- CH_3). Anal. Calcd for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, $\text{C}_{53}\text{H}_{47}\text{FeN}_5$: C, 78.61; H, 5.85; N, 8.65. Found: C, 78.35; H, 6.11; N, 8.38.

Physical Measurements.

^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded on an Agilent 400 MHz spectrometer, JEOL 400 MHz YH spectrometer, or a Varian INOVA 600 MHz spectrometer. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. Assignments of resonances for paramagnetic compounds are based on integration and only reported in the experimental procedures for conclusive cases. High resolution mass spectra were obtained on a Thermo Finnigan Linear Trapping Quadrupole mass spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Room temperature magnetic susceptibility measurements were performed with

a Johnson Matthey Mark 1 instrument that was calibrated with $\text{HgCo}(\text{SCN})_4$. Zero field ^{57}Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a $^{57}\text{Co}/\text{Rh}$ radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/N_2 cryostat within an accuracy of ± 0.3 K. The data were calibrated relative to α -iron at 298 K with minimum experimental line widths of 0.23 mm/s. The fitting procedure to extract quantitative spectral parameters uses a least squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a $\text{Mo K}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)⁶⁷ was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames, followed by reflection indexing and least-squares refinement, produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods

(SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.⁶⁸

Density Functional Theory Calculations.

All DFT calculations were performed with the ORCA program package.⁶⁹ Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.⁷⁰⁻⁷² The all-electron Gaussian basis sets were those developed by the Ahlrichs group.⁷³⁻⁷⁵ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SVP basis sets were used that were of double- ζ quality in the valence region and contained a polarizing set of d functions on the nonhydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)⁷⁶⁻⁷⁸ approach were chosen to match the orbital basis.⁷⁹⁻⁸¹ All molecular orbital and spin density plots were generated using the program Gabedit.⁸² Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.⁸³ The Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{84,85}

Accession Codes

CCDC 1869113-1869118 contain the supplementary crystallographic data for this chapter.

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CHAPTER III: REACTIVITY OF HIGH-SPIN IRON(II) PYRIDINE BISPYRROLIDE COMPLEXES WITH ORGANIC AZIDES

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3.1 Abstract

The reactions of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ ($\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}} = 2,6\text{-bis}(5\text{-(2,4,6-trimethylphenyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine}$) with organic azides have been studied. The identity of the azide substituent had a profound impact on the transformation type and nature of the observed products. Reaction with aromatic p-tolyl azide, N_3Tol , resulted in exclusive formation of the corresponding iron tetrazene complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$. In contrast, the use of bulky 1-adamantyl azide or 4-azido-4-methylpentylbenzene led to clean intramolecular C–H amination of one of the benzylic C–H bonds of a mesityl substituent on the pyridine dipyrrolide, PDP, supporting ligand. The smaller aliphatic substituent in benzyl azide allowed for the isolation of two different compounds from distinct reaction pathways. One product is the result of double C–H amination of the PDP ligand via nitrene transfer, while the second one contains a dibenzyl tetrazene and a benzaldimine ligand. The bulky aromatic mesityl azide, MesN_3 , allows for suppression of tetrazene formation and the spectroscopic observation of the reactive imidyl radical intermediate $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. This complex decomposes in the presence of the weak

benzylic bonds of the ^{Mes}PDP^{Ph} supporting ligand to form the C-H amination product Fe(NHMe-^{Mes}PDP^{Ph}). All isolated complexes were characterized using a combination of X-ray crystallography, solid state magnetic susceptibility measurements, ¹H NMR and ⁵⁷Fe Mössbauer spectroscopy, and density functional theory (DFT), and their electronic structures were elucidated. Potential electronic structures for putative iron(IV) imido or iron(III) iminyl radical complexes were explored via DFT calculations.

3.2 Introduction

Reactions between organic azides and various transition metal complexes have been intensively studied due to their relevance in nitrogen-group transfer reactions.¹ As a consequence of this research, nitrene transfer to olefins and insertion into C-H bonds has become a viable strategy for the synthesis of important nitrogen-containing organic compounds such as aziridines and functionalized amines, respectively.²⁻⁸ Inspired initially by the related oxygen atom-transfer reactivity of P450⁹ and nonheme iron enzymes,¹⁰ nitrene transfer via iron catalysis has received particular attention.¹¹⁻¹⁵ Based on the seminal work on biomimetic iron porphyrin complexes that promote C-H amination and the presence of iron-oxo intermediates in biological systems,¹⁶⁻¹⁹ a substantial number of isoelectronic iron-imido species with numerous supporting ligand systems has been prepared and studied over the last two decades.²⁰⁻⁴⁶ This class of compounds displays a remarkable range of different electronic structures with iron centers in oxidation states from +II to +V and various spin states combined with dianionic imido (NR²⁻) or monoanionic iminyl radical (NR^{•1-}) ligands. In addition to iron-imido species, iron-tetrazene complexes, formed via [2 + 3] cycloaddition of an Fe=NR unit with an additional equivalent of organic azide, can often be isolated in reactions with organic azides as the nitrene source.⁴⁶⁻⁵³ Due to the redox-active nature of the tetrazene ligand, which can exist in three different oxidation states, multiple distinct

electronic structures are possible in combination with iron and have been explored by a number of researchers.⁵⁴ While many iron tetrazene complexes are inert, several examples have recently been suggested as intermediates in the formation of azoarenes via nitrene homocoupling, and catalytic protocols for azoarene synthesis from aromatic organic azides have been developed.^{54,55} Additionally, Jenkins and co-workers have shown that iron tetrazene complexes can be competent intermediates in catalytic aziridination reactions.⁵² For both types of reactivity, the iron tetrazenes were proposed to act as a “masked form” of a reactive iron-imido species. Despite the ever-growing sample size of well-characterized intermediates obtained from the reaction of organic azides with iron precursors, the exact factors that govern the diverse reactivity of iron compounds in nitrene transfer reactions continue to be unclear. Specifically, examples of C–H amination facilitated by iron catalysts remain scarce.^{2,4} The most successful and best-understood catalyst system was reported by Betley and co-workers using dipyrromethenes as the supporting ligand.^{43-46,56-59} The ability of this ligand system to support high-spin ferric imido or iminyl species has been proposed as a key feature to allow facile intra- and intermolecular C–H amination via nitrene transfer. An interesting characteristic of dipyrromethene ligands is their close relationship to the porphyrin ligands used in the initial discovery of iron mediated C–H amination (Figure 3.1).

Figure 3.1. Iron complexes with pyrrole-based ligands employed in nitrene transfer reactions.

In a similar manner, pyridine dipyrrolide (PDP) ligands with two anionic pyrrolide moieties separated by a neutral pyridine donor can be viewed as a porphyrin fragment (Figure 3.2). However, the pincer-type ligand structure allows for the stabilization of different coordination geometries and resulting electronic structures compared to both the parent macrocycle and dipyrromethenes. For example, we have recently shown that the PDP platform supports unusual high-spin ferrous configurations in a distorted square-planar ligand field.⁶⁰ Based on these observations, we were curious to investigate whether PDP ligands are capable of supporting rare high-spin Fe^{III}-iminyl or Fe^{IV}-imido complexes that can facilitate nitrene transfer. The steric profile of the PDP ligand was identified as a critical parameter to fine tune the desired electronic structure. Mindiola, Caulton, and co-workers recently reported the synthesis and characterization of the stable Fe^{IV} imido complex (^tBuPDP^tBu)Fe(N^IAd) (H₂^tBuPDP^tBu = 2,6-bis(3,5-di-tert-butyl-1H-pyrrol-2-yl)pyridine).²⁸ As established by their thorough electronic structure analysis, the unusual cis-divacant octahedral geometry enforced by the bulky ^tBuPDP^tBu ligand results in a low-spin Fe^{IV} (*S* = 0) configuration with a closed-shell NR²⁻ ligand. In line with the proposed requirement for high-spin ferric imido/iminyl intermediates for nitrene transfer, this complex is remarkably inert toward nitrene transfer to both olefins and C–H

bonds.⁶¹ We hypothesized that opening of a coordination site *trans* to the central pyridine donor by using ^{Mes}PDP^{Ph} as a supporting ligand could result in four-coordinate square-planar or five-coordinate square-pyramidal nitrene intermediates exhibiting higher spin states and increased reactivity. Herein, we describe the reactivity of organic azides with the Fe^{II} complex (^{Mes}PDP^{Ph})Fe(thf) to yield iron tetrazene complexes and products resulting from intramolecular C–H amination.

Mindiola, Caulton, 2014

This Study

Figure 3.2. Pyridine dipyrrole (PDP) iron complexes with distinct coordination geometries investigated for their reactivity with organic azides.

3.3 Reactivity of (^{Mes}PDP^{Ph})Fe(L) (L = Et₂O or thf) with 1-Adamantyl Azide

The addition of one equivalent of N₃¹Ad to dark-red solutions of (^{Mes}PDP^{Ph})Fe(OEt₂) or (^{Mes}PDP^{Ph})Fe(thf) in benzene-*d*₆ resulted in complete conversion of the starting complex within 1

h to a new paramagnetic species, as detected by ^1H NMR spectroscopy. No obvious color change was observed during the reaction; however, upon addition of azide, evolution of N_2 was observed. The absence of a signal for an azide stretching mode in the IR spectrum of the crude reaction mixture indicated complete consumption of 1-adamantyl azide and ruled out formation of a simple iron azide adduct. The appearance of a signal at 3198 cm^{-1} suggested the formation of an N–H bond. Based on the ^1H NMR data, the symmetry of the product is significantly reduced compared to the C_{2v} symmetric starting material, as evidenced by a total of 24 paramagnetically shifted resonances between -96.42 and 203.45 ppm , which indicates a C_1 symmetric molecule. Reactions with excess azide under otherwise identical conditions yielded the same paramagnetic product in the presence of unreacted N_3^1Ad . Following recrystallization from toluene/pentane mixtures, the new complex was obtained as red microcrystalline needles and further characterized by zero-field ^{57}Fe Mössbauer spectroscopy (Figure 3.3). The large isomer shift, δ , of 0.75 mm s^{-1} is consistent with a central high-spin Fe^{II} metal center, which was further supported by a room temperature effective magnetic moment, μ_{eff} , of $5.2\ \mu_{\text{B}}$. Deviation from the spin-only value expected for four unpaired electrons is typical for PDP iron complexes and is likely due to contributions from unquenched orbital angular momentum.^{28,60} Previously reported Mössbauer data for high-spin ferrous PDP complexes by Mindiola and co-workers and our group provide further insight into the likely coordination environment around the metal center (Table 3.1). The unusually small quadrupole splitting, $|\Delta\text{E}_\text{Q}|$, of 0.41 mm s^{-1} for a high-spin ferrous species is indicative of a four coordinate species with planar geometry.⁶⁰ In contrast, well characterized examples for five-coordinate Fe^{II} PDP complexes exhibit significantly larger values of $|\Delta\text{E}_\text{Q}|$,⁶⁰ while the cis-divacant high-spin Fe^{II} complex $(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{OEt}_2)$ is characterized by a splitting of intermediate size at 1.12 mms^{-1} .²⁸ In combination, the collected

analytical data are most consistent with nitrene insertion into a benzylic C–H bond of an ortho-methyl group of one of the mesityl substituents. The product of this intramolecular group transfer reaction was tentatively assigned as $\text{Fe}(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ shown in Scheme 3.1.

Scheme 3.1. Synthesis of $\text{Fe}(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})$.

Despite repeated efforts, single crystalline samples suitable for X-ray diffraction studies could not be obtained from hydrocarbon solvents. Interestingly, the solid state Mössbauer data for $\text{Fe}(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ indicated the presence of a minor impurity (<10%) of a second iron species with parameters $\delta = 0.94 \text{ mm s}^{-1}$ and $\Delta E_Q = 2.14 \text{ mm s}^{-1}$, which are indicative of a five coordinate PDP iron complex (Figure 3.6). Based on the previously established ability of the starting material ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$) to reversibly bind an additional THF ligand, this minor species was attributed to a diethyl ether or THF adduct of $\text{Fe}(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ due to the presence of ethereal solvents in the glovebox atmosphere. Notably, dissolution of $\text{Fe}(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ in $\text{THF-}d_8$ resulted in an immediate color change from intense red to orange and led to substantial changes to the chemical shifts observed in the ^1H NMR spectrum (Scheme 3.2 and Figure 3.3).

Scheme 3.2. Synthesis of (NH¹Ad-MesPDP^{Ph})Fe(thf). Note, for clarity the mesityl substituent of one pyrrole has been truncated and is denoted as “Mes”.

Figure 3.3. Comparison of the ¹H NMR spectra of Fe(NH¹Ad-MesPDP^{Ph}) in benzene-*d*₆ and (NH¹Ad-MesPDP^{Ph})Fe(thf) in THF-*d*₈ (bottom).

Further support for the formation of a new species was obtained from the Mössbauer spectrum recorded in THF solution (Figure 3.5), which shows a complete absence of the signal for the

four-coordinate complex and a majority quadrupole doublet with parameters $\delta = 1.12 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 2.16 \text{ mm s}^{-1}$. These values are similar to those of the minor species from the solid state measurement and consistent with a five-coordinate high-spin ferrous species $(\text{NH}^1\text{Ad-MesPDP}^{\text{Ph}})\text{Fe}(\text{thf})$. The second observed species, with Mössbauer parameters of $\delta = 0.46 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 0.99 \text{ mm s}^{-1}$, likely stems from decomposition encountered during sample preparation, as the values are consistent with those reported for colloidal $\text{FeO}(\text{OH})$ (rust).⁶²

Figure 3.4. Zero-field Mössbauer spectrum of $\text{Fe}(\text{NH-}^1\text{Ad}^{\text{MesPDP}^{\text{Ph}}})$ acquired at 80 K. For the composite spectrum (left), the white circles indicate the experimental data and the blue line corresponds to the fit. For the component spectrum (right), the white circles indicate experimental data and the blue and red lines are the fits for $\text{Fe}(\text{NH-}^1\text{Ad}^{\text{MesPDP}^{\text{Ph}}})$ and a species tentatively assigned as $(\text{NH-}^1\text{Ad}^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{thf}/\text{OEt}_2)$, respectively.

Table 3.1. Summary of ^{57}Fe Mössbauer spectroscopic data for PDP iron complexes.

	δ / mms^{-1}	$ \Delta E_Q / \text{mms}^{-1}$	Ref
$(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}^{\text{II}}(\text{OEt}_2) (S = 2)$	0.86	1.12	28
$(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}^{\text{III}}(\text{Cl}) (S = 5/2)$	0.39	2.38	28
$(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}^{\text{IV}}(\text{N}^{\text{I}}\text{Ad}) (S = 0)$	-0.09	2.78	28
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{thf})(\mu\text{-Cl})\text{Li}(\text{thf})_3 (S = 2)$	1.09	2.63	60
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{OEt}_2) (S = 2)$	0.87	0.50	60
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{thf}) (S = 2)$	0.78	0.48	60
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{thf})_2^a (S = 2)$	1.09	2.76	60
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{py})_2 (S = 2)$	0.98	2.92	60
$\text{Fe}^{\text{II}}(\text{NH}^{\text{I}}\text{Ad-}^{\text{Mes}}\text{PDP}^{\text{Ph}}) (S = 2)$	0.75	0.41	<i>This work</i>
$(\text{NH}^{\text{I}}\text{Ad-}^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{thf})^a (S = 2)$	1.12	2.16	<i>This work</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{III}}(\text{N}_4\text{Tol}_2^{\bullet}) (S = 0)$	0.12	3.12	<i>This work</i>
$\text{Fe}^{\text{II}}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}}) (S = 2)$	0.93	1.48	<i>This work</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{II}}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh}) (S = 0)$	0.15	2.26	<i>This work</i>

^aRecorded in frozen THF solution.

Figure 3.5. Zero-field Mössbauer spectrum of $(\text{NH}^{\text{I}}\text{Ad-MesPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ acquired at 80 K. For the composite spectrum (left), the white circles indicate the experimental data and the blue line corresponds to the fit. For the component spectrum (right), the white circles indicate experimental data and the blue and red lines are the fits for $(\text{NH}^{\text{I}}\text{Ad-MesPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and a species tentatively assigned as $\text{FeO}(\text{OH})$, respectively. Note: The spectrum was acquired in frozen THF solution.

Slow diffusion of pentane into a concentrated THF solution of the new compound resulted in the isolation of red-orange single crystals identified as $(\text{NH}^{\text{I}}\text{Ad-MesPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ by X-ray crystallography. The molecular structure shown in Figure 3.6 confirms intramolecular nitrene insertion into a benzylic C–H bond of an ortho-methyl group of one of the mesityl substituents. The five-coordinate geometry around the iron center can be described as heavily distorted square pyramidal or trigonal bipyramidal with N(2)–Fe(1)–(N4), N(2)–Fe(1)–O(1), and O(1)–Fe(1)–N(4) angles of $118.46(7)^\circ$, $149.61(6)^\circ$, and $91.04(6)^\circ$, respectively. Due to the small bite angle of the pincer ligand, the two pyrrole nitrogen atoms N(1) and N(3) are not perfectly

trans to each other with an N(1)–Fe(1)–N(3) angle of 147.17(7)°. The long Fe–N and Fe–O bond lengths (Table 3.1) are consistent with a high-spin iron center. The angles around N(4) indicate the presence of a neutral amine ligand, and the N–H hydrogen atom was located in the electron density map.

Figure 3.6. ORTEP of (NH¹Ad-MesPDP^{Ph})Fe(thf) displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of the amine H), co-crystallized solvent molecules, and a mesityl pyrrole substituent (with exception of the *ipso* carbon) have been excluded for clarity.

3.4 Reactivity with the Aromatic Azide Paratolyl Azide

Encouraged by the observed intramolecular C–H activation using ¹AdN₃, reactions using an aromatic azide were targeted next to explore whether the different electronic and steric properties of the nitrene source would enable intermolecular C–H amination reactions. Addition of one equivalent of paratolyl azide to (MesPDP^{Ph})Fe(thf) in aromatic solvents at room temperature resulted in an immediate color change from red to brown. Analysis of the reaction mixture by ¹H NMR spectroscopy revealed the formation of a new diamagnetic species but revealed incomplete consumption of the starting material. An approximate ratio of 1:1 for the

new complex and the starting material was determined via integration of the 4-pyridine proton resonances. Repeating the experiment with an organic azide to (^{Mes}PDP^{Ph})Fe(thf) ratio of 2:1 produced the new diamagnetic complex with complete consumption of (^{Mes}PDP^{Ph})Fe(thf). Recrystallization from toluene/pentane solutions at $-35\text{ }^{\circ}\text{C}$ yielded a dark brown, microcrystalline solid identified as the tetrazene complex (^{Mes}PDP^{Ph})Fe(N₄Tol₂) (Scheme 3.3).

Scheme 3.3. Synthesis of (^{Mes}PDP^{Ph})Fe(N₄Tol₂). R denotes *p*-tolyl.

Single crystals suitable for characterization by X-ray diffraction were obtained via slow diffusion of pentane into a concentrated solution of (^{Mes}PDP^{Ph})Fe(N₄Tol₂) in toluene at $-35\text{ }^{\circ}\text{C}$. The molecular structure of the complex is illustrated in Figure 3.7 and contains an iron center in a distorted square pyramidal coordination environment. The short Fe–N bond distances (Table 3.1) suggest a low-spin configuration consistent with the diamagnetic ground state.

Table 3.2. Selected bond lengths (Å) and angles (deg) for (NH¹Ad-^{Mes}PDP^{Ph})Fe(thf) and (^{Mes}PDP^{Ph})Fe(N₄Tol₂).

	(^{Mes} PDP ^{Ph})Fe(N ₄ Tol ₂)	(NH ¹ Ad- ^{Mes} PDP ^{Ph})Fe(thf)	
Fe(1)–N(1)	1.946(3)	Fe(1)–N(1)	2.092(2)
Fe(1)–N(2)	1.943(3)	Fe(1)–N(2)	2.130(2)
Fe(1)–N(3)	1.955(3)	Fe(1)–N(3)	2.128(2)
Fe(1)–N(4)	1.867(3)	Fe(1)–N(4)	2.240(2)
Fe(1)–N(7)	1.803(3)	Fe(1)–O1	2.144(2)
N(4)–N(5)	1.299(4)	N(1)–Fe(1)–N(2)	75.10(6)
N(5)–N(6)	1.336(4)	N(1)–Fe(1)–N(3)	147.17(7)
N(6)–N(7)	1.318(4)	N(2)–Fe(1)–N(3)	76.26(6)
N(1)–Fe(1)–N(2)	79.87(11)	N(2)–Fe(1)–N(4)	118.46(7)
N(1)–Fe(1)–N(3)	153.02(11)	N(2)–Fe(1)–O(1)	149.61(6)
N(2)–Fe(1)–N(3)	79.80(11)	N(4)–Fe(1)–O(1)	91.04(6)
N(2)–Fe(1)–N(4)	174.94(12)	-	-
N(2)–Fe(1)–N(7)	96.34(12)	-	-
N(4)–Fe(1)–N(7)	78.75(12)	-	-

Figure 3.7. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized solvent molecules have been excluded for clarity.

However, due to the well-established redox activity of tetrazene ligands, a broader analysis of the structural features is necessary to establish the oxidation states of the iron center and the N_4Tol_2 fragment. Several studies have shown that the redox state of tetrazene ligands can be determined via inspection of the N–N bond lengths in the MN_4 chelate ring.⁶³ For $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$, the N–N distances within the iron tetrazene unit (N(4)–N(5) 1.299(4) Å, N(5)–N(6) 1.336(4) Å, N(6)–N(7) 1.318(4) Å) are most consistent with a tetrazene radical anion and infer an oxidation state of +III for the iron center. Antiferromagnetic coupling between the ligand radical ($S_L = 1/2$) and a low-spin ferric ion (d^5 , $S_{\text{Fe}} = 1/2$) gives rise to the overall $S = 0$ ground state. The Mössbauer parameters for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ of $\delta = 0.12 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 3.12 \text{ mm s}^{-1}$ are also consistent with a low-spin Fe^{III} center (Figure 3.8).

Figure 3.8. Zero-field Mössbauer spectrum of (^{Mes}PDP^{Ph})Fe(N₄Tol₂) acquired at 80 K. The white circles indicate the experimental data and the blue line corresponds to the fit.

While the observed isomer shift would be unusually high for an alternative assignment as a low-spin Fe^{IV} complex with a dianionic tetrazene ligand, the large quadrupole splitting is inconsistent with a low-spin Fe^{II} configuration with a neutral tetrazene fragment. For the latter electronic configuration, a nearly isotropic electric field gradient and a resulting small quadrupole splitting are expected due to three doubly filled d orbitals (d_{xz} , d_{yz} , d_{xy}) for the low-spin d⁶ ion under the influence of a square-pyramidal ligand field. Further evidence for an unusual electronic structure was obtained from NMR spectroscopy. The ¹H NMR spectrum of (^{Mes}PDP^{Ph})Fe(N₄Tol₂) exhibits 12 resonances consistent with C_{2v} symmetry in solution on the NMR time scale (Figure 3.9). Whereas, in the solid-state the structure exhibits approximate C_s symmetry, the wagging motion of the tetrazene ligand renders the top and bottom faces of the PDP ligand and the two tolyl substituents of the tetrazene ligand equivalent, thus affording a higher effective symmetry in

solution. Variable-temperature NMR (VT-NMR) data collected over a range of -90 to 90 $^{\circ}\text{C}$ in toluene- d_8 (Figure 3.10) indicate that the energy barrier for this dynamic process is too low to observe discrete C_s symmetric isomers while maintaining fluid toluene solution. However, significant broadening of the resonances assigned to the protons of the tolyl and mesityl groups at -90 $^{\circ}\text{C}$ suggests that the sample is close to the decoalescence temperature of two C_s -symmetric conformations. More importantly, and relevant to the electronic structure assignment, the chemical shifts of several resonances are highly sensitive to changes in temperature.

Figure 3.9. ^1H NMR spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ at 400 MHz in benzene- d_6 .

Figure 3.10. Variable temperature ^1H NMR spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ at 400 MHz in toluene- d_8 . Resonances marked by an asterisk are due to small amounts of pentane in the sample.

The most striking temperature-dependent shifts are observed for resonances associated with the protons of the tetrazene moiety, the 3-pyridine protons, and the pyrrole protons. This behavior is consistent with thermal population of paramagnetic excited states. However, the persistence of clearly resolved J couplings for the proton resonances of the phenyl substituents and the 4-pyridine proton suggests only minor contributions from the paramagnetic state(s) even at the highest experimentally probed temperature of 90 °C.

Broken-symmetry DFT computational studies were conducted to complement the experimental electronic structure assignment for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$. Within the broken symmetry formalism, the notation $\text{BS}(m,n)$ describes a state with m unpaired spin-up electrons

and n unpaired spin-down electrons localized on separate fragments of the molecule. Several computational models were tested in full molecule geometry optimizations at the B3LYP level of theory to account for possible electronic structures of the diamagnetic ground state and potentially low-lying paramagnetic excited states. A comparison of the computed structural parameters can be found in Table 3.3. For the ground state, a BS(1,1) approach was employed to provide an open-shell singlet configuration with a tetrazene radical anion antiferromagnetically coupled to a low-spin ferric ion, and a restricted Kohn–Sham (RKS) approach was used to enforce an alternative closed-shell singlet configuration describing either a low-spin Fe^{II} complex with a neutral tetrazene ligand or a low-spin Fe^{IV} species with a dianionic tetrazene unit. Both formalisms yielded optimized structures that are in excellent agreement with the experimental data from crystallography and reproduced the Mössbauer parameters within generally accepted computational accuracy (Table 3.3).⁶⁴ Therefore, neither solution can be excluded based on structural or spectroscopic arguments. A comparison of the obtained total energies showed that the BS(1,1) solution is only 1.9 kcal/mol more stable than the RKS solution. The modest energy lowering induced by symmetry breaking reflects singlet diradical character for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$, albeit lower than in many previously reported open-shell singlet systems.⁶⁵ This is also apparent from the relatively large spatial overlap between the magnetic orbitals of $S = 0.70$. As a result, the spin density values on iron and the tetrazene moiety deviate significantly from the idealized values of one unpaired electron for each fragment (Figure 3.11). To investigate the nature of potentially low-lying paramagnetic states, calculations were performed assuming triplet and quintet configurations. For $S = 1$ states, a BS(3,1) approach and a simple unrestricted Kohn–Sham (UKS3) calculation converged to identical broken-symmetry solutions representing an intermediate-spin Fe^{III} center antiferromagnetically coupled

to a tetrazene radical anion (BS(3,1)). Surprisingly, this broken-symmetry triplet state was found to be 6.6 kcal/mol lower in energy than the open-shell singlet BS(1,1) state. However, the computed structural parameters for the BS(3,1) solution are inconsistent with the experimentally observed values for (^{Mes}PDP^{Ph})Fe(N₄Tol₂). Most notably, the Fe–N bond to the apical nitrogen donor of the tetrazene unit (Fe(1)–N(7): 2.121 Å) is significantly elongated, reflecting occupation of the σ -antibonding d_{z^2} orbital in an intermediate-spin Fe^{III} configuration. Providing further evidence that the BS(3,1) solution does not represent the ground state of (^{Mes}PDP^{Ph})Fe(N₄Tol₂), the calculated Mössbauer isomer shift deviates substantially from the experimentally observed values (Table 3.3). Additionally, two distinct $S = 2$ states were located at moderately higher energies than the triplet configuration but slightly below the computed energy of the diamagnetic BS(1,1) state. A BS(5,1) configuration representing a high spin Fe^{III} ion antiferromagnetically coupled to a tetrazene radical anion was found to be only 2.9 kcal/mol above the BS(3,1) solution. Using a UKS5 approach, a different quintet state corresponding to an intermediate-spin Fe^{III} center ferromagnetically coupled to a tetrazene radical was identified at 6.4 kcal/mol above the lowest energy BS(3,1) solution. As is the case for the BS(3,1) solution, the calculated geometries and Mössbauer parameters for the quintet configurations are inconsistent with the experimental data. These computational studies highlight that the reliable prediction of accurate spin state energetics remains a substantial challenge for DFT methods and often requires higher levels of theory that are beyond the scope of this work. For hybrid functionals such as B3LYP, the relative energies of different spin states depend strongly on the admixed fraction of exact Hartree–Fock exchange and an overestimation of the stability of higher spin states is typical for molecules with low-lying high-spin states or spin-crossover behavior.⁶⁶

Figure 3.11. Spin density distributions obtained via Mulliken population analysis for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ using BS(1,1) (top-left), BS(3,1) (top-right), BS(5,1) (bottom-left), and UKS5 (bottom-right) computational approaches.

Table 3.3. Relative energies and calculated Mössbauer parameters from DFT calculations

		$\Delta E / kcal\ mol^{-1}$	δ / mms^{-1}	$ \Delta E_Q / mms^{-1}$
$S = 0$	RKS	8.5	0.14	-3.16
	BS(1,1)	6.6	0.16	-3.23
$S = 1$	BS(3,1)/UKS3	0	0.29	2.53
$S = 2$	BS(5,1)	2.9	0.43	2.91
	UKS5	6.4	0.21	3.20

Altogether, the experimental and computational characterization of $(^{Mes}PDP^{Ph})Fe(N_4Tol_2)$ suggests that the ground state is best described as $(^{Mes}PDP^{Ph})Fe^{III}(N_4Tol_2^{\bullet 1-})$ with strong antiferromagnetic coupling between the tetrazene radical and the low-spin Fe^{III} ion. Several low-lying paramagnetic states identified via computational analysis contain a Fe^{III} ion in intermediate- or high-spin configurations and a tetrazene radical anion, indicating that the paramagnetic contributions observed by VT-NMR are due to spin state changes at the metal center. While an alternative ground state description of a closed-shell singlet composed of the two resonance structures $(^{Mes}PDP^{Ph})Fe^{II}(N_4Tol_2^0) \leftrightarrow (^{Mes}PDP^{Ph})Fe^{IV}(N_4Tol_2^{2-})$ cannot be excluded by comparison with experimental data from Mössbauer spectroscopy and X-ray diffraction, the prevalence of a tetrazene radical anion next to an Fe^{III} center in all identified excited states favors the open-shell singlet description. Based on a recent compilation of known iron tetrazene complexes by Groysman and co-workers,⁵⁴ the open shell singlet configuration with a low-spin ferric center of $(^{Mes}PDP^{Ph})Fe(N_4Tol_2)$ is unique and expands the range of available electronic structures for this compound class.

3.5 Reactivity of (^{Mes}PDP^{Ph})Fe(L) (L= thf or Et₂O) with Benzyl Azide

The divergent reactivity of N₃(p-tolyl) and N₃¹Ad raised the question whether tetrazene formation versus C–H amination, respectively, was due to the steric profiles or the electronic properties of the azide substituents. To address this question, benzyl azide, N₃Bn, was chosen as an example for an alkyl-substituted nitrene source with reduced steric bulk compared to N₃¹Ad. Addition of 1 equivalent of N₃Bn to (^{Mes}PDP^{Ph})Fe(thf) provided a mixture of two major products, one diamagnetic and one paramagnetic iron complex in addition to minor unidentified paramagnetic species. Conducting the reaction using excess N₃Bn (three equivalents) resulted in complete consumption of the iron starting material and yielded the two new species in an approximate 1:1 ratio as determined by ¹H NMR spectroscopy (Scheme 3.4). Mössbauer spectroscopy performed on a sample of the crude reaction mixture after complete removal of all volatiles confirmed the presence of two iron complexes with clearly distinguishable quadrupole doublets (Figure 3.12). Simulation of the data confirmed the 1:1 ratio obtained via ¹H NMR spectroscopy and provided parameters of $\delta = 0.93 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 1.48 \text{ mm s}^{-1}$, indicative of high-spin Fe^{II}, for product A and $\delta = 0.15 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 2.26 \text{ mm s}^{-1}$, consistent with a low-spin configuration, for product B.

Figure 3.12. Zero-field Mössbauer spectra of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ at 80 K. For the composite spectrum (left), the white circles indicate the experimental data and the blue line corresponds to the fit. For the component spectrum (right), the white circles indicate experimental data and the purple and dark-blue lines are the fits for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ and $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$, respectively.

Despite our best efforts, a reliable separation of these two compounds on a preparative scale has so far been unsuccessful. However, cooling a concentrated toluene/pentane solution of the mixture to $-35\text{ }^{\circ}\text{C}$ yielded single crystals suitable for X-ray analysis allowing the structural characterization of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$. A representation of the molecular structure is shown in Figure 3.13 and confirms double C–H amination of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand via nitrene insertion into one methyl group of each mesityl substituent.

Figure 3.13. ORTEP of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2$ displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of amine hydrogens) and co-crystallized solvent molecules have been excluded for clarity.

The newly generated pendent amines are coordinated to the iron center and in combination with the PDP pincer enforce a distorted trigonal-bipyramidal ligand environment. Taking into account the dianionic charge of the newly formed $(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})^{2-}$ ligand and the long Fe–N bond lengths (Table 3.4), the iron center is in a high-spin ferrous configuration consistent with component A observed by Mössbauer spectroscopy. Analysis of the remaining crystals by ^1H NMR spectroscopy confirmed that $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ is indeed the paramagnetic product observed in the reaction, as evidenced by the symmetric and paramagnetically shifted resonances. A second recrystallization via slow diffusion of pentane into a toluene solution of the crude reaction mixture yielded single crystals of the diamagnetic component B identified as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ (Figure 3.14). The low-spin configuration of the central Fe ion is supported by short Fe–N bond distances to the PDP pincer ligand (Table 3.4). The N–N distances in the tetrazene fragment are consistent with the fully oxidized, neutral form of the ligand with short bond lengths between the terminal and internal

nitrogen atoms (N(4)–N(5) 1.303(2) Å and N(6)–N(7) 1.302(2) Å) and longer bond lengths between the internal nitrogen atoms (N(5)–N(6) 1.350(2) Å). The sixth coordination site in the distorted octahedral complex is occupied by a benzaldimine ligand, which is an isomer of benzyl nitrene. The short C(58)–N(8) bond length of 1.271(2) Å confirms the presence of a double bond, and the aldimine and the imine protons were located in the electron density map.

Figure 3.14. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of imine *NH* and *CH*), co-crystallized toluene, and a pyrrole mesityl substituent (with exception of the *ipso* carbon) have been excluded for clarity.

Figure 3.15. ^1H - ^{13}C HSQC spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ in benzene- d_6 indicating aldimine CH correlation.

Figure 3.16. ^1H - ^{15}N HSQC spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ in benzene- d_6 indicating aldimine NH correlation.

Scheme 3.4. Synthesis of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$. Bn denotes benzyl and Mes denotes mesityl.

The presence of the imine ligand was also confirmed by ^1H NMR spectroscopy with diagnostic doublet resonances at 7.54 ppm ($\text{HN}=\text{CHPh}$) and 10.39 ppm ($\text{HN}=\text{CHPh}$) featuring a large coupling constant of 22 Hz. The structure was confirmed via a combination of 2D NMR experiments, including ^1H - ^{13}C and ^1H - ^{15}N HSQC (Figures 3.15 and 3.16).

As a whole, the experimental data for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ are consistent with an electronic structure containing a low-spin Fe^{II} center, a neutral dibenzyl tetrazene unit, and a benzaldimine ligand. Crystallographically characterized N-protio imine complexes of transition metals are rare. However, examples for benzaldimine formation via reaction of benzyl azide with second and third row transition metals (Ru, Os, and Ir) have been reported.⁶⁷⁻⁷⁰ For these transformations, the mechanism of imine formation is proposed to proceed via metal

nitrene formation by N₂ extrusion followed by a 1,2-shift of a benzylic hydrogen atom. A similar mechanism was recently proposed by Betley and co-workers for reactions of iron and cobalt complexes with primary alkyl azides.⁵⁹⁻⁷¹ However, no coordination of the resulting imine products to the metal center was observed in these cases. The only known crystallographically characterized example of a benzaldimine iron complex was reported by Chirik and co-workers.⁷² In their study, the complex (ⁱPrPDI)Fe(NH=CHPh) (ⁱPrPDI = 2,6-(2,6-ⁱPr₂-C₆H₃N=CMe₂)₂C₅H₃N) was derived in a bimolecular fashion from the reaction of phenyl diazomethane with (ⁱPrPDI)Fe(N₂)₂. Despite a lack of clear mechanistic information, the two products observed in the reaction between (^{Mes}PDP^{Ph})Fe(L) (L = OEt₂ or thf) and N₃Bn suggest three distinct pathways that are all consistent with a reactive iron imido/iminylnitrene intermediate: (a) intramolecular C–H amination; (b) tetrazene formation likely to proceed via [2 + 3]-cycloaddition with a second equivalent of azide; and (c) aldimine formation via 1,2-shift in the presence of C–H bonds in the α-position to the nitrogen atom.

Table 3.4. Selected bond lengths (Å) and angles (deg) for Fe($\{NHBn\}_2$ -^{Mes}PDP^{Ph}) and (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh).

Fe($\{NHBn\}_2$ - ^{Mes} PDP ^{Ph}) ^a		(^{Mes} PDP ^{Ph})Fe(N ₄ Bn ₂)(HN=CHPh)	
Fe(1)–N(1)	2.064(1)	Fe(1)–N(1)	1.996(1)
Fe(1)–N(2)	2.131(2)	Fe(1)–N(2)	1.938(1)
Fe(1)–N(3)	2.191(1)	Fe(1)–N(3)	1.995(1)
N(1)–Fe(1)–N(2)	75.62(3)	Fe(1)–N(4)	1.848(1)
N(1)–Fe(1)–N(1)'	151.23(6)	Fe(1)–N(7)	1.855(1)
N(2)–Fe(1)–N(3)	131.20(3)	Fe(1)–N(8)	1.983(1)
N(3)–Fe(1)–N(3)'	97.59(7)	N(4)–N(5)	1.303(2)
-	-	N(5)–N(6)	1.350(2)
-	-	N(6)–N(7)	1.302(2)
-	-	N(8)–C(58)	1.271(2)
-	-	N(1)–Fe(1)–N(2)	80.85(6)
-	-	N(1)–Fe(1)–N(3)	160.11(6)
-	-	N(2)–Fe(1)–N(3)	79.88(5)
-	-	N(2)–Fe(1)–N(7)	174.00(6)
-	-	N(4)–Fe(1)–N(8)	172.46(6)

^aThe molecule lies on a crystallographic 2-fold rotation axis that passes through Fe(1), N(2), and C(7). Coordinates for the symmetry-related primed (') atoms were generated via the symmetry relationship: 1 – x, y, 0.5 – z.

3.6 Reactivity of (^{Mes}PDP^{Ph})Fe(thf) with Mesityl Azide

The disparate reaction outcomes for (^{Mes}PDP^{Ph})Fe(thf) with various organic azides suggested that careful tuning of the substitution of the azide used as the nitrene source may render intermediate (^{Mes}PDP^{Ph})Fe(NR) species isolable. Accordingly, a benzene-*d*₆ solution of (^{Mes}PDP^{Ph})Fe(thf) was treated with one equivalent of bulky aryl azide, mesityl azide, MesN₃. An

immediate color change of the solution from dark-red to dark-brown was noted. ^1H NMR spectroscopy of the crude reaction mixture evidenced complete consumption of starting material and the formation of a new paramagnetic species featuring apparent C_{2v} symmetry. 12 paramagnetically shifted and broadened resonances were observed spanning a range of -214.36 to 21.74 ppm, prompting tentative assignment of the species as either the azido adduct, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_3\text{Mes})$, or the iron bound nitrene, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ (Scheme 3.5). Recently, Mindiola and coworkers have disclosed the synthesis and characterization of a related cobalt azido species, $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Co}(\text{N}_3^1\text{Ad})$, via the reaction of $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Co}(\text{OEt}_2)$ and $^1\text{AdN}_3$.⁶¹ This compound readily extrudes dinitrogen when irradiated to generate the fleeting nitrene intermediate $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Co}(\text{N}^1\text{Ad})$, as evidenced by the clean intramolecular C-H amination of a proximal tert-butyl group of the $(^{\text{tBu}}\text{PDP}^{\text{tBu}})$ supporting ligand, yielding $\text{Co}(\text{NH}^1\text{Ad}-^{\text{tBu}}\text{PDP}^{\text{tBu}})$. In consideration of this result and the plausibility that a C_{2v} symmetric ^1H NMR spectrum may be consistent with either $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_3\text{Mes})$ or $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, an IR spectrum was acquired of the crude product in a KBr matrix. The resulting IR spectra is devoid of any feature consistent with an azido functionality, inconsistent with the assignment of the product as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_3\text{Mes})$.

Scheme 3.5. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$.

Monitoring solutions of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ in benzene- d_6 over time demonstrated significant product decomposition to a new paramagnetic species, as discerned by ^1H NMR spectroscopy. Similarly, an aliquot of the preparative scale reaction mixture of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with MesN_3 in benzene- d_6 was subjected to ^1H NMR analysis after 12 hours and demonstrated spectral features consistent with the presence of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and the unidentified paramagnetic species. Based on the number of paramagnetically shifted resonances, consistent with a C1 symmetric $\text{MesPDP}^{\text{Ph}}$ ligand environment, this species was tentatively assigned as $\text{Fe}(\text{NHMes-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$, proposed to have arisen from the intramolecular C-H amination of one mesityl group of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ supporting ligand.

In an attempt to obtain structural characterization of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ or the decomposition product, pentane was diffused into a crude benzene- d_6 solution, resulting in the isolation of red crystals amenable to characterization via X-ray crystallography. The resulting structure allowed for the unambiguous identification of the crystalline material as $\text{Fe}(\text{NHMes-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ (Figure 3.17). This compound is anticipated to have resulted from intramolecular C-H amination of a benzylic C-H bond of the mesityl substituent of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ chelate ligand, reactivity akin to that observed with $^1\text{AdN}_3$ and benzyl azide as the nitrene source (Scheme 3.6).

Scheme 3.6. Synthesis of Fe(NHMe^{Mes}PDP^{Ph}) from (Me^{Mes}PDP^{Ph})Fe(thf).

Fe(NHMe^{Mes}PDP^{Ph}) crystallizes in the triclinic space group P-1 and the hydrogen of the newly formed amine moiety was located in the electron difference map.. The geometry about the iron center is similar to that of the starting material, (Me^{Mes}PDP^{Ph})Fe(thf), as the amine nitrogen is lowered beneath the plane established by the PDP chelate. The N2-Fe1-N4 bond angle was found to be 144.47(9)°, compared to the N2-Fe1-O1 angle of 152.99 in (Me^{Mes}PDP^{Ph})Fe(thf). This deviation demonstrates a more significant departure from planarity in the solid-state for Fe(NHMe^{Mes}PDP^{Ph}). Bond lengths of 2.012(2) for Fe1-N1, 2.073(2) for Fe1-N2, 2.017(2) for Fe1-N3, and 2.134(2) for Fe1-N4 are consistent with a high-spin state for the iron center. Consideration of the retention of the dianionic charge in the modified dipyrroliide ligand prompts an assignment of the electronic structure of Fe(NHMe^{Mes}PDP^{Ph}) as a high-spin ferrous species. It should be highlighted that in the case of the reaction of ¹AdN₃ with (Me^{Mes}PDP^{Ph})Fe(thf), a product assignment as Fe(NH¹Ad-Me^{Mes}PDP^{Ph}) was in part based upon a Mössbauer spectra consistent with a planar or pseudo square planar high-spin Fe^{II} PDP complex. The isolation and characterization of Fe(NHMe^{Mes}PDP^{Ph}) as a four-coordinate species devoid of coordinated THF ligand lends further credence to this previously made assignment, in lieu of its unambiguous solid-state characterization via X-ray crystallography.

Figure 3.17. ORTEP of $\text{Fe}(\text{NHMe-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ at 30% probability ellipsoids. Hydrogen atoms (with exception of the amine H) and cocrystallized benzene solvent have been removed for clarity. A mesityl substituent of the ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$) ligand has been truncated (with exception of the arene *ipso* carbon) for clarity.

Interestingly, the isolation of $\text{Fe}(\text{NHMe-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ using the bulky aromatic azide MesN_3 as the nitrene source contrasts with the observed reactivity for the less bulky aromatic azide pTolN_3 , where no ligand C-H amination was observed. For example, an experiment probing the addition of one molar equivalence of pTolN_3 to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in benzene- d_6 solution resulted in the metallotetrazene $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$ and unreacted $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ being the only species discernable by ^1H NMR spectroscopy (*vide supra*). Alternatively, in the case of reaction of one molar equivalence of MesN_3 with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in benzene- d_6 solution, no evidence of metallotetrazene formation was observed via ^1H NMR. An additional experiment was conducted where a benzene- d_6 solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was treated with two molar equivalents of MesN_3 . Analysis of the resulting ^1H NMR spectrum indicated the presence of paramagnetically shifted and broadened resonances consistent with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and unreacted MesN_3 and no evidence of formation of the corresponding tetrazene complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Mes}_2)$. These results prompt two hypotheses about the fate of the spectroscopically characterized intermediate $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$: 1.) Intramolecular nitrene

insertion into a benzylic C-H bond kinetically outcompetes metallotetrazene formation via the [2+3]-cycloaddition of a second equivalent of MesN₃ to form the species (^{Mes}PDP^{Ph})Fe(N₄Mes₂).

2.) The 2,6-dimethyl substitution of the organic fragment of the imparts steric protection of intermediate (^{Mes}PDP^{Ph})Fe(NMes) and disallows [2+3] cycloaddition by a second azide equivalent of MesN₃, based solely on steric grounds. In consideration of the combined data for the (^{Mes}PDP^{Ph})Fe(NR) system, the steric argument is favored at this time. This insights suggest that for metastable (^{Mes}PDP^{Ph})Fe(NR) intermediates to be isolated and fully characterized, significantly bulky aryl nitrene fragments are necessitated.

3.7 Reactivity of (^{Mes}PDP^{Ph})Fe(thf) with 4-Azido-4-methylpentylbenzene

Considering the propensity for intermediate (^{Mes}PDP^{Ph})Fe(NR) species to undergo a variety of reaction pathways, including ligand C-H amination, iron tetrazene formation, and hydrogen atom abstraction, it was hypothesized that careful tailoring of the azide as a nitrene source may allow for productive intramolecular C-H amination of aliphatic azides to form saturated N-heterocycles. In consideration of these details, it was anticipated that selection of an azide possessing both alpha substitution (to eliminate hydrogen atom abstraction), steric hindrance (to suppress tetrazene formation), and weak benzylic C-H bonds (to suppress ^{Mes}PDP^{Ph} C-H amination) would be a suitable substrate to explore. Recently, 4-azido-4-methylpentylbenzene and related α-geminal dimethyl substituted azides have been identified as a suitable substrates for intramolecular benzylic C-H amination via pyrrole based iron and cobalt platforms.^{56,71}

Scheme 3.7. Proposed formation of (^{Mes}PDP^{Ph})Fe bound 2,2-dimethyl-5-phenylpyrrolidine via direct C-H bond amination from 4-azido-4-methylpentylbenzene.

Accordingly, a benzene-*d*₆ solution of (^{Mes}PDP^{Ph})Fe(thf) was treated with one equivalent of 4-azido-4-methylpentylbenzene anticipating the formation of a (^{Mes}PDP^{Ph})Fe bound 2,2-dimethyl-5-phenylpyrrolidine adduct, as demonstrated in Scheme 3.7. Notably, no discernable color change of the solution or N₂ evolution was observed upon addition of the azide. The reaction progress was monitored via ¹H NMR spectroscopy and after eight hours complete consumption of the starting materials was observed, concomitant with the presence of a new paramagnetic species with apparent C₁ symmetry, as evidenced by 31 paramagnetically shifted and broadened resonances spanning a range of -92.76 to 202.64 ppm. Removal of volatiles and subsequent crystallization by diffusion of pentane into a concentrated benzene solution at ambient temperature afforded red single crystals suitable for X-ray crystallographic analysis. The X-ray crystallographic study identified the reaction product as Fe(NH(C(CH₃)₂(CH₂)₃Ph)-^{Mes}PDP^{Ph}), arising from intramolecular C-H amination of a benzylic C-H bond of the ^{Mes}PDP^{Ph} ligand (Figure 3.18 and Scheme 3.8). This result suggests that kinetically the C-H amination of

the ^{Mes}PDP^{Ph} chelate outcompetes the intramolecular amination of a benzylic C-H bond of the intermediate nitrene.

Figure 3.18. ORTEP of $\text{Fe}(\text{NH}(\text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph})\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of the amine H) and co-crystallized pentane solvent have been excluded for clarity.

The proximity of benzylic C-H bonds of the mesityl PDP substituent is likely to account for this preference. $\text{Fe}(\text{NH}(\text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph})\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ was found to crystallize in the triclinic space group P-1. The geometry about the iron center is highly distorted. A limiting geometric description of a see-saw coordination geometry is appropriate, as evidenced by the bent N2-Fe-N4 bond angle of $130.22(5)^\circ$. This is further reinforced via the τ_4 value of 0.57. In regard to the electronic structure of the iron center, a high-spin ferrous formulation is inferred from the relatively long iron nitrogen bond distances of 2.0149(13) (Fe-N1), 2.0624(13) (Fe-N2), 1.9973(13) (Fe-N3), and 2.1321(13) (Fe-N4). These values are in reasonable agreement with the $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ (*vide supra*), which Mössbauer spectroscopy has characterized as possessing a high-spin Fe^{II} center. The slightly contracted bond lengths of

$\text{Fe}(\text{NH}(\text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph})-\text{MesPDP}^{\text{Ph}})$ relative to $\text{Fe}(\{\text{NHBn}\}_2-\text{MesPDP}^{\text{Ph}})$ is attributed to the less congested coordination environment present in the four vs. five-coordinate structure. The amine proton was identified in the electron difference map, confirming the tetrahedral coordination environment about the nitrogen atom and formal nitrene insertion. The structural metrics are summarized in Table 3.5 for comparison to isostructural $\text{Fe}(\text{NHMe}-\text{MesPDP}^{\text{Ph}})$.

Scheme 3.8. Synthesis of $\text{Fe}(\text{NH}(\text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph})-\text{MesPDP}^{\text{Ph}})$.

Table 3.5. Selected bond lengths (Å) and angles (deg) for Fe(NHMeS-MesPDP^{Ph}) and Fe(NH(C(CH₃)₂(CH₂)₃Ph)-MesPDP^{Ph}).

	Fe(NHMeS-MesPDP ^{Ph})	Fe(NH(C(CH ₃) ₂ (CH ₂) ₃ Ph)-MesPDP ^{Ph})
Fe(1)–N(1)	2.012(2)	2.0149(13)
Fe(1)–N(2)	2.073(2)	2.0624(13)
Fe(1)–N(3)	2.017(2)	1.9973(13)
Fe(1)–N(4)	2.134(2)	2.1321(13)
N(1)–Fe(1)–N(2)	78.43(9)	78.90(5)
N(1)–Fe(1)–N(3)	150.85(9)	149.37(5)
N(1)–Fe(1)–N(4)	110.67(9)	110.22(5)
N(2)–Fe(1)–N(3)	77.43(9)	77.15(5)
N(2)–Fe(1)–N(4)	144.47(9)	130.22(5)
N(3)–Fe(1)–N(4)	98.48(9)	99.80(5)

In consideration of this experimental outcome, it has become obvious that in order to leverage productive C-H amination reactivity within the Fe-PDP system three critical design parameters must be included. These considerations are as follows: 1.) The PDP pincer ligand must possess a chemically robust substitution pattern, excluding weak benzylic C-H bonds susceptible to intramolecular C-H amination. 2.) The steric environment must afford access to nitrene coordination *trans* to the central pyridine unit comprising the tridentate pincer ligand. This critical geometric concern affords access to electronic structures featuring higher spin states and destabilization of the iron bound nitrene. Consequently, destabilization of the Fe=NR fragment results in increased reactivity that is not observed in systems with the nitrene unit coordinated *cis* to the pyridine (i.e. (^tBuPDP^tBu)Fe(N¹Ad), featuring a *cis*-divacant octahedral geometry). 3.) Steric considerations about the nitrene must also be made. In combination, these

results demonstrate that insufficiently bulky nitrene sources, i.e. unsubstituted aryl azides, suffer from kinetically rapid tetrazene formation as a reaction outcome, suggesting that intercepting nitrene intermediates of this nature is a significant challenge. Furthermore, the utilization of azides lacking substitution alpha to the intermediate nitrene are susceptible to kinetically competitive α -HAA.

3.8 Calculations of Putative (^{Mes}PDP^{Ph})Fe(NR) Intermediates

To gain further insight into the electronic structures and differences in reactivity of potential imido/iminylnitrene intermediates formed for the three different organic azides, broken symmetry DFT calculations were performed at the B3LYP level. An important question in these studies was the interplay of molecular geometry and electronic structure to address the marked difference in reactivity between Caulton and Mindiola's isolable imido complex (^{tBu}PDP^{tBu})Fe(N¹Ad) and the proposed reactive intermediates employing the ^{Mes}PDP^{Ph} supporting ligand. Therefore, all computations were conducted using untruncated structures to account for the potential steric interplay between the ^{Mes}PDP^{Ph} ligand and the substituent on nitrogen. Unless otherwise noted, all geometry optimizations were started from planar structures with a N_{py}-Fe-N_{im} angle of 180°. In the absence of information on the spin states of the proposed intermediates several computational approaches were taken to account for a wide range of potential electronic structures: (a) a spin restricted approach (RKS) was used to model a closed-shell singlet ground state representing either a low-spin Fe^{II} complex with a neutral singlet nitrene, a low-spin Fe^{IV} center with a dianionic imido ligand, or a resonance form of both; (b) a BS(1,1) approach was chosen to represent a low-spin ferric ion (S_{Fe} = 1/2) antiferromagnetically coupled to an iminylnitrene radical (S = 1/2); (c) spin-unrestricted triplet (UKS3) and quintet (UKS5) approaches were taken to represent a number of different electronic structure possibilities

including intermediate- spin ($S = 1$) and high-spin Fe^{IV} ($S = 2$) configurations with a dianionic imido ligand; (d) BS(3,1) and BS(5,1) calculations were performed to test for electronic structures with intermediate-spin ($S_{\text{Fe}} = 3/2$) or high-spin Fe^{III} ($S_{\text{Fe}} = 5/2$) centers antiferromagnetically coupled to an iminyl radical ($S = 1/2$). Table 3.6 summarizes the relative energies and important structural features of the $\text{Fe}=\text{NR}$ unit for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ with $\text{R} = {}^1\text{Ad}$, Bn , Tol , and Mes obtained after geometry optimization. For all four R groups, the lowest energy solution is a BS(3,1) state, which corresponds to a $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{III}}(\text{NR}^{\bullet 1-})$ electronic structure with an intermediate spin ferric ion. Reassuringly, the UKS3 calculations provided the same solution as the BS(3,1) approach with spontaneous symmetry breaking, indicating that this state is the lowest energy configuration on the triplet surface. Spin density plots visualizing this configuration for all four derivatives are shown in Figure 3.20, and a representative qualitative molecular orbital diagram for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{III}}(\text{N}^1\text{Ad}^{\bullet 1-})$ is shown in Figure 3.19. Consistent with iminyl radical character, the nitrogen atoms of the $\text{Fe}=\text{NR}$ moieties carry significant spin density. The spin density map of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NBn})$ shows substantial delocalization of the unpaired electron onto the benzylic protons of the iminyl substituent, which could favor facile 1,2-hydrogen atom shift to furnish the experimentally observed benzaldimine fragment. Even stronger delocalization into the aromatic substituent is observed for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NTol})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. Betley and co-workers have recently suggested that the concentration of spin density on the iminyl/imido nitrogen atom (i.e., iminyl radical character) could play an important role in C–H functionalization processes.⁴⁶ Based on this assumption, the complete lack of iminyl radical character in $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{N}^1\text{Ad})$, which is best described as a low-spin Fe^{IV} species with a dianionic imido ligand, could also be responsible for the poor reactivity of this complex toward C–H bonds. A closer inspection of the structural parameters reveals that the

$N_{py}-Fe-N_{im}$ angle for all four compounds is close to 180° ($165.1-177.7^\circ$), indicating nearly planar coordination environments around the iron centers. This structural motif favors an intermediate-spin iron center by strongly destabilizing the $d_{x^2-y^2}$ orbital. The $Fe-N_{im}-C_{im}$ angles show a clear deviation from linearity for the $Fe=NR$ unit independent of the substituent, which suggests that this bend is due to electronic rather than steric effects. However, the bulky 1Ad group causes a significant twist of the mesityl substituents away from the nearly coplanar arrangement observed for the benzyl, tolyl, and mesityl derivatives. This distortion results in a complete steric protection of the $Fe=NR$ unit and is consistent with the lack of tetrazene formation in the reaction of N_3^1Ad with $(^{Mes}PDP^{Ph})Fe(thf)$ or $(^{Mes}PDP^{Ph})Fe(OEt_2)$. Independent of substituent, the closed-shell singlet state (RKS) is found slightly higher in energy than the BS(3,1) triplet state and shows a much smaller $N_{py}-Fe-N_{im}$ angle consistent with the cis-divacant octahedral geometry reported for diamagnetic $(^{tBu}PDP^{tBu})Fe^{IV}(N^1Ad^{2-})$.

Figure 3.19. Qualitative molecular orbital diagram visualizing the electronic structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{III}}(\text{N}^1\text{Ad}^{\bullet 1-})$ showing the d orbital occupation of the intermediate-spin Fe^{III} ion and the singly occupied molecular orbital of the iminyl ligand radical.

The preference for this geometry and electronic structure given an $S = 0$ ground state is consistent with Caulton and Mindiola's calculations of their compound using identical computational methods to those employed in the study presented herein (functional, basis sets, ORCA program suite). Nevertheless, our results challenge their conclusion that the *cis*-divacant octahedral structure of $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{N}^1\text{Ad})$ is enforced by electronic effects rather than steric

bulk of the supporting ligand. Allowing a more planar coordination environment results in an energetically preferable electronic structure change in our computational study. However, it should be noted that the accurate calculation of spin state energetics remains a substantial challenge for modern DFT methods and can depend on the functional used. Given that all solutions calculated by us to cover the numerous potential electronic configurations are within less than 10 kcal mol⁻¹ of each other for all (^{Mes}PDP^{Ph})Fe(NR) complexes, more sophisticated computational methods may be necessary to elucidate the complex ground states of these compounds. The close energy of the remaining computational approaches highlights this phenomenon. The BS(1,1) approach converges to a diamagnetic BS(2,2) state that is best described as containing an intermediate-spin Fe^{II} ion ($S_{\text{Fe}} = 1$) antiferromagnetically coupled to a triplet nitrene ($S = 1$). Furthermore, the two quintet solutions obtained via BS(5,1) and UKS5 approaches provide two additional electronic structures of only slightly higher energy than the BS(3,1) ground state and correspond to electronic configurations best described by a high-spin ferric metal center antiferromagnetically coupled to an iminyl radical and an intermediate-spin ferric metal center exhibiting a ferromagnetic interaction with an iminyl radical, respectively. It should be noted that a bent starting geometry was required to converge on a BS(5,1) solution. The otherwise employed linear Fe=NR starting structure led to convergence to the UKS5 solution despite using the BS formalism. The presence of several electronic states within a few kilocalories per mole of each other is consistent with the proposal of two-state reactivity for the iron-mediated amination of hydrocarbons by the Fe=NH⁺ ion in the gas phase.⁷³

Figure 3.20. Spin density distributions obtained via Mulliken population analysis for (^{Mes}PDP^{Ph})Fe(N¹Ad) (top-left), (^{Mes}PDP^{Ph})Fe(NBn) (top-right), (^{Mes}PDP^{Ph})Fe(NTol) (bottom-left) and (^{Mes}PDP^{Ph})Fe(NMes) (bottom-right) using a BS(3,1) or UKS3 computational approach.

Table 3.6. Calculated energies and selected structural parameters for different electronic structures of $(^{Mes}PDP^{Ph})Fe(NR)$ (R = ¹Ad, Tol, Bn, Mes) obtained from DFT calculations.

		$\Delta Energy / \text{kcal mol}^{-1}$	$N_{py}-Fe-N_{im} / ^\circ$	$Fe-N_{im}-C_{im} / ^\circ$	$Fe-N_{im} / \text{\AA}$
$(^{Mes}PDP^{Ph})Fe(N^1Ad)$	RKS	+4.7	120.9	138.2	1.603
	BS(2,2)	+3.2	149.0	152.8	1.743
	BS(3,1)/UKS3 ^a	0	165.4	133.5	1.722
	UKS5 ^b	+0.9	165.1	147.4	1.782
	BS(5,1) ^c	+4.8	136.5	160.4	1.772
$(^{Mes}PDP^{Ph})Fe(NBn)$	RKS	+4.8	114.6	131.4	1.610
	BS(2,2)	+6.7	139.6	137.2	1.721
	BS(3,1)/UKS3 ^a	0	177.7	129.2	1.732
	UKS5 ^b	+3.5	176.0	146.9	1.758
	BS(5,1) ^c	+3.9	173.89	144.07	1.764
$(^{Mes}PDP^{Ph})Fe(NTol)$	RKS	+9.7	119.1	138.9	1.631
	BS(2,2)	+5.5	146.9	146.9	1.759
	BS(3,1)/UKS3 ^a	0	172.4	145.7	1.734
	UKS5 ^b	+2.1	177.6	166.2	1.778
	BS(5,1) ^c	+4.3	128.2	165.3	1.795
$(^{Mes}PDP^{Ph})Fe(NMes)$	RKS	+8.7	131.51	152.71	1.623
	BS(2,2)	+7.6	166.92	169.05	1.791
	BS(3,1)/UKS3 ^a	0	173.42	149.56	1.732
	UKS5 ^b	+2.2	175.27	162.17	1.784
	BS(5,1) ^c	+2.6	153.86	167.58	1.791

^aantiferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl radical ($S = 1/2$). ^bferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl(1-) radical ($S = 1/2$). ^cantiferromagnetic coupling between h.s. Fe^{III} ($S = 5/2$) and iminyl(1-) radical ($S = 1/2$).

To compliment this study, additional calculations were performed on the hypothetical nitrene complex ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^1\text{Ad})$), featuring the unsubstituted parent PDP ligand. This hypothetical complex was explored *in silico* via Caulton, Mindiola, and coworkers to examine the possibility of steric bias that tert-butyl substitution at the five position of the PDP pyrrolide imparts on the corresponding iron nitrene. An RKS calculation was performed on ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^1\text{Ad})$) which demonstrated that the complex maintains an electronic preference for the cis-divacant octahedral geometry when in a closed-shell diamagnetic configuration. The aforementioned computational study of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) complexes highlights that by altering the substitution of the PDP ligand, an electronic preference exists for the nitrene fragment to adopt a planar coordination geometry trans to the central pyridine in paramagnetic electronic structural configurations. Taking this result into consideration, the computational study was extended to include the hypothetical ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^1\text{Ad})$) to further explore this phenomena. The same array of computational approaches that were explored for ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) were probed for ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^1\text{Ad})$). Interestingly, in agreement with ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) computations, the UKS3 calculation for ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^1\text{Ad})$) spontaneously converges to a BS(3,1) solution with the imide fragment existing in a planar geometry, with an $\text{N}_{\text{py}}\text{-Fe-N}_{\text{im}}$ angle of 175.68° . This renders the geometric configuration of the complex square planar. The bent $\text{Fe-N}_{\text{im}}\text{-C}_{\text{im}}$ angle of 146.15° and the Fe-N_{im} bond length of $1.712 \text{ \AA}$ are also in good agreement with the values obtained from the BS(3,1) computations for the ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) complexes. The most intriguing discovery is that the BS(3,1) solution featuring a square planar geometry lies $10.8 \text{ kcal mol}^{-1}$ lower in energy than the corresponding RKS solution with *cis*-divacant octahedral geometry. The spin density plot obtained via Mulliken population analysis of this computation is presented in Figure 3.20 and clearly demonstrates the square-planar geometry adopted by $^{\text{H}}\text{PDP}^{\text{H}}\text{FeN}^1\text{Ad}$ as well as the

significant radical character imparted throughout the nitrene fragment. These result are in excellent agreement with the aforementioned computational study performed on (^{Mes}PDP^{Ph})Fe(NR) derivatives and highlights that the preference for a square-planar intermediate-spin Fe^{III} center engaged in antiferromagnetic coupling with an iminyl radical ligand vs. a low-spin Fe^{IV} iron imide in *cis*-divacant octahedral geometry is a sterically driven phenomena that can be influenced via the identity of the substituent at the 5-position of the PDP pyrrolides.

Table 3.7. Calculated energies and selected structural parameters for different electronic structures of (^HPDP^H)Fe(N¹Ad) obtained from DFT calculations.

	$\Delta Energy / kcal\ mol^{-1}$	$N_{py}-Fe-N_{im} / ^\circ$	$Fe-N_{im}-C_{im} / ^\circ$	$Fe-N_{im} / \text{\AA}$
RKS	+10.8	124.16	141.75	1.595
BS(1,1) ^a	+9.8	129.53	139.76	1.667
BS(3,1)/UKS3 ^b	0	175.68	146.15	1.712
BS(5,1)/UKS5 ^c	+12.4	129.76	147.08	1.778

^aantiferromagnetic coupling between l.s. Fe^{III} (S=1/2) and iminyl radical (S=1/2). ^bantiferromagnetic coupling between i.s. Fe^{III} (S = 3/2) and iminyl radical (S = 1/2). ^cantiferromagnetic coupling between h.s. Fe^{III} (S = 5/2) and iminyl(1-) radical (S = 1/2).

Figure 3.21. Spin density plot obtained from Mulliken population from BS(3,1)/UKS3 calculation of (^HPDP^H)Fe(N¹Ad).

3.9 Conclusion

The reaction of the square-planar high-spin Fe^{II} complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ or $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, with organic azides proceeds readily to provide products consistent with intramolecular C–H amination, tetrazene formation via [2 + 3]-cycloaddition, α -HAA, and a reactive but spectroscopically observable Fe^{III} iron iminyl radical species. The observed reactivity depends strongly on the nature of the organic azide and reflects the steric and electronic properties of the organic substituent. This reactivity is in stark contrast to the previously reported reaction of cis-divacant octahedral $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{OEt}_2)$ with N_3^1Ad that furnishes an isolable and remarkably inert Fe^{IV} imido complex. For the planar compounds described herein, reactions with 1-adamantyl azide yield the C–H amination products $\text{Fe}(\text{NH}^1\text{Ad}-^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and $(\text{NH}^1\text{Ad}-^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, depending on the solvent environment. Both complexes were characterized by ^1H NMR and Mössbauer spectroscopy and magnetic susceptibility measurements. Structural characterization for $(\text{NH}^1\text{Ad}-^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ confirms C–N and N–H bond formation via nitrene insertion.

The non-bulky aromatic organic azide N_3Tol enables exclusive formation of the iron tetrazene complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$, which was characterized structurally and spectroscopically. The electronic structure of this complex is unprecedented for iron tetrazenes and is best described as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}^{\text{III}}(\text{N}_4\text{Tol}_2^{\bullet 1-})$ according to the combined experimental and computational data. The small aliphatic nitrene source benzyl azide provides the structurally and spectroscopically characterized complexes $\text{Fe}(\{\text{NHBn}\}_2-^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$, highlighting the availability of both C–H amination and tetrazene formation pathways. Additional reactivity resulting in benzaldimine ligand formation is enabled by the presence of α -hydrogen atoms in benzyl azide. The bulky azide, MesN_3 allows for

suppression of tetrazene formation and the spectroscopic observation of the reactive imidyl radical intermediate ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NMes})$) via ^1H NMR. This complex decomposes in the presence of the weak benzylic bonds of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ supporting ligand to form the C-H amination product $\text{Fe}(\text{NHMe}-^{\text{Mes}}\text{PDP}^{\text{Ph}})$, characterized via X-ray crystallography.

Finally, in an attempt to sequester C-H amination of the PDP chelate and intercept the reactive nitrene fragment with other weak benzylic C-H bonds, 4-azido-4-methylpentylbenzene was explored as a nitrene source. The clean conversion to $\text{Fe}(\text{NH}(\text{C}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph})-^{\text{Mes}}\text{PDP}^{\text{Ph}})$, characterized via X-ray crystallography, demonstrates that the C-H amination of the mesityl group of the PDP ligand kinetically outcompetes the C-H amination of a benzylic C-H bond of the iron bound 4-methylpentylbenzene nitrene fragment, disallowing formation of the desired 2,2-dimethyl-5-phenylpyrrolidine product.

All reaction products observed in this study are consistent with the formation of highly reactive $\text{Fe}=\text{NR}$ intermediates. DFT studies for the proposed four-coordinate intermediates show several energetically close lying electronic states and do not allow a conclusive evaluation of the exact ground state configuration consistent with potential two-state reactivity. However, it is clear that different spin states favor distinct iron imido/imidyl/nitrene geometries. The lowest energy configuration for all studied intermediates ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) contains an intermediate-spin Fe^{III} ion antiferromagnetically coupled to an imidyl radical and favors a planar coordination environment. In contrast, diamagnetic singlet configurations prefer substantially bent structures. Furthermore, the computed structure of the hypothetical parent PDP nitrene complex, ($^{\text{H}}\text{PDP}^{\text{H}}\text{Fe}(\text{N}^{\text{I}}\text{Ad})$), are consistent with the results obtained for ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{NR})$) complexes. In combination, these studies provide strong evidence that the electronic structure of the iron nitrene fragment is directly attenuated by the steric profile of the PDP ligand, which is governed

by the substituents located at the five position of the pyrrolide heterocycles. Furthermore, these results provide direct insight into the divergent reactivity of PDP iron complexes with different coordination environments and suggests that the stability of the PDP iron nitrene fragment can be controlled by careful design of the appropriate ligand environment.

3.10 Experimental Procedures

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH₂ and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Deuterated benzene (benzene-*d*₆) and tetrahydrofuran (THF-*d*₈) for NMR spectroscopy were distilled from sodium metal and sodium benzophenone, respectively. 1-Adamantyl azide was obtained from Sigma-Aldrich, dried under high vacuum, and recrystallized at -35°C from pentane prior to use. (^{Mes}PDP^{Ph})Fe(thf),⁶⁰ (^{Mes}PDP^{Ph})Fe(OEt₂),⁶⁰ para-tolyl azide,⁷⁴ mesityl azide,⁷⁵ benzyl azide,⁷⁶ and 4-azido-4-methylpentylbenzene⁷¹ were synthesized according to literature procedures.

Safety Considerations.

Organic azides are known energetic materials that may decompose violently via explosion upon input of energy from external sources (heat, light, pressure). While we did not encounter any problems or dangerous situations during the course of this study, all experiments involving organic azides were performed on small scale with less than 100 mg of azide material. All manipulations outside of the glovebox were performed behind a blast shield. The organic

azides were stored in the dark at $-35\text{ }^{\circ}\text{C}$ in the glovebox. $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$ is thermally stable upon heating to $80\text{ }^{\circ}\text{C}$ in benzene- d_6 .

Preparation of $\text{Fe}(\text{NH}^1\text{Ad-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$.

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 200 mg (0.28 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in 10 mL of benzene, affording a dark red solution. In a separate vial, 54 mg (0.30 mmol, 1.07 eq.) of 1-adamantyl azide was dissolved in 5 mL of benzene. The adamantyl azide solution was added dropwise to the solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ over a period of approximately 10 min. Upon addition of the azide, evolution of N_2 was observed, as evidenced by bubbling of the solution. The reaction mixture was allowed to stir for 12 h, at which time it was reduced to dryness. The resulting red powder was dissolved in a minimum amount of toluene, approximately 5 mL, and filtered through a pipet containing a pad of Celite supported on a glass microfiber plug. The resulting solution was layered with 10 mL of pentane and stored at $-35\text{ }^{\circ}\text{C}$. After 12 h, red crystalline needles had formed and were isolated via vacuum filtration on a medium porosity glass frit. The crystalline product was washed with 10 mL of pentane and dried *in vacuo*. Yield: 151 mg (0.19 mmol, 68%). $\mu_{\text{eff}} = 5.2\text{ }\mu_{\text{B}}$ (295 K). ^1H NMR (600 MHz, benzene- d_6 ; δ/ppm): 203.45, 117.17, 111.70, 107.54, 105.35, 23.00, 14.32, 13.84, 10.72, 8.98, 7.04, 4.62, 3.88, 3.57, 0.89, -1.33 , -1.81 , -5.14 , -9.34 , -10.92 , -15.71 , -17.16 , -47.02 , -96.42 . Anal. Calcd for $\text{Fe}(\text{NH}^1\text{Ad-}^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{C}_{53}\text{H}_{52}\text{FeN}_4$: C, 79.49; H, 6.54; N, 7.00. Found: C, 79.66; H, 6.28; N, 7.41.

Preparation of $(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$.

A 20 mL scintillation vial was charged with 15 mg of $\text{Fe}(\text{NH}^1\text{Ad-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and 500 μL of THF- d_8 . The solution was filtered through a glass microfiber plug into a J. Young NMR tube, affording a homogeneous red/orange solution. The tube was sealed, removed from the glovebox,

and a ^1H NMR spectrum was acquired. Analysis of the resulting spectrum demonstrated quantitative conversion to $(\text{NH}^1\text{Ad}^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$. ^1H NMR (600 MHz, $\text{THF}-d_8$; δ/ppm): 149.52, 133.21, 111.62, 99.72, 95.92, 82.49, 39.90, 12.82, 12.16, 11.98, 11.85, 10.27, 9.16, 5.92, 5.07, 4.40, -1.07, -3.54, -15.14, -16.67, -22.12, -57.79, -67.96.

Preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$.

In the glovebox, 200 mg (0.28 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was transferred to a 20 mL scintillation vial equipped with a magnetic stirrer. 10 mL of toluene was added to the solid affording a dark red solution. In a separate vial, 74 mg (0.56 mmol, 2.0 eq.) of p-tolyl azide was dissolved in approximately 5 mL of toluene. The toluene solution of p-tolyl azide was added dropwise to the stirring solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, resulting in evolution of N_2 and an immediate color change of the solution to dark-brown. The reaction mixture was allowed to stir for 2 h, at which time the solvent was removed, affording a dark brown powder. The crude material was dissolved in a minimum amount of toluene and filtered through a pipet fitted with a microfiber glass plug. The solution was collected in a separate 20 mL vial and layered with 10 mL of pentane. Storage of the solution at -35°C for 48 h afforded dark-brown/black crystalline material which was isolated via vacuum filtration on a medium porosity frit. The crystals were washed with three-5 mL aliquots of pentane, and dried in vacuo. Yield: 165 mg, 0.19 mmol, 67%. Single crystals of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ were obtained via slow diffusion of pentane into a concentrated toluene solution at -35°C . ^1H NMR (400 MHz, benzene- d_6 , δ/ppm) 11.11 (s, 4H, *ortho*-tolyl-H), 7.68 (t, $J = 7.4$ Hz, 4H, *meta*-phenyl-H), 6.72 (d, $J = 7.5$ Hz, 4H, *ortho*-phenyl-H), 6.30 (overlapping s and t, 6H (total), *meta*-mesityl-H (s, 4H), *para*-phenyl-H (t, 2H)), 5.75 (t, $J = 7.5$ Hz, 1H, 4-pyridine-H), 4.65 (s, 4H, *meta*-tolyl-H), 3.73 (d, $J = 7.7$ Hz, 2H, 2-pyridine-H), 1.93 (s, 6H, *para*-mesityl- CH_3), 1.87 (s, 12H, *ortho*-mesityl- CH_3), -0.93 (s, 2H, pyrrole-H),

–5.49 (s, 6H, *para*-tolyl-CH₃). ¹³C NMR (150 MHz, benzene-*d*₆, δ/ppm) 187.10, 178.73, 165.66, 163.42, 159.36, 151.36, 144.32, 141.96, 136.27, 131.45, 128.35, 127.04, 126.94, 126.24, 124.28, 121.53, 116.28, 104.74, 91.78, 21.45, 19.37. (^{Mes}PDP^{Ph})Fe(N₄Tol₂) crystallizes as a toluene solvate. Analysis calcd for (^{Mes}PDP^{Ph})Fe(N₄Tol₂)·C₇H₈ C₅₃H₅₂FeN₄: C, 78.27; H, 6.06; N, 9.98. Found: C, 77.87; H, 5.95; N, 10.27.

Preparation of (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh).

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 150 mg (0.21 mmol) of (^{Mes}PDP^{Ph})Fe(thf) in 10 mL of benzene. In a separate vial, 85 mg (0.64 mmol) of benzyl azide was dissolved in 3 mL of benzene. The azide solution was added to the solution of the iron complex dropwise over the course of several minutes, inducing a darkening of the solution, accompanied by effervescence of N₂. The reaction mixture was allowed to stir for 12 h. The crude reaction mixture was filtered through a plug of Celite supported on a glass microfiber filter and collected in a 50 mL round-bottom flask. Here, 1 mL portions of benzene were used to extract the products from the Celite plug until washings were clear. Solvent was removed in vacuo, and a sample of the resulting red powder was subjected to ¹H NMR analysis, indicating the presence of (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh). Analysis of the crude reaction mixture via Mössbauer spectroscopy indicated Fe({NHBn}₂-^{Mes}PDP^{Ph}) and (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) as the only iron containing species present in the sample, in approximate 1:1 ratio. Crystallization via slow diffusion of pentane into a toluene solution of Fe({NHBn}₂-^{Mes}PDP^{Ph}) and (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) afforded crystals of (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) suitable for study via X-ray. ¹H NMR (600 MHz, benzene-*d*₆; δ/ppm): 10.39 (d, *J* = 22.0 Hz, 1H, imine-NH), 7.71 (d, *J* = 7.1 Hz, 4H, Ar), 7.54 (d, *J* = 22.0 Hz, 1H, imine-CH), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.25 (t, *J* = 7.6 Hz, 4H, Ar), 7.10–7.07 (m, 4H, Ar),

6.98–6.82 (m, 4H, Ar), 6.79 (m, 2H, Ar), 6.50 (d, $J = 8.4$ Hz, 4H, Ar), 6.11 (s, 2H, pyrrole-H), 4.69 (s, 2H, benzyl-CH₂), 4.27 (s, 2H, benzyl-CH₂), 2.27 (s, 6H, mesityl-CH₃), 1.88 (s, 6H, mesityl-CH₃), 1.43 (s, 6H, mesityl-CH₃). Eight aryl protons could not be located and assigned unambiguously as they are obscured by benzene and toluene residual solvent peaks present in the ¹H NMR spectrum. ¹³C NMR (151 MHz, benzene-*d*₆, δ/ppm) 174.06, 155.79, 147.68, 139.31, 138.91, 137.52, 137.25, 135.96, 135.78, 134.77, 134.72, 134.63, 132.64, 132.61, 131.49, 130.77, 130.59, 129.97, 129.57, 129.21, 128.65, 127.28, 126.88, 126.57, 126.35, 118.14, 109.98, 69.91, 66.22, 22.06, 21.44, 20.76. Three resonances were not located.

(^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) crystallizes as a toluene solvate. Analysis calcd for C₆₄H₅₈FeN₈·C₇H₈: C, 78.44; H, 6.12; N, 10.31. Found: C, 78.21; H, 5.90; N, 10.36.

Preparation of Fe({NHBn}₂-^{Mes}PDP^{Ph})₂.

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 150 mg (0.21 mmol) of (^{Mes}PDP^{Ph})Fe(thf) in 10 mL of benzene. In a separate vial, 85 mg (0.64 mmol) of benzyl azide was dissolved in 3 mL of benzene. The azide solution was added to the solution of the iron complex dropwise over the course of several minutes, inducing a darkening of the solution, accompanied by effervescence of N₂. The reaction mixture was allowed to stir for 12 h. The crude reaction mixture was filtered through a plug of Celite supported on a glass microfiber filter and collected in a 50 mL round-bottom flask. One mL portions of benzene were used to extract the products from the Celite plug until washings were clear. Solvent was removed in vacuo and a sample of the resulting red powder was subjected to ¹H NMR analysis, indicating the presence of Fe({NHBn}₂-^{Mes}PDP^{Ph}). Analysis of the crude reaction mixture via Mössbauer spectroscopy indicated Fe({NHBn}₂-^{Mes}PDP^{Ph}) and (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) as the only iron containing species present in the sample, in approximate 1:1 ratio. Crystallization via

slow diffusion of pentane into a toluene solution of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{-Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ afforded crystals of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$ suitable for study via X-ray crystallography. Analysis of the crystalline sample via ^1H NMR confirmed its identity as $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$. ^1H NMR (400 MHz, benzene- d_6 ; δ/ppm): 166.29, 107.61, 107.13, 55.16, 39.34, 34.09, 12.41, 12.18, 11.89, 8.84, 4.43, -6.07, -12.48, -71.38, -81.52. Difficulty in attaining bulk purity of the compound, due to challenges associated with fractional crystallization of $\text{Fe}(\{\text{NHBn}\}_2\text{-}^{\text{Mes}}\text{PDP}^{\text{Ph}})_2$ away from $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ precluded obtaining a sample suitable for elemental analysis.

Preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$.

To a J. Young NMR tube was added containing 10 mg (0.012 mmols) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and 500 μL of benzene- d_6 , , affording a dark-red solution. In a separate dram vial was added 2 mg (0.012 mmols, 1.0 eq.) of mesityl azide and 100 μL of benzene- d_6 . The resulting azide solution was added to the NMR tube containing the solution of the iron complex, inducing an immediate color change of the solution to dark-brown. A ^1H NMR spectrum was acquired and indicated quantitative conversion of the starting material to a new paramagnetic species assigned as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. ^1H NMR (400 MHz, benzene- d_6 ; δ/ppm): -214.36 (3H, $p\text{-MesCH}_3$), -155.87 (6H, $o\text{-MesCH}_3$), -48.17 (2H, $m\text{-MesCH}$), -6.89 (12H, $o\text{-MesCH}_3$), -5.96 (2H), 2.80 (6H, $p\text{-MesCH}_3$), 3.02 (2H), 3.22 (4H), 11.28 (4H), 13.61 (4H), 21.74 (2H). Note, the 4-pyridine resonance could not be unambiguously assigned. Additionally, resonances for free THF were not observed at 3.57 and 1.40 ppm, respectively, complicating the unambiguous assignment of the ^1H NMR spectrum.

Preparation of Fe(NHMe^s-^{Mes}PDP^{Ph}).

In a 20 mL scintillation vial, 48 mg (0.066 mmol) of (^{Mes}PDP^{Ph})Fe(thf) was dissolved in 5 mL of benzene affording a dark-red solution. In a separate vial, 10 mg of mesityl azide (0.062 mmol) was dissolved in approximately 5 mL of benzene. The azide solution was added to the solution of the iron complex, which induced a gradual darkening of the solution to brown-red. The mixture was allowed to stir for 18 hrs. Solvent was removed *in vacuo* leaving a dark residue. ¹H NMR analysis in benzene-*d*₆ of the crude reaction mixture revealed two paramagnetic species, one of which was identified as (^{Mes}PDP^{Ph})Fe(NMe^s) via comparison to an authentic sample. A crystallization was performed via diffusion of pentane into a concentrated benzene solution of the crude mixture and after 48 hrs. red crystals had formed that were found to be suitable for X-ray crystallography, which identified the additional product as Fe(NHMe^s-^{Mes}PDP^{Ph}).

Preparation of Fe(NH(C(CH₃)₂(CH₂)₃)^{Mes}PDP^{Ph}).

In a 20 mL scintillation vial equipped with a magnetic stirrer was combined 25 mg (0.035 mmols) of (^{Mes}PDP^{Ph})Fe(thf) and approximately 500 μ L of benzene-*d*₆. Vigorous stirring resulted in dissolution of all solids and formation of a dark-red solution. In a separate vial, 8 mg (0.039 mmols, 1.1 eq.) of 4-azido-4-methylpentylbenzene was dissolved in approximately 100 μ L of benzene-*d*₆, yielding a colorless solution. The solution of 4-azido-4-methylpentylbenzene was added dropwise via pipette to the stirring solution of (^{Mes}PDP^{Ph})Fe(thf). No evident color change or evolution of N₂ gas was noted. The mixture was stirred for five minutes and then filtered through a glass microfiber plug into a J. Young NMR tube. After 8 hrs, ¹H NMR analysis indicated complete consumption of the starting material and quantitative formation of Fe(NH(C(CH₃)₂(CH₂)₃)^{Mes}PDP^{Ph}). The solvent was removed *in vacuo*, leaving a dark-red film,

subsequent trituration and washing with pentane which afforded a red powder. The material was taken up in a minimum amount of benzene (1 mL) and filtered through a pipette fitted with a glass microfiber plug into a dram vial. Diffusion of pentane into the benzene solution at ambient temperature afforded ruby colored plates of the title compound suitable for X-ray crystallographic analysis. ^1H NMR (400 MHz, benzene- d_6) δ -92.76, -63.86, -10.93, -8.73, -4.55, -2.38, -1.59, -1.04, -0.46, 1.82, 3.21, 3.33, 3.86, 6.51, 7.77, 7.98, 8.34, 10.44, 11.18, 11.65, 13.72, 14.44, 16.46, 23.28, 97.45, 104.03, 104.94, 107.83, 112.98, 116.60, 202.64.

Physical Measurements.

^1H and ^{13}C { ^1H } NMR spectra were acquired at 25 °C on a Varian Unity INOVA 600 MHz spectrometer equipped with a 5 mm inverse broadband PFG probe, on an Agilent 400 MHz DD2 spectrometer equipped with a 5 mm One NMR probe, or a JNM-ECZ400S/L1 spectrometer equipped with a 5 mm ROYAL NMR probe. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Room temperature magnetic susceptibility measurements were performed with a Johnson Matthey Mark 1 instrument that was calibrated with $\text{HgCo}(\text{SCN})_4$. Zero field ^{57}Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a $^{57}\text{Co}/\text{Rh}$ radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/ N_2 cryostat within an accuracy of ± 0.3 K. The data were calibrated relative to α -iron at 298 K. The fitting procedure to extract quantitative spectral parameters uses a least-squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)⁷⁷ was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.⁷⁸

Density Functional Theory Calculations.

All DFT calculations were performed with the ORCA program package.⁷⁹ Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.⁸⁰⁻⁸² The all-electron Gaussian basis sets were those developed by the Ahlrichs group.⁸³⁻⁸⁵ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center

were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SVP basis sets were used that were of double- ζ quality in the valence region and contained a polarizing set of d functions on the nonhydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)⁸⁶⁻⁸⁸ approach were chosen to match the orbital basis.⁸⁹⁻⁹¹ Throughout this chapter computational results are described by using the broken-symmetry (BS) approach by Ginsberg⁹² and Noodleman.⁹³ Because several broken symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation BS(m,n) has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. All molecular orbital and spin density plots were generated using the program Gabedit.⁹⁴ Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.⁹⁵ Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{64,96}

Accession Codes

CCDC entries 1918285–1918288 contain the supplementary crystallographic data for some of the compounds described in this chapter.

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Reactivity of Pyridine Dipyrrolide Iron(II) Complexes with Organic Azides: C-H Amination and Iron Tetrazene Formation

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CHAPTER IV: SYNTHESIS AND CHARACTERIZATION OF HIGH-SPIN IRON(II) COMPLEXES OF VARIOUS PYRIDINE DIPYRROLIDE LIGANDS

4.1 Abstract

A family of high-spin Fe^{II} complexes carrying the new pyridine dipyrrolide ligands $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$, $\text{H}_2^{4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$ was synthesized and structurally characterized. For $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, it was discovered that four-coordinate $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ or five-coordinate complexes $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$, and $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ could be isolated depending on the identity of the exogenous Lewis base employed during synthesis. $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ was found to undergo loss of the diethyl ether ligand in non-coordinating solvent, forming the dimeric species $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^{\text{tBu}}\text{PDP}^{\text{Ph}})_2$, as evidenced ^1H NMR and Mössbauer spectroscopies. For $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}}\text{PDP}^{\text{Ph}}$, the four coordinate thf adducts $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ were synthesized. $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was found to exhibit an equilibrium between four- and five-coordinate species in solution, which was supported by ^1H NMR and ^{57}Fe Mössbauer spectroscopy. For $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$, the five coordinate bis-pyridine adducts $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and $(\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ have been also been synthesized.

4.2 Introduction

The manipulation of the coordination environments available to high-spin Fe^{II} PDP complexes has been demonstrated to have a profound impact upon the electronic structure of the resulting complexes.¹⁻³ Recently, our group has reported a convenient synthetic procedure that allows access to pyridine dipyrrolide ligands with various substitution patterns at the 3- and 5-pyrrolide positions as well as at the 4-pyridine position via tandem Stetter and Paul-Knorr reactions.⁴⁻⁶ The development of this protocol has allowed for the development of a library of PDP ligands which may find utility in systematically modifying the steric and electronic properties of the resulting iron complexes for desired applications. In the context of nitrene group transfer, it has been previously demonstrated that high-spin Fe^{II} PDP complexes are capable of decomposing organic azides to forming iron imido/iminyl complexes.^{3,7} The Mindiola and Caulton groups have shown that when a bulky tert-butyl substituent is present at the 5-position of the PDP pyrrolide rings unusual cis-divacant octahedral iron complexes can be isolated, including a diamagnetic Fe^{IV} imido complex.^{2,3,8} Surprisingly, this genuine Fe^{IV} complex is unreactive towards C-H bonds, possibly due to a lack of destabilization of the iron imido nitrogen bond.⁹ Alternatively, as demonstrated in Chapter 3, experimental and computational evidence demonstrates that when the 5-position of the PDP pyrrolides is a mesityl group, planar imido complexes best described as intermediate spin Fe^{III} ions antiferromagnetically coupled to iminyl radicals are formed.^{7,10} These complexes are highly reactive and facilitate intramolecular C-H amination of benzylic C-H bonds present on the mesityl group of the PDP ligand. (^{Mes}PDP^{Ph})Fe(NR) intermediates have also been shown to undergo tetrazene formation when the nitrene source is not sufficiently bulky, or alpha hydrogen atom abstraction, when hydrogen atoms are available in the position alpha to the intermediate

nitrene. In consideration of the susceptibility for the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ supporting ligand to undergo facile C-H amination, even when other benzylic C-H bonds are present in the substrate, PDP ligands featuring more robust arene substitution were envisioned. It was anticipated that such ligands may be suitable for imparting stability onto ($^{\text{Ar}}\text{PDP}^{\text{Ph}}$)Fe(NR) complexes and render them suitable for study and potential use as intermolecular group transfer reagents. Herein is described the synthesis and spectroscopic characterization of a new family of high-spin ferrous PDP complexes featuring robust substitution patterns at the 5-position of the pyrrole heterocycles, including $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, $\text{H}_2^{2,6\text{-ClPh}}\text{PDP}^{\text{Ph}}$, $\text{H}_2^{4\text{-MeO}^{2,6\text{Cl}_2\text{Ph}}}\text{PDP}^{\text{Ph}}$, and $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$.

4.3 Synthesis and Characterization of ($^{\text{tBu}}\text{PDP}^{\text{Ph}}$) High-Spin Fe^{II} Complexes

Due to unusual physical characteristics of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(L) (where L = OEt_2 or THF), and ($^{\text{tBu}}\text{PDP}^{\text{tBu}}$)Fe(OEt_2),^{1,3} (i.e., coordination environment and electronic structure), the synthesis of other high-spin Fe^{II} PDP iron complexes was pursued. The synthesis of the new PDP ligand $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, an analogue to previously described $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{tBu}}$, was accomplished on a multigram scale via a tandem Stetter and Paul-Knorr reactions (Scheme 4.1) in 65 % yield.^{1,4,5}

Scheme 4.1. Synthesis of pyridine dipyrrolide ligands via tandem Stetter and Knorr reactions.

Figure 4.1. Pyridine dipyrrolide ligands used in this study.

In consideration of the diverse coordination chemistry of the previously described $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})_n$ species, metalation of the new ligand precursors was explored via a variety of conditions. For $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, treatment of a diethyl ether solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ with a slurry of the ligand in the same solvent induced an immediate color change to red orange accompanied by precipitation of an orange solid. Following isolation by filtration, analysis of the resulting solid in benzene- d_6 solution via ^1H NMR spectroscopy indicated a C_{2v} symmetric major product with nine paramagnetically shifted and broadened resonances. Integrations relative to the 4-pyridine proton (25.87 ppm) and tert-butyl protons (33.52 ppm) were consistent with a product assignment as a diethyl ether adduct, $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$. The minor species, also paramagnetic in nature, was noted to have apparent C_{2v} symmetry based on a total of seven observed resonances. Relative integrations of the tert-butyl methyl protons (30.86 ppm) and the 4-pyridine proton (-0.91 ppm) along with the absence of resonances attributed to a diethyl ether ligand

suggested an initial product assignment as a three-coordinate pyridine dipyrrolide iron complex, $\text{Fe}(\text{tBuPDP}^{\text{Ph}})$ (Figure 4.1).

Crystallization of the crude orange solid from a concentrated diethyl ether solution at -35°C afforded a single crystal suitable for analysis via X-ray crystallography. The structural analysis confirmed the identity of the major species present in the ^1H NMR spectrum as the mono-diethyl ether adduct, $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (Figure 4.2). $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ was found to crystallize in the orthorhombic unit cell $\text{Pca}2_1$ in a *cis*-divacant octahedral geometry, consistent with the closely related analogue $(\text{tBuPDP}^{\text{tBu}})\text{Fe}(\text{OEt}_2)$, recently reported by Caulton et al.³ Relatively long bond lengths of 2.020(2), 2.031(2), 2.020(2), and 2.105(2) Å from the iron center to N1, N2, N3, and O1, are consistent with a high-spin ferrous state. The presence of an $S = 2$ iron center was confirmed via a room-temperature magnetic moment of $5.1 \mu_{\text{B}}$. In order to further probe the two species that were present in the crude benzene- d_6 ^1H NMR spectrum, a zero-field Mössbauer spectrum was acquired of a powder sample obtained from the crude reaction mixture. Surprisingly, the Mössbauer spectrum indicated the presence of only a single quadrupole doublet with parameters $\delta = 0.91 \text{ mms}^{-1}$ and $|\Delta E_{\text{Q}}| 1.25 \text{ mms}^{-1}$, in good agreement with $\delta = 0.86 \text{ mms}^{-1}$ and $|\Delta E_{\text{Q}}| 1.21 \text{ mms}^{-1}$ measured for $(\text{tBuPDP}^{\text{tBu}})\text{Fe}(\text{OEt}_2)$ and confirming the high-spin Fe^{II} ground state of $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$.³ Intrigued by the observation of only a single quadrupole doublet, a benzene- d_6 solution of the crude orange material obtained from the reaction of $\text{H}_2\text{tBuPDP}^{\text{Ph}}$ and $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ was monitored via ^1H NMR spectroscopy over time. Interestingly, the ratio of the two species slowly changed over a period of hours, with the concentration of $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ diminishing over time cleanly to the species tentatively assigned as the three-coordinate $\text{Fe}(\text{tBuPDP}^{\text{Ph}})$ complex. In an attempt to drive the observed reaction to completion, samples of the crude orange material were suspended in pentane and

vigorously stirred. A color change of the suspension from orange to dark-red/brown was observed within minutes. The resulting suspension was reduced to dryness and extracted into benzene. Filtration through celite and subsequent removal of the solvent *in vacuo* afforded a dark-red/brown powder. Analysis of the resulting material via ^1H NMR in benzene- d_6 revealed the presence of only the species assigned as $\text{Fe}(\text{tBuPDP}^{\text{Ph}})$, suggesting lability and loss of the diethyl ether ligand of $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ upon dissolution in hydrocarbon solvent.

A single crystal of this material grown from diffusion of pentane into a concentrated benzene solution allowed for unambiguous assignment of the identity of the compound via X-ray crystallography. Surprisingly, the identity of the crystalline material was found to be the helical dimeric species $\text{Fe}_2(\mu_2-\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$, and not the anticipated three coordinate complex $\text{Fe}(\text{tBuPDP}^{\text{Ph}})$. The formation of $\text{Fe}_2(\mu_2-\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$ demonstrates loss of a diethyl ether ligand from two $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ complexes and subsequent reorganization of the PDP ligand coordination motif to form the observed structure. Furthermore, the resulting migration of one arm pyrrolide arm of a PDP ligand to a second iron center suggests that loss of a diethyl ether ligand induces iron pyrrolide nitrogen bond breaking and bond forming events. Unfortunately, due to the weak diffraction of the sample, only atomic connectivity of the molecule was established, precluding meaningful discussion of the structural metrics. The synthesis and X-ray structures of $(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $\text{Fe}_2(\mu_2-\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$ (preliminary) are presented in Scheme 4.2 and Figure 4.2.

Mixture of $(t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ & $\text{Fe}_2(\mu_2-\kappa^2-t\text{BuPDP}^{\text{Ph}})_2$

Figure 4.2. ^1H NMR spectra of the mixture of $(t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $\text{Fe}_2(\mu_2-\kappa^2-t\text{BuPDP}^{\text{Ph}})_2$ (top) and isolated $\text{Fe}_2(\mu_2-\kappa^2-t\text{BuPDP}^{\text{Ph}})_2$ (bottom) at 400 MHz in benzene- d_6 . The unmarked resonances correspond to pentane present in the samples.

Scheme 4.2. Synthesis of $(^t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $\text{Fe}_2(\mu_2-\kappa^2-^t\text{BuPDP}^{\text{Ph}})_2$.

Figure 4.3. ORTEP of $(^t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (left) and $\text{Fe}_2(\mu_2-\kappa^2-^t\text{BuPDP}^{\text{Ph}})_2$ (right) at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent are omitted for clarity. For $\text{Fe}_2(\mu_2-\kappa^2-^t\text{BuPDP}^{\text{Ph}})_2$ only the quaternary carbons of the tert-butyl substituents are depicted.

In lieu of a high-resolution X-ray crystal structure of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$, a zero-field Mössbauer spectrum was acquired at 80 K to interrogate the electronic structure(s) and potential electronic communication between the two iron centers. The resulting spectrum (Figure 4.3) features a single quadrupole doublet with $\delta = 0.82 \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.68 \text{ mms}^{-1}$, unambiguous evidence of both iron centers adopting a high-spin ferrous configuration. It should be noted that the observed doublet possesses asymmetry, with linewidths of $\Gamma_L = 0.44 \text{ mms}^{-1}$ and $\Gamma_R = 0.38 \text{ mms}^{-1}$, respectively. This observation hints that in the solid state slightly different coordination environments may exist for each iron center, resulting in similar but non identical spectra.

Previously, the Mindiola group has described the synthesis and characterization of a similar helical, dimeric high-spin Fe^{II} PDP complex, $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{tBu}})_2$.¹¹ The ^1H NMR spectrum of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{tBu}})_2$ is also in good agreement with $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$ which displays five paramagnetically shifted resonances spanning a range of 0.50 to 82.5 ppm in benzene- d_6 solution. The apparent C_{2v} symmetry is ascribed to fluxional behavior of the complex in solution at room-temperature. The solid-state zero field Mössbauer parameters of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{tBu}})_2$, $\delta = 0.80(1) \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.76(1) \text{ mms}^{-1}$, are essentially identical to those of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$.

Figure 4.4. Zero-field ^{57}Fe Mössbauer spectra of $(^t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (left) and $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^{\text{Ph}})_2$ (right) recorded at 80 K.

Investigations of the magnetic behavior of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^t\text{Bu})_2$ were performed via the Evans method, revealing μ_{eff} value of $6.9 \mu_{\text{B}}$ at room temperature in benzene- d_6 . A complementary SQUID magnetization measurement spanning a temperature range of 20-300 K revealed a temperature dependence to the magnetic moment of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^t\text{Bu})_2$, as demonstrated by an increase in μ_{eff} from 3.02 to $7.50 \mu_{\text{B}}$ over the measured conditions.¹¹ Similarly, the room temperature magnetic moment $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^{\text{Ph}})_2$ was found to be $7.0 \mu_{\text{B}}$, consistent with weak coupling between two independent high-spin Fe^{II} centers, as demonstrated by agreement with the high temperature spin-only value of $6.9 \mu_{\text{B}}$ for two uncoupled $S = 2$ spin systems. This was further verified via a density functional theory study. A BS(4,4) calculation performed at the B3LYP level converged to an optimized structure featuring two antiferromagnetically coupled $S = 2$ iron centers. This was evidenced via analysis of the

Mulliken spin populations of the iron atoms, with spin-density values of -3.78 and 3.78, respectively (Figure 4.4). The energy difference between the high-spin state and broken symmetry solution was calculated to be 120.439 cm⁻¹ and the exchange coupling constant, J , was calculated to be -7.53 cm⁻¹. These values were obtained using the following Hamiltonian (top) and formula (bottom), where E_{BS} is the energy of the low-spin solution, E_{HS} is the energy of the high-spin solution, and S_{max}^2 is the total spin of the high-spin state.^{12,13}

$$H = -2J\vec{S}_{Fe1} \cdot \vec{S}_{Fe2}$$

$$J = -\frac{E_{HS} - E_{BS}}{S_{max}^2}$$

Previously, the Betley group has reported a similar diiron dimer within the context of a pyrrole based dipyrromethene ligand environment.¹⁴ This complex, [(^tBuL)FeCl]₂ (^tBuL = 1,9-di-*tert*-butyl-5-(2,6-dichlorophenyl)dipyrromethene), which is best described as featuring two antiferromagnetically coupled high-spin Fe^{II} centers is characterized by Mössbauer parameters of $\delta = 0.94$ mms⁻¹ and $\Delta E_Q = 1.96$ mms⁻¹ and magnetic moment of 7.2 μ_B determined via SQUID magnetometry at 295 K, in good agreement with experimentally determined magnetic susceptibilities of Fe₂(μ_2 - κ^2 -^tBuPDP^{tBu})₂ and Fe₂(μ_2 - κ^2 -^tBuPDP^{Ph})₂. A very similar coupling constant of $J = -6.92$ cm⁻¹ was calculated for this complex via a BS(4,4) calculation using the same functional and the ORCA program suite and is in good agreement with the experimentally determined value of -1.95 cm⁻¹. Furthermore, Mössbauer parameters obtained from the same BS(4,4) calculation computed identical isomer shifts of 0.69 mms⁻¹ for both iron centers in Fe₂(μ_2 - κ^2 -^tBuPDP^{Ph})₂. However, different quadrupole splittings for the two iron nuclei, -1.62 mms⁻¹ and -1.71 mms⁻¹, were computed, which may explain the origin of the broadness and asymmetry present in the experimentally determined Mössbauer spectra of Fe₂(μ_2 - κ^2 -^tBuPDP^{Ph})₂.

Figure 4.5. Spin-density plot obtained from Mulliken population analysis of BS(4,4) calculation of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$.

Due to the lability of the diethyl ether ligand in solution for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, exploration of metalation protocols in the presence of stronger Lewis bases was also studied to gain more insight into the coordination chemistry of the $(^{\text{tBu}}\text{PDP}^{\text{Ph}})^{2-}$ ligand. The reaction of a THF solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$ in the same solvent was found to immediately afford a red homogenous mixture. The ^1H NMR spectrum of the crude product in benzene- d_6 suggested clean and quantitative conversion to the corresponding thf adduct, as evidenced by nine paramagnetically shifted and broadened resonances spanning a chemical shift range of 110.80 to 1.87 ppm. In totality, integration of the diagnostic tert-butyl methyl groups signal (36.27 ppm, 18H) and the 4-pyridine proton (26.82 ppm, 1H) were consistent with a preliminary product assignment as the five-coordinate bis-THF adduct, $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$. The presence of the 4-pyridine proton at 26.82 ppm is consistent with the chemical shift values for the related five-coordinate PDP high-spin Fe^{II} complexes, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, which

were found to have 4-pyridine proton resonances at 20.32 and 21.54 ppm in THF-*d*₈ and benzene-*d*₆, respectively. Importantly, monitoring benzene-*d*₆ solutions of (^tBuPDP^{Ph})Fe(thf)₂ via ¹H NMR demonstrated no irreversible solvent ligand lability, as no resonances consistent with the formation of Fe₂(μ₂-κ₂-^tBuPDP^{Ph})₂ and free THF were observed. Recrystallization of the crude product from a concentrated THF solution layered with pentane at -35°C afforded large red blocks suitable for analysis via X-ray crystallography. The X-ray analysis confirmed the identity of the product as the pentacoordinate bis-THF adduct (Figure 4.5). The structural metrics are consistent with previously characterized high-spin Fe^{II} PDP complexes and are summarized in Table 4.1. Within the context of the previously reported (^tBuPDP^tBu) ligand, a high-spin Fe^{II} THF adduct was reported via treatment of (^tBuPDP^tBu)Fe(OEt₂) with THF or alternatively via a deprotonation and metalation procedure from H₂^tBuPDP^tBu and FeCl₂ in THF solvent. The product of these reactions was assigned as a mono-THF adduct, based upon ¹H NMR analysis.³

Figure 4.6. ORTEPs of (^tBuPDP^{Ph})Fe(thf)₂ (left) and (^tBuPDP^{Ph})Fe(py)₂ (right) at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent are omitted for clarity.

In consideration of the unprecedented coordination geometry of (^tBuPDP^{Ph})Fe(thf)₂ for high-spin ferrous PDP complexes, a zero-field Mössbauer spectrum was acquired at 80 K. The

resulting single quadrupole doublet featured $\delta = 1.07 \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.42 \text{ mms}^{-1}$. The high isomer shift value is consistent with a high-spin Fe^{II} center and is in good agreement with that of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ which features $\delta = 1.09 \text{ mms}^{-1}$.¹ The large deviation in the quadrupole splitting in $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (1.42 mms^{-1}) relative to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (2.76 mms^{-1}) is consistent with the markedly different coordination geometries for the two complexes with *trans*- and *cis*-coordinating THF ligands, respectively. This is reflected in the DFT calculated asymmetry parameter of the electric field gradient, η , which is 0.56 for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and 0.89 for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$. The isomer shift is also noticeably lower than the four-coordinate *cis*-divacant octahedral diethyl ether adducts of $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{OEt}_2)$ ($0.86(1) \text{ mms}^{-1}$).³

A final metalation protocol of $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$ was explored with the iron dialkyl reagent $\text{Fe}(\text{Ns})_2(\text{py})_2$, as previously demonstrated for $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$.¹ Accordingly, treatment of a solution of $\text{Fe}(\text{Ns})_2(\text{py})_2$ in a mixture of pentane and toluene with a toluene solution of $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$ resulted in a gradual color change from purple to red. Upon removal of volatiles, ^1H NMR analysis of the crude mixture evidenced clean and quantitative conversion to a C_{2v} symmetric product, as evidenced by 10 paramagnetically shifted and broadened resonances spanning a chemical shift range of 4.43 to 104.00 ppm. Relative integrations compared to the 4-pyridine proton (30.33 ppm) were consistent with assignment of the product as the bis-pyridine adduct, $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$. Furthermore, the appearance of the 4-pyridine resonance downfield from its diamagnetic reference value is consistent with previously characterized five-coordinate high-spin ferrous PDP complexes.¹

Recrystallization of the crude product via diffusion of pentane into a concentrated toluene solution afforded orange single crystals suitable for X-ray crystallography. The structural

analysis identified the sample as a penta-coordinate bis-pyridine adduct, $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, which adopts a geometry analogous to that observed for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ in the solid-state with trans apical pyridine ligands (Figure 4.5). The Mössbauer parameters of a solid sample of $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ were found to be $\delta = 1.02 \text{ mms}^{-1}$ and $|\Delta E_{\text{Q}}| = 1.94 \text{ mms}^{-1}$ in good agreement for the five-coordinate analogue $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$. The difference in the quadrupole splitting values between the $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ is not entirely clear at this time and is tentatively ascribed to solid-state effects, as the coordination environments of the two compounds and iron THF-oxygen and pyridine-nitrogen bonds are very similar ($\sim 2.25 \text{ \AA}$). In all, the characterization data suggests that the substitution of the stronger Lewis basic ligand pyridine for THF imparts no significant perturbation on the electronic structure of the resulting compound, and the high-spin ferrous state is retained. The Mössbauer spectra for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ are depicted in Figure 4.6 and a complete summary of available Mössbauer parameters for all $(^{\text{tBu}}\text{PDP}^{\text{Ph}})$ and $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}^{\text{II}}$ iron complexes is provided in Table 4.13. Solid-state magnetic susceptibility values of 5.1 and $5.4 \mu_{\text{B}}$ (magnetic susceptibility balance) at room temperature for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ and $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, respectively, are in agreement with high-spin Fe^{II} formulations for the central metal ions, as inferred from X-ray crystallography and Mössbauer spectroscopy.

Figure 4.7. Zero-field ^{57}Fe Mössbauer spectra of $(^t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (left) and $(^t\text{BuPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ (right) recorded at 80 K.

Table 4.1. Selected bond lengths (Å) and angles (deg) for (^tBuPDP^{Ph})Fe(OEt₂), (^tBuPDP^{Ph})Fe(thf)₂, and (^tBuPDP^{Ph})Fe(py)₂.

	(^t BuPDP ^{Ph})Fe(OEt ₂)	(^t BuPDP ^{Ph})Fe(thf) ₂	(^t BuPDP ^{Ph})Fe(py) ₂
Fe(1)–N(1)	2.020(2)	2.0609(8)	2.0937(15)
Fe(1)–N(2)	2.031(2)	2.0628(8)	2.0624(15)
Fe(1)–N(3)	2.020(2)	2.0611(8)	2.0825(15)
Fe(1)–N(4)	-	-	2.2561(15)
Fe(1)–N(5)	-	-	2.2491(15)
Fe(1)–O(1)	2.105(2)	2.2478(7)	-
Fe(1)–O(2)	-	2.2897(7)	-
N(1)–Fe(1)–N(2)	79.23(9)	79.07(3)	78.50(6)
N(1)–Fe(1)–N(3)	146.55(8)	157.26(3)	156.60(6)
N(2)–Fe(1)–N(3)	79.38(9)	78.31(3)	78.13(6)
N(2)–Fe(1)–O(1)	107.31(8)	100.01(3)	-
N(2)–Fe(1)–O(2)	-	95.76(3)	-
N(2)–Fe(1)–N(4)	-	-	92.48(6)
N(2)–Fe(1)–N(5)	-	-	100.57(6)

4.4 Synthesis and Characterization of (ArPDP^{Ph}) High-Spin Fe^{II} Complexes

With the disparate geometric and electronic structures observed for (^tBuPDP^R) complexes relative to (^{Mes}PDP^{Ph}) high-spin Fe^{II} complexes, the iron coordination chemistry of other aryl substituted PDP ligands was explored. The synthesis of the new PDP ligand H₂^{C₆F₅}PDP^{Ph} was accomplished in a 64% yield in a two-step one pot reaction sequence akin to previously described PDP ligands synthesized in our group. H₂^{2,6-Cl₂Ph}PDP^{Ph} was also synthesized in a similar manner from 2,6-pyridinecarboxaldehyde and the corresponding chalcone, 1-(2,6-dichlorophenyl)-3-phenyl-2-propen-1-one.^{1,4} However, Paul-Knorr cyclization of the intermediate diketone in ethanol which has been successful for the synthesis of a variety of

$\text{H}_2^{\text{R}}\text{PDP}^{\text{R}}$ ligands did not proceed. This is likely due to poor solubility of the intermediate diketone in this solvent. Solvent screening found that glacial acetic acid afforded the desired $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ in a moderate yield of 67% (50% over the two steps). The corresponding 4-methoxy pyridine analogue $\text{H}_24\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ was also synthesized, yielding the corresponding diketone in 62% from 4-methoxy-2,6-pyridinecarboxaldehyde and 1-(2,6-dichlorophenyl)-3-phenyl-2-propen-1-one under analogous Stetter conditions. Treatment of the diketone with an excess of NH_4OAc in refluxing glacial acetic acid afforded $\text{H}_24\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ in 43% yield (unoptimized). X-ray structures of both $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_24\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ were determined at 100 K and an ORTEP of each is depicted in Figures 4.7 and 4.8. The structure of $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ is monomeric and features hydrogen bonding interactions to a dimethylsulfoxide solvent molecule. In contrast, $\text{H}_24\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$, which was crystallized from dichloromethane solvent, is characterized by a dimeric structure. This is due to the absence of a solvent molecule in the crystal lattice capable of participating in hydrogen bonding with the pyrrole protons.

Figure 4.8. ORTEP of $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ excluding DMSO solvent (left) and $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ (right) depicting the hydrogen bonding interaction between the pyrrole hydrogens and DMSO oxygen atom. Both structures displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of pyrrole hydrogens) are excluded for clarity.

Figure 4.9. ORTEP of the hydrogen bonded dimer $[\text{H}_{24}\text{-MeO}^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}}}]_2$ (left) and $\text{H}_{24}\text{-MeO}^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}}}$ (right) displayed at 30% probability ellipsoids. Co-crystallized solvent molecules and hydrogen atoms (with exception of pyrrole hydrogens) are removed for clarity.

Metalation of $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ was first explored via treatment of $\text{Fe}(\text{Ns})_2(\text{py})_2$ with the corresponding ligand in toluene solvent (Scheme 4.3). In each case, precipitation of the corresponding iron bis-pyridine compounds, $(^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, was observed and the compounds were isolated in high purity via filtration followed by washing with pentane in yields of 88 and 56%, respectively.

Scheme 4.3. Synthesis of $(^{\text{R}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ complexes. $\text{R} = ^t\text{Bu}$, C_6F_5 , or $2,6\text{-Cl}_2\text{Ph}$.

In benzene- d_6 solution, $(^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ show nine and eleven paramagnetically shifted resonances, respectively, consistent with the anticipated number

of resonances for a C_{2v} symmetric ($^R\text{PDP}^R$)Fe(py)₂ environment in solution. ^{19}F NMR analysis of ($^{C6F5}\text{PDP}^{\text{Ph}}$)Fe(py)₂ demonstrated 3 paramagnetically broadened resonances in relative 1:2:2 ratio, consistent with the symmetry observed in the ^1H NMR measurement for this complex. A single crystal of ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ was grown via slow evaporation of a concentrated dichloromethane solution of the compound and allowed for confirmation of its structure via X-ray crystallography. An ORTEP of the complex is shown in Figure 4.9. The structure of ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ in the solid state is C_s symmetric, very similar to ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(py)₂, existing in a square pyramidal geometry about the iron center. Presumably, as with ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(py)₂, dynamic movement of the pyridine ligands of ($^{C6F5}\text{PDP}^{\text{Ph}}$)Fe(py)₂ and ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ above and below the plane of the PDP pincer renders the two ligands equivalent on the ^1H NMR time scale, hence the observed C_{2v} symmetric spectrum.

Figure 4.10. ORTEP of ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent are omitted for clarity. Only the *ipso* carbon of one 2,6-dichlorophenyl pyrrole substituent is depicted.

Zero-field Mössbauer spectra acquired on powder samples of ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ (Figure 4.13) and ($^{C6F5}\text{PDP}^{\text{Ph}}$)Fe(py)₂ (Figure 4.10) at 80 K were fit satisfactorily with parameters $\delta = 0.99 \text{ mms}^{-1}$ and $|\Delta E_Q| = 3.12 \text{ mms}^{-1}$ for ($^{2,6-\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(py)₂ and $\delta = 1.08 \text{ mms}^{-1}$ and $|\Delta E_Q| = 2.91 \text{ mms}^{-1}$ for ($^{C6F5}\text{PDP}^{\text{Ph}}$)Fe(py)₂. These values are nearly identical to the Mössbauer

parameters of $\delta = 0.98 \text{ mms}^{-1}$ and $|\Delta E_Q| = 2.92 \text{ mms}^{-1}$ determined for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ measured under the same conditions.

Figure 4.11. Zero-field ^{57}Fe Mössbauer spectrum of $(^{\text{C6F5}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ recorded at 80 K.

The metalation of $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ was performed by treatment of FeCl_2 with the deprotonated ligand (Scheme 4.4). To stirring solutions of either $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ in THF solvent was added a solution of LiHMDS in the same solvent, resulting in a rapid color change of the solution from colorless to a luminescent yellow. Addition of the solution of the *in situ* generated doubly deprotonated ligand to a THF suspension of FeCl_2 resulted in an immediate color change to red-orange. After stirring overnight, the resulting solution was concentrated *in vacuo* and pentane was added, inducing precipitation of an orange microcrystalline solid. Filtration, subsequent extraction of the material into dichloromethane solvent, and filtration through a pad of celite afforded a dark-red solution. The resulting filtrate was concentrated and triturated multiple times, affording

(^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) and (4-MeO^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) as bright orange powders in 74 and 77% yields, respectively.

Scheme 4.4. Synthesis of (R^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) complexes. R = H or OMe.

Red single crystals of both complexes could be obtained from diffusion of pentane into concentrated benzene solutions at room temperature. Interestingly, in a departure from (^{Mes}PDP^{Ph})Fe(thf), (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) and (4-MeO^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) both feature geometries that are not pseudo-square planar. The presence of the *ortho* chloride substitution patterns on the arene ring results in an iron-chloride (Fe(1)-Cl(2)) interaction in the solid state, with the experimentally determined Fe...Cl interatomic distances being 2.7161(5) and 2.6853(6) Å for (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) and (4-MeO^{2,6}-Cl₂PhPDP^{Ph})Fe(thf), respectively. ORTEP depictions of each compound are depicted in Figure 4.11, demonstrating their solid-state structures as determined by X-ray crystallography. The solid-state C₁ symmetric structures are in disagreement with the solution phase ¹H NMR spectrum, which evidences C_{2v} symmetry. For a discrete C₁ structures, 19 resonances would be expected for (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) and (4-MeO^{2,6}-Cl₂PhPDP^{Ph})Fe(thf), assuming free rotation of the PDP pyrrolide 3-phenyl substituents and iron bound THF ligands. Presumably, the weak interaction between the iron and chlorides of the 2,6-dichlorophenyl substituents of the PDP ligand is dynamic in solution, and the THF ligand is on average planar, resulting in the observed C_{2v} symmetric spectrum. Due to their similarities

only the structural metrics of ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf) will be described in further detail. A more complete description of both the structural features of ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf) and ($^{4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}}$)Fe(thf) can be found in Table 4.2. In ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf), the THF ligand is bent below the plane established by the PDP pincer. The Fe-O1 bond to the THF oxygen is 2.0555(13) Å, the Fe-N1 and N3 bonds to the pyrrolide nitrogens are 2.0732(15) and 2.0599(14) Å, and the Fe1-N2 bond to the pyridine nitrogen is 2.0749(14) Å. These values are in good agreement with the observed structure of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(thf) and are consistent with other high-spin Fe^{II} PDP complexes.^{1,3} Notably, however, is one structural discrepancy in the ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf), the N2-Fe1-O1 bond angle is bent at 135.32(6)°, whereas in ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(thf) the same bond angle is much closer to planarity, measured at 152.99(5)°.¹

Figure 4.12. ORTEP of ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf) (left) and ($^{4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}}$)Fe(thf) (right) at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

In light of the observation of the chloride substituents perturbing the coordination environment about iron, both ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(thf) and ($^{4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}}$)Fe(thf) were analyzed by zero-field ^{57}Fe Mössbauer spectroscopy to assess their electronic structures relative to previously prepared high-spin Fe^{II} PDP complexes. The observed quadrupole doublets were

each fitted as one component spectra with identical isomer shifts, $\delta = 0.96 \text{ mms}^{-1}$, and $|\Delta E_Q| = 1.43 \text{ mms}^{-1}$ and 2.00 mms^{-1} , confirming the high-spin ferrous formulation of the iron centers (Figure 4.12). The DFT computed values for both compounds were found to be $\delta = 0.81 \text{ mms}^{-1}$ and $\Delta E_Q = 2.00 \text{ mms}^{-1}$, and are in good agreement with the experimental data. However, it should be noted that the discrepancy between the computed and experimental quadrupole splitting values of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ are not clear at this time. The quadrupole splitting is known to be sensitive to subtle changes in the coordination environment, and thus, the deviation between the experimental values in the two complexes is tentatively attributed to solid-state packing effects. Consequently, the iron-chloride interactions observed in the solid state structures of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(4\text{-MeO}^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ may be the primary reason for the significant increase in their quadrupole splitting values relatives to those obtained from the corresponding Mössbauer spectra of the four-coordinate square planar complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$.¹

Figure 4.13. Zero-field ^{57}Fe Mössbauer spectra of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(4\text{-MeO}^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ recorded at 80 K.

Dissolution of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in $\text{THF-}d_8$ and acquisition of an ^1H NMR spectrum demonstrated significant shifts in the chemical shifts of the observed resonances (Figure 4.13). For $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ the 4-pyridine proton resonances was identified at 22.14 ppm in $\text{THF-}d_8$, while in $\text{benzene-}d_6$ the 4-pyridine proton resonance for $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was observed at 0.36 ppm, consistent with five and four coordinate high-spin Fe^{II} PDP complexes, respectively.¹ Note that for $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ resonances corresponding to the THF protons were not observed due to rapid equilibrium with $\text{THF-}d_8$. For $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ the resonances at 106.58 and 98.12 ppm are assigned to the 3-pyridine and 4-pyrrole protons, respectively. Alternatively, for $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$, the resonances at 85.40 and 65.88 ppm are assigned as the 3-pyridine and 4-pyrrole protons. The shift in the frequency of the resonances corresponding to the 4-pyridine, 3-pyridine, and 4-pyrrole protons is due to changes in the

amount of spin density imparted on the respective nuclei. Our group has previously demonstrated that the origin of this subtle phenomena is a change in the ground-state electronic structure between four and five coordinate high-spin Fe^{II} PDP complexes.¹

Figure 4.14. Comparison of the ¹H NMR spectra of (2,6-Cl₂Ph)PDP^{Ph})Fe(thf)₂ in THF-*d*₈ (top) and (2,6-Cl₂Ph)PDP^{Ph})Fe(thf) in benzene-*d*₆ (bottom). Note, in the top spectrum the unmarked resonances correspond to THF while in the bottom spectrum the unmarked resonances are DCM and toluene present in the sample.

To further validate the existence of discrete four- and five-coordinate thf adducts, a powder sample of (2,6-Cl₂Ph)PDP^{Ph})Fe(thf) was dissolved in THF and a zero-field Mössbauer spectrum was acquired. The resulting spectrum contained a single quadrupole doublet which was satisfactorily fit with $\delta = 1.20 \text{ mms}^{-1}$ and $|\Delta E_Q| = 3.02 \text{ mms}^{-1}$. Note that these values are markedly

different that the solid-state Mössbauer parameters of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and are in good agreement with the previously reported values for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$.¹ Furthermore, these values are in excellent agreement with the Mössbauer parameters of five-coordinate $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, which further evidences this assignment. Both spectra are depicted in Figure 4.14.

Figure 4.15. Zero-field ^{57}Fe Mössbauer spectra of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ (left, in frozen THF solution) and $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ (right) recorded at 80 K.

A preliminary X-ray structure of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ was obtained allowing for assignment of the atom connectivity and confirmation of the identity of the species. Akin to $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$, $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ was found to adopt a square pyramidal geometry in the solid state. The addition of the second solvent ligand further congests the coordination sphere and interrupts the interaction between an *ortho*-phenyl chloride substituent(s) and the iron center that was observed in the four-coordinate THF analogue. This consistent with the apparent

C_{2v} symmetry observed in the ^1H NMR spectrum of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$. An ORTEP of the preliminary X-ray structure of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ is presented in Figure 4.15.

Table 4.2. Selected bond lengths (Å) and angles (deg) for $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, $(4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$. Note, the apical pyridine in $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ is disordered over two positions. Only metrics for one pyridine ring position are disclosed.

	$(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	$(4\text{-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	$(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$
Fe(1)–N(1)	2.0732(15)	2.0695(16)	2.072(3)
Fe(1)–N(2)	2.0749(14)	2.0735(16)	2.073(3)
Fe(1)–N(3)	2.0599(14)	2.0553(16)	2.077(3)
Fe(1)–N(4)	-	-	2.118(4)
Fe(1)–N(5)	-	-	2.112(3)
Fe(1)–O(1)	2.0555(13)	2.0477(14)	-
Fe(1)–Cl(1)	2.7161(5)	2.6853(6)	-
N(1)–Fe(1)–N(2)	77.03(6)	76.51(6)	76.26(13)
N(1)–Fe(1)–N(3)	154.40(6)	153.82(6)	146.10(13)
N(2)–Fe(1)–N(3)	77.50(6)	77.78(6)	76.37(13)
N(2)–Fe(1)–O(1)	135.32(6)	131.84(6)	-
N(2)–Fe(1)–N(4)	-	-	174.15(15)
N(2)–Fe(1)–N(5)	-	-	87.56(16)

Figure 4.16. ORTEP of $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$ at 30% probability ellipsoids. Hydrogen atoms and a co-crystallized diethyl ether solvent molecule are omitted for clarity.

Table 4.3. Experimental and calculated Mössbauer parameters for high-spin Fe^{II} PDP complexes

	δ / mms^{-1} (calc)	$\Delta E_Q / \text{mms}^{-1}$ (calc) ^a	$\eta^{b,c}$
$(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$	0.91 (0.76)	1.25 (1.75)	0.913
$\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-tBuPDP}^{\text{Ph}})_2$	0.82 (0.69)	1.68 (-1.62)	0.375
	0.82 (0.69)	1.68 (-1.71)	0.546
$(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$	1.07 (0.87)	1.42 (1.85)	0.557
$(\text{tBuPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$	1.02 (0.85)	1.94 (4.66)	0.507
$(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$	0.96 (0.81)	1.43 (2.14)	0.417
$(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})_2^d$	1.20 (0.93)	3.02 (2.81)	0.866
$(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{py})_2$	0.99 (0.86)	3.12 (3.01)	0.802
$(^{\text{C}_6\text{F}_5\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$	1.08 (0.85)	2.91 (2.96)	0.716
$(4\text{-MeO}^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$	0.96 (0.81)	2.00 (2.14)	0.417

^aSign not determined experimentally. ^bAsymmetry parameter of the electronic field gradient.

^cNot determined experimentally. ^dMeasured in frozen THF solution.

4.5 Conclusion

A family of high-spin Fe^{II} complexes carrying the new pyridine dipyrrolide ligands $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$, $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$ was synthesized and structurally characterized. The new PDP ligands $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ were characterized via X-ray crystallography. $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ was found to exist as a discrete monomeric structure with a dimethyl sulfoxide solvent molecule acting as a hydrogen bond donor to the pyrrolide nitrogen protons. Alternatively, $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ was found to exist as a hydrogen bonded dimer in absence of coordinating solvent, akin to the previously reported analogue, $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$.

For $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$, it was discovered that four or five coordinate high-spin Fe^{II} complexes could be isolated depending on the identity of the exogenous Lewis base employed during synthesis. The resulting compounds $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$, $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})_2$, and $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ were characterized via a combination of ^1H NMR and Mössbauer spectroscopies as well as magnetic measurements. The solid-state structures of these new Fe^{II} synthons were unambiguously confirmed via single crystal X-ray diffraction. Four-coordinate $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ was found to undergo loss of the diethyl ether solvento ligand in non-coordinating solvent, affording the diiron helical dimer $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^{\text{tBu}}\text{PDP}^{\text{Ph}})_2$, as evidenced ^1H NMR and ^{57}Fe Mössbauer spectroscopies. A preliminary X-ray crystallographic analysis of this complex has also been performed, confirming its atomic connectivity.

For $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$, the four coordinate THF adducts $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(\text{4-MeO}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ were synthesized and characterized crystallographically. $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was found to exhibit an equilibrium between four- and five-coordinate species in solution, which was supported by ^1H NMR and ^{57}Fe Mössbauer

spectroscopies. A preliminary X-ray structural analysis of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ confirming atomic connectivity is also disclosed. For $\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ and $\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}}$, the five coordinate bis-pyridine adducts $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ and $(\text{H}_2^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ have been synthesized and structurally characterized. The derivation of the aryl substituent at the 5-position of the pyrrolide ring of the PDP ligand has been determined to have no impact upon the coordination environment and resulting electronic structure of the bis-THF and bis-pyridine adducts, relative to the previously reported analogue $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$.

In totality, these results reiterate the disparate electronic ground states operative in four- and five- coordinate high-spin Fe^{II} PDP complexes. Furthermore, the facile extension of the modular PDP ligand synthesis and iron metalation protocols to the new compounds presented here demonstrates that the synthesis of other new high-spin Fe^{II} PDP derivatives with varying coordination numbers, geometries, and PDP ligand substitution patterns are synthetically accessible. Importantly, the development of these new high-spin Fe^{II} PDP synthons will allow for future exploration of their application in potential stoichiometric and catalytic group transfer reactions.

4.6 Experimental Procedures

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH_2 and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Deuterated benzene ($\text{benzene-}d_6$) and tetrahydrofuran ($\text{THF-}d_8$) for NMR spectroscopy were distilled from sodium

metal and sodium benzophenone, respectively. Deuterated dichloromethane (CD_2Cl_2) was distilled from calcium hydride. CDCl_3 and $\text{DMSO}-d_6$ were obtained from Cambridge Isotopes and used as received. $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$,^{15,16} $\text{Fe}(\text{Cl})_2(\text{py})_4$,¹⁷ 4,4-dimethyl-1-phenyl-1-penten-3-one,¹⁸ 1-(2,3,4,5,6-pentafluorophenyl)-3-phenyl-2-propen-1-one,¹⁹ 1-(2,6-dichlorophenyl)-3-phenyl-2-propen-1-one,¹⁹ 2,6-pyridinedicarboxaldehyde,²⁰ and 4-methoxy-2,6-pyridinedicarboxaldehyde²¹ were prepared according to literature procedures. FeCl_2 , LiHMDS, trimethylsilylmethyl lithium, ammonium acetate, 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride, sodium tert-butoxide, were purchased from commercial vendors and used as received. All solvents were purchased from commercial vendors and used as received.

Preparation of 2,6-Bis(5-(tert-butyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine, $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$.

In a Schlenk flask equipped with a magnetic stirrer was added 2.88 g (21.3 mmol) of 2,6-pyridinecarboxaldehyde, 8.04 grams (42.7 mmol, 2.05 eq.) of 4,4-dimethyl-1-phenyl-1-penten-3-one, 8.62 grams (32.0 mmol, 1.5 eq.) of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride, and 150 mL of absolute ethanol. A condenser was affixed to the flask and the apparatus was attached to a Schlenk line. The system was purged with argon for five minutes, degassed, and the argon atmosphere was replenished. This procedure was repeated an additional four times. Under a heavy flow of argon, a 100 mL solution of absolute ethanol and 3.08 grams (32.0 mmol, 1.5 eq.) of sodium tert-butoxide was added via syringe through the sidearm of the flask, resulting in an immediate color change of the solution from yellow to dark-brown. The solvent was brought to a reflux, which was maintained for 28 hrs. A yellow-orange precipitate was evident at this time, which was isolated via filtration and washed with three aliquots of cold ethanol. ^1H NMR analysis (CDCl_3) confirmed the identity of the solid as the desired 1,4-diketone intermediate, which was utilized in the next step without further purification. The diketone, 20 g

(260 mmol, 12.2 eq) of ammonium acetate, and 100 mL of absolute ethanol were combined in a round bottom flask equipped with a magnetic stirrer. The solvent was brought to a reflux was maintained for 96 hours, at which time a yellow precipitate was evident in the reaction mixture. The precipitate was isolated via vacuum filtration and washed with copious amounts of cold ethanol. Drying under high vacuum for 48 hours afforded anhydrous $H_2^{tBu}PDP^{Ph}$, a pale yellow solid which was stored in the glovebox for subsequent use. Yield: 6.50 grams, 13.7 mmol, 64%. 1H NMR (benzene- d_6 , 400 MHz, δ , ppm): 9.26 (s, pyrrole-NH, 2H), 7.60 (d, $J = 7.0$ Hz, *ortho*-PhH, 4H), 7.20 (t, $J = 7.4$ Hz, *meta*-PhH, 4H), 7.12 (d, $J = 7.9$ Hz, 3-pyridineH, 2H), 6.71 (t, $J = 7.9$ Hz, 4-pyridineH, 1H), 6.21 (d, $J = 3.2$ Hz, pyrrole-CH, 2H), 1.24 (s, *t*Bu-CH₃, 18H). 1H NMR (CDCl₃, 400 MHz, δ , ppm): 9.16 (s, pyrrole-NH, 2H), 7.47 (d, $J = 7.0$ Hz, *ortho*-PhH, 4H), 7.35 (t, $J = 7.5$ Hz, *meta*-PhH, 4H), 7.27 (t, $J = 7.3$, *para*-PhH, 2H), 7.16 (t, $J = 7.8$ Hz, 4-pyridineH, 1H), 6.95 (d, $J = 7.9$ Hz, 3-pyridineH, 2H), 6.08 (d, $J = 3.2$ Hz, pyrrole-CH, 2H), 1.40 (s, 18H, *t*Bu-CH₃). ^{13}C NMR (CDCl₃, 600 MHz, δ , ppm): 150.20, 142.97, 137.33, 136.10, 129.12, 128.35, 126.34, 124.94, 124.67, 116.57, 107.40, 31.51, 30.46. HRMS (ESI) calcd for C₃₃H₃₆N₃⁺ [M + H]⁺ 474.2904 m/z. Found 474.2900.

Preparation of 2,6-Bis(5-(2,3,4,5,6-pentafluorophenyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine, $H_2^{C6F5}PDP^{Ph}$.

In a Schlenk tube equipped with a magnetic stirrer was added 332 mg (2.46 mmols) of 2,6-pyridinecarboxaldehyde, 1.50 grams (5.03 mmol, 2.05 eq.) of 1-(2,3,4,5,6-pentafluorophenyl)-3-phenyl-2-propen-1-one, and 131 milligrams (0.489 mmols, 0.20 eq.) of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride, and 15 mL of dry 1,4-dioxane. A condenser was affixed to the flask and the apparatus was attached to a Schlenk line. The system was purged with argon for five minutes, degassed, and replenished with a fresh argon

atmosphere. This procedure was repeated an additional four times. Under a heavy flow of argon, 110 μL of triethylamine (0.783 mmol, 0.32 eq.) dissolved in 1 mL of dry 1,4-dioxane was added via syringe, resulting in an immediate color change from yellow to dark-green. The solvent was brought to a reflux, which was maintained for 16 hrs. A yellow-orange precipitate was evident at this time. The entirely crude reaction mixture was transferred to a round bottom flask. Three five -mL aliquots of dichloromethane were used to rinse the Schlenk flask. The extracts were combined and the solvent was removed *in vacuo*, yielding an orange solid. ^1H and ^{19}F NMR analysis (CDCl_3) confirmed the identity of the solid as the desired 1,4-diketone intermediate. The crude material was used without further purification for the second step. 10 mL of absolute ethanol was added to a round bottom flask containing the diketone, along with 4.00 grams (51.9 mmol, 21.1 eq.) of ammonium acetate. The mixture was stirred vigorously, and the solvent was brought to a reflux, which was maintained for 16 hrs. The resulting yellow precipitate was isolated via vacuum filtration on a medium porosity glass frit and washed with three 10 mL aliquots of 0°C ethanol. Drying the material under high vacuum at 100°C for 48 hours afforded the title compound as a pale yellow powder. Yield: 1.09 grams, 1.57 mmol, 64%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.68 (d, J = 2.3 Hz, 2H, pyrrole-NH), 7.50 – 7.39 (m, 9H, *ortho*- and *meta*-Ph-H, and 4-pyH), 7.37 – 7.30 (t, J = 7.0 Hz, 2H, *para*-PhH), 7.00 (d, J = 7.9 Hz, 2H, 3-pyH), 6.67 (d, J = 2.4 Hz, 2H, pyrrole-CH). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -141.78 (d, J = 26.6 Hz, 4F, *ortho*-F), -156.89 (t, J = 22.4 Hz, 2F, *para*-F), -162.85 (td, J = 24.5, 6.5 Hz, 4F, *meta*-F). HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{18}\text{N}_3\text{F}_{10}^+$ [$\text{M} + \text{H}$] $^+$ 694.1336 m/z. Found 694.1339.

Preparation of 1,1'-(2,6-pyridinediyl)bis[2-phenyl-4-(2,6-dichlorophenyl)]-1,4-butanedione.

In a 250 ml Schlenk flask, 595 mg (4.41 mmol) of 2,6-pyridinecarboxaldehyde, 2.5 grams (9.02 mmol) of 1-(2,6-dichlorophenyl)-3-phenyl-2-propen-1-one, and 890 mg (3.30 mmol) of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride were combined with a

magnetic stirrer and 15 mL of absolute ethanol. A reflux condenser was affixed to the flask and the apparatus was attached to a Schlenk line and purged for 5 minutes with argon. The apparatus was then degassed, and again purged with argon. This procedure was repeated four additional times. In a separate flask, 317 mg (3.30 mmol) of sodium tert-butoxide was dissolved in 5 mL of absolute ethanol. The sodium tert-butoxide solution was added to the Schlenk flask under a heavy flow of argon via the sidearm. An immediate color change to dark-brown was observed. The mixture was then brought to a gentle reflux, which was maintained for 12 hrs. The resulting tan precipitate was isolated on a medium porosity frit and washed with three 10 mL aliquots of cold ethanol. Yield: 2.28 grams (3.1 mmol), 75%. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, J = 7.8 Hz, 2H), 7.95 – 7.87 (m, 1H), 7.66 – 7.58 (d, J = 7.2 Hz, 4H), 7.36 – 7.27 (m, 10H), 7.19 (t, J = 7.4 Hz, 2H), 6.34 (dd, J = 10.1, 3.7 Hz, 2H), 4.17 (dd, J = 19.0, 10.1 Hz, 2H), 3.46 (dd, J = 19.0, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 45.46, 47.27, 126.46, 127.64, 128.26, 129.13, 129.20, 130.78, 137.08, 138.29, 139.21, 151.27, 198.24, 200.23, one resonance was not detected. HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{26}\text{N}_1\text{O}_4\text{Cl}_4^+$ $[\text{M} + \text{H}]^+$ 688.0610 m/z. Found 688.0620. IR: 1699 cm^{-1} (broad, C=O).

Preparation of 2,6-Bis(5-(2,6-dichlorophenyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine, $\text{H}_2^{2,6-\text{Cl}_2\text{Ph}}\text{PDPPh}$.

A 250 mL round bottom flask was loaded with 2.28 grams (3.31 mmol) of 1,1'-(2,6-pyridinediyl)bis[2-phenyl-4-(2,6-dichlorophenyl)]-1,4-butanedione, 3.00 grams (38.9 mmol, 11.75 eq) of ammonium acetate, and a magnetic stirrer. 25 mL of glacial acetic acid was added to the mixture. A condenser was affixed to the flask and the mixture was brought to a vigorous reflux, which was maintained for approximately 48 hrs. The resulting yellow powder was then isolated via vacuum filtration and washed with three 15 mL aliquots of cold ethanol. The solid was extracted into dichloromethane and purified via passage through a plug of basic alumina.

Removal of the solvent *in vacuo* afforded a light yellow powder. Yield: 1.45 g (2.22 mmol), 67%. Single crystals suitable for study via X-ray crystallographic analysis were obtained from a concentrated dimethyl sulfoxide solution of the compound. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 11.54 (d, $J = 2.5$ Hz, 2H, pyrrole-NH), 7.62 (d, $J = 8.2$ Hz, 4H), 7.43 (m, 10H), 7.31 (m, 3H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.30 (d, $J = 2.9$ Hz, 2H, pyrrole-CH). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 113.55, 116.43, 124.45, 126.20, 126.64, 127.16, 128.60, 128.66, 129.03, 130.83, 131.44, 135.84, 136.39, 136.76, 149.69. HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{24}\text{N}_3^+$ $[\text{M} + \text{H}]^+$ 650.0719 m/z . Found 650.0767.

Preparation of 1,1'-(4-methoxy-2,6-pyridinediyl)bis[2-phenyl-4-(2,6-dichlorophenyl)]-1,4-butanedione.

In an oven dried Schlenk flask equipped with a magnetic stirrer was combined 291 mg (1.76 mmol) of 4-methoxy-2,6-pyridinedicarboxaldehyde, 1.00 g (3.61 mmol, 2.05 eq) 1-(2,6-dichlorophenyl)-3-phenyl-2-propen-1-one, 359 mg (1.33 mmol, 0.75 eq.) of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride and 10 mL of absolute ethanol. A reflux condenser was equipped to the flask which was attached to a Schlenk line. The apparatus was purged with argon and then degassed, this procedure was repeated four subsequent times. In a separate flask was combined 128 mg (1.33 mmol, 0.75 eq.) of sodium tert-butoxide and 4 mL absolute ethanol. Under a heavy argon flow, the sodium tert-butoxide solution was added via syringe to the Schlenk flask and the reaction mixture was brought to reflux. After 20 hrs. the reaction mixture was cooled to room temperature, and a yellow precipitate was observed. The precipitate was isolated via vacuum filtration on a medium porosity glass frit and washed three times with five mL aliquots of cold ethanol, dried in air, and used without further purification. Yield: 788 mg, 1.1 mmol, 62%. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.71 (s, 2H, 3-pyridineH), 7.68 – 7.45 (m, 9H, Ar), 7.37 – 7.03 (m, 7H, Ar), 6.20 (dd, $J = 10.5, 3.3$ Hz, 2H, CH), 4.12 (dd, $J = 19.1, 10.3$ Hz,

2H, Ar), 3.94 (s, 3H, 4-pyridine-OCH₃), 3.47 (dd, $J = 18.8, 3.2$ Hz, 2H, CH). HRMS (ESI) calcd for C₃₈H₂₈Cl₄NO₅⁺ [M + H]⁺ 718.0716 m/z. Found 718.0732.

Preparation of 2,6-Bis(5-(2,6-dichlorophenyl)-3-phenyl-1H-pyrrol-2-yl)-4-methoxy-pyridine H₂4-MeO^{2,6-Cl₂Ph}PDP^{Ph}.

In a 100 mL round bottom flask equipped with a magnetic stirrer was added 788 mg (1.1 mmol) of 4-methoxy pyridine-2,6-(2,6-dichlorophenyl)-diketone and 1.71 grams (22 mmol, 20 eq.) of ammonium acetate. 10 mL of glacial acetic acid was added to the mixture and stirred vigorously. The solvent was brought to a gentle reflux, which was maintained for 24 hrs. Cooling to room temperature induced abundant precipitation of a yellow solid, which was isolated on a medium porosity frit and washed with three aliquots of cold ethanol. The crude solid was extracted into dichloromethane and washed through a plug of basic alumina to remove any residual acetic acid. Removal of the solvent in vacuo left an off-white/tan powder, identified as the title compound. Crystals suitable for study via X-ray diffraction were obtained from evaporation of a concentrated dichloromethane solution over 4 days. Yield: 324 mg, 0.475 mmol, 43%. ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.48 (s, 2H, pyrrole-NH), 7.62 (d, $J = 8.1$ Hz, 4H), 7.49 – 7.39 (m, 11H), 7.28 (t, $J = 7.4$ Hz, 2H), 6.53 (s, 2H), 6.28 (d, $J = 2.9$ Hz, 2H, pyrrole-CH), 3.32 (s, 3H, 4-pyridine-OCH₃). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 54.36, 102.51, 113.44, 124.52, 126.01, 126.71, 127.04, 128.59, 129.24, 130.85, 131.44, 135.85, 136.75, 150.89, 165.09, one resonance was not detected. HRMS (ESI) calcd for C₃₉H₂₅N₃Cl₄O⁺ [M + H]⁺ 680.0824 m/z. Found 680.0830.

Preparation of (^tBuPDP^{Ph})Fe(OEt₂).

In the glovebox, a round bottom flask equipped with a magnetic stirrer, 239 mg (0.635 mmol) of Fe[N(SiMe₃)₂]₂ was dissolved in 10 mL of diethyl ether. In a separate 20 mL

scintillation vial, 300 mg of $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$ (0.633 mmol) was slurried in 10 mL of diethyl ether. The ligand slurry was added to the solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$, resulting in an immediate color change to red. The reaction mixture was allowed to stir for 24 hrs. The resulting orange precipitate was isolated on a medium porosity glass frit, washed with three 1.5 mL aliquots of diethyl ether, and dried briefly *in vacuo*. Yield: 286 mg, 0.475 mmol, 75%. $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ^1H NMR (400 MHz, benzene- d_6) δ 111.47 (singlet, 2H), 86.61 (singlet, 2H), 33.52 (singlet, $^{\text{tBu}}\text{CH}_3$, 18H), 25.87 (singlet, 4-pyridine- H , 1H), 22.60 (singlet, $\text{Et}_2\text{O-CH}_2$, 4H), 11.13 (singlet, 4H), 7.47 (singlet, 4H), 4.65 (singlet, 2H), -1.63 (singlet, $\text{Et}_2\text{O-CH}_3$, 6H). Anal. Calcd for $(^{\text{tBu}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ $\text{C}_{37}\text{H}_{43}\text{FeN}_3\text{O}$: C, 73.87; H, 7.20; N, 6.98. Found: C, 71.86; H, 6.95; N, 6.97.

Preparation of $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^{\text{tBu}}\text{PDP}^{\text{Ph}})_2$.

In the glovebox, a round bottom flask equipped with a magnetic stirrer, 239 mg (0.635 mmol) of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ was dissolved in 10 mL of diethyl ether. In a separate 20 mL scintillation vial, 300 mg of $\text{H}_2^{\text{tBu}}\text{PDP}^{\text{Ph}}$ (0.633 mmol) was slurried in 10 mL of diethyl ether. The ligand slurry was added to the solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$, resulting in an immediate color change to red. The reaction mixture was allowed to stir for 24 hrs. The resulting orange precipitate was isolated on a medium porosity glass frit, washed with three-1.5 mL aliquots of diethyl ether, and dried briefly *in vacuo*. The resulting powder was combined in a round bottom flask equipped with a magnetic stirrer, and 15 mL of pentane was added. The suspension was stirred vigorously for four hours, at which time a color change from orange to dark-red/brown was noted. The mixture was then reduced to a solid *in vacuo*. The solid residue was extracted into the minimum amount of benzene and filtered through a pipette fitted with a celite column supported by a microfiber glass plug into a separate flask. The solvent was then removed in

vacuo affording a dark powder. Yield: 240 mg, 0.227 mmol, 71%. $\mu_{\text{eff}} = 7.0 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ^1H NMR (400 MHz, benzene- d_6) δ 78.99 (singlet, 2H), 48.99 (singlet, 2H), 30.68 (singlet, $^t\text{BuCH}_3$, 18H), 15.25 (singlet, 4H), 8.80 (singlet, 4H), 2.08 (singlet, 2H), -0.91 (singlet, 4-py- H , 1H). Anal. Calcd for $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^{\text{Ph}})_2$, $\text{C}_{66}\text{H}_{66}\text{Fe}_2\text{N}_6$: C, 75.14; H, 6.31; N, 7.97. Found: C, 74.37; H, 6.35; N, 7.42. Note, despite the low carbon content evidenced by CHN analysis, Mössbauer spectroscopy evidences $\text{Fe}_2(\mu_2\text{-}\kappa^2\text{-}^t\text{BuPDP}^{\text{Ph}})_2$ as the only iron containing species present within the sample.

Preparation of ($^t\text{BuPDP}^{\text{Ph}}$)Fe(thf) $_2$.

In the glovebox, 300 mg (0.633 mmol) of $\text{H}_2^t\text{BuPDP}^{\text{Ph}}$ was dissolved in 10 mL of THF in a 20 mL scintillation vial equipped with a magnetic stirrer. Rapid stirring induced complete dissolution of $\text{H}_2^t\text{BuPDP}^{\text{Ph}}$. In a separate round bottom flask, 280 mg (0.743 mmol) of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ was dissolved in 10 mL of THF, affording a homogeneous pale green solution. With rapid stirring, the solution of the $\text{H}_2^t\text{BuPDP}^{\text{Ph}}$ was added dropwise via pipette to the solution of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$, resulting in an immediate color change to orange/red. The mixture was allowed to stir for 16 hrs. Subsequent removal of the solvent resulted in an orange film. The crude mixture was extracted into a minimum amount of THF and the resulting solution was filtered through a celite plug supported by a glass microfiber filter in a 20 mL scintillation vial. The solution was layered with 15 mL of pentane and stored at -35°C for 48 hrs. The resulting red blocks were isolated on a medium porosity glass frit, washed with three-5 mL aliquots of pentane, and dried *in vacuo*. The resulting filtrate was concentrated and a second crystallization was performed. The combined yield from two crops of crystallizations was 286 mg, 0.426 mmol, 67%. $\mu_{\text{eff}} = 5.4 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ^1H NMR (400 MHz, benzene- d_6) δ 110.80 (singlet, 2H), 89.17 (singlet, 2H), 36.27 (singlet, $^t\text{Bu-CH}_3$, 18H), 26.82 (singlet, 4-

pyridine-*H*, 1H), 11.01 (singlet, 4H), 6.00-9.26 (overlapping singlets, 12H), 4.64 (singlet, 2H), 1.87 (singlet, THF-CH₂, 8H). Anal. Calcd for (^tBuPDP^{Ph})Fe(thf)₂, C₄₁H₄₉FeN₃O₂: C, 73.31; H, 7.35; N, 6.26. Found: C, 69.08; H, 6.46; N, 6.33. Single crystals suitable for study via X-ray crystallography were obtained from the aforementioned procedure.

Preparation of (^tBuPDP^{Ph})Fe(py)₂.

In the glovebox, 99 mg (0.223 mmol) of Fe(Cl)₂(py)₄ was suspended in 5 mL of pentane in a 20 mL scintillation vial equipped with a magnetic stirrer. In a separate vial, 43 mg of neosilyl lithium (0.457 mmol, 2.05 eq) was dissolved in 5 mL of pentane and added to the stirring yellow suspension, inducing a color change to purple. The reaction mixture was allowed to stir for 2 hrs. The resulting crude suspension was filtered through a plug of celite supported by a glass microfiber filter. The dark purple filtrate was concentrated to 1 mL. In a separate vial was combined 107 mg (0.226 mmol) of H₂^tBuPDP^{Ph} and 5 mL of toluene, yielding a homogeneous pale yellow solution. The solution of the proligand was added dropwise to the solution of the iron complex, affording a dark-red solution. The reaction mixture was allowed to stir for two hours, at which time 10 mL of pentane was added. Storage at -35°C for 12 hrs resulted in the formation of orange/red plates which were isolated via vacuum filtration over a medium porosity glass frit. The material was washed with three 5 mL aliquots of pentane, and dried *in vacuo*. Yield: 94 mg, 0.137 mmol, 61 %. A single crystal suitable for X-ray analysis was grown from slow diffusion of pentane into a concentrated solution of toluene at -35°C. $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ¹H NMR (400 MHz, benzene-*d*₆) δ 104.00 (singlet, 2H), 88.95 (singlet, 2H), 67.82 (broad singlet, 4H), 36.60 (singlet, ^tBu-CH₃, 18H), 30.33 (singlet, 4-pyridine-*H*, 1H), 27.62 (singlet, 4H), 9.79-11.00 (overlapping singlets, 6H), 6.68 (singlet, 4H),

4.43 (singlet, 2H). Anal. Calcd for (^tBuPDP^{Ph})Fe(py)₂, C₄₃H₄₃FeN₅: C, 75.32; H, 6.32; N, 10.21
Found: C, 75.49; H, 6.54; N, 8.49.

Preparation of (2,6-Cl₂PhPDP^{Ph})Fe(thf).

In the glovebox, 500 mg (0.768 mmol) of H₂(^{2,6}-Cl₂PhPDP^{Ph}) and 10 mL of THF were loaded in a 100 mL flask equipped with a magnetic stirrer. In a separate vial, 265 mg (1.58 mmol) of LiHMDS was combined with 3 mL of THF. While vigorously stirring, the solution of LiHMDS was added to the solution of H₂(^{2,6}-Cl₂PhPDP^{Ph}), resulting in an immediate color change from tan to a brilliant luminescent yellow. The mixture was stirred for approximately two hours. In a separate 250 mL round bottom flask, 97 mg (0.765 mmol) of FeCl₂, 20 mL of THF, and a magnetic stirrer were combined. While vigorously stirring, the solution of deprotonated ligand was added to the THF slurry of FeCl₂, resulting in an immediate color change to an intense dark-red. After 12 hours, the mixture was homogenous and the volume of solvent was reduced to approximately 3 mL. 75 mL of diethyl ether was added, and immediate precipitation of a bright orange solid was observed. The resulting solid was isolated on a medium porosity glass frit and dried *in vacuo*. The solid was transferred to a 20 mL vial and combined with 5 mL of toluene, 10 mL of pentane, and a magnetic stirrer. Rapid stirring of the mixture induced precipitation of lithium chloride. The suspension was then filtered over a medium porosity frit containing a one inch pad of celite. The red compound was washed from the celite first with toluene, and then with dichloromethane, until all washings were clear. Removal of solvent *in vacuo*, followed by trituration with pentane afforded the title compound as an orange-red powder, which could be recrystallized from a concentrated dichloromethane solution layered with pentane at -35°C for 48 hrs. Yield: 445 mg (0.572 mmol), 74%. $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ¹H NMR (400 MHz, benzene-*d*₆) δ 106.09 (singlet, 2H), 97.77 (singlet, 2H), 16.53 (broad singlet,

4H), 13.45 (singlet, 4H), 12.23 (singlet, 4H), 11.91 (singlet, 4H), 9.76 (singlet, 2H), 7.99 (singlet, 4H), 0.33 (1H, 4-pyridine-*H*). One resonance could not be located. Anal. Calcd for (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf), C₄₁H₂₉Cl₄FeN₃O: C, 63.35; H, 3.76; N, 5.41. Found: C, 62.64; H, 3.75; N, 5.23. The low carbon value observed in the CHN analysis suggests that despite multiple extractions of the compound via hydrocarbon solvents 1/3 eq. of LiCl is still present in the sample. Anal. Calcd for (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf)•1/3(LiCl), C₄₁H₂₉Cl_{4.33}FeLi_{0.33}N₃O: C: 62.23; H: 3.69; N: 5.31. Found: 62.64; H, 3.75; N, 5.23. Single crystals suitable for an X-ray study were grown from diffusion of a pentane into a concentrated benzene solution of the title compound over 48 hrs.

Preparation of (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf)₂.

15 mg of (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) was weighed into a one dram vial. A 500 μL aliquot of THF solvent was added, resulting in dissolution of the compound. The resulting mixture was filtered into a J. Young NMR tube, affording a homogeneous orange solution. On a high-vacuum line, the THF solvent was removed and the sample was evacuated for two hours. THF-*d*₈ was then vacuum transferred onto the sample, again affording a homogeneous orange solution. An ¹H NMR spectrum was acquired and demonstrated quantitative conversion of (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) to (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf)₂, as demonstrated by the downfield shift of the resonance corresponding to the para-pyridine proton. The J. Young tube was returned to the glovebox and one drop of pentane was added to the sample as a secondary internal standard. A ¹H NMR spectrum was again acquired, with the resonances corresponding to (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf)₂ unchanged. ¹H NMR (400 MHz, THF-*d*₈) δ 85.38 (singlet, 2H), 65.88 (singlet, 2H), 22.15 (singlet, 4-pyridine-*H*, 1H), 8.02 (singlet, 4H), 7.08 (singlet, 4H), 6.86 (singlet, 2H), 6.41 (singlet, 4H), 5.97 (singlet,

2H). Note, resonances for the THF ligands were not observed due to rapid exchange with THF-*d*₈.

Synthesis of (2,6-Cl₂PhPDP^{Ph})Fe(py)₂.

In a 20 mL vial equipped with a magnetic stirrer was added 153 mg (0.345 mmol) of Fe(Cl)₂(py)₄ and 15 mL of pentane. Vigorous stirring afforded a yellow suspension. In a separate vial 65 mg (0.690 mmol, 2.0 eq.) of neosilyl lithium was dissolved in approximately 5 mL of pentane. The neosilyl lithium solution was added to the suspension of Fe(Cl)₂(py)₄, inducing a rapid color change to dark-purple. The reaction mixture was allowed to stir for two hours, at which time it was filtered through a pad of celite supported on a glass microfiber filter into a round bottom flask. In a separate vial, 225 mg (0.345 mmol) of H₂^{2,6-Cl₂PhPDP^{Ph}} was suspended in 5 mL of toluene and 10 mL of pentane. The ligand suspension was added dropwise to the stirring solution of Fe(Ns)₂(py)₂, inducing a color change to yellow-orange within minutes accompanied by abundant precipitation of an orange solid. After one hour, the precipitate was collected on a medium porosity glass frit and washed with three 5 mL aliquots of pentane, and dried *in vacuo*. Yield: 167 mg, 0.193 mmol, 56%. Single crystals of the compound were grown from slow evaporation of a dichloromethane solution over 36 hrs. $\mu_{\text{eff}} = 4.7 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance). ¹H NMR (400 MHz, benzene-*d*₆) δ 110.77 (broad singlet, 4H), 83.19 (singlet, 2H), 76.19 (singlet, 2H), 38.08 (singlet, 4H), 24.23 (singlet, 4-pyridineH, 1H), 9.41 (singlet, 4H), 7.48-8.08 (overlapping broad singlets, 6H), 7.25 (singlet, 2H), 7.04 (singlet, 4H), 5.31 (singlet, 2H). ¹⁹F NMR (376 MHz, benzene-*d*₆) δ -162.59 (broad singlet, 2F), -160.88 (broad singlet, 1F, *para*Ph-F), -71.52 (broad singlet, 2F). Anal. Calcd for (2,6-Cl₂PhPDP^{Ph})Fe(py)₂, C₄₇H₃₁Cl₄FeN₅: C, 65.38; H, 3.62; N, 8.11. Found: C, 64.93; H, 3.98; N, 7.80.

Preparation of (4-MeO^{2,6}-Cl₂Ph)PDP^{Ph})Fe(thf).

In a 20 mL scintillation vial 250 mg (0.367 mmol) of H₂4-MeO^{2,6}-Cl₂PhPDP^{Ph} was dissolved in 10 mL of THF, affording a colorless homogenous solution. In a separate vial 128 mg of LiHMDS (0.765 mmol, 2.08 eq) was dissolved in 5 mL of THF. The LiHMDS solution was added dropwise to the solution of H₂4-MeO^{2,6}-Cl₂PhPDP^{Ph}, inducing an immediate color change to bright yellow. The reaction mixture was allowed to stir for two hours. In a separate 50 mL round bottom flask, 47 mg of FeCl₂ (0.371 mmol, 1.01 eq.) was suspended in 10 mL of THF via vigorous stirring. Dropwise addition of the deprotonated ligand solution to the FeCl₂ suspension induced an immediate color change to amber, accompanied via gradual dissolution of FeCl₂. The reaction mixture was stirred for 16 hrs. The solvent was then concentrated *in vacuo* to approximately 2 mL and pentane (25 mL) was added. Vigorous stirring induced the precipitation of a bright orange microcrystalline solid. This solid was isolated on a fine porosity glass frit via vacuum filtration and subsequently transferred to a 20 mL scintillation vial. The solid was then extracted into 2 mL of toluene and pentane (15 mL) was added, resulting in precipitation of an orange microcrystalline powder. The suspended powder was passed over a medium porosity glass frit with a one inch pad of celite. The organic extracts were collected via vacuum filtration, and the celite pad was washed with three 25 mL aliquots of dichloromethane, or until the washings were clear. Removal of the solvent *in vacuo* and subsequent trituration with pentane afforded a bright orange powder. Yield 227 mg, 0.281 mmol, 77 %. ¹H NMR (400 MHz, benzene-*d*₆) δ 101.94 (singlet, 2H), 98.43 (singlet, 2H), 18.67 (broad singlet, 4H), 14.43 (singlet, 4H), 12.34 (singlet, 4H), 11.90 (singlet, 4H), 11.12 (singlet, 3H, 4-pyridine-OCH₃), 10.34 (singlet, 2H), 8.76 (singlet, 4H). One resonance could not be located. Anal. Calcd for

(4-MeO^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf), C₄₂H₃₁Cl₄FeN₃O₂: C, 62.48; H, 3.87; N, 5.20. Found: C, 60.35; H, 3.76; N, 5.04. The low carbon value observed in the CHN analysis suggests that despite multiple extractions of the compound via hydrocarbon solvents 1/2 eq. of LiCl is still present in the sample. Anal. Calcd for (4-MeO^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf)•1/2(LiCl), C₄₂H₃₁Cl_{4.5}FeLi_{0.5}N₃O₂: C: 60.88; H: 3.77; N: 5.07. Found: 60.35; H: 3.76; N: 5.04. Single crystals suitable for study via X-ray crystallography were grown from diffusion of pentane into a concentrated benzene solution of the compound over 48 hrs.

Synthesis of (C⁶F⁵PDP^{Ph})Fe(py)₂.

In a 20 mL vial equipped with a magnetic stirrer was added 64 mg (0.144 mmol) of Fe(Cl)₂(py)₄ and 10 mL of pentane. Vigorous stirring afforded a yellow suspension. In a separate vial 27 mg (287 mmol, 2.0 eq.) of neosilyl lithium was dissolved in approximately 3 mL of pentane. The neosilyl lithium solution was added to the suspension of Fe(Cl)₂(py)₄, inducing a rapid color change to dark-purple. The reaction mixture was allowed to stir for two hours, at which time it was filtered through a pad of celite supported on a glass microfiber filter into a 50 mL round bottom flask. In a separate vial, 100 mg (0.144 mmol, 1.0 eq) of H₂^{C⁶F⁵}PDP^{Ph} was slurried in 1.5 mL of toluene and 5 mL of pentane. The ligand suspension was added dropwise to the stirring solution of Fe(Cl)₂(py)₂, inducing a color change to yellow-orange and within minutes abundant precipitation of an orange solid was observed. After one hour, the precipitate was collected on a medium porosity glass frit and washed with three 1.5 mL aliquots of pentane, and dried *in vacuo*. Yield: 115 mg, 127 mmol, 88%. Recrystallization was accomplished via layering a concentrated toluene solution of the title compound with excess pentane and storing the resulting solution at -35°C for 36 hrs. ¹H NMR (400 MHz, benzene-*d*₆) δ 83.08 (broad singlet, 4H), 78.78 (singlet, 2H), 73.83 (singlet, 2H), 32.96 (singlet, 4H), 26.13 (singlet, 1H, 4-

pyridine-*H*), 8.88 (singlet, 4H), 8.01 (singlet, 2H), 7.59 (singlet, 4H), 5.88 (singlet, 2H). $\mu_{\text{eff}} = 5.3 \mu_{\text{B}}$ (295 K, magnetic susceptibility balance) Anal. Calcd for ($\text{C}_6\text{F}_5\text{PDP}^{\text{Ph}}$)Fe(py)₂, C₄₇H₂₅F₁₀FeN₅: C, 62.34; H, 2.78; N, 7.73. Found: C, 62.19; H, 2.90; N, 7.84.

Physical Measurements.

¹H and ¹³C {¹H} NMR spectra were recorded on an Agilent 400 MHz spectrometer, JEOL 400 MHz YH spectrometer, or a Varian INOVA 600 MHz spectrometer. All chemical shifts are reported relative to SiMe₄ using ¹H (residual) chemical shifts of the solvent as a secondary standard. Assignments of resonances for paramagnetic compounds are based on integration and only reported in the experimental procedures for conclusive cases. High resolution mass spectra were obtained on a Thermo Finnigan Linear Trapping Quadrupole mass spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Room temperature magnetic susceptibility measurements were performed with a Johnson Matthey Mark 1 instrument that was calibrated with HgCo(SCN)₄. Zero field ⁵⁷Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a ⁵⁷Co/Rh radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/N₂ cryostat within an accuracy of ± 0.3 K. The data were calibrated relative to α -iron at 298 K with minimum experimental line widths of 0.23 mm/s. The fitting procedure to extract quantitative spectral parameters uses a least squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a

Triumph monochromator, a Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)²² was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames, followed by reflection indexing and least-squares refinement, produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.²³

Density Functional Theory Calculations.

All DFT calculations were performed with the ORCA program package.²⁴ Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.²⁵⁻²⁷ The all-electron Gaussian basis sets were those developed by the Ahlrichs group.²⁸⁻³⁰ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SVP basis sets were used that were of double- ζ quality in the valence region and contained a polarizing set of d functions on the nonhydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)³¹⁻³³ approach were chosen to match

the orbital basis.³⁴⁻³⁶ Throughout this chapter computational results are described by using the broken-symmetry (BS) approach by Ginsberg³⁷ and Noodleman.³⁸ All molecular orbital and spin density plots were generated using the program Gabedit.³⁹ Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.⁴⁰ The Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{41,42}

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CHAPTER V: REACTIVITY OF A ROBUST HIGH-SPIN IRON(II) PYRIDINE BISPYRROLIDE COMPLEX WITH ORGANIC AZIDES

5.1 Abstract

Reaction of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ ($\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$ = 2,6-Bis(5-(2,6-dichlorophenyl)-3-phenyl-1H-pyrrol-2-yl)-pyridine) with various organic azides has been studied. The identity of the azide substituent has been found to have a profound impact on the transformation type and identity of the reaction products. Treatment of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with bulky 1-adamantyl azide resulted in the formation of the *cis*-divacant octahedral diamagnetic low-spin Fe^{IV} imide, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$. In a divergent manner, reaction with the bulky aryl azides, mesityl azide (mesityl = 2,4,6-trimethylphenyl), or xylyl azide (xylyl = 2,6-dimethylphenyl) resulted in the exclusive formation of the paramagnetic iron iminyl complexes $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NXyl})$. Reaction with the sterically unhindered aryl azides, *para*fluorophenyl azide, pFPhN_3 , or 4-*tert*butylphenyl azide, which lack sufficient steric protection of the intermediate iron nitrene, resulted in the exclusive formation of the corresponding Fe^{III} tetrazene complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{p}^t\text{BuPh})_2)$. A reaction with 1-(4-azidobutyl)benzene was also explored and resulted in the isolation of

(^{2,6}-Cl₂PhPDP^{Ph})Fe(N₄(nBuPh)₂)(HN=CH(CH₂)₃Ph), a low-spin Fe^{II} complex carrying a neutral tetrazene and aldimine ligand. All complexes were characterized using a combination of X-ray crystallography, ¹H NMR, and ⁵⁷Fe Mössbauer spectroscopy. Complementary density functional theory (DFT) studies have been undertaken to explore potential electronic structures for the isolated iron(IV) imido and iron(III) iminyl radical complexes.

5.2 Introduction

Significant attention has recently been devoted to the renewed study of base metal catalyzed reactions.¹ Specifically, researchers have identified iron as a potential surrogate for precious metals in a variety of valuable synthetic transformations, principally due to its ubiquity and benign nature. One specific class of reactions in which iron has shown significant promise is atom or group transfer reactions, such C-H hydroxylation or amination.² Decades ago, this field was pioneered by Breslow and coworkers, who disclosed the success of biomimetic iron porphyrin systems as catalysts in C-H amination.³ Following this report, modern investigations from the Betley and Milsman groups have included the development of similar pyrrole based ligand platforms that have demonstrated the capability to perform intramolecular C-H amination of mesityl groups of the supporting ligands (Figure 5.1).^{4,5} The pyrrole based ligands utilized in these systems include the dipyrromethene and pyridine dipyrrolide classes of ligands, which can be viewed as porphyrin fragments. Despite the initial promise of the intramolecular reactivity observed in these reports, subsequent investigations have demonstrated that the high reactivity of the intermediate iron nitrenes responsible for the observed C-H amination are susceptible to other competing degradation pathways, including tetrazene formation via [2+3] cycloaddition with a second equivalent of organic azide, or α -hydrogen atom abstraction from the nitrene substituent. These challenges underscore the necessity for the careful development and steric

attenuation of both the supporting ligand and the nitrene fragments in these systems in order to circumvent undesired reactivity.

In consideration of these necessities, the Betley group has demonstrated that the installation of inert and sterically encumbering 2,4,6-triphenylbenzene substitutions in place of mesityl groups on the dipyrromethene ligand render reactive iron nitrene complexes isolable and amenable to spectroscopic characterization. In depth spectroscopic and computational studies have elegantly demonstrated that these complexes do not contain canonical dianionic imidos, but instead feature high-spin Fe^{III} ions antiferromagnetically coupled to iminyl radical ligands. The same group has subsequently invoked the participation of similar intermediates in their catalytic protocol to form N-heterocycles via the decomposition of alkyl azides. The radical character imparted onto the iminyl ligand nitrogen is considered a critical component responsible for the success of this system.⁶ Mechanistically, this transformation is proposed to proceed via a C-H abstraction/radical rebound mechanism, invoking a direct comparison to the C-H hydroxylation of hydrocarbons via iron oxo porphyrins in P450 enzymes.⁷

Figure 5.1. Examples of pyrrole based ligands susceptible to intramolecular C-H amination.

Inspired by this success, it was envisioned that the installation of chemically robust aryl substituents at the 5-position of the PDP ligand pyrrolides may render the corresponding iron nitrene complexes amenable to isolation and spectroscopic study. The work presented in chapter 3 has demonstrated that by tailoring the nitrene source in reactions with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, the Fe^{III} iminyl radical complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ could be spectroscopically characterized via ^1H NMR spectroscopy.⁸ This complex has been shown to engage in the direct C-H amination of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand, as it decomposes in solution to the corresponding nitrene group transfer product, $\text{Fe}(\text{MesNH-}^{\text{Mes}}\text{PDP}^{\text{Ph}})$. Interestingly, despite the analogous reactivity to dipyrromethene complexes, calculations have suggested disparate ground states exist for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$

and dipyrromethene iron iminyl complexes. Computational analysis suggests a square-planar intermediate-spin ferric ion engaged in antiferromagnetic coupling to an iminyl radical ligand may best describe the electronic structure of this complex. In hopes of developing analogous square-planar iron iminyl complexes, we turned to $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, presented in Chapter 4. The similar substitution pattern of this ligand was envisioned to closely emulate that of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, used in the generation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. Further, the replacement of the mesityl methyl groups with chloride substituents should prevent intramolecular C-H amination and possibly make the corresponding iron nitrene adducts more amenable to crystallization. Herein is described initial reactivity studies and computational analysis of a variety of products arising from the reactivity of $(^{2,6\text{-ClPh}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with organic azides, including iron imide complexes.

Figure 5.2. Dipyrromethene (left) and pyridine dipyrroliide (middle, right) iron nitrene complexes.

5.3 Reactivity of (2,6-Cl₂PhPDP^{Ph})Fe(thf) with Adamantyl Azide

Considering the propensity for the ^{Mes}PDP^{Ph} ligand framework to undergo facile C-H amination of the mesityl substituent when treated with various organoazides, the complex (2,6-Cl₂PhPDP^{Ph})Fe(thf) was chosen as an alternative synthon that led to the successful synthesis of (2,6-Cl₂PhPDP^{Ph})Fe(NR) complexes. It was hypothesized that by maintaining an aryl substitution pattern at the five position of the pyrrolide would afford a ligand steric profile and corresponding electronic structure similar to that of ^{Mes}PDP^{Ph}. Accordingly, treatment of a homogeneous red solution of (2,6-Cl₂PhPDP^{Ph})Fe(thf) in benzene-*d*₆ with one equivalent of adamantyl azide at room temperature was found to induce no reaction, as determined by ¹H NMR spectroscopy. Heating the mixture at 60°C induced a color change of the solution to dark brown within minutes. Analysis of the crude reaction mixture via ¹H NMR spectroscopy demonstrated complete consumption of the starting material with concomitant appearance of a new C_{2v} symmetric diamagnetic species, as indicated by relative integrations to the 4-pyridine triplet resonance (5.28 ppm). Removal of volatiles *in vacuo* and subsequent crystallization via slow evaporation of a diethyl ether solution afforded red single crystals suitable for analysis via X-ray diffraction. The X-ray analysis confirmed the identity of the reaction product as the iron imido complex, (2,6-Cl₂PhPDP^{Ph})Fe(N¹Ad) (Scheme 5.1). An ORTEP of the molecular structure is depicted in Figure 5.4.

Scheme 5.1. Synthesis of $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$.

The coordination geometry about the iron center is best described as a *cis*-divacant octahedron. The short iron-nitrogen bond lengths of are consistent with a low spin state, in agreement with the apparent diamagnetism observed via ^1H NMR spectroscopy. Distances of 1.887(4) Å and 1.894(4) Å to N1 and N3 of the pyrrolide N atoms, 1.898 (4) Å to N2, the pyridine nitrogen. The iron-imide nitrogen bond distance is 1.620(4) Å. In totality, the solid-state structure of $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ is very similar to the previously studied analogue $(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{N}^1\text{Ad})$, reported by Caulton, Mindiola, et al.⁹ For comparison, important structural metrics determined via the X-ray crystallographic analysis of $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ and $(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{N}^1\text{Ad})$ are provided in Table 5.2. Despite the similarity in the iron PDP nitrogen and iron imide bond lengths, a subtle but evident difference in the coordination geometry of the two complexes is present in the $\text{N}_{\text{pyridine}}\text{-Fe-N}_{\text{imide}}$ bond angle. For *cis*-divacant octahedral $(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{N}^1\text{Ad})$ this angle was found to be 116.6(2),⁹ while for $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ the imide fragment is more bent, with a $\text{N}_{\text{pyridine}}\text{-Fe-N}_{\text{imide}}$ angle of 123.12(19)°. Despite the slight departure from *cis*-divacant octahedral geometry for $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ relative to $(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{N}^1\text{Ad})$, the $\text{Fe-N}_{\text{imide}}\text{-C}_{\text{imide}}$ bond angles are 139.94(4) and 140.5(3) degrees, respectively.

Caulton, Mindiola, and coworkers have previously reported the density functional theory (DFT) characterization of (^tBuPDP^tBu)Fe(N¹Ad) and cited an electronic and not steric preference for the imide to occupy an apical coordination site, resulting in a *cis*-divacant octahedral geometry. (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad) offers the possibility of testing this proposal, as a planar geometry should be accessible for the complex due to the smaller steric profile of the 2,6-dichlorophenyl substituents at the 5 position of the pyrrolides. Notably, the observed C_{2v} symmetric ¹H NMR spectrum (Figure 5.3), suggests that the imido fragment is engaged in rapid equilibration above and below the plane of the ^{2,6}-Cl₂PhPDP^{Ph} chelate faster than can be observed on the NMR timescale. This is in contrast to (^tBuPDP^tBu)Fe(N¹Ad), which displays a C_s symmetric ¹H NMR spectrum due to its inability to access to a planar structure owing to the steric environment enforced by the tert-butyl groups at the 5 position of the pyrrolide heterocycles of the ^tBuPDP^tBu pincer. Interestingly, the chemical shifts of (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad) were found to be significantly deviated from those reported for (^tBuPDP^tBu)Fe(N¹Ad) (Table 5.1) and largely removed from their diamagnetic references values. For example, the 4-pyridine resonance in (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad) is observed at 5.28 ppm vs. 6.28 ppm in (^tBuPDP^tBu)Fe(N¹Ad). This behavior is similar to (^{Mes}PDP^{Ph})Fe(N₄pTol₂), discussed in Chapter 3, which features a 4-pyridine resonance at 5.75 ppm.⁵ Computational analysis and variable temperature NMR studies suggest that low-lying paramagnetic excited states may be accessible for (^{Mes}PDP^{Ph})Fe(N₄pTol₂), resulting in the observed anomalous chemical shifts as a result of paramagnetic contributions to the chemical shifts. A similar situation may be operative for (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad), as suggested by computational analysis (*vide infra*).

Figure 5.3. ^1H NMR spectrum of $(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ at 400 MHz in benzene- d_6 .

Table 5.1. ^1H NMR chemical shifts (ppm) of *cis*-divacant octahedral PDP iron imides.

	$(^t\text{BuPDP}^t\text{Bu})\text{Fe}(\text{N}^1\text{Ad})^a$	$(^{2,6\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$
4-Pyridine H	6.28 ^b	5.28
3-Pyridine H	6.28 ^b	7.97
Pyrrole- CH	6.64	4.78
Adamantyl- CH_2	2.23	3.65
Adamantyl- CH_2	1.46	1.70-1.56 ^c
Adamantyl- CH	1.56	-0.21

^a Values obtained from reference 9. ^b Overlapping resonances.

^c multiplet resonance.

Figure 5.4. ORTEP depictions of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ displayed at 30% probability ellipsoids. The bottom perspective view has one pyrrolide 2,6-dichlorophenyl substituent (with exception of the *ipso* carbon) and hydrogen atoms omitted for clarity.

Table 5.2. Selected bond lengths (Å) and angles (deg) obtained from X-ray crystallography for (^tBuPDP^tBu)Fe(N¹Ad) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N¹Ad).

	(^t BuPDP ^t Bu)Fe(N ¹ Ad) ^a	(^{2,6-Cl₂Ph} PDP ^{Ph})Fe(N ¹ Ad)
Fe(1)–N(1)	1.910(2)	1.887(4)
Fe(1)–N(2)	1.867(3)	1.898(4)
Fe(1)–N(3) ^d	-	1.894(4)
Fe(1)–N(4)	1.640(4)	1.620(4)
Fe(1)–C(38)–N(4)	140.5(3)	139.94(4)
N(1)–Fe(1)–N(2)	82.13(7)	81.21(17)
N(1)–Fe(1)–N(3) ^d	-	151.59(18)
N(1)–Fe(1)–N(4)	106.21(7)	100.82(19)
N(2)–Fe(1)–N(3) ^d	-	80.67(17)
N(2)–Fe(1)–N(4)	116.6(2)	123.12(19)
N(3)–Fe(1)–N(4) ^d	-	107.38(19)

^aValues obtained from reference 9. ^b Values obtained from RKS calculation of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N¹Ad). ^dN1 and N3 of (^tBuPDP^tBu)Fe(N¹Ad) are symmetry related.

5.4 Reactivity of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf) with 4-Substituted Aryl Azides

Considering the disparate outcome of the reaction of adamantyl azide with (^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf) relative to (^{Mes}PDP^{Ph})Fe(thf), it was surmised that the possibility of isolating an iron nitrene with aryl substitution may exist within the framework of the ^{2,6-Cl₂Ph}PDP^{Ph} ligand. Accordingly, addition of a benzene-*d*₆ solution containing one equivalent of parafluorophenyl azide to a (^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf) solution in the same solvent led to an instantaneous color change from of the solution from red to dark brown. Analysis of the crude reaction mixture by ¹H NMR spectroscopy indicated an approximate 1:1 ratio of starting material to a new diamagnetic species based on integrations of the 4-pyridine proton resonances. Repetition of the experiment with two molar equivalents of *para*-fluorophenyl azide led to

complete consumption of the starting material and clean formation of the new diamagnetic product, as ascertained by NMR. ^{19}F NMR analysis confirmed the presence of one fluorine environment in the sample, as evidenced by a broad singlet resonance at -121.86 ppm (benzene- d_6 , Figure 5.5). Performing the reaction on a preparative scale afforded a dark-brown powder after workup (*vide infra*), which was subjected to analysis via zero-field Mössbauer spectroscopy. The observed quadrupole doublet (Figure 5.4) gave a satisfactory fit with parameters $\delta = 0.13$ mms^{-1} and $|\Delta E_Q| = 2.97$ mms^{-1} . These values are in good agreement with the Mössbauer parameters of $\delta = 0.12$ mms^{-1} and $|\Delta E_Q| = 3.12$ mms^{-1} for the related species $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$, previously presented in Chapter 3.⁵

Figure 5.5. Zero-field Mössbauer spectrum of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ acquired at 80 K. The white circles indicate the experimental data and the blue line corresponds to the fit.

Based on the available spectroscopic data, a tentative assignment of the species as the iron tetrazene complex $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ was made. Consistent with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ is characterized by unusual chemical shifts for some resonances in the ^1H NMR spectrum (i.e.: 5.75 ppm for 4-pyridine*H*), some of which are broadened and devoid of coupling (i.e.: Ar*H*, 0.46 ppm), reminiscent of paramagnetically broadened and shifted resonances. This is further evidenced by the broad ^{19}F resonance (Figure 5.6) that is entirely devoid of coupling to the protons on the phenyl ring of the tetrazene. For $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$ this behavior was ascribed to accessible paramagnetic excited states.

Evaporation of a concentrated dichloromethane solution of the pure material at room temperature afforded dark-brown single crystals suitable for study via X-ray crystallography. The solid-state structural analysis performed at 100 K confirmed the identity of the product as the iron tetrazene complex, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$. $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$, which was crystallized in the triclinic space group P-1, was found to exist as a two-component non-merohedral twin, featuring a major domain of 71.51(8)%. The coordination environment about the iron center is best described as a pseudo-square pyramidal in nature, and is isostructural with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$. This result contrasts the apparent C_{2v} symmetry observed in the solution phase as determined by NMR spectroscopy. As previously discussed for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$, this likely arises from rapid wagging of the tetrazene ligand above and below the plane of the PDP chelate on the timescale of the NMR experiment. The low energy barrier associated with this dynamic behavior in solution prevents the observation of discrete C_s symmetric isomers which are “frozen-out” under crystallography conditions at 100 K.⁴ Relevant bond lengths and angles for $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ are summarized in Table 5.3. Notable bond distances include the nitrogen-nitrogen bonds within the tetrazene ligand, which were found to be 1.317(4)

Å for N(4)-N(5), 1.328(4) Å for N(5)-N(6), and 1.317(4) Å for N(6)-N(7), consistent with the retention of the radical monoanionic tetrazene formulation in this compound. Similarly, the iron PDP nitrogen distances were also found to be similar to those observed in (^{Mes}PDP^{Ph})Fe(N₄pTol₂), with distances of 1.938(3) for Fe-N1, 1.936(3) for Fe-N2, 1.950(3) for Fe-N3, 1.875(3) for Fe-N4, and 1.795(3) for Fe-N7. These bond lengths, which are consistent with a low-spin iron center, prompt an overall electronic structural assignment for the complex as containing a low-spin ferric center engaged in apparent antiferromagnetic coupling to a radical monoanionic tetrazene ligand.

In spite of the steric bulk of the para-substituted tert-butyl group, the reaction of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf) with *para*-^tBu-phenylazide proceeded with the formation of the tetrazene derivative, (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(p^tBuPh)₂) (Scheme 5.2). The ¹H NMR spectrum of this compound (Figure 5.7, bottom) features NMR characteristics (broad resonances, unusual chemical shifts, etc.) similar to (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(pFPh)₂) and (^{Mes}PDP^{Ph})Fe(N₄pTol₂).⁵

Figure 5.6. ORTEP depictions of two perspective views of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized dichloromethane have been excluded for clarity.

Figure 5.7. ^1H NMR spectra of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ (top) and $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{p}'\text{BuPh})_2)$ (bottom) at 400 MHz in CDCl_3 . Top-right: ^{19}F NMR spectra of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ at 376 MHz in CDCl_3 .

Scheme 5.2. Synthesis of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pRPh})_2)$ complexes. R denotes fluoro or tert-butyl.

Table 5.3. Selected bond lengths (Å) and angles (deg) for (^{Mes}PDP^{Ph})Fe(N₄Tol₂) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(pFPh)₂).

	(^{Mes} PDP ^{Ph})Fe(N ₄ Tol ₂)	(^{2,6-Cl₂Ph} PDP ^{Ph})Fe(N ₄ (pFPh) ₂)
Fe(1)–N(1)	1.946(3)	1.938(3)
Fe(1)–N(2)	1.943(3)	1.936(3)
Fe(1)–N(3)	1.955(3)	1.950(3)
Fe(1)–N(4)	1.867(3)	1.875(3)
Fe(1)–N(7)	1.803(3)	1.795(3)
N(4)–N(5)	1.299(4)	1.317(4)
N(5)–N(6)	1.336(4)	1.328(4)
N(6)–N(7)	1.318(4)	1.317(4)
N(1)–Fe(1)–N(2)	79.87(11)	80.45(12)
N(1)–Fe(1)–N(3)	153.02(11)	152.95(12)
N(2)–Fe(1)–N(3)	79.80(11)	79.20(12)
N(2)–Fe(1)–N(4)	174.94(12)	176.88(13)
N(2)–Fe(1)–N(7)	96.34(12)	92.88(13)
N(4)–Fe(1)–N(7)	78.75(12)	79.01(13)

In order to further support the electronic structure assignment of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(pFPh)₂) made based upon ¹H NMR and X-ray crystallographic analysis, a full molecule DFT computational study was performed at the B3LYP level of theory using (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(pFPh)₂) as a representative example. BS(1,1), BS(2,2), and RKS approaches were employed, covering a gamut of potential electronic structures for the system. The BS(1,1) solution converged to the corresponding broken-symmetry solution, representing a low-spin Fe^{III} center antiferromagnetically coupled to a tetrazene radical monoanion. The resulting optimized structure is in good agreement with the structural metrics obtained

experimentally from X-ray crystallography. A high spatial overlap value of $S = 0.67$ was computed, suggesting a highly covalent interaction between the metal and ligand fragments. Mössbauer parameters were computed from the optimized structure and were found to be in excellent agreement with the experimentally obtained values, $\delta = 0.18 \text{ mms}^{-1}$ and $\Delta E_Q = -3.03 \text{ mms}^{-1}$. Analysis of the Mulliken population analysis obtained from the calculation obviated the presence of approximately one iron-centered spin as well as significant spin density of the opposite sign delocalized throughout the nitrogen atoms and aromatic system of one phenyl group of the tetrazene ligand, as demonstrated by the spin density plot depicted in Figure 5.7. The BS(2,2) computation converged spontaneously to the BS(1,1). Furthermore, the RKS calculation, accounting for either a low-spin Fe^{II} center ligated by a neutral, fully oxidized tetrazene ligand, or low-spin Fe^{IV} ion ligated by a dianionic tetrazene, was found to be only $1.9 \text{ kcal mol}^{-1}$ higher in energy than the BS(1,1) solution. The small energetic favorability observed by symmetry breaking in this context is identical to that observed in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$, also displaying a calculated energy difference of $1.9 \text{ kcal mol}^{-1}$ between the BS(1,1) and RKS-optimized structures.⁵ The computed Mössbauer parameters for the RKS calculation were found to have an identical isomer shift to the BS(3,1) computed structure, $\delta = 0.18 \text{ mms}^{-1}$, while the calculated quadrupole splitting $\Delta E_Q = -2.73 \text{ mms}^{-1}$ for the RKS solution is slightly deviated from the experimentally observed value of $|2.97| \text{ mms}^{-1}$. Table 5.4 summarizes the experimental and calculated Mössbauer data for $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$. Consistent with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{pTol}_2)$, a definitive assessment of the electronic structure of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPh})_2)$ cannot be made on the basis of computations alone, and the high-resolution crystal structure coupled with the diamagnetism observed via NMR are the most telling pieces of information and are consistent with the assignment of a low-spin ferric ion

ligated by a radical monoanionic tetrazene ligand in the $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}\text{Fe}(\text{N}_4(\text{pRPh})_2)$ complexes presented here.

Figure 5.8. Spin density plot obtained from the Mulliken population analysis of a BS(1,1) calculation of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}\text{Fe}(\text{N}_4(\text{pFPh})_2)$.

Table 5.4. Experimental and calculated Mössbauer parameters for $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}\text{Fe}(\text{N}_4(\text{pFPh})_2)$.

	δ / mms^{-1} (calc)	ΔE_Q / mms^{-1}	η^a
Experimental	0.13	$ 2.97 ^b$	$-^c$
RKS	0.18	-2.73	0.683
BS(1,1)	0.18	-3.03	0.537

^a Asymmetry parameter of the electronic field gradient. ^b Sign not determined experimentally. ^c Value not determined experimentally.

5.5 Reactivity of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}\text{Fe}(\text{thf}))$ with Mesityl and Xylyl Azide

Having isolated and characterized $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}\text{Fe}(\text{N}^1\text{Ad}))$, it was anticipated that a sterically encumbered aryl nitrene congener may also be isolable. Hence, the bulky aryl azide mesityl azide (MesN_3) was selected as a suitable first candidate. To a red/orange benzene- d_6

solution of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was added a solution of one molar equivalence of MesN_3 in the same solvent, inducing a rapid color change of the solution to dark brown. Analysis of the crude reaction mixture via ^1H NMR spectroscopy indicated complete consumption of the high-spin Fe^{II} starting material and the appearance of eleven new paramagnetically shifted resonances spanning a chemical shift range of 23.45 to -224.83 ppm. The 11 paramagnetically shifted broad singlet resonances is consistent with a C_{2v} symmetric $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})$ ligand environment and mesityl fragment. Integrations of the observed signals relative to the 4-pyridine resonance (-4.41 ppm) were consistent with an initial assignment of the product as either an organoazide adduct, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_3\text{Mes})$ or an iron nitrene $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$. A comparison of the ^1H chemical shifts obtained from the NMR spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ indicate that the two complexes are chemically similar, and prompts a tentative assignment of the product as the iron imide, as opposed to the plausible azide adduct.

In order to probe the generality of the ability to observe 2,6-disubstituted aryl nitrenes, an analogous reaction with 2,6-dimethylphenyl azide (xylyl azide) was performed in benzene- d_6 solution. Similar to the reaction with mesityl azide, an instantaneous color change of the solution to dark brown was observed. Analysis of a ^1H NMR spectrum (Figure 5.9) acquired of the crude reaction mixture demonstrated clean conversion to a new species featuring 11 paramagnetically shifted resonances spanning a range of 171.20 to -133.78 ppm. The ^1H NMR spectra is consistent with a C_{2v} symmetric complex and prompted an assignment of the product as $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NXyl})$. Qualitatively, the ^1H NMR spectra of $(^{2,6\text{-ClPh}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NXyl})$ are very similar with the exception of two resonances. $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NXyl})$ is characterized by one extremely downfield shifted resonance observed at 171.20 ppm. This resonance is absent in the ^1H NMR spectrum of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$.

Integration of this resonance relative to the 4-pyridine resonance (-5.07 ppm) demonstrated a 1:1 ratio, prompting an assignment as the *para*-phenyl proton of the 2,6-dimethylphenyl group of the nitrene unit. The absence of this resonance is consistent with the *para*-methyl substitution in the mesityl analogue, which has a corresponding chemical shift of -224.83 ppm, a feature which is absent in spectrum of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(NXyl).

Scheme 5.3. Synthesis of (^{2,6-ClPh}PDP^{Ph})Fe(NMes) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(NXyl).

Figure 5.9. ^1H NMR spectra of $(^{2,6}\text{-Cl}_2\text{Ph})\text{PDP}^{\text{Ph}}\text{Fe}(\text{NMes})$ (bottom) and $(^{2,6}\text{-Cl}_2\text{Ph})\text{PDP}^{\text{Ph}}\text{Fe}(\text{NXyl})$ (top) in benzene- d_6 .

5.6 Reactivity of $(^{2,6}\text{-Cl}_2\text{Ph})\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$ with 1-(4-Azidobutyl)benzene

With the observed propensity to form nitrene species via the decomposition of azides in the presence of $(^{2,6}\text{-Cl}_2\text{Ph})\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$, attempts were made to determine if productive C-H amination could be leveraged in this system (Scheme 5.4). Accordingly, the substrate 1-(4-azidobutyl)benzene was chosen as a model substrate, as it has been demonstrated to undergo intramolecular C-H amination at the benzylic position to form the corresponding 2-phenylpyrrolidine product following the generation of reactive nitrenes of iron.⁶ Reactions of this type have been proposed to occur via initial formation of the metal nitrene species followed by hydrogen atom abstraction from the benzylic position of the butylbenzene fragment to form a

metal amido and a benzylic radical. Radical rebound of the carbon-based radical with the metal amido species gives rise to the phenyl pyrrolidine product.

Scheme 5.4. Proposed synthesis of iron-bound 2-phenylpyrrolidine via decomposition of 1-(4-azidobutyl)benzene in the presence of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$.

Treatment of a benzene-*d*₆ solution of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with a solution of one equivalent of 1-(4-azidobutyl)benzene in the same solvent yielded no discernable color change. Analysis of the crude reaction mixture via ¹H NMR spectroscopy indicated the generation of a new diamagnetic species as well as unreacted starting material. The new diamagnetic product was characterized via a distinct downfield doublet resonance at 9.62 ppm with ³J_{H-H} of 21.6 Hz, suggesting the incorporation of an imine functionality into the product. The experiment was repeated using three molar equivalents of the azide reagent, and full consumption of the starting materials was evidenced by ¹H NMR analysis. The volatiles were removed *in vacuo*, and crystallization of the crude product was accomplished by diffusion of pentane into a concentrated benzene solution of the new iron complex. Abundant crystallization of red plates suitable for analysis by X-ray crystallography were generated from this method. The structural analysis revealed the identity of the crystal as $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{nBuPh})_2)(\text{HN}=\text{CH}(\text{CH}_2)_3\text{Ph})$ carrying both tetrazene and imine ligands sourced from the azide starting material (Figure 5.10). This

compound is an analogue of the low-spin Fe^{II} species (^{Mes}PDP^{Ph})Fe(N₄Bn₂)(HN=CHPh) presented in Chapter 3, which was obtained as one of the products in the reaction of (^{Mes}PDP^{Ph})Fe(thf) with benzyl azide. The identity of the second product was determined to be the high-spin Fe^{II} species Fe({NHBn}₂-^{Mes}PDP^{Ph}), which arises from two consecutive C-H amination events of the ^{Mes}PDP^{Ph} ligand.⁵ Presumably, the lack of benzylic C-H bonds on the PDP ligand in close proximity to an intermediate nitrene renders the formation of the tetrazene and imine-ligated product as the sole reaction outcome. At this time, the mechanistic pathway that accounts for the formation of this unusual compound is not entirely clear. However, the observation of a tetrazene ligand suggests that the initially generated iron nitrene intermediate undergoes a rapid [2+3] cycloaddition to form the corresponding tetrazene. Subsequent capture and formation of another nitrene intermediate followed by hydrogen atom abstraction would account for the observed product (Scheme 5.5).

In regard to the details of the structural analysis of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(nBuPh)₂)-(HN=CH(CH₂)₃Ph), the complex was found to crystallize in the triclinic space group P-1. The iron-nitrogen bond distances of 1.9794(14) Å and 1.9941(14) Å to N1 and N3 (pyrrolide nitrogens), 1.9503(14) Å to N3 (pyridine nitrogen), 1.8526(14) Å and 1.8502(15) Å to N4 and N7 (tetrazene nitrogens), and 2.0016(16) Å to N8 (imine nitrogen) are in agreement with the low-spin state inferred from the diamagnetism of the compound observed via ¹H NMR. Analysis of the nitrogen-nitrogen bonds comprising the tetrazene ligand revealed distances of 1.299(2) Å for N4-N5, 1.351(2) Å for N5-N6, and 1.294(2) Å for N6-N7, consistent with a fully oxidized neutral tetrazene ligand.¹⁰ The short N(8)-C(58) distance of 1.272(2) confirms the presence of a double bond in the imine fragment and the imine hydrogen atom was successfully identified in

Scheme 5.5. Synthesis of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{nBuPh})_2)(\text{HN}=\text{CH}(\text{CH}_2)_3\text{Ph})$.

Table 5.5. Selected bond lengths (Å) and angles (deg) for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)(\text{HN}=\text{CHPh})$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{nBuPh})_2)(\text{HN}=\text{CH}(\text{CH}_2)_3\text{Ph})$.

	$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Bn}_2)-$ (HN=CHPh)	$(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}-$ (N ₄ (nBuPh) ₂)(HN=CH(CH ₂) ₃ Ph)
Fe(1)–N(1)	1.996(1)	1.9794(14)
Fe(1)–N(2)	1.938(1)	1.9503(14)
Fe(1)–N(3)	1.995(1)	1.9941(14)
Fe(1)–N(4)	1.848(1)	1.8526(14)
Fe(1)–N(7)	1.855(1)	1.8502(15)
Fe(1)–N(8)	1.983(1)	2.0016(16)
N(4)–N(5)	1.3030(2)	1.299(2)
N(5)–N(6)	1.350(2)	1.351(2)
N(6)–N(7)	1.302(2)	1.294(2)
N(8)–C(58)	1.271(2)	1.272(2)
N(1)–Fe(1)–N(2)	80.85(6)	80.20(6)
N(1)–Fe(1)–N(3)	160.11(6)	159.05(6)
N(2)–Fe(1)–N(3)	79.88(5)	79.61(6)
N(2)–Fe(1)–N(7)	174.00(6)	174.25(6)
N(4)–Fe(1)–N(8)	172.46(6)	175.80(6)

The observation of iron tetrazene and imine formation in the product $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{nBuPh})_2)(\text{HN}=\text{CH}(\text{CH}_2)_3\text{Ph})$ is another example of the highly reactive nature of the nitrenoid intermediates formed within the context of the PDP Fe system. Furthermore, the observation of the aldimine ligand formation demonstrates that an intermediate iron nitrene is competent for a C-H functionalization reaction in the context of the new 2,6-dichlorophenyl-substituted PDP supporting ligand. This result hints that the elimination of C-H bonds alpha to an intermediate iron nitrene fragment may allow for the systematic leveraging of a C-H functionalization reaction to occur in a controlled fashion. Studies involving the evaluation of α -geminal dimethyl-substituted alkyl azides¹¹ in reactions with $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ are currently underway in our laboratory (See Chapter 7 for future outlooks).

5.7 Calculations of Isolated Iron Imides and Iminyl Radical Complexes

In Chapter 3, computational evidence was presented that suggested the intermediacy of paramagnetic $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ complexes as potential intermediates in C-H amination, tetrazene formation, and α -hydrogen atom abstraction. The observation of paramagnetic complexes $(^{\text{Ar}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ (where Ar = 2,6-Cl₂Ph or mesityl and R = Mesityl or Xylyl) by ¹H NMR spectroscopy has further solidified this claim. However, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ is apparently diamagnetic which is inconsistent with the paramagnetic description ascribed to the unobserved intermediate $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ probed computationally. Furthermore, the unusual ¹H NMR chemical shifts of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ suggested that low-lying paramagnetic excited states may be available to this complex. With these details in mind, a full molecule computational analysis of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ was undertaken to better understand what potential paramagnetic electronic structures may be available to this complex and determine their

proximity in energy to the apparently diamagnetic ground state. With this in mind, RKS and BS(1,1) calculations were chosen to scan the singlet surface, UKS3 and BS(3,1) calculations on the triplet surface, and UKS5 and BS(5,1) computations were performed on the pentet energy surface. For consistency, the same computational methods employed in the study presented in Chapter 3 were utilized in this work (ORCA 3.02/B3LYP functional).

The RKS calculation converged to an optimized solution in excellent agreement with the experimental structure obtained via X-ray crystallography. Notably the iron-imide bond length, Fe-N4, was calculated to be 1.598 Å, similar to the experimentally obtained value of 1.620(4) Å. Furthermore, the N2-Fe1-N4 bond angle, spanning the pyridine nitrogen, iron, and imide nitrogen, was accurately reproduced via DFT with a value of 120.42°, vs. an experimental value of 123.12(19)°, consistent with a *cis*-divacant octahedral geometry. The BS(1,1) calculation was found to converge on a BS(2,2) solution with $S_{\text{Fe}} = 1$ and $S_{\text{L}} = 1$ (of the opposite sign convention) for the imide fragment. The spin-density map illustrating this is presented in Figure 5.11. Analysis of the Fe-N_{imide} bond length revealed a distance of 1.920 Å, significantly deviated from the experimental value of 1.620(4) Å. The geometry of this structure trends away from *cis*-divacant octahedral and is best described as bent, as evidenced by a N2-Fe1-N4 bond angle of 141.37°. Despite the significant geometric discrepancies present between the RKS and BS(2,2) optimized structures, these solutions are only separated by only a mere 0.5 kcal mol⁻¹. The UKS3 calculation spanning the triplet energy surface spontaneously converged to a BS(3,1) solution, which was found to be approximately 1.7 kcal mol⁻¹ lower in energy than the RKS solution. The prevalence for this electronic structure seems to be pervasive in the PDP system when planarity is allowed for the nitrene fragment, as BS(3,1) solutions have also been observed to be energetically favored for the optimized triplet structures of all (^{Mes}PDP^{Ph})Fe(NR) fragments that

have been analyzed computationally. Similarly, the BS(3,1) electronic structure in this context can be described as an intermediate spin ferric ion ($S_{\text{Fe}} = 3/2$) engaged in antiferromagnetic coupling with an iminyl based radical ligand, accounting for an overall $S = 1$ state. A high spatial overlap value of 0.66 was computed for the non-orthogonal magnetic orbitals. Analysis of the structural metrics demonstrates that the iron-iminyl fragment adopts a bent structure, consistent with the aforementioned analogues of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand. The N2-Fe1-N4 angle of 138.20° deviates from the experimentally observed angle of 123.12(19)°, while the iron-imide/iminyll bond distance is significantly elongated from 1.620(4) Å in the X-ray structure to 1.709 Å. The N_{im}-C_{im} bond length is reduced from 1.440(6) Å to 1.412 Å in the optimized BS(3,1) structure, indicating a trend towards a double bond and iminyl character. Mulliken population analysis confirmed the presence of approximately three spins located on the iron center, with significant radical character of the opposite sign present on the imide fragment, as depicted by the spin density plot in Figure 5.11.

UKS5 and BS(5,1) calculations also converged on the same solution, which was found to be the to be the lowest in energy and slightly favored over the BS(3,1) solution by 0.9 kcal mol⁻¹. This is in contrast to the computational study of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$)Fe(N¹Ad) and nitrene analogues, where BS(3,1) solutions were consistently identified to be the lowest energy solutions, albeit, modestly favored over other electronic structures. Despite this difference, all optimized geometries of ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(N¹Ad) are computed to exist within 3.1 kcal mol⁻¹ of one another. This result again underscores that it would be impossible to definitively identify the ground state of ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}$)Fe(N¹Ad) solely via computational methods.¹² The UKS5 solution is found to possess three iron centered spins ($S_{\text{Fe}} = 3/2$) and one imide centered spin ($S_{\text{L}} = 1/2$) of the same sign (Figure 5.11). Formally, such as solution could be described as an intermediate

spin Fe^{III} ion ($S_{\text{Fe}} = 3/2$) engaged in ferromagnetic coupling with a monoanionic iminyl radical ligand ($S_{\text{L}} = 1/2$) to account and overall $S = 2$ state. The Fe-N_{im} bond length of 1.781 Å is significantly elongated and relative to the experimentally determined value of 1.620(4) Å. A summary of the metrics obtained from this computational study is presented in Table 5.6.

Table 5.6. Calculated energies and selected structural parameters for different electronic structures of ^{(2,6-Cl₂Ph)₂PDP^{Ph}}Fe(N¹Ad) obtained from DFT calculations.

	$\Delta\text{Energy} / \text{kcal mol}^{-1}$	$N_{\text{py}}\text{-Fe-N}_{\text{im}} / ^{\circ}$	$\text{Fe-N}_{\text{im}}\text{-C}_{\text{im}} / ^{\circ}$	$\text{Fe-N}_{\text{im}} / \text{\AA}$
RKS	+2.6	120.42	141.58	1.598
BS(2,2) ^a	+3.1	141.37	146.86	1.920
BS(3,1)/UKS3 ^b	+0.9	138.23	159.23	1.709
UKS5 ^c	0	158.83	140.92	1.781

^aAntiferromagnetic coupling between i.s. Fe^{II} ($S = 1$) and triplet nitrene ($S = 1$). ^bAntiferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl radical ($S = 1/2$). ^cFerromagnetic coupling ferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl radical (1-) ($S = 1/2$).

Figure 5.11. Spin density plots obtained from the Mulliken population analysis of BS(3,1)/UKS3 (top), BS(2,2) (middle), and UKS5 (bottom) calculations of $(^{2,6}\text{-Cl}_2\text{P}^{\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$.

Although these computational results may seem to disfavor the relevance or the contribution of a BS(3,1) electronic structure (or other paramagnetic electronic structures) to the ground state of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$, attention is returned to the solution phase structure of the molecule, which possesses apparent C_{2v} symmetry, as ascertained by ^1H NMR spectroscopy. This result suggests that on the timescale of the ^1H NMR experiment, $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ has access to a planar structure in solution, and thus, if the electronic structure departs from a diamagnetic state in a planar structure, the resulting paramagnetic states become highly relevant. The observed anomalous ^1H NMR shifts of the compound lend further credence to this argument, as occupation of the imide in a planar site between the two extremes of a *cis*-divacant octahedron may render spin-state changes. Complex electronic structures featuring multiconfigurational ground states have also recently been identified in other 3d transition metal complexes carrying pyrrole and nitrene ligands that are competent in C-H amination reactions.¹³⁻

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In consideration of the results obtained from the computational study of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$, aryl substituted PDP nitrene complexes were also investigated computationally using $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ as a representative example to determine if they would be consistent with related $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ analogues. The same computational approaches utilized for the study of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ complexes, with exclusion of RKS and BS(1,1) calculations, as both $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{Xyl})$ were observed to be paramagnetic by ^1H NMR spectroscopy. With both complexes displaying similar NMR characteristics, and presumably possessing similar electronic structures, $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ was chosen as a representative example for study, as the $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ analogue has previously been computed.

The UKS3 calculation spanning the triplet surface spontaneously converged to the corresponding BS(3,1) solution, consistent with $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$. Analysis of the optimized structure demonstrates excellent agreement with the previously investigated $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NR})$ complexes.⁵ The structure of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ is best described as square planar, with a $\text{N}_{\text{pyridine}}\text{-Fe-N}_{\text{imide}}$ bond angle of 176.39° . The short iron-nitrene bond length of $1.74 \text{ \AA}$ implies significant multiple bond character. Further scrutiny of the bond distances in the computed structure demonstrate significant distortions throughout the nitrene aryl substituent. A $\text{N}_{\text{imide}}\text{-C}_{\text{ipso}}$ bond length of $1.33 \text{ \AA}$ is computed, intermediate between carbon-nitrogen double and single bond lengths. For reference, the high-spin Fe^{II} aryl amine complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NH}_2\text{Mes})$ has an amine nitrogen to aryl *ipso* carbon bond length of $1.45 \text{ \AA}$ (See Appendix A.2.8). This observation, coupled with the computed bond lengths of $1.45 \text{ \AA}$ from the *ipso* carbon to the *ortho* carbon and $1.41 \text{ \AA}$ for the *meta* to *para* carbon of the mesityl aryl ring (which depart from the $1.39 \text{ \AA}$ bond lengths in benzene)¹⁶ suggest that as a whole nitrene fragment is best described as an iminyl radical ligand (Figure 5.13). This claim is supported by analysis of the spin density distribution (Figure 5.14) obtained from Mulliken population analysis. Spin density values of 2.64 on the iron center and -0.30 on the iminyl nitrogen are consistent with an intermediate spin ferric ion ($S_{\text{Fe}} = 3/2$) engaged in antiferromagnetic coupling with an iminyl radical ligand ($S_{\text{L}} = 1/2$). Notably, significant spin density is also found on the mesityl substituent, consistent with the significantly perturbed bond distances of the arene as well as the highly shifted ^1H NMR resonances of the protons of the mesityl group.

On the pentet surface the UKS5 calculation converged to an optimized structure best described as an intermediate-spin ferric ion ($S_{\text{Fe}} = 3/2$) engaged in ferromagnetic with an iminyl (1^-) radical ($S_{\text{L}} = 1/2$), consistent with an alignment of the iron and iminyl radical spins. The spin

density map (Figure 5.14) depicts approximately three iron centered spins along with significant spin present on the NMes fragment. Consistent with the BS(3,1) calculation, a nearly planar geometry is adopted by this structure with a $N_{py}\text{-Fe-}N_{im}$ angle of 168.11° and $\text{Fe-}N_{im}$ bond length of $1.792 \text{ \AA}$. It should be added that this structure is analogous to the UKS5 solution obtained for the $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$.

The BS(5,1) solution converged to an optimized structure that is similar to that for the BS(5,1) solution of $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$, with an $S_{\text{Fe}} = 5/2$ center and one spin located on the nitrene fragment, $S_L = 1/2$. Analysis of the bond metrics reveals a Fe-N distance of $1.81 \text{ \AA}$, again, consistent with multiple bond character. Notably, the increase in the bond distance from $1.74 \text{ \AA}$ in the BS(3,1) optimized structure to $1.81 \text{ \AA}$ in the BS(5,1) structure is consistent with an increase of the iron spin-state from intermediate ($S_{\text{Fe}} = 3/2$) to high-spin ($S_{\text{Fe}} = 5/2$). Also consistent with the previously discussed structures is the observation that the mesityl fragment possesses a similarly contracted $N_{imide}\text{-C}_{ipso}$ bond length of $1.32 \text{ \AA}$ and perturbed aryl carbon-carbon bond distances (Figure 5.13). Additionally, the same contracted $N_{imide}\text{-C}_{ipso}$ and perturbed aryl carbon-carbon bond distances within the nitrene mesityl substituent are present that are observed in the BS(3,1) and UKS5 geometry optimized structures. Overall, this solution can be formally described as an intermediate spin Fe^{III} center engaged in ferromagnetic coupling with an iminyl based radical ligand to account for an overall $S = 2$ state. An additional detail of interest in the optimized BS(5,1) structure is the presence of spin density (0.04, Figure 5.14) on a Cl atom of the $^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}$ supporting ligand. This chloride is presumably engaged in a weak Lewis-acid/base interaction, as evidenced by the Fe-Cl distance of $2.734 \text{ \AA}$, similar to $(^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{thf})$ where a similar chloride interaction is also present and measures $2.7161(5) \text{ \AA}$ (Figure 5.12).

Figure 5.12. BS(5,1) optimized structure of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ indicating Fe-Cl interaction. Note, color scheme is as follows: red (iron), grey (carbon), blue (nitrogen), green (chlorine).

Although the solid-state structure has yet to be determined for $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, these computational results, in combination with the observation of the paramagnetic ^1H NMR spectrum of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ sheds light on possible electronic structures for the compound. All three paramagnetic electronic structures study here suggest the presence of a destabilized iron-iminyl interaction, departing from a classical dianionic imido type ligand, although the ground state electronic configuration cannot be unambiguously assigned using DFT computational methods alone. This result is consistent with DFT calculations on isolable $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, which are also predicted to have numerous electronic structure configurations within only a few kcal mol^{-1} (Table 5.8).

Figure 5.13. Comparison of bond lengths from the X-ray crystal structure of $(^{Ar}L)FeCl(N(p\text{-}^tBuC_6H_4))_4$ and the optimized structures obtained from UKS3/BS(3,1) (top-right), UKS5 (bottom-left), and BS(5,1) (bottom-right) DFT calculations of $(^{2,6-Cl_2Ph}PDP^{Ph})Fe(NMes)$. Note: ^{Ar}L = 1,9-(2,4,6- $Ph_3C_6H_2$)-5-mesityldipyromethene.

Table 5.7. Calculated energies and selected structural parameters for different electronic structures of $(^{2,6-Cl_2Ph}PDP^{Ph})Fe(NMes)$ obtained from DFT calculations.

	$\Delta E_{\text{energy}} / \text{kcal mol}^{-1}$	$N_{\text{py}}\text{-Fe-}N_{\text{im}} / ^\circ$	$\text{Fe-}N_{\text{im}}\text{-}C_{\text{im}} / ^\circ$	$\text{Fe-}N_{\text{im}} / \text{\AA}$
BS(3,1)/UKS3 ^a	0	176.39	141.76	1.738
UKS5 ^b	+1.4	168.11	143.57	1.792
BS(5,1) ^c	+1.9	131.97	158.15	1.805

^aantiferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl radical ($S = 1/2$).

^bferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl(1-) radical ($S = 1/2$).

^cantiferromagnetic coupling between h.s. Fe^{III} ($S = 5/2$) and iminyl(1-) radical ($S = 1/2$).

Figure 5.14. Spin density plots obtained from the Mulliken population analysis of BS(3,1)/UKS3 (top), BS(5,1) (middle), and UKS5 (bottom) calculations of $(^{2,6}\text{-Cl}_2\text{Ph})\text{PDP}^{\text{Ph}}\text{Fe}(\text{NMes})$.

Table 5.8. Calculated energies for different electronic structures of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ obtained from DFT calculations.

$\Delta\text{Energy} / \text{kcal mol}^{-1}$		
$(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$	RKS	+ 2.6
	BS(2,2) ^a	+ 3.1
	BS(3,1)/UKS3 ^b	+ 0.9
	UKS5 ^c	0
$(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$	BS(3,1)/UKS3 ^b	0
	UKS5 ^c	+ 1.4
	BS(5,1) ^d	+ 1.9
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$	RKS	+8.7
	BS(2,2) ^a	+7.6
	BS(3,1)/UKS3 ^b	0
	UKS5 ^c	+2.2
	BS(5,1) ^d	+2.6

^aAntiferromagnetic coupling between i.s. Fe^{II} ($S = 1$) and triplet nitrene ($S = 1$) or antiferromagnetic coupling between i.s. Fe^{IV} ($S = 1$) and triplet nitrene ($S=1$). ^bAntiferromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl radical ($S = 1/2$). ^cFerromagnetic coupling between i.s. Fe^{III} ($S = 3/2$) and iminyl(1-) radical ($S = 1/2$).

^dAntiferromagnetic coupling between h.s. Fe^{III} ($S = 5/2$) and iminyl(1-) radical ($S = 1/2$).

5.8 Conclusion

Reaction of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ ($\text{H}_2^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}} = 2,6\text{-Bis}(5\text{-(2,6-dichlorophenyl)-3-phenyl-1H-pyrrol-2-yl-pyridine})$) with a variety of organic azides has been studied. The identity of the azide substituent has been found to have a substantial impact on the observed reaction products. Treatment of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with the bulky aliphatic 1-adamantyl azide resulted in the formation of the *cis*-divacant octahedral diamagnetic low-spin Fe^{IV} imide, $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}^1\text{Ad})$. Alternatively, reaction with either *para*-fluorophenyl-azide or *para*-tert-butylphenylazide, pFPhN_3 , which lacks steric protection of the nitrene, resulted in the exclusive formation of the corresponding Fe^{III} tetrazene complexes $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{pFPhN}_3)_2)$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{p}^t\text{BuPhN}_3)_2)$. In contrast, by using bulky aryl azide, such as mesityl azide, the paramagnetic iron iminyl complex $(^{2,6\text{-Cl}_2\text{Ph}}\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ has been characterized via ^1H NMR. Finally, the reaction of 4-azidobutylbenzene was also explored in attempt to leverage intramolecular C-H amination to the corresponding cyclic pyrrolidine. Instead, a low-spin Fe^{II} complex carrying a tetrazene and aldimine ligand $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4(\text{nBuPh})_2)(\text{HN}=\text{CH}(\text{CH}_2)_3\text{Ph})$ was isolated as the sole reaction product.

A complementary density functional theory (DFT) study has also been undertaken to explore potential paramagnetic electronic structures available to $(^{2,6\text{-Cl}_2\text{Ph}}\text{PhPDP}^{\text{Ph}})\text{Fe}(\text{NMes})$, which suggest this complex may feature an iminyl radical ligand. These results suggest that careful attention of the ancillary PDP ligand may allow for the isolation of iron nitrene complexes with discrete geometries and hence, electronic structures. Furthermore, it is anticipated that this will allow for the informed design of future systems leveraging discrete molecular iron complexes for nitrene group transfer.

5.9 Experimental Procedures

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH₂ and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Deuterated benzene (benzene-*d*₆) for NMR spectroscopy were distilled from sodium metal. Deuterated dichloromethane (dichloromethane-*d*₂) was distilled from calcium hydride. 1-Adamantyl azide was obtained from Sigma-Aldrich, dried under high vacuum, and recrystallized at -35°C from pentane prior to use. *Para*-fluorophenyl azide,¹⁷ *para*-tertbutylphenyl azide,¹⁷ mesityl azide,¹⁷ and 1-(4-azidobutyl)benzene⁶ were synthesized according to literature procedures.

Preparation of (2,6-Cl₂PhPDP^{Ph})Fe(N¹Ad).

In the glovebox, 24 mg (0.031 mmol) of (2,6-Cl₂PhPDP^{Ph})Fe(thf) was suspended in 500 μL of benzene-*d*₆ in a J. Young NMR Tube. In a separate dram vial, 6 mg (0.034 mmol, 1.1 eq.) of ¹AdN₃ was dissolved in 500 μL of benzene-*d*₆. The azide solution was added to the NMR tube and the tube was sealed. The mixture was shaken vigorously for thirty seconds and then the NMR tube was removed from the glovebox and placed in a 60°C oil bath. The tube was heated for 30 minutes and a ¹H NMR spectrum was acquired, which indicated the presence of (2,6-Cl₂PhPDP^{Ph})Fe(N¹Ad). The tube was then returned to the glovebox and poured into a 20 mL vial. The J. Young tube was washed three times with 1.5 mL of benzene. The benzene solutions were combined and reduced to approximately 1 mL. Addition of 5 mL of pentane induced the precipitation of a dark brown powder which was isolated via vacuum filtration on a medium

porosity frit. The powder was washed three times with 1.5 mL of pentane and dried *in vacuo*.

Yield: 11 mg, 0.013 mmol, 40%. ^1H NMR (400 MHz, benzene- d_6) δ 7.97 (d, J = 7.4 Hz, 2H, 3-pyridineH), 7.47 (d, J = 7.5 Hz, 4H, *ortho*-PhH), 7.36 (t, J = 7.5 Hz, 4H, *meta*-PhH), 7.03 (d, J = 8.0 Hz, 4H, *ortho*-PhH), 6.95 (t, J = 7.2 Hz, 2H, *para*-PhH), 6.62 – 6.52 (t, J = 8.0 Hz, 2H, *para*-PhH), 5.28 (t, J = 7.8 Hz, 1H, 4-pyridineH), 4.78 (s, 2H, pyrrole-CH), 3.65 (s, 6H, adamantyl-CH₂), 1.80 – 1.46 (m, 6H, adamantyl-CH₂), -0.21 (s, 3H, adamantyl-CH). ^{13}C NMR (101 MHz, benzene- d_6) δ 27.52, 36.99, 107.35, 117.86, 128.59, 128.80, 128.94, 130.54, 130.84, 133.74, 135.10, 136.10, 138.15, 149.05, 155.95, 170.52 (three resonances were not located). Single crystals were grown via slow evaporation of a concentrated diethyl ether solution.

Preparation of ($^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}$)Fe($\text{N}_4(\text{pFPh})_2$).

In a 20 mL scintillation vial equipped with a magnetic stirrer was combined 95 mg (0.122 mmol) of ($^{2,6}\text{-Cl}_2\text{PhPDP}^{\text{Ph}}$)Fe(thf) and 10 mL of benzene. In a separate vial, 38 mg (0.277 mmol, 2.27 eq.) of parafluorophenyl azide and 5 mL of benzene were combined. With vigorous stirring, the azide solution was added dropwise to the suspension of the iron compound. An immediate color change from red to dark-red/brown was observed upon addition, accompanied by effervescence of the solution. After 12 hrs the solvent was removed, leaving a brown powder. The powder was transferred to a medium porosity glass frit and washed with three 5-mL aliquots of pentane and dried *in vacuo*. Single crystals suitable for study by X-ray diffraction were grown from slow evaporation of a concentrated dichloromethane solution of the compound. Yield: 95 mg, 82%. ^1H NMR (400 MHz, dichloromethane- d_2) δ 8.89 (s, 4H), 7.63 (t, J = 7.6 Hz, 4H), 7.07 (d, J = 7.4 Hz, 4H), 6.96 (t, J = 7.6 Hz, 2H), 6.84 (d, J = 7.8 Hz, 4H), 6.79 – 6.71 (t, 2H), 6.66 (t, J = 7.9 Hz, 1H), 6.04 (s, 4H), 5.09 (d, J = 5.1 Hz, 2H), 2.28 (s, 2H). Satisfactory ^{13}C NMR data

could not be acquired due to the extremely poor solubility of the compound in hydrocarbon solvents. ^{19}F NMR (376 MHz, benzene- d_6) δ -121.86.

Preparation of ($^{2,6}\text{-Cl}_2\text{Ph}$ PDP $^{\text{Ph}}$)Fe($\text{N}_4\text{p}^t\text{BuPh}_2$).

In a 20 mL scintillation vial equipped with a magnetic stirrer was combined 102 mg (0.131 mmol) of ($^{2,6}\text{-Cl}_2\text{Ph}$ PDP $^{\text{Ph}}$)Fe(thf) and 10 mL of benzene. In a separate vial, 50 mg (0.285 mmol, 2.18 eq.) of para tert-butylphenyl azide and 5 mL of benzene were combined. With vigorous stirring, the azide solution was added dropwise to the suspension of the iron compound. An immediate color change from red to dark-red/brown was observed upon addition, accompanied by effervescence of the solution. After 12 hrs the solvent was removed, leaving a brown powder. The powder was transferred to a medium porosity glass frit and washed with three 5-mL aliquots of pentane and dried *in vacuo*. ^1H NMR (400 MHz, benzene- d_6) δ 9.39 (s, 4H), 7.45 (t, J = 7.6 Hz, 4H), 7.10 (d, J = 7.6 Hz, 4H), 6.70 (t, J = 7.4 Hz, 2H), 6.60 (d, J = 8.1 Hz, 4H), 6.10 (t, J = 8.1 Hz, 2H), 5.94 (t, J = 7.9 Hz, 1H, 4-pyH), 5.75 (s, 4H), 4.87 (d, J = 7.8 Hz, 2H, 3-pyH), 2.05 (s, 2H), 0.93 (s, 18H, p -Ph(CH_3) $_3$). Satisfactory ^{13}C NMR data could not be acquired due to the poor solubility of the compound in hydrocarbon solvents.

Preparation of ($^{2,6}\text{-Cl}_2\text{Ph}$ PDP $^{\text{Ph}}$)Fe(NHCH(CH_2) $_3$ Ph)($\text{N}_4(n\text{BuPh})_2$).

50 mg (0.064 mmol) of ($^{2,6}\text{-Cl}_2\text{Ph}$ PDP $^{\text{Ph}}$)Fe(thf) was slurried in 5 mL of benzene in a 20 mL vial equipped with a magnetic stirrer. A 5 mL solution of 36 mg (0.205 mmol, 3.2 eq.) of 1-(4-azidobutyl)benzene was added to the vial. A color change from orange to red was noted accompanied by dissolution of all solids. The resulting homogeneous mixture was stirred for 24 hours. The solvent was then removed *in vacuo*, leaving a red residue which was washed three times with pentane. Yield: 32 mg, 0.027 mmols, 42%. ^1H NMR (400 MHz, benzene- d_6 ; δ , ppm): 9.62 (d, J = 22.0 Hz, 1H, aldimine-NH), 7.72 (d, J = 7.5 Hz, 4H, ArH), 7.41 (d, J = 7.9 Hz, 2H,

ArH), 7.22 (t, $J = 7.7$ Hz, 4H, ArH), 7.14 – 7.00 (m, 13H, ArH), 6.97 (t, $J = 7.2$ Hz, 4H, ArH), 6.90 – 6.73 (m, 6H, ArH), 6.30 (t, $J = 8.0$ Hz, 2H, ArH), 6.22 (s, 2H, pyrrole-CH), 3.59 (m, 2H, -CH₂), 3.25 (m, 2H, -CH₂), 2.50-2.47 (m, 2H, -CH₂), 2.37 – 2.29 (m, 2H, -CH₂), 1.98 (t, $J = 7.4$ Hz, 2H, CH₂), 1.82 – 1.65 (m, 2H, -CH₂), 1.60 – 1.49 (m, 2H, -CH₂) 1.48 – 1.19 (m, 8H, (4) -CH₂). Red single crystals of the compound were grown from diffusion of pentane into a concentrated benzene solution at room temperature.

Preparation of (^{2,6}-Cl₂PhPDP^{Ph})Fe(NMes).

In the glovebox, 50 mg (0.064 mmol) of (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf) was suspended in 500 μ L of benzene-*d*₆ in a J. Young NMR tube. In a separate dram vial, 12 mg (0.074 mmol, 1.16 eq.) of mesityl azide was dissolved in 100 μ L of benzene-*d*₆. The azide solution was added to J. Young tube inducing an immediate color change of the suspension from red to dark brown. The tube was sealed and shaken vigorously for thirty seconds, and a ¹H NMR spectrum was acquired, indicating quantitative conversion of (^{2,6}-Cl₂PhPDP^{Ph})Fe(thf). The NMR tube was returned to the glovebox and the solution was passed through a column of celite supported by a glass microfiber plug and collected in a 20 mL scintillation vial. The solvent was immediately removed *in vacuo*, affording a dark residue which was triturated with pentane. The resulting solid was transferred to a medium porosity glass frit and washed with three-3 mL aliquots of pentane and dried *in vacuo*. Yield: 35 mg, 0.042 mmol, 65%. ¹H NMR (400 MHz, benzene-*d*₆) δ 23.45 (s, 2H), 13.30 (s, 4H), 12.83 (s, 2H), 11.17 (s, 4H), 3.75 (s, 4H), 3.62 (s, 2H, *para*-phenylH), -4.41 (s, 1H, 4-pyridineH), -5.44 (s, 2H), -52.54 (s, 2H, *meta*-mesitylH), -159.03 (s, 6H, *ortho*-mesityl-CH₃), -224.83 (s, 3H, *para*-mesityl-CH₃).

Preparation of (2,6-Cl₂Ph)*PDP*^{Ph})Fe(NmXyl).

In a J. Young Tube 14 mg (0.018 mmol) of (2,6-Cl₂Ph)*PDP*^{Ph})Fe(thf) was dissolved in 500 μ L of benzene-*d*₆. In a separate vial, 5 mg (0.034 mmol, 1.9 eq.) of 2,6-dimethylphenyl azide was dissolved in 100 μ L of benzene-*d*₆. The azide solution was added to the NMR tube containing the solution of the iron complex. The tube was sealed and shaken rapidly for 30 seconds. A color change from red to brown as observed immediately. ¹H NMR spectroscopy indicated quantitative conversion to the product. ¹H NMR (400 MHz, benzene-*d*₆; δ , ppm): -133.78 (6H, *ortho*-CH₃), -48.61 (2H, *meta*-Ph), -5.07 (1H, 4-pyridine*H*), 3.27 (4H), 3.36 (2H), 3.90 (4H), 11.18 (4H), 12.22 (2H), 12.88 (4H), 24.36 (2H), 171.20 (1H, *para*-Ph*H*). Note, resonances for free THF were not observed at 1.40 and 3.57 ppm, respectively, thus, complicating the unambiguous assignment of ¹H NMR resonances.

Physical Measurements.

¹H and ¹³C {¹H} NMR spectra were acquired at 25 °C on a Varian Unity INOVA 600 MHz spectrometer equipped with a 5 mm inverse broadband PFG probe, on an Agilent 400 MHz DD2 spectrometer equipped with a 5 mm One NMR probe, or a JNM-ECZ400S/L1 spectrometer equipped with a 5 mm ROYAL NMR probe. All chemical shifts are reported relative to SiMe₄ using ¹H (residual) chemical shifts of the solvent as a secondary standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Room temperature magnetic susceptibility measurements were performed with a Johnson Matthey Mark 1 instrument that was calibrated with HgCo(SCN)₄. Zero field ⁵⁷Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a ⁵⁷Co/Rh radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/N₂ cryostat within an accuracy of $\pm$ 0.3 K. The data were calibrated

relative to α -iron at 298 K. The fitting procedure to extract quantitative spectral parameters uses a least-squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)¹⁸ was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.¹⁹

Density Functional Theory Calculations.

All DFT calculations were performed with the ORCA program package.²⁰ Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.²¹⁻²³ The all-electron Gaussian basis sets were those developed by the Ahlrichs group.²⁴⁻²⁶ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SVP basis sets were used that were of double- ζ quality in the valence region and contained a polarizing set of d functions on the nonhydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)²⁷⁻²⁹ approach were chosen to match the orbital basis.³⁰⁻³² Throughout this chapter computational results are described by using the broken-symmetry (BS) approach by Ginsberg³³ and Noodleman.³⁴ Because several broken symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation BS(m,n) has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. All molecular orbital and spin density plots were generated using the program Gabedit.³⁵ Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.³⁶ Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{37,38}

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CHAPTER VI: SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF A PYRIDINE DIPYRROLIDE IRON CARBENE COMPLEX

6.1 Abstract

The paramagnetic iron carbene complexes ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) and ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) have been prepared by the decomposition of diphenyldiazomethane in the presence of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$) and ($^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$), respectively. For ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) a thorough structural and spectroscopic study has been conducted, including X-ray crystallographic characterization as well as ^1H NMR and variable-temperature and applied-field Mössbauer spectroscopies. A complementary density functional theory study has also been conducted to further elucidate the electronic structure of this complex, which may be described as containing an intermediate spin iron(III) ion engaged in antiferromagnetic coupling to a carbene radical monoanion, ($\text{CR}_2^{1\bullet}$).

Preliminary reactivity studies of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) with carbon monoxide and isocyanides have also been investigated. Addition of carbon monoxide to ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) resulted in the insertion of the diphenylidene fragment, (CPh_2), into an iron pyrrolide nitrogen bond, forming a new carbon-nitrogen bond. This group transfer reaction is accompanied by ligation of two molecules of CO to the iron center. The resulting product,

(CPh₂^{Mes}PDP^{Ph})Fe(CO)₂, has been characterized by X-ray crystallography, and NMR and Mössbauer spectroscopies, confirming its structure and assigning its diamagnetic low-spin iron Fe^{II} electronic ground state. Similarly, the reaction of (^{Mes}PDP^{Ph})Fe(CPh₂) with 2,6-dimethylphenyl isocyanide results in an analogous carbene group transfer reaction, producing the isocyanide complex (CPh₂^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₂, which has also been thoroughly characterized. In benzene-*d*₆ solution, (CPh₂^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₂ is observed to undergo further carbene group transfer to an isocyanide ligand, resulting in the production of the corresponding ketenimine, Ph₂C=C=N-(2,6-(CH₃)₂Ph) and (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃, as determined by ¹H NMR spectroscopy. The iron containing product of this reaction has been identified as the diamagnetic Fe^{II} tris-isocyanide complex (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃, arising from isocyanide ligand redistribution. Alternatively, when (^{Mes}PDP^{Ph})Fe(CPh₂) is treated with one equivalent of the sterically encumbered isocyanide, C≡N-¹Ad, the diamagnetic carbene isocyanide species (^{Mes}PDP^{Ph})Fe(CPh₂)(C≡N-¹Ad) is produced and has been characterized via ¹H NMR and X-ray crystallography. These results suggests the competency of isocyanide-ligated iron carbene species in carbene group transfer to isocyanides.

6.2 Introduction

Carbene complexes have become ubiquitous intermediates in the field of organometallic catalysis, having achieved widespread notoriety and recognition for their utility in a variety of synthetic methodologies.¹⁻³ Of the many synthetic transformations that carbenes may facilitate, attractive examples include insertions into hydrogen-element (i.e. C-H, N-H, and O-H) bonds, cyclopropanation, and most notably, the olefin metathesis reaction.⁴⁻¹⁴ Historically, carbene complexes have been classified into two limiting classes depending on the nature of the electronic structure of the carbene fragment. Electrophilic carbenes are known as Fischer-type,

while alternatively, Schrock-type carbenes are nucleophilic in nature. Fischer carbenes possess a bonding interaction between a lone pair with singlet carbene parentage and a vacant metal orbital of appropriate symmetry. The additional interaction of a filled metal d orbital with a vacant carbene p orbital results in a donor-acceptor bonding motif. Additional stabilization of the vacant p orbital of the Fischer-carbene is imparted by the presence of heteroatoms possessing lone pairs adjacent to the carbene, commonly oxygen and nitrogen atoms.¹⁵ In contrast, Schrock carbenes, which are comprised strictly of hydrocarbon structures, possess triplet ground states. The triplet carbene is engaged in highly covalent bonding with a triplet metal center, with the bonding being polarized towards the carbene, rendering it nucleophilic.¹⁵ More recently, the Grubbs family of catalysts, which features ruthenium (II) centers and an electrophilic carbene ligand distinct from the Fischer description has been recognized as a privileged class of catalysts in olefin metathesis chemistry.¹¹ Schrock type carbenes are also highly active in olefin metathesis reactions and have received significant attention in their own right (Figure 6.1).^{9,10}

Figure 6.1. Examples of popular Schrock (left) and Grubbs (right) metathesis catalysts.

Although tremendous success has been realized by the Schrock and Grubbs catalyst systems over the past decades, each does possess inherent limitations. Notably, the Schrock type catalysts are air and moisture sensitive organometallic reagents, while the air-stable Grubbs catalyst systems employ precious ruthenium. In light of the latter, researchers have developed an

interest in extending the olefin metathesis reaction to iron, the 3d congener of ruthenium. The development of an iron-catalyzed olefin metathesis reaction is highly attractive in consideration of the cost reduction associated with the replacement of scarce ruthenium with a base metal alternative. In addition to iron being the most abundant of the transition metals, it also is recognized as benign. In consideration of the potential impact of an iron-catalyzed olefin metathesis reaction, researchers have sought to prepare iron complexes bearing carbene or alkylidene type ligands to explore their reactivity profiles. A host of examples are presented in Figure 6.2.

Despite the recent interest in the development of a molecular iron metathesis catalyst, evidence for iron carbene complexes actually predate Schrock's initial report of the first transition metal alkylidene complex.¹⁶ In early reports, Jolly and Green detailed suggested the production of the parent iron methyldiene complex, $[(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-CH}_2)\text{Fe}(\text{CO})_2][\text{BF}_4]$, by treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_3)$ with strong acids.^{17,18} A decade later, the first spectroscopic characterization of an iron carbene was accomplished by Brookhart and coworkers. ¹³C NMR spectroscopy identified a doublet carbon resonance at 342.4 ppm with $^1J_{\text{C-H}}=146$ Hz, consistent with the iron benzyldiene complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CHPh})]$.¹⁹ Subsequently, the research of iron carbenes has seen steady growth and now is a mature field with complexes characterized within a number of coordination environments.

The first examples of crystallographically characterized iron carbene complexes were reported, by Jones et al. Structural analysis of $[(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_7\text{H}_6)\text{Fe}(\text{CO})_2][\text{PF}_6]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_{11}\text{H}_8)\text{Fe}(\text{CO})_2][\text{PF}_6]$ determined the iron carbene bond distances in these complexes to be 1.979(3) and 1.996(2) Å, respectively.^{20,21} Lapinte then reported the structural characterization of the iron-ethylidene complex, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{dppe})(\text{C}(\text{H})\text{Me})][\text{OTf}]$, where

dppe = ethylenebis(diphenylphosphine), featuring an iron carbene bond distance of 1.787(8) Å.²² Guerchais followed with the X-ray crystallographic analysis of related $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})\text{-}\{\eta^2\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$ with an iron carbene bond length of 1.857(6) Å.²³

Complimentary synthetic investigations have included the exploration of macrocyclic ligands as supporting platforms for iron carbene fragments. Floriani and coworkers have reported the characterization of two diamagnetic (tmtaa)Fe(CPh₂) (tmtaa = tetramethyldibenzotetraazaannulene) complexes.^{24,25} An additional report from the same group described the X-ray studies of the paramagnetic calixarene complexes $[\{p^t\text{Bu-calix[4]-(O)}_2(\text{OR})_2\}\text{Fe}(\text{CPh}_2)]$, where R = Me or SiMe₃. The iron carbene bond lengths were found to be 1.943(8) Å and 1.958(5) Å. SQUID magnetometry measurements are consistent with high-spin Fe^{II} electronic structures for these species.²⁶ A crystal structure of the diamagnetic porphyrin ligated-iron carbene (TPFPP)Fe(CPh₂) (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrinato dianion) with a short iron-carbon bond length of 1.794(3) Å has been reported by the Che group.²⁷ An initial assignment of this compound as a low-spin Fe^{IV} complex with a dianionic alkylidene ligand was made based on Mössbauer spectroscopic measurements. Li and coworkers have disclosed an in depth study revisiting the electronic structure of (TPFPP)Fe(CPh₂) as well as the closely related dichlorocarbene analogues, (TPP)Fe(CCl₂), and (TTP)Fe(CCl₂). A combination of X-ray crystallography, Fe K-edge X-ray absorption near edge spectroscopy (XANES), and variable temperature applied field Mössbauer spectroscopy has elucidated the electronic structure of these compounds as low-spin ferrous species with highly covalent iron carbene interactions.²⁸ More recently, Che et al. have also recently reported a closely related family of diamagnetic iron porphyrin adamantylidene complexes, including structurally characterized (TPFPP)Fe(Ad).²⁹ A combined theoretical and experimental study has concluded that these complexes also feature

low-spin Fe^{II} centers with ancillary neutral carbene donors. These electronic structural assignments for the iron porphyrin carbene derivatives are in agreement with extensive computational studies and other extensive experimental investigations that have been conducted by other groups.³⁰⁻³²

In contrast to the ever growing number of porphyrin based iron carbene complexes, Jenkins and coworkers have reported the synthesis and X-ray crystallographic characterization of a unique “all carbene” iron complex, featuring a tetra-N-heterocyclic carbene macrocycle and diphenylidene ligand.³³ Akin to other macrocycle supported iron carbenes, [(^(S,S)-1,2-Cy,BMe₂TC^H)Fe(CPh₂)] is also diamagnetic and features a short iron-carbene bond length of 1.814(4) Å. A preliminary assignment as a low-spin Fe^{IV} complex has been made on the basis of electrochemical experiments and the diamagnetism of the complex observed by ¹H NMR spectroscopy.

The first examples of pincer ligand iron alkylidene complexes were structurally characterized by Chirik.³⁴ Paramagnetic (^{Et}PDI)Fe(CPh₂) and (^{Me}EtPDI)Fe(CPh₂) (^{Et}PDI = 2,6-(2,6-Et₂C₆H₃N=CMe)₂C₅H₃N) and ^{Me}EtPDI = 2,6-(2,6-Me₂C₆H₃N=CEt)₂C₅H₃N)) are the first examples of iron complexes featuring carbene radical ligands. A combined experimental and computational study of these compounds suggested the presence of high-spin Fe^{II} centers engaged in antiferromagnetic coupling with redox-active bis(imino)pyridine and carbene radical ligands. Although these complexes are not active cyclopropanation catalysts, a reaction protocol has recently been designed that demonstrates related Fe PDI complexes as highly active carbene transfer catalysts.³⁵ Additionally, carbene radical complexes have been identified as important intermediates in cobalt and iron catalyzed cyclopropanation catalysis.³⁶⁻⁴⁰ Other strategies for synthesizing iron carbene complexes have recently been disclosed by the Holland and

Wolczanski groups, respectively.⁴¹⁻⁴⁴ Table 6.1 summarizes a number of the notable iron carbene complexes that have been discussed and also includes their iron-carbene bond lengths, oxidation states, and spin states.

Figure 6.2. Examples of selected crystallographically characterized mononuclear iron carbene complexes and their corresponding iron carbene bond lengths.

Table 6.1. Oxidation state, spin state, and iron carbene bond distances for selected crystallographically characterized iron carbene complexes.

	<i>Oxidation State</i>	<i>Spin State^a</i>	<i>Fe-Carbene Bond Distance / Å</i>	<i>Ref</i>
$[(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_7\text{H}_6)\text{Fe}(\text{CO})_2][\text{PF}_6]$	Fe ^{II}	0	1.996(2)	21
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{dppe})(\text{C}(\text{H})\text{Me})][\text{OTf}]$	Fe ^{II}	0	1.787(8)	22
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})\{\eta^2\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$	Fe ^{II}	0	1.857(6)	23
$(\text{tmtaa})\text{Fe}(\text{CPh}_2)$	Fe ^{II}	0	1.794(3)	24
$\{[p^t\text{Bu-calix[4]}-(\text{O})_2(\text{OCH}_3)_2]\text{Fe}(\text{CPh}_2)\}$	Fe ^{II}	2	1.943(8)	26
$(\text{TPFPP})\text{Fe}(\text{CPh}_2)$	Fe ^{II}	0	1.794(3)	27
$[(\text{S,S})\text{-1,2-Cy,BMe}_2\text{TC}^H]\text{Fe}(\text{CPh}_2)$	Fe ^{IV}	0	1.814(4)	33
$(^{\text{Me}}\text{EtPDI})\text{Fe}(\text{CPh}_2)$	Fe ^{II}	2	1.936(2)	34
$[\text{mer-}\{\kappa\text{-C,N,C-(2-C}_6\text{H}_4)\text{CH=N(1,2-C}_6\text{H}_4)\text{C}(\text{tPr})\}\text{Fe}(\text{PMe}_3)_3][\text{BAr}^{\text{F}}_4]$	Fe ^{II}	0	1.899(3)	41
$[\text{MeC}[\text{C}(\text{Me})\text{N-(2,6-Me}_2\text{C}_6\text{H}_3)]_2\text{Fe}_2(\text{C}(\text{H})(\text{SiMe}_3))$	Fe ^{II}	2	1.956(6)-1.973(6)	40
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$	Fe ^{III}	1	1.850(2)	<i>This work</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N-}^1\text{Ad})$	Fe ^{II}	0	1.801(3)	<i>This work</i>

^aThe spin-state equals 2S, where S is the total number of unpaired electrons in the compound.

Despite the growing number of iron carbene complexes which feature various ligands, oxidation states, and coordination motifs, to date none of these examples have demonstrated activity in the olefin metathesis reaction. Based on orbital analysis, Hoffman has suggested the necessity of an iron alkylidene complex in the +4 oxidation state for the realization of an active metathesis catalyst of iron.⁴⁵ In consideration of this suggestion, the electronic rich, dianionic pyridine dipyrrolide (PDP) ligand framework was identified as a potential platform for the stabilization of formally Fe^{IV} iron alkylidene species. Recently, Mindiola and coworkers have reported the first example of a pyridine dipyrrolide iron complex featuring a metal-ligand multiple bond.⁴⁶ Spectroscopic and computational characterization of diamagnetic

(^tBuPDP^tBu)Fe(N¹Ad) confirmed its identity as a genuine Fe^{IV} complex featuring a closed-shell dianionic imido ligand.

Following this report, the synthesis of the closely related analogues (^{Mes}PDP^{Ph})Fe(NMes), (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N¹Ad), and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(NMes) has been accomplished and presented in Chapters 3 and 5 of this dissertation, respectively.⁴⁷ Crystallographically characterized (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N¹Ad) also possesses a low-spin Fe^{IV} center and similar coordination environment to (^tBuPDP^tBu)Fe(N¹Ad). The precedent provided by these complexes featuring metal-ligand multiple bonds suggests that access to an Fe^{IV} alkylidene within the pyridine dipyrrolide ligand framework may also be possible. In contrast to (^RPDP^R)Fe(N¹Ad) analogues, spectroscopically characterized (^{Mes}PDP^{Ph})Fe(NMes) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(NMes) are paramagnetic in nature. Computational analysis has suggested square-planar coordination geometries for these complexes and an electronic structure description of intermediate spin ferric centers ($S_{\text{Fe}} = 3/2$) engaged in antiferromagnetic coupling to iminyl radical ligands ($S_{\text{L}} = 1/2$), invoking assignment of an overall $S = 1$ ground state. The observed line broadening and paramagnetic shifts of the ¹H NMR resonances for these iron imide species is strong evidence of their paramagnetic ground state electronic structures.

With these details in mind, the question arose as to whether hypothetical (^{Ar}PDP^{Ph})Fe(CR₂) complexes would adopt closed-shell diamagnetic Fe^{IV} ground states with dianionic alkylidene ligands in a *cis*-divacant octahedral geometry, or alternatively, if the coordination environment available within (^{Ar}PDP^{Ph}) ligand motifs would afford square-planar carbene complexes featuring paramagnetic electronic structures with higher spin states. Herein is described the synthesis, characterization, and reactivity of iron carbene species synthesized from the reaction of high-spin (^{Ar}PDP^{Ph})Fe(thf) complexes and diphenyldiazomethane.

6.3 Reactivity of (^{Ar}PDP^{Ph})Fe(thf) Complexes with Diphenyldiazomethane

Akin to the generation of iron imides in the context of pyridine dipyrrolide (PDP) iron complexes, it was reasoned that high-spin Fe(II) PDP solvento complexes would offer efficient access to potential high-valent Fe carbene complexes via the decomposition of diazo reagents and subsequent carbene capture at iron.⁴⁷ Treatment of benzene-*d*₆ solutions of (^{Mes}PDP^{Ph})Fe(thf) or (^{2,6-Cl₂Ph}PDP^{Ph})Fe(thf) with a diphenyldiazomethane solution of the same solvent at room temperature afforded a gradual color change from dark red to dark brown over 16 hrs. ¹H NMR spectroscopic analysis revealed the complete consumption of the high-spin Fe^{II} starting materials with concomitant formation of new paramagnetic species, as evidenced by 12 and 10 resonances spanning a range of -55.22 ppm to -91.41 ppm and -55.35 ppm to 92.33 ppm for the (^{Mes}PDP^{Ph})Fe(CPh₂) (Figure 6.3) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(CPh₂), respectively. The number of observed resonances suggested C_{2v} symmetric products, and relative integrations of the resonances were consistent with either the diazoalkane adducts (^{Ar}PDP^{Ph})Fe(N₂CPh₂), or carbenes of the formulation (^{Ar}PDP^{Ph})Fe(CPh₂).

Figure 6.3. ^1H NMR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ at 600 MHz in benzene- d_6 . The unmarked resonances corresponds to pentane present in the sample.

In consideration of these results, isolation of the product arising from the reaction of diphenyldiazomethane with $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ was pursued on a preparative scale. Accordingly, treatment of a diethyl ether slurry of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with a diphenyldiazomethane solution of the same solvent at room temperature afforded after a gradual color change from dark red to dark brown accompanied by a precipitate after 16 hrs. The solid was collected via vacuum filtration and after workup (*vide infra*) was isolated as a dark brown powder. An infrared spectrum of the product was acquired in KBr (Figure 6.4) and was devoid of any discernable N=N diazo stretching mode (2032 cm^{-1} in CPh_2N_2)⁴⁸, which suggested that the identity of the product was unlikely to be the diazoalkane adduct $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_2\text{CPh}_2)$.

Figure 6.4. IR spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ (KBr).

Single crystals of the product suitable for X-ray crystallography were obtained by diffusion of pentane into a toluene solution of the purified material at -35°C . The X-ray study identified the species as the iron carbene complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ (Scheme 6.1). The compound was determined to be a toluene solvate and crystallized in the monoclinic space group $\text{P2}_1/\text{n}$. An ORTEP representation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ is depicted in Figure 6.5.

The geometry about the iron center is best described as square planar, as defined by the κ^3 -PDP pincer and diphenylidene ligand ($\tau_4 = 0.17$). It should be however be noted that an idealized square-planar structure cannot be realized for pyridine dipyrrolide ligand complexes as the geometric constraints imposed by the bite angles of the PDP chelate rigorously enforces distorted structures. In $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, this is evidenced by the N1-Fe1-N2, N2-Fe1-N3, and N1-Fe1-N3 bond angles of $80.27(8)^\circ$, $159.35(8)^\circ$, and $79.58(8)^\circ$. The carbene fragment is nearly planar, as evidenced by the N2-Fe1-C44 angle of $176.20(9)^\circ$ and the overall C_{2v}

symmetric square planar geometry of (^{Mes}PDP^{Ph})Fe(CPh₂) in the solid state is in agreement with the solution phase ¹H NMR spectrum. Furthermore, the bond angles about the carbene carbon, C44, are consistent with sp² hybridization.

Scheme 6.1. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$.

Figure 6.5. ORTEP of (^{Me}S₂PDP^{Ph})Fe(CPh₂) depicted at 30% probability ellipsoids. Hydrogen atoms and a cocrystallized toluene solvent molecule are excluded for clarity.

Notably, the square planar geometry of (^{Mes}PDP^{Ph})Fe(CPh₂) is an unprecedented coordination motif for an iron carbene complex. Currently, the closest structural analogues to (^{Mes}PDP^{Ph})Fe(CPh₂) are the four-coordinate (^RPDI)Fe(CPh₂) carbene radical species reported by Chirik.³⁴ The X-ray structures for these pincer compounds feature carbene ligands positioned above the plane of the PDI chelate by 0.647 Å and 0.706 Å for (^{Et}PDI)Fe(CPh₂) and (^{Me}EtPDI)Fe(CPh₂), respectively. This distortion, which is accompanied by bent N_{pyridine}-Fe-carbene bond angles of 147.82° and 147.52° for these two compounds is consistent with a trend away from square planarity towards a tetrahedral geometry. The Fe-C bond distance of 1.850(2) Å for (^{Mes}PDP^{Ph})Fe(CPh₂) is indicative of multiple bond character. This distance is intermediate relative to the iron carbene bond distances of 1.979(3) Å in [(η^5 -C₅H₅)(η^1 -C₇H₆)Fe(CO)₂][PF₆] and 1.787(8) Å in [(η^5 -C₅Me₅)Fe(dppe)(C(H)Me)][OTf].^{21,22} Alternatively, the Chirik carbene radical complexes feature significantly longer iron carbene bond distances of 1.921(2) Å and 1.936(2) Å for (^{Et}PDI)Fe(CPh₂) and (^{Me}EtPDI)Fe(CPh₂), respectively. These observations are consistent with high-spin ferrous centers present in each of these compounds.³⁴

Furthermore, the iron carbene bond distance in (^{Mes}PDP^{Ph})Fe(CPh₂) is significantly elongated from the iron imido nitrogen bonds in the diamagnetic Fe^{IV} PDP complexes (^tBuPDP^tBu)Fe(N¹Ad) and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N¹Ad), which have crystallographically determined iron imide nitrogen bond lengths of 1.640(4) Å and 1.620(4) Å, respectively.^{46,47} This is consistent with significantly more metal ligand multiple bond character in these complexes than in (^{Mes}PDP^{Ph})Fe(CPh₂). For (^{Mes}PDP^{Ph})Fe(CPh₂), iron nitrogen contacts to the PDP pincer were found to be 1.9581(19) Å and 1.9455(19) Å for the pyrrolides N1 and N3, and 1.9779(19) Å for the central pyridine nitrogen, N2. For comparison, the Fe1-N1, Fe-N2, and Fe1-N3 distances for

the iron pyrrolide and iron pyridine nitrogen bonds in (^tBuPDP^tBu)Fe(N¹Ad) are 1.910(2) Å, 1.910(2) Å, and 1.867(3) Å. Similarly, the bond distances for the same contacts in (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad) are 1.887(4) Å, 1.894(4) Å, and 1.898(4) Å. It is clear that the iron nitrogen bond distances are significantly elongated in the formally Fe^{IV} complex (^{Mes}PDP^{Ph})Fe(CPh₂) relative to authentic Fe^{IV} complexes (^tBuPDP^tBu)Fe(N¹Ad) and (^{2,6}-Cl₂PhPDP^{Ph})Fe(N¹Ad).

Finally, a comparison of the structural metrics of the square planar high-spin Fe^{II} PDP starting material, (^{Mes}PDP^{Ph})Fe(thf), suggests that assignment of (^{Mes}PDP^{Ph})Fe(CPh₂) as a high-spin ferrous ion with a weak field ancillary carbene ligand is unlikely. (^{Mes}PDP^{Ph})Fe(thf) is characterized by relatively long iron PDP nitrogen bond distances ranging from 2.0693(13)-2.0419(14) Å, inconsistent with the observed bond lengths to the nitrogens of the PDP pincer ligand in (^{Mes}PDP^{Ph})Fe(CPh₂).⁴⁹ A more complete summary of the structural metrics obtained for (^{Mes}PDP^{Ph})Fe(CPh₂) via X-ray crystallography is provided later in Table 6.5.

The room-temperature magnetic moment of (^{Mes}PDP^{Ph})Fe(CPh₂) was found to be 3.8 μ_B (magnetic susceptibility balance), intermediate relative to the spin-only values expected for an S = 1 (2.83 μ_B) or S = 2 system (4.90 μ_B). In consideration of this ambiguity surrounding the oxidation state and spin-state of the iron center in (^{Mes}PDP^{Ph})Fe(CPh₂), a zero-field Mössbauer spectrum was acquired on a powder sample of the complex at 80 K. A single symmetric quadrupole doublet was fit satisfactorily with parameters of δ = 0.20 mms⁻¹, |ΔE_Q| = 2.75 mms⁻¹, and Γ_L = Γ_R = 0.30 mms⁻¹ (Figure 6.6). The low isomer shift value is consistent with the short metal-ligand bond lengths observed crystallographically; however, it is significantly higher than the isomer shift value of -0.09(1) mms⁻¹ reported for the diamagnetic Fe^{IV} complex (^tBuPDP^tBu)Fe(N¹Ad).⁴⁶ This result is consistent with the paramagnetism of the complex observed

by ^1H NMR spectroscopy and is further evidence that the square-planar carbene complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ and *cis*-divacant iron imide complex $(^{\text{tBu}}\text{PDP}^{\text{tBu}})\text{Fe}(\text{N}^1\text{Ad})$ have disparate electronic structures, despite supporting isoelectronic carbene and nitrene fragments.

Figure 6.6. Zero-field ^{57}Fe Mössbauer spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ acquired at 80 K.

In order to further interrogate the electronic structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, additional spectroscopic analysis was pursued via variable-temperature and variable-field Mössbauer spectroscopy. Two samples of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ were prepared and analyzed, one in frozen toluene solution and a second powder sample frozen in mineral oil. The spectroscopic data for both samples was in good agreement, excluding the possibility of potential intermolecular magnetic interactions in the solid state. Thus, the data presented and described herein originates from the powder sample. The zero-field Mössbauer spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ acquired at 4.2 K was consistent with the 80 K measurement, with $\delta = 0.30 \text{ mms}^{-1}$ and $\Delta E_{\text{Q}} = 2.86 \text{ mms}^{-1}$ (Figure 6.7). Subsequent measurements spanning applied fields of 0.1 to 7 T and temperatures of

4.2 K to 100 K were performed (Figures 6.7 and 6.8). A negative sign for the quadrupole splitting (-2.86 mms^{-1}) and a value for the asymmetry parameter of the electronic field gradient (η), 0.413, were determined through the high temperature, high field measurement (100 K, 7 T). Satisfactory simulation of the data as an $S = 1$ system was achieved with g values of 4.80, 2.50, and $2.00 \mu_B$ for g_x , g_y , and g_z . The overall magnetic splitting features exhibited under variable-field conditions were only successfully reproduced with a strong anisotropic ^{57}Fe hyperfine tensor, or internal field. The A_{xx} , A_{yy} , and A_{zz} values utilized in the fit were +73.4, -5.9, and -9.1 T, respectively. The extremely large and atypical A_{xx} value suggests a remarkably large unquenched angular momentum in this direction rendering the system unusually and largely anisotropic.^{50,51} Overall, the isomer shift and quadrupole splitting of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ are more similar to reported intermediate spin ($S = 1$) Fe^{IV} systems.⁵² The fit parameters utilized for simulation of the data are found in Table 6.2.

Figure 6.7. Zero-field and applied-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ acquired at temperatures from 4.2 K to 100 K and field strengths of 0 to 7 T.

Figure 6.8. Zero-field and applied-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ acquired at temperatures from 4.2 K to 30 K and fields strengths of 2 to 7 T.

Table 6.2. Fit parameters utilized in modeling experimental data obtained for (^{Mes}PDP^{Ph})Fe(CPh₂) via variable-temperature applied-field Mössbauer spectroscopy.

<i>Quantity</i>	<i>Value</i>
<i>S</i>	1
<i>D</i>	10 cm ⁻¹
<i>E/D</i>	0.2
<i>g</i>	4.80, 2.50, 2.00
<i>δ</i>	0.20 mms ⁻¹
<i>ΔE_Q</i>	-2.86 mms ⁻¹
<i>η</i>	0.413
<i>A/g_Nβ_N</i>	[+73.4, -5.9, -9.1] T
Area	0.93
<i>Γ</i>	0.300 mms ⁻¹

In consideration of the combined characterization obtained by means of ¹H NMR, zero-field Mössbauer spectroscopy, and X-ray crystallography, multiple possible electronic structures could be considered for (^{Mes}PDP^{Ph})Fe(CPh₂). However, the *S* = 1 state suggested by variable-temperature applied-field Mössbauer narrows the potential possibilities to two limiting electronic structure configurations for (^{Mes}PDP^{Ph})Fe(CPh₂). The first being an intermediate spin Fe^{IV} center (*S*_{Fe} = 1) ligated by a closed-shell dianionic alkylidene ligand (*S*_L = 0). The second possibility is an intermediate-spin Fe^{III} center (*S*_{Fe} = 3/2) engaged in antiferromagnetic coupling to a monoanionic carbene radical ligand (*S*_L = 1/2), which would afford an overall *S* = 1 ground state. However, despite the wealth of physical characterization available for (^{Mes}PDP^{Ph})Fe(CPh₂), an unambiguous assignment of a limiting electronic structure for the complex is not possible from the currently available experimental data.

Furthermore, due to the scarcity of paramagnetic iron carbene complexes, compounds suitable for close comparison do not exist in the literature at this time. Despite the lesser developed chemistry of paramagnetic iron carbenes, a number of paramagnetic iron imido complexes featuring non-innocent ligands have been recently synthesized and offer interesting comparisons within the context of iron ligand multiple bonding. One noteworthy complex is the intermediate-spin Fe(III) imido species ($i^{\text{Pr}}\text{PDI}\text{Fe}(\text{N}(2,6\text{-}i^{\text{Pr}}_2\text{-C}_6\text{H}_3))$) ($i^{\text{Pr}}\text{PDI} = (2,6\text{-}i^{\text{Pr}}_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) reported by Chirik.^{53,54} This complex has a magnetic moment consistent with a $S = 1$ system ($2.8 \mu_{\text{B}}$ from 20 to 300 K) and Mössbauer isomer shift, $\delta = 0.302$ mm/s, similar to that of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$). X-ray crystallographic analysis of ($i^{\text{Pr}}\text{PDI}\text{Fe}(\text{N}(2,6\text{-}i^{\text{Pr}}_2\text{-C}_6\text{H}_3))$) identified an iron imide nitrogen bond length of 1.7048(16) Å, consistent with a closed shell diamagnetic dianionic imide. Despite this metal ligand bonding interaction being consistent with double bond character, the PDI chelate in this complex exists as a monoreduced ligand radical engaged in antiferromagnetic coupling with the ferric center. This electronic structural motif offers precedent for a ligand radical bound to an intermediate spin Fe(III) ion in the context of a complex featuring a metal ligand multiple bond. Thus, the possibility of an intermediate-spin Fe^{III} center ($S_{\text{Fe}} = 3/2$) engaged in antiferromagnetic coupling to a monoanionic carbene radical ligand ($S_{\text{L}} = 1/2$) in ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$) should be carefully considered.

6.4 Density Functional Theory Study of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$)

In light of the ambiguity surrounding the electronic structure of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$), we turned to density functional theory (DFT) calculations to gain further insight. Utilizing atomic coordinates obtained from X-ray crystallography, full molecule geometry optimizations were performed at the B3LYP level of theory for a variety of possible paramagnetic electronic

structure descriptions. Unrestricted Kohn-Sham (UKS) calculations including UKS3 and UKS5 approaches, corresponding to triplet and quintet states, respectively, were utilized to account for possible $S = 1$ or $S = 2$ electronic structures. These include a Fe^{IV} intermediate spin ion ($S_{\text{Fe}} = 1$) with a diamagnetic dianionic alkylidene ligand ($S_{\text{L}} = 0$) and a high spin Fe^{II} ion with an ancillary carbene ligand ($S_{\text{L}} = 0$). Broken symmetry (BS) calculations were employed to account for the possibility of intermediate-spin $\text{Fe}(\text{III})$ ($S_{\text{Fe}} = 5/2$) and high-spin $\text{Fe}(\text{III})$ ($S_{\text{Fe}} = 3/2$) ions antiferromagnetically coupled to carbene radicals ($S_{\text{L}} = 1/2$), via BS (3,1) and BS(5,1) calculations, respectively.

Analysis of the results from the BS(3,1) and UKS calculations demonstrated convergence to identical electronic structures, consistent with an intermediate-spin Fe^{III} ion antiferromagnetically coupled to a carbene radical ligand. This is supported by examination of the spin distribution obtained via Mulliken population analysis, which demonstrates a value of 2.68 on the iron center and -0.53 on the carbene carbon. Significant spin density is also present throughout the phenyl substituents of the carbene fragment (Figure 6.10). The high spatial overlap value of 0.80 is consistent with a highly covalent bonding interaction between the iron center and carbene ligand. Furthermore, the convergence of the UKS3 calculation to a BS(3,1) solution is consistent with this optimized structure being the lowest energy on the triplet surface.

Analysis of the BS(5,1) calculation and the corresponding spin-density populations reveals a computed electronic structure consistent with a high-spin ferric ion antiferromagnetically coupled to a carbene-based radical. Spin density values of 3.96 and -0.24 were computed for the iron center and carbene carbon, respectively, while a significant portion of the remaining negative spin density is located throughout the phenyl substituents of the carbene (-0.29). The deviation of the spin density from the expected value of five for a high-spin

Fe^{III} center is rationalized by spin polarization that imparts spin density onto the nitrogens of the PDP ligand. Similar to the BS(3,1) calculation, the spin density map of the Mulliken population analysis obtained from the BS(5,1) calculation also has significant spin density imparted onto the phenyl substituents of the carbene fragment. Importantly, upon examination of the structural metrics of the optimized BS(5,1) structure, it was observed that the calculated metrics were not in good agreement with the crystallographically determined structure of (^{Mes}PDP^{Ph})Fe(CPh₂). In the optimized BS(5,1) structure, the carbene fragment is drastically lifted out of the plane and the resulting geometry is most consistent with a bent structure intermediate to limiting planar and *cis*-divacant descriptions. This is obviated by the N2-Fe1-C44 bond angle of 120.26°. Furthermore, the Fe-carbene bond distance is drastically elongated to 2.001 Å, which is consistent with the high-spin state of the iron center. Although the optimized structure for the BS(5,1) calculation is only 3.1 kcal mol⁻¹ higher in energy than the BS(3,1) calculation, this solution is currently disfavored in consideration of the inconsistency of the structural metrics with the experimentally determined structure from X-ray crystallography.

Interestingly, the UKS5 calculation did not converge to the corresponding BS(5,1) solution, but instead converges to an electronic structure solution that is consistent with an intermediate-spin Fe^{III} center ferromagnetically coupled to a carbene radical ligand. Spin-density values of 3.12 and 0.50 were computed for the iron center and the carbene carbon, consistent with an *S* = 2 state. This electronic structure is consistent with a spin flip at the carbene carbon relative to the BS(3,1) solution. A stark energetic penalty is clear in consideration of this electronic structural change, as the optimized structure for the UKS5 solution lies 15.7 kcal mol⁻¹ higher in energy than the corresponding BS(3,1)/UKS3 solution. Despite the excellent agreement of the structural metrics with those obtained by X-ray crystallography, the large energy

difference between the computed structures suggests that this electronic structure is not a likely description of the electronic structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$.⁵⁵ The spin-density plots obtained from each computational approach are depicted in Figure 6.10 and a summary of experimental and computation metrics obtained for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ are compiled in Table 6.3. Additionally, a qualitative molecular orbital diagram of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ developed from the results of the BS(3,1) calculation is depicted in Figure 6.9.

With these optimized structures in hand, Mössbauer parameters were calculated for all to use in comparison to the experimentally determined values. The computed isomer shift values are in excellent agreement with the experimental data, however, analysis of the quadrupole splitting values clearly favors the BS(3,1) electronic structure (Table 6.3). Although there is deviation between the computed (-4.04) and experimentally determined values (-2.86), DFT is able to correctly predict the negative sign associated with the quadrupole splitting of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ determined by applied-field Mössbauer. In contrast, the BS(5,1) and UKS5 computed values predict an incorrect positive sign for the quadrupole splitting. Furthermore, the difference the experimental and computed quadrupole splittings, -2.86 vs. -4.40 mms^{-1} , is rationalized on the basis of an inherent limitation to DFT, namely, the exclusion of unquenched orbital angular momentum. This leads to exclusion of spin orbit coupling and ultimately the observed inconsistency in computed ΔE_Q value. In consideration of the combined physical and computational characterization of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, an electronic structural assignment of the complex as an intermediate-spin ferric ion engaged in antiferromagnetic coupling to a carbene radical is favored at this time, in agreement with previously studied square-planar iron iminyl radical complexes of the PDP ligand.⁴⁷ Notably, this makes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ the first example

of an iron carbene complex in the formal oxidation state of +3, whereas previous examples have been limited to Fe(II) and Fe(IV) ions.

Table 6.3. Summary of physical and computational metrics for (^{Mes}PDP^{Ph})Fe(CPh₂).

	$\Delta Energy$ / $kcal\ mol^{-1}$	$Fe-C_{carbene}$ / $\text{\AA}$	$N_{pyridine}-Fe-C_{carbene}$ / °	δ / mms^{-1}	ΔE_Q / mms^{-1}	η^a
Experimental	-	1.850(2)	176.20(9)	0.20	- 2.86	0.413
BS(3,1)/UKS3	0	1.881	179.94	0.24	- 4.04	0.208
BS(5,1)	+ 15.7	1.996	120.26	0.27	3.15	0.856
UKS5	+ 3.14	2.001	179.98	0.22	4.36	0.624

Figure 6.9. Qualitative molecular orbital diagram derived from the Unrestricted Corresponding Orbitals (UCO) obtained from BS(3,1)/UKS3 DFT calculations.

Figure 6.10. Spin-density plots obtained from Mulliken population analysis of UKS3/BS(3,1) (top), BS(5,1) (middle), and UKS5 (bottom) DFT calculations.

6.5 Reactivity Studies of (^{Mes}PDP^{Ph})Fe(CPh₂)

With an established understanding of the electronic structure of (^{Mes}PDP^{Ph})Fe(CPh₂), an evaluation of its utility in carbene group transfer was pursued. Previously, carbene group transfer reactions have been demonstrated by a variety of isolable late 3d metal carbene complexes including those of iron³⁴, cobalt⁵⁶⁻⁵⁸, nickel⁵⁹⁻⁶³, and copper⁶⁴⁻⁶⁶. In these instances, the ability to transfer the carbene ligand to organic substrates such as carbon monoxide, isocyanides, and organic azides is well documented. In particular, the carbene radical complex (^{Me}PDI)Fe(CPh₂) reported by Chirik was found to facilitate carbene group transfer to CO, H₂, and organic azides. No cyclopropanation, C-H abstraction, or metathesis reactivity was observed for the compound, which was attributed to the lack of alkylidene or Schrock carbene character present in this complex, consistent with the presence of a high-spin Fe^{II} ion.³⁴

In order to assess the possibility of carbene group transfer from (^{Mes}PDP^{Ph})Fe(CPh₂), reactions were first probed with carbon monoxide. The addition of 1 atm of CO to a benzene-*d*₆ solution of (^{Mes}PDP^{Ph})Fe(CPh₂) at room temperature resulted in a rapid color change of the solution from dark green to red brown. Analysis of the crude reaction mixture by ¹H NMR spectroscopy demonstrated complete conversion of the starting material and quantitative formation of a new diamagnetic species. The ¹H NMR spectrum evidenced a diamagnetic product, with apparent C₁ symmetry in solution. Six distinct singlets of equal intensity were identified within the range of 1.96 ppm to 2.44 ppm, consistent with six chemically inequivalent methyl groups for the ^{Mes}PDP^{Ph} ligand. Furthermore, ¹³C-{¹H} NMR in benzene-*d*₆ revealed two downfield resonances at 208.92 ppm and 220.67 ppm, suggesting the incorporation of two unique carbonyl ligands in the product. Analysis by infrared spectroscopy (KBr) confirmed the

incorporation of terminal CO ligands into the product, with two strong CO stretches identified at 2023 cm^{-1} and 1954 cm^{-1} (Figure 6.11).

Figure 6.11. IR spectrum of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ (KBr).

In consideration of the complex ^1H NMR spectrum, a zero-field Mössbauer spectrum was acquired of the product following workup (*vide infra*) and indicated clean transformation of the starting material to a single new iron-containing species with $\delta = 0.13 \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.75 \text{ mms}^{-1}$. These Mössbauer parameters inferred a low-spin Fe(II) ground state for the new complex, consistent with the diamagnetism observed via ^1H NMR spectroscopy. The X-ray crystallographic analysis of single crystals obtained from the evaporation of a concentrated diethyl ether of solution of the compound revealed an iron complex having undergone insertion of the diphenylidene fragment into an iron-pyrrolide nitrogen bond (Scheme 6.2). Two carbonyl ligands were also bound to the iron center, in agreement with the ^{13}C NMR spectrum, as well as

the modified PDP ligand, now a tridentate C,N,N chelate featuring an N alkylated pyrrole moiety. The modified PDP ligand maintains a dianionic charge, by way of one pyrrolide moiety and the newly formed alkyl ligand. The C44-N1 bond distance of 1.472(3) Å is consistent with a C-N single bond. Overall, the solid-state structure of (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂ is consistent with the apparent C₁ symmetry observed by NMR spectroscopy. ORTEP depictions of (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂ are presented in Figure 6.12, and important bond distances are summarized in Table 6.3. The metal-ligand bond distances are 1.9846(17), 1.9687(18), 2.076(2), 1.796(2), and 1.742(2) for the iron pyridine nitrogen (Fe-N2), pyrrolide nitrogen (Fe-N3), carbon (Fe-C51), and CO carbons (Fe-C57 and Fe-C58), respectively, are consistent with a low-spin Fe^{II} ion.

Scheme 6.2. Synthesis of (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂. One mesityl PDP substituent in (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂ has been denoted “Mes”.

The observation of the diphenylidene fragment in (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂ bridging the iron center and a pyrrolide nitrogen is not an unprecedented coordination motif. Related examples of bridging carbene ligands have also been documented for porphyrin complexes and implicated as key intermediates in iron and cobalt catalyzed cyclopropanation.^{36,37,67-71}

Figure 6.12. ORTEP depictions of two perspectives of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{CO})_2$ at 30% probability ellipsoids. Co-crystallized diethyl ether solvent and hydrogen atoms are omitted for clarity.

Having noted the carbene insertion chemistry upon reaction of $(^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{CPh}_2)$ with carbon monoxide, we sought out to explore the reactivity of this species with other organic substrates. Previously, catalytic carbene transfer to isocyanides has been demonstrated by cobalt and nickel systems to form the corresponding ketenimines.^{57,63} In consideration of this precedent, the reactivity of $(^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{CPh}_2)$ was explored with isocyanide reagents. The addition of two equivalents of 2,6-dimethylphenylisocyanide to a stirring benzene solution of

$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ resulted in an immediate color change from dark green to red. ^1H NMR analysis of the crude reaction mixture in benzene- d_6 indicated complete consumption of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ with concomitant formation of a new diamagnetic product. Eight singlet resonances were identified in the upfield region of the spectrum with relative integrations of 3 and a ninth singlet resonance with a relative integration of 6. These resonances suggested a preliminary assignment of the product as a 2,6-dimethylphenylisocyanide analogue to $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ with the six chemically distinct methyl groups corresponding to a C_1 symmetric $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand environment. The three remaining singlet resonances, of 3:3:6 relative intensity, were assigned as two distinct 2,6-dimethylphenyl isocyanide ligands. An isocyanide ligand orthogonal to the PDP chelate plane undergoing fast rotation on the NMR timescale and consequently one methyl group signal accounting for the integration of six. A second isocyanide ligand in the plane of the PDP chelate was proposed to possess two chemically inequivalent methyl groups, resulting in the observation of the two additional singlet resonances with relative integrations of 3 and 3, respectively. The observation of these two distinct signals on the timescale of the ^1H NMR experiment is attributed to restricted rotation of the isocyanide ligand, likely as a result of the sterically congested environment about the Fe center.

The IR spectrum (KBr) of the product features two intense bands isocyanide $\text{C}\equiv\text{N}$ stretches at 2102 and 1999 cm^{-1} , consistent with the incorporation of 2,6-dimethylphenyl isocyanide ligands into the observed product (Figure 6.13).

Figure 6.13. IR spectrum of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2 (\text{KBr})$.

Furthermore, the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of the new species contains two ^{13}C resonances at 195.33 and 179.73 ppm, which provides further evidence of the presence of two chemically inequivalent isocyanide ligand environments. Gratifyingly, single crystals of the product suitable for analysis via X-ray crystallography were grown from a mixture of toluene and pentane at -35°C . The structural analysis confirmed the identity of the product as $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$, consistent with the C_1 symmetric NMR spectrum and other spectroscopic data (Scheme 6.3 and Figure 6.16).

Scheme 6.3. Synthesis of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$. Note: For $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ one mesityl PDP substituent has been abbreviated “Mes” and the 2,6-dimethylphenylisocyanide ligands have been abbreviated “CNAr”.

Akin to $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$, the formation of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ is accounted for by insertion of the diphenylidene fragment into an iron pyrrolide bond, accompanied by ligation of two diphenyl isocyanide ligands. Interestingly, in accord with $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$, the insertion of the diphenylidene fragment into an iron-pyrrolide nitrogen bond resulted in the formation of a new carbon-nitrogen single bond. The sp^3 -hybridized alkyl carbon was detected in the $^{13}\text{C}\{-^1\text{H}\}$ NMR in dichloromethane- d_2 at 72.15 ppm. Unambiguous assignment of this resonance was accomplished via a combination of HSQC, HMBC, DEPT 135, and APT NMR experiments. HSQC analysis indicated a lack of correlation with any ^1H resonance, consistent with assignment as a quaternary carbon. A HMBC experiment indicated correlations between the ^{13}C resonance at 72.15 ppm to ^1H resonances at 7.84, 6.69, and 6.25 ppm. These resonances were assigned as three of the four unique *ortho*-phenyl protons of the CPh_2 fragment (Figure 6.13). The combination of DEPT 135 and APT experiments are also consistent with the assignment of this resonance as a quaternary carbon (Figure 6.14 and 6.15).

Figure 6.14. ^1H - ^{13}C HMBC spectrum of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_2$ in dichloromethane- d_2 .

Figure 6.15. ^{13}C (bottom), DEPT 135 (middle), and APT (top) spectra of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_2$ in dichloromethane- d_2 .

In regard to the structural analysis of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_2$, notable bond lengths include 1.7570(15) Å (Fe1-C44) and 1.8461(14) Å (Fe1-C53) for the apical and in-plane isocyanide carbons, 1.9837(12) Å (Fe1-N1) and 1.9776(12) Å (Fe1-N2) for the pyrrolide and pyridine nitrogens, and 2.0683(14) Å (Fe1-C62) for the alkyl carbon. The C62-N3 distance of 1.4773(17) Å is consistent with a carbon-nitrogen single bond. The structural data for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_2$ and $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ is overall similar. Key bond distances and bond angles are summarized in Table 6.4 and an ORTEP of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_2$ is presented in Figure 6.16.

Notably, $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ and $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ are the first examples of iron-alkyl complexes within the context of pyridine dipyrrolide iron chemistry. The iron alkyl bond distances are consistent with previously reported low-spin ferrous alkyls of related pyridine based pincer ligands.⁷² With $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ and $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ being the first structurally characterized examples of low-spin Fe^{II} PDP compounds, zero-field Mössbauer spectra of each were acquired to further characterize the respective complexes. The spectra obtained from solid samples of each compound both revealed a single quadrupole doublet with $\delta = 0.13 \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.75 \text{ mms}^{-1}$ for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ and $\delta = 0.18 \text{ mms}^{-1}$ and $|\Delta E_Q| = 1.51 \text{ mms}^{-1}$ for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ (Figure 6.17). These values are consistent with the low-spin $\text{Fe}(\text{II})$ electronic structure inferred from the diamagnetism of the complexes observed by NMR. The slightly lower isomer shift value for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ is consistent with the contracted metal carbonyl bond distances in this complex relative to the isocyanides in $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$. This minor discrepancy between the two structures is likely a result of steric crowding about the iron center imparted by the bulkier isocyanide ligands.

Figure 6.16. ORTEP depictions of two perspectives of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-(\text{CH}_3)_2(\text{Ph})_2)_2$ at 30% probability ellipsoids. Note, in addition to hydrogen atoms and co-crystallized solvent, the bottom image has PDP mesityl substituents and 2,6-dimethylphenyl isocyanide substituents truncated to depict solely the *ipso* carbons.

Table 6.4. Selected bond lengths (Å) and angles (deg) for (CPh₂^{Mes}PDP^{Ph})Fe(CO)₂, (CPh₂^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₂, and (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃.

	(CPh ₂ ^{Mes} PDP ^{Ph})- Fe(CO) ₂	(CPh ₂ ^{Mes} PDP ^{Ph})- Fe(C≡N-2,6-(CH ₃) ₂ Ph) ₂	(^{Mes} PDP ^{Ph})- Fe(C≡N-2,6-(CH ₃) ₂ Ph) ₃		
Fe1–N2	1.9846(17)	Fe1-N1	1.9837(12)	Fe1-N1	2.007(3)
Fe1–N3	1.9687(18)	Fe1-N2	1.9776(12)	Fe1-N2	1.954(3)
Fe1–C44	2.076(2)	Fe1-C44	1.7570(15)	Fe1-N3	1.999(3)
Fe1-C57	1.796(2)	Fe1-C53	1.8461(14)	Fe1-C44	1.885(3)
Fe1-C58	1.742(2)	Fe1-C62	2.0683(14)	Fe1-C53	1.845(4)
N1-C44	1.472(3)	N3-C62	1.4733(17)	Fe1-C62	1.902(3)
N2–Fe1–N3	81.44(7)	N1-Fe1-N2	81.54(5)	N1-Fe1-N2	80.14(11)
C44-Fe1-C58	99.49(9)	C44-Fe1-C62	95.64(6)	N1-Fe1-N3	160.25(11)
N1-C44-Fe1	115.06(13)	N3-C62-Fe1	115.37	N2-Fe1-N3	80.15(11)
N2–Fe1–C44	91.46(8)	N2-Fe1-C44	86.32(6)	N1-Fe1-C44	87.52(13)
N2-Fe1-C58	85.85(9)	N2-Fe1-C62	89.68(5)	N1-Fe1-C53	99.78(13)
N3-Fe1-C44	153.23(8)	N1-Fe1-C44	108.63(6)	N1-Fe1-C62	86.40(13)
C44-Fe1-C57	93.74(9)	C44-Fe1-C53	88.83(6)	N2-Fe1-C44	88.26(13)
N2-Fe1-C57	173.14(9)	N2-Fe1-C53	172.84(6)	N2-Fe1-C53	179.44(14)
N3-Fe1-C57	95.79(8)	N1-Fe1-C53	95.06(5)	N1-Fe1-C62	89.42(13)
N3-Fe1-C58	105.64(9)	N1-Fe1-C62	153.46(5)	N3-Fe1-C44	90.72
-	-	-	-	N3-Fe1-C53	99.92(13)
-	-	-	-	N3-Fe1-C62	94.56(13)

Figure 6.17. Zero-field ^{57}Fe Mössbauer spectra of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{CO})_2$ (left) and $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ (right) recorded at 80 K.

6.6 Reactivity Studies of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$

Based on the known propensity for 3d transition metal carbene compounds to undergo carbene transfer group to isocyanides^{57,60,61,63}, thermal decomposition studies of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ were conducted. It was found that heating a benzene- d_6 solution of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ at 80°C for 48 hrs resulted in complete decomposition of the starting material to multiple diamagnetic and paramagnetic products, as determined by ^1H NMR spectroscopy. Anticipating an iron isocyanide complex as a likely reaction product, the independent synthesis and characterization of a $(^{\text{MesPDP}^{\text{Ph}}})\text{Fe}-(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})$ species was pursued, in order to determine unambiguously the presence of such a species in the crude reaction mixture.

The preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_3$ and the related complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$ was accomplished by the addition of a benzene solution containing three molar equivalents of the corresponding isocyanide to a solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ in the same solvent (Scheme 6.4). Both $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_3$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$ precipitated from the crude reaction mixture and were isolated as analytically pure yellow ($\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph}$) or orange ($\text{C}\equiv\text{N}-^1\text{Ad}$) powders, following filtration and subsequent washing with pentane. Analysis by IR spectroscopy (KBr) indicated strong $\text{C}\equiv\text{N}$ stretches at 2103 cm^{-1} and 2150 cm^{-1} for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6(\text{CH}_3)_2\text{Ph})_3$, Figure 6.18, and 2123 cm^{-1} for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$, Figure 6.19.

Figure 6.18. IR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-(\text{CH}_3)_2\text{Ph})_3$ (KBr).

Figure 6.19. IR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$ (KBr).

Scheme 6.4. Independent synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{NR})_3$ complexes. “Mes” denotes a mesityl substituent of the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand.

The ^1H NMR spectra of both species in benzene- d_6 or dichloromethane- d_2 are consistent with C_{2v} symmetric structures in solution. X-ray studies performed on single crystals of both complexes and unambiguously confirmed their identities. Despite repeated efforts, only poorly

diffracting crystals could be obtained for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N-}^1\text{Ad})_3$; thus, only the structure of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N-2,6}(\text{CH}_3)_2\text{Ph})_3$ will be discussed in further detail. $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N-2,6}(\text{CH}_3)_2\text{Ph})_3$ was found to crystallize in the triclinic space group P-1 and an ORTEP of the solid-state structure is presented in Figure 6.20. The short iron PDP nitrogen bond lengths of 2.007(3) Å (Fe1-N1), 1.954(3) Å (Fe1-N2), and 1.999(3) Å (Fe1-N3) are consistent with a diamagnetic ferrous ground state. For example, comparison of these metrics to previously characterized high-spin Fe^{II} ($S = 2$) $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ complexes is consistent with this assessment (see Table 6.5), as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$ both feature iron nitrogen bond lengths well in excess of 2 Å. Furthermore, the iron isocyanide carbon bond lengths of 1.885(3) Å (Fe-C44), 1.845(4) Å (Fe1-C53), and 1.902(3) Å (Fe1-C62) for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N-2,6}(\text{CH}_3)_2\text{Ph})_3$ are similar to the iron isocyanide carbon distances of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N-2,6}(\text{CH}_3)_2\text{Ph})_2$. A more complete presentation of the structural metrics obtained from crystallography is presented in Table 6.4 (*vide supra*).

Figure 6.20. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph)}_3$ depicted at 30% probability ellipsoids. Note only one of the two independent molecules in the unit cell is depicted. Additionally, co-crystallized benzene, hydrogen atoms, and a mesityl substituent of the PDP ligand (with exception of the *ipso* carbon) are excluded for clarity.

Table 6.5. Iron-PDP nitrogen bond lengths ($\text{\AA}$) in high- and low-spin Fe^{II} $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ complexes.

	<i>Spin-State</i>	<i>Fe-N_{Pyridine}/\AA</i>	<i>Fe-N_{pyrrole}/\AA</i>	<i>Fe-N_{pyrrole}/\AA</i>
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$	2	2.0693(14)	2.0596(14)	2.0419(14)
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{py})_2$	2	2.1126(13)	2.0968(13)	2.0863(13)
$(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$	0	1.9846(17)	1.9687(18)	-
$(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph})_2$	0	1.9776(12)	1.9837(12)	-
$(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph})_3$	0	1.954(3)	2.007(3)	1.999(3)

Zero-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph})_3$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$ acquired at 80 K revealed quadrupole doublets with $\delta = 0.11 \text{ mms}^{-1}$ and $|\Delta E_Q| = 0.48 \text{ mms}^{-1}$ for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6\text{-(CH}_3)_2\text{Ph})_3$ and $\delta = 0.15 \text{ mms}^{-1}$ and $|\Delta E_Q| = 0.76 \text{ mms}^{-1}$ for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-^1\text{Ad})_3$ (Figure 6.21). The isomer shift values are consistent with a

low-spin Fe^{II} ion present in both species and in good agreement with $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ and $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$, while the small quadrupole splitting values are consistent with symmetric charge distributions at the iron centers. A summary of all experimentally and computationally determined Mössbauer parameters for the compounds studied in this chapter is presented in Table 6.7.

Figure 6.21. Zero-field ^{57}Fe Mössbauer spectra of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$ (left) $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-1\text{Ad})_3$ (right) recorded at 80 K.

Table 6.6. Experimental and calculated Mössbauer parameters for ^{Mes}PDP^{Ph} complexes in this chapter.

	$\delta / \text{mms}^{-1} (\text{calc})$	$\Delta E_Q / \text{mms}^{-1} (\text{calc})$	$\eta^{a,b}$
(^{Mes} PDP ^{Ph})Fe(CPh ₂)	0.20 (0.24) ^c	-2.86 (-4.04) ^c	0.208 ^c
(CPh ₂ ^{Mes} PDP ^{Ph})Fe(CO) ₂	0.13 (0.11)	1.75 (2.00)	0.672
(CPh ₂ ^{Mes} PDP ^{Ph})Fe(C≡N-2,6-(CH ₃) ₂ Ph) ₂	0.18 (0.22)	1.51 (1.72)	0.224
(^{Mes} PDP ^{Ph})Fe(C≡N- ¹ Ad) ₃	0.15 (0.20)	0.76 (1.15)	0.089
(^{Mes} PDP ^{Ph})Fe(C≡N-2,6-(CH ₃) ₂ Ph) ₃	0.11	0.48	-

^aAsymmetry parameter of the electronic field gradient. ^bNot determined experimentally. ^cObtained from BS(3,1)/UKS3 calculation.

With established spectroscopic markers in hand for (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃, a comparison of its ¹H NMR chemical shifts was made to the mixture of decomposition products produced from the thermal decomposition of (CPh₂^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₂. The presence of (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃ in the mixture was confirmed by diagnostic singlet resonances at 2.14 ppm and 2.27 ppm each with relative integration of 12, albeit, as a minor component of the mixture. These resonances correspond to the mesityl *ortho* methyl groups of the ^{Mes}PDP^{Ph} chelate and the apical 2,6-dimethylphenylisocyanide ligands. The second diamagnetic decomposition product was determined to be the ketenimine, *N*-(2,2-diphenylethenylidene)-2,6-dimethyl-benzenamine (Ph₂C=C=N-(CH₃)₂Ph), based on comparison of the ¹H chemical shifts and relative integrations to the literature reported values (Figure 6.22 and 6.23).⁵⁷ Furthermore, (^{Mes}PDP^{Ph})Fe(CPh₂) was also identified in the ¹H NMR spectrum, also in low concentration, as determined by relative integration to the two diamagnetic species. Lastly, the second paramagnetic compound present in the mixture was determined to be the majority iron containing species, based on integration relative (^{Mes}PDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃ and (^{Mes}PDP^{Ph})Fe(CPh₂). The integration relative to the ketenimine product was determined to be approximately 1:1. The 11 paramagnetically shifted and broadened resonances of the new

paramagnetic complex are consistent with a PDP iron species possessing apparent C_{2v} symmetry in solution. The number of resonances and their relative integrations (Figure 6.24) are consistent a tentative assignment of this species as a mono isocyanide adduct, $(^{Mes}PDP^{Ph})Fe-(C\equiv N-2,6-(CH_3)_2Ph)$. Diagnostic resonances at 12.27, -1.01, and -23.69 ppm were determined to have relative integrations of 12:6:6 and are anticipated to correspond to the *ortho* and *para* mesityl methyl groups of the $^{Mes}PDP^{Ph}$ pincer and the *ortho* methyl groups of the isocyanide ligand. Scheme 6.5 summarizes the products of thermal decomposition of $(CPh_2^{Mes}PDP^{Ph})Fe-(C\equiv N-2,6-(CH_3)_2Ph)_2$.

Scheme 6.5. Thermal decomposition of $(CPh_2^{Mes}PDP^{Ph})Fe(C\equiv N-2,6-(CH_3)_2Ph)_2$.

Figure 6.22. ^1H NMR spectra (600 MHz) in benzene- d_6 of upfield aliphatic resonances of an independently prepared sample of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$ (top) and the crude reaction mixture obtained from heating $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ to 80°C for approximately 48 hrs (bottom). Blue circles indicate peaks assigned as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$ and pink circles indicated peaks assigned as $\text{Ph}_2\text{C}=\text{C}=\text{N}-2,6-(\text{CH}_3)_2\text{Ph}$.

Figure 6.23. ^1H NMR spectra (600 MHz) in benzene- d_6 of downfield aryl resonances of an independently prepared sample of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$ (top) and the crude reaction mixture obtained from heating $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ to 80°C for approximately 48 hrs (bottom). Blue circles indicate peaks assigned as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$ and pink circles indicated peaks assigned as $\text{Ph}_2\text{C}=\text{C}=\text{N}-2,6-(\text{CH}_3)_2\text{Ph}$.

Figure 6.24. ^1H NMR spectrum (400 MHz) in benzene- d_6 from -50 to 20 ppm of crude reaction mixture obtained from heating $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ to 80°C for approximately 48 hrs. Note: The resonances and relative integrations for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$, and $\text{Ph}_2\text{C}=\text{C}=\text{N}-2,6-(\text{CH}_3)_2\text{Ph}$ have been omitted for clarity.

6.7 Synthesis of a Monoisocyanide Carbene Adduct

Intrigued by the observed reactivity with carbon monoxide and 2,6-dimethylphenyl isocyanide, the question of mechanistic formation of the observed products arose. It was postulated that multiple disparate reaction pathways could account for the observation of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ and $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$: 1) Ligation of one CO/isocyanide ligand to the $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, forming a mixed species $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{CE})$ (where $\text{E} = \text{O}$, or NR , and $\text{R} = 2,6-(\text{CH}_3)_2\text{Ph}$), followed by carbene insertion into an iron-pyrrolide bond and subsequent ligation of a second equivalent of CO/isocyanide, or 2) ligation of two CO/isocyanide ligands, forming a $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{CR})_2$ species, followed by subsequent carbene insertion into an iron-pyrrolide bond. These two mechanistic possibilities are depicted in Figure 6.25.

Proposed pathway 1:

Proposed pathway 2:

Figure 6.25. Possible mechanisms for the formation of $(\text{CPh}_2^{\text{MesPDP}^{\text{Ph}}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ from $(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$.

In lieu of this mechanistic ambiguity, reactions with the bulky isocyanide $\text{C}\equiv\text{N}^{-1}\text{Ad}$ were explored to see if a kinetically more stable mono- or bis-isocyanide carbene complex could be isolated and characterized. Accordingly, it was found that careful addition of a dilute benzene solution of one equivalent of $\text{C}\equiv\text{N}^{-1}\text{Ad}$ to a solution of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ in the same solvent resulted in an instantaneous color change of the solution from green to red brown. After removal of volatiles, crystallization of the product via slow evaporation of a diethyl ether solution afforded single crystals suitable for analysis via X-ray crystallography. The resulting structure was found to be the carbene mono isocyanide complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ (Figure 6.24 and Scheme 6.6.). In the solid state $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ adopts a distorted square pyramidal geometry. This distorted geometry is enforced by the bite angle of the PDP ligand and results in a τ_5 value of 0.46.^{73,74} Analysis of the bond metrics obtained from the X-ray analysis realized a significant contraction of the iron-carbene bond distance from 1.850(2) Å in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ to 1.801(3) Å in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$. This value is similar to the highly contracted iron-carbene bond distances previously reported for diamagnetic cyclopentadienyl-ligated iron carbenes and various macrocyclic iron diphenylidene complexes (Table 6.1). Furthermore, the significantly contracted $\text{Fe}-\text{C}_{\text{carbene}}$ bond distance in $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ relative to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ is consistent with the likelihood of alternative electronic structures for the two species.^{22,24,27,33}

Scheme 6.6. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$.

Figure 6.26. ORTEP of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ depicted at 30% probability ellipsoids. Co-crystallized solvent molecules, hydrogen atoms, and a PDP mesityl substituent (with exception of the *ipso* carbon) are omitted for clarity.

Analysis of the remaining crystalline material by ^1H NMR spectroscopy in benzene- d_6 solution revealed the diamagnetic nature of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ (Figure 6.25). The identification of three distinct upfield singlet resonances at 2.78, 2.53, and 2.14 ppm, respectively, is consistent with inequivalent mesityl methyl groups, suggesting a C_s symmetric $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand environment. The observation of three additional aliphatic resonances at 1.60, 1.25, and 0.76 ppm, in a relative 3:6:6 ratio, were attributed to the symmetric $\text{C}\equiv\text{N}^{-1}\text{Ad}$ ligand.

Overall, the solution phase ^1H NMR spectrum is consistent with the structure obtained by X-ray crystallography (Figure 6.19).

Figure 6.27. ^1H NMR spectrum of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}^{-1}\text{Ad})$ at 600 MHz in $\text{benzene-}d_6$. The inset depicts a range of 6–8 ppm for closer examination of the aryl proton resonances.

Table 6.7. Selected bond lengths (Å) and angles (deg) for (^{Mes}PDP^{Ph})Fe(CPh₂) and (^{Mes}PDP^{Ph})Fe(CPh₂)(C≡N-¹Ad).

	(^{Mes} PDP ^{Ph})Fe(CPh ₂)	(^{Mes} PDP ^{Ph})Fe(CPh ₂)(C≡N- ¹ Ad)
Fe1–N1	1.9581(19)	1.955(2)
Fe1–N2	1.9779(19)	1.930(2)
Fe1–N3	1.9455(19)	1.949(2)
Fe1–C44	1.850(2)	1.801(3)
Fe1–C57	-	1.886(3)
N1–Fe1–N2	80.27(8)	79.58(10)
N1–Fe1–N3	159.35(8)	148.31(10)
N2–Fe1–N3	79.58(8)	80.75(9)
C44–Fe1–N1	100.88(9)	102.51(11)
N2–Fe1–C44	176.20(9)	92.88(11)
C44–Fe1–N3	99.52(9)	103.06(11)
C44–Fe1–C57	-	90.61(12)
C57–Fe1–N1	-	97.60(11)
C57–Fe1–N2	-	175.92(11)
C57–Fe1–N3	-	100.53(11)

In regard to the electronic structure of (^{Mes}PDP^{Ph})Fe(CPh₂)(C≡N-¹Ad), the highly contracted iron-carbene bond distance suggests significant multiple-bond character. Assignment of the carbene fragment as a dianionic alkylidene ligand would infer a low-spin Fe^{IV} formal oxidation state, in agreement with the diamagnetism of the complex indicated by ¹H NMR spectroscopy. Alternatively, if assigned as an ancillary carbene ligand, a diamagnetic low-spin Fe^{II} assignment would be appropriate. It should be noted that the previously reported diamagnetic macrocyclic iron carbene complexes have withstood longstanding debate about their

electronic structures due to similar ambiguity in the assignment of a formal oxidation state for the iron center. It is anticipated that future spectroscopic and theoretical studies may offer further insight into the uncertainty surrounding the formal oxidation state of the iron center in

6.8 Conclusion

The paramagnetic iron carbene complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ have been prepared via the decomposition of diphenyldiazomethane and in the presence of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$. For $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, a combination of ^1H NMR, variable-temperature and applied-field ^{57}Fe Mössbauer, and X-ray crystallography has unambiguously assigned the solution- and solid-state structures of the complex. A complementary density functional theory study of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ has also been performed, which suggests this compound may be described as an intermediate spin iron(III) ion engaged in antiferromagnetic coupling to a monoanionic carbene radical ligand ($\text{CR}_2^{1-\bullet}$).

Preliminary reactivity studies of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ with carbon monoxide and isocyanides have also been performed. It has been found that $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ reacts rapidly with carbon monoxide to form the diamagnetic complex $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$. This product is accounted for by insertion of the diphenylidene fragment into an iron-pyrrolide nitrogen bond, accompanied by ligation of two molecules of CO to the iron center. Excitingly, $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ constitutes CPh_2 group transfer by the formation of a new carbon-nitrogen bond, forming a modified N-alkylated PDP ligand. Similarly, addition of 2,6-dimethylphenyl isocyanide to $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ results in an analogous carbene insertion, carbon-nitrogen bond formation, and PDP ligand modification. Notably, no reaction intermediates are observed in either of these contexts.

Heating benzene- d_6 solutions of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$ induces further carbene group transfer to an isocyanide ligand, resulting in the production of the corresponding ketenimine $\text{Ph}_2\text{C}=\text{C}=(2,6-(\text{CH}_3)_2\text{Ph})$, the isocyanide complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$, and the parent carbene $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, as determined by ^1H NMR spectroscopy. This result suggests that carbene group transfer to the nitrogen of a pyrrolide ligand is a reversible process, consistent with previously investigated iron porphyrin systems.

Lastly, when $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ is treated with one equivalent of the sterically encumbered isocyanide, $\text{C}\equiv\text{N}-^1\text{Ad}$, the diamagnetic carbene isocyanide species, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}-^1\text{Ad})$, is produced. This complex, which has been characterized by ^1H NMR and X-ray crystallography, offers valuable information concerning the identity of transition metal complexes that are mechanistically relevant to carbene group transfer to isocyanides. Furthermore, the existence of this complex suggests that PDP iron carbene complexes may find future utility in other stoichiometric or catalytic carbene group transfer reactions by tuning of the electronic structure of the iron center by the addition of ancillary ligands.

6.9 Experimental Procedures

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH_2 and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Carbon monoxide was

purchased from Matheson and used as received. 2,6-dimethylphenylisocyanide was purchased from Fluka. 1-Adamantyl isocyanide was obtained from TCI and sublimed under high-vacuum prior to use. Deuterated benzene (benzene- d_6) and dichloromethane (dichloromethane- d_2) for NMR spectroscopy were distilled from sodium metal and calcium hydride, respectively.

$\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ were prepared according to previously reported procedures.⁴⁹

Safety Considerations.

Diazo reagents are known energetic materials that may decompose violently via explosion upon input of energy from external sources (heat, light, pressure). While we did not encounter any problems or dangerous situations during the course of this study, all experiments involving diazo reagents were performed on small scale with 1 g or less of material. All manipulations outside of the glovebox were performed behind a blast shield in a fumehood. The diazo reagents were stored in the dark at $-35\text{ }^\circ\text{C}$ in the glovebox.

Preparation of diphenyldiazomethane.

Diphenyldiazomethane was prepared according to a modified literature procedure.⁷⁵

Note: diazo reagents are known to be potentially energetic materials. Thus, all synthetic manipulations outside of the glovebox were performed behind a blast shield in a fumehood. In a round bottom flask equipped with a magnetic stirrer was combined 1.00 g (5.1 mmol) of benzophenone hydrazone and 12 mL of dichloromethane, affording a colorless homogeneous solution. The flask was immersed in an ice bath and cooled to 0°C . Subsequently, 1.15 g (13.1 mmol, 2.6 eq.) of activated MnO_2 was added slowly, inducing an immediate color change of the solution to dark purple. The flask was wrapped in aluminum foil and allowed to stir overnight. After 16 hr the crude reaction mixture was passed through a plug of basic alumina. The resulting purple solution was removed, affording a viscous dark-purple oil. The crude

diphenyldiazomethane was transferred to an oven dried flask and freeze/pump/thaw degassed three times on a high-vacuum line. The material was transferred to the glovebox where it was stored over 4 Å molecular sieves for 24 hrs. Extraction into 10 mL of pentane, subsequent passage through a pipette column of basic alumina, and removal of solvent *in vacuo* afforded pure diphenyldiazomethane (devoid of solvent and water), as discerned by ^1H NMR spectroscopy. Yield: 561 mg, 2.89 mmol, 57%. The ^1H NMR data were consistent with previously reported literature values.

Preparation of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$).

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 500 mg (0.691 mmol) of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{thf})$) and 5 mL of diethyl ether. Vigorous stirring of the mixture afforded a maroon suspension. In a separate vial, 175 mg (1.3 eq, 0.902 mmol) of diphenyldiazomethane was dissolved in 5 mL of diethyl ether. The solution of diphenyldiazomethane was added dropwise to the suspension containing the iron compound. After 16 hrs, a dark precipitate was evident. The material was isolated on a medium porosity glass frit and dried *in vacuo*. The resulting dark solid was transferred to a separate vial and extracted into a minimum amount of benzene, resulting in an olive green solution. The benzene extracts were then passed through a plug of celite and collected in a tared flask. Additional benzene (10 mL) was utilized to completely wash the celite plug until washings were completely clear. Removal of volatiles and subsequent trituration with pentane afforded a dark brown solid identified as ($^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{Fe}(\text{CPh}_2)$). Yield: 362 mg (0.443 mmol, 64%). $\mu_{\text{eff}} = 3.8(2) \mu_{\text{B}}$ (295 K, magnetic susceptibility balance), $\mu_{\text{eff}} = 3.4(3) \mu_{\text{B}}$. ^1H NMR (600 MHz, benzene- d_6 ; δ , ppm): 9.141 (s, 2H), 4.122 (s, 4H), 15.83 (s, 4H), 13.47 (s, 12H, *ortho*-mesityl- CH_3), 12.78 (s, 4H), 7.47 (s, 4H), 6.98 (apparent triplet, $J = 7.0$ Hz, $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ 4-PhH), 1.39 (s, 2H), -2.23 (s, 6H, *para*-mesityl-

CH_3), -16.39 (s, 2H), -16.56 (s, 1H, 4-pyridineH), -55.22 (s, 4H). Anal. Calcd for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, $\text{C}_{56}\text{H}_{47}\text{FeN}_3$: C, 82.24; H, 5.79; N, 5.14. Found: C, 82.24; H, 5.90; N, 5.06. Slow evaporation of a diethyl ether solution at -35°C provided dark single crystals of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ suitable for X-ray diffraction.

Preparation of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$.

To a J. Young NMR tube was added 25 mg (0.032 mmol) of $(^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and 500 μL of benzene- d_6 affording a turbid red/orange suspension. In a dram vial 12 mg (0.062 mmol, 0.94 eq.) of diphenyldiazomethane was dissolved in 100 μL of benzene- d_6 . The solution of diphenyldiazomethane was added to the J. Young tube containing the iron complex, resulting in an immediate color change of the solution to dark brown. The tube was sealed, shaken for thirty seconds, and a ^1H NMR spectrum was acquired which demonstrated quantitative conversion to the title compound. ^1H NMR (600 MHz, benzene- d_6 ; δ , ppm): -55.35 (4H), -20.56 (2H), -12.73 (1H), -2.57 (2H), 3.63 (4H), 12.19 (4H), 15.71 (4H), 53.43 (4H), 92.33 (2H), 2 resonances not located.

Preparation of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$.

In the glovebox, a 50 mL thick walled glass vessel was loaded with a magnetic stirrer, 190 mg (0.232 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$, and 15 mL of toluene. The vessel was sealed and removed from the glovebox, attached to a high-vacuum line, and degassed. To the vessel was added 1 atm of CO, inducing an immediate color change of the solution from olive green to dark red/brown. The vessel was sealed and the reaction mixture was allowed to stir for 12 hrs. Removal of CO and solvent on the high-vacuum line afforded a dark brown residue. The vessel was returned to the glovebox and the resulting material was extracted into a minimum amount of diethyl ether. The resulting extract was filtered through a plug of celite into a 20 mL scintillation

vial. Complete removal of volatiles afforded a dark brown residue which was triturated with pentane to afford the title compound as a brown solid. Yield: 150 mg (0.172 mmol, 74%). ^1H NMR (400 MHz, benzene- d_6 ; δ , ppm) δ 7.87 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 7.0 Hz, 2H), 7.37 (d, J = 8.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 2H), 7.21-7.17 (m, 2H), 7.14 – 7.02 (m, 3H), 7.02 – 6.92 (m, 2H), 6.88-6.81 (m, 5H), 6.73 (t, J = 7.6 Hz, 1H), 6.44 (t, J = 7.4 Hz, 1H), 6.38 – 6.26 (m, 5H), 6.24 (s, 1H), 6.21 (t, J = 7.6 Hz, 1H), 2.44 (s, 3H, Mesityl- CH_3), 2.40 (s, 3H, Mesityl- CH_3), 2.17 (s, 3H, Mesityl- CH_3), 2.02 (overlapping singlets, 6H, Mesityl- CH_3), 1.96 (s, 3H, Mesityl- CH_3). ^{13}C NMR (101 MHz, benzene- d_6) δ 20.79 (Mesityl- CH_3), 21.03 (Mesityl- CH_3), 21.32 (Mesityl- CH_3), 21.33 (Mesityl- CH_3), 22.68 (Mesityl- CH_3), 22.69 (Mesityl- CH_3), 76.01 (CPh_2), 104.58, 114.67, 116.26, 116.66, 120.31, 121.07, 123.58, 126.16, 126.75, 126.94, 127.20, 127.23, 128.59, 128.65, 128.92, 129.26, 129.44, 129.54, 129.80, 129.83, 130.00, 131.18, 131.35, 131.81, 132.30, 132.66, 134.67, 135.91, 136.02, 136.29, 136.40, 137.14, 137.21, 137.33, 137.45, 137.89, 139.23, 139.29, 139.85, 145.69, 149.71, 152.60, 157.27, 208.93 (CO), 220.67 (CO). IR (KBr pellet): 1954 cm^{-1} ($\text{C}\equiv\text{O}$) and 2023 cm^{-1} ($\text{C}\equiv\text{O}$). Single crystals of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$ suitable for study via X-ray were grown from slow evaporation of a diethyl ether solution at -35°C . Anal. Calcd for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CO})_2$, $\text{C}_{58}\text{H}_{47}\text{FeN}_4\text{O}_2$: C, 79.72; H, 5.42; N, 4.81. Found: C, 79.22; H, 5.94; N, 4.56.

Preparation of $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$.

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 250 mg (0.306 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ and 10 mL of benzene. In a separate vial, 86 mg (0.656 mmol, 2.14 eq.) of 2,6-dimethylphenylisocyanide was dissolved in 5 mL of benzene. The isocyanide solution was added dropwise to the solution containing the iron complex, resulting in an immediate color change from olive green to dark red. The reaction mixture was stirred for 12 hrs

at room temperature. The solvent was then removed *in vacuo*, affording a red/brown powder. The powder was extracted into benzene and filtered through a plug of celite into a round bottom flask. The celite plug was washed with additional aliquots of benzene until the washings were completely clear. Removal of the solvent *in vacuo* afforded the title compound as a red/brown solid. Yield: 318 mg (0.294 mmol, 96%). ¹H NMR (600 MHz, dichloromethane-*d*₂; δ, ppm): 7.84 (d, *o*-PhH, 1H), 7.38 (m, *o*-PhH, 1H), 7.32 (d, *o*-PhCH₃, 4H), 7.32 (*m*-PhCH₃, 2H), 7.16 (*p*-PhCH₃, 2H), 7.16 (*m*-PhH, 1H), 7.15 (*m*-PhH, 1H), 7.06 (*m*-PhH, 1H), 7.06 (*p*-PhH, 1H), 7.01 (*m*-PhH, 2H), 7.01 (*p*-PhH, 1H), 6.99 (*m*-PhH, 2H), 6.92 (*o*-PhH, 2H), 6.92 (*m*-ArH, H), 6.85 (3-pyH, 1H), 6.84 (3-pyH, 1H), 6.84 (*p*-ArH, H), 6.75 (*m*-ArH, H), 6.69 (*o*-PhH, 1H), 6.63 (m, 4-pyH, 1H), 6.47 (s, *m*-MesCH, 1H), 6.42 (s, *m*-MesCH, 1H), 6.39 (*m*-PhH, 1H), 6.37 (s, *m*-MesCH, 1H), 6.27 (s, *m*-MesCH, 1H), 6.25 (*m*-PhH, 1H), 6.17 (*m*-PhH, 1H), 5.99 (s, pyrroleCH, 1H), 5.95 (t, *p*-PhH, 1H), 5.90 (s, pyrroleCH, 1H), 2.42 (s, *o*-MesCH₃, 3H), 2.35 (s, *o*-CH₃, 3H), 2.12 (s, *o*-MesCH₃, 3H), 2.07 (s, *o*-MesCH₃, 6H), 2.06 (s, *o*-MesCH₃, 3H), 2.01 (s, *o*-MesCH₃, 3H), 1.98 (s, *p*-MesCH₃, 3H), 1.73 (s, *o*-CH₃, 3H), 1.39 (s, *p*-MesCH₃, 3H). ¹³C NMR (151 MHz, dichloromethane-*d*₂; δ, ppm): 195.33 (C53/C62), 179.73 (C53/C62), 157.86 (C3), 153.27 (C22), 149.36 (C11), 147.23 (C41), 139.68 (C6), 139.26 (C25), 138.86 (C13), 138.22 (C30), 137.87 (C32), 137.52 (C15), 137.17 (C12), 136.98 (C36), 136.84 (C17), 136.32 (C34), 135.96 (C46), 135.67 (C4), 134.83 (C64), 134.78 (C57), 134.09 (C55), 133.28 (C59), 133.12 (C31), 132.31 (C63), 131.77 (C51), 131.54 (C23), 131.36 (C49), 129.94 (C54), 129.55 (C26), 129.17 (C7), 129.10 (C48), 128.92 (C27), 128.64 (C8), 128.59 (C5), 128.59 (C24), 128.54 (C35), 128.27 (C65), 127.78 (C16), 127.76 (C14), 127.45 (C50), 127.32 (C58), 127.27 (C56), 127.13 (C33), 127.13 (C45), 126.53 (C43), 126.53 (C66), 126.37 (C28), 126.17 (C21), 125.42 (C9), 124.35 (C44), 123.54 (C42), 120.76 (C1), 120.76 (C2), 120.50 (C47), 115.77 (C10), 115.58 (C29),

102.06 (C52), 72.15 (C40), 23.08 (C38), 22.98 (C37), 22.98 (C60), 22.08 (C19), 21.74 (C18), 20.87 (C39), 20.56 (C20), 19.03 (C67), 18.61 (C61). IR (KBr pellet): 1999 cm^{-1} ($\text{C}\equiv\text{N}$) and 2102 cm^{-1} ($\text{C}\equiv\text{N}$). Single crystals suitable for study via X-ray were grown via diffusion of pentane into a concentrated toluene at -35°C . Anal. Calcd for $(\text{CPh}_2^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-(2,6-(\text{CH}_3)_2\text{Ph})_2)$, $\text{C}_{74}\text{H}_{65}\text{FeN}_5$: C, 82.28; H, 6.07; N, 6.48. Found: C, 82.43; H, 6.06; N, 6.40.

Figure 6.28. ^{13}C NMR labeling scheme for $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_2$.

Preparation of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}\equiv\text{N}-2,6-(\text{CH}_3)_2\text{Ph})_3$.

A 20 mL scintillation vial was loaded with a magnetic stirrer, 250 mg (0.345 mmol) of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$, and 5 mL of benzene, affording a homogenous dark red solution. In a separate vial, 140 mg (1.07 mmol, 3.1 eq.) of 2,6-dimethylphenylisocyanide was dissolved in 5 mL of benzene. The isocyanide solution was added to slowly, dropwise, to the solution of the iron compound, resulting in an immediate color change of the solution from dark red to orange. Within minutes, an abundant yellow/orange precipitate was evident. The reaction mixture was allowed to stir for 12 hours. The resulting precipitate was isolated on a medium porosity glass frit and washed with three 5 mL aliquots of pentane. Drying *in vacuo* afforded the title compound as an analytically pure yellow powder. Yield: 322 mg (0.308 mmol, 89%). ^1H NMR (600 MHz, dichloromethane- d_2 ; δ , ppm): 7.49 (AA'BB'C, $J_{\text{AB}} = 7.64$ Hz, $J_{\text{AB}'} = 0.51$ Hz, $J_{\text{AA}'} =$

1.94 Hz, $J_{AC} = 1.31$ Hz, *o*-PhH, 4H), 7.35 (AA'BB'C, $J_{AB} = 7.64$ Hz, $J_{AB'} = 0.51$, $J_{BB'} = 1.44$ Hz, $J_{BC} = 7.43$ Hz, *m*-PhH, 4H), 7.22 (AB₂, $J_{AB} = 8.0$ Hz, 4-pyH, 4H), 7.20 (AA'BB'C, $J_{BC} = 7.43$ Hz, $J_{AC} = 1.31$ Hz, *p*-PhH, 1H), 7.11 (AB₂, $J_{AB} = 8.0$ Hz, 3-pyH, 2H), 7.09 (AB₂, $J_{AB} = 7.80$ Hz, *p*-PhH, 2H (apical isocyanides)), 7.03 (AB₂, $J_{AB} = 7.50$ Hz, *p*-PhH (equatorial isocyanide)), 7.02 (AB₂, $J_{AB} = 7.8$ Hz, *m*-PhH, 4H (apical isocyanides)), 6.95 (AB₂, $J_{AB} = 7.5$ Hz, *p*-PhH, 1H (apical isocyanide)), 6.40 (s, *m*-MesH, 4H), 5.71 (s, pyrroleH, 2H), 2.37 (s, *m*-CH₃, 6H (equatorial isocyanide)), 2.19 (s, *m*-CH₃, 12H (apical isocyanides)), 2.03 (s, *o*-MesCH₃, 12H), 1.46 (s, *p*-MesCH₃, 6H). ¹³C NMR (151 MHz, dichloromethane-*d*₂; δ, ppm): 178.15 (C24), 176.68 (C18), 157.58 (C3), 147.35 (C11), 139.89 (C6), 137.85 (C13), 137.63 (C15), 136.69 (C12), 136.59 (C4), 136.05 (C1), 135.86 (C20), 134.47 (C26), 130.05 (C5), 130.01 (25), 129.70 (C7), 128.69 (C8), 128.51 (C22), 128.42 (C19), 128.35 (C21), 127.54 (C27), 127.36 (C14), 127.20 (C28), 125.66 (C9), 115.05 (C10), 109.12 (C2), 21.79 (C16), 20.86 (C17), 19.84 (C29), 19.07 (C23). IR (KBr pellet): 2103 cm⁻¹ (C≡N) and 2150 cm⁻¹ (C≡N). Anal. Calcd for (MesPDP^{Ph})Fe(CN-(2,6-(CH₃)₂Ph)₃, C₇₀H₆₄FeN₆: C, 80.44; H, 6.17; N, 8.04. Found: C, 80.17; H, 6.07; N, 7.99. Single crystals suitable for analysis via X-ray were grown from diffusion of pentane into a concentrated benzene solution of (MesPDP^{Ph})Fe(C≡N-(2,6-(CH₃)₂Ph)₃ at room temperature.

Figure 6.29. ¹³C NMR labeling scheme for (MesPDP^{Ph})Fe(C≡N-2,6-(CH₃)₂Ph)₃.

Preparation of $(^{Mes}PDP^{Ph})Fe(C\equiv N-^1Ad)_3$.

A 20 mL scintillation vial was loaded with a magnetic stirrer, 250 mg (0.345 mmol) of $(^{Mes}PDP^{Ph})Fe(thf)$, and 5 mL of benzene. Vigorous stirring of the mixture resulted in a homogenous dark red solution. In a separate vial, 173 mg (1.07 mmol, 3.1 eq.) of 1-adamantylisocyanide ($C\equiv N-^1Ad$) was dissolved in 5 mL of benzene. The isocyanide solution was added dropwise, to the solution of the iron compound, resulting in an immediate color change of the solution from dark red to red/brown. The reaction mixture was allowed to stir for 12 hours. To the resulting suspension was added 5 mL of pentane, which induced precipitation of yellow/orange microcrystalline material. The precipitate was isolated on a medium porosity glass frit and washed with three 5 aliquots of pentane, affording the title compound as an analytically pure yellow powder. Yield: 316 mg (0.278 mmol, 81%). 1H NMR (600 MHz, dichloromethane- d_2 ; δ , ppm): 7.48 (AA'BB'C, $J_{AB} = 7.79$ Hz, $J_{AA'} = 1.91$ Hz, $J_{AC} = 1.29$ Hz, $J_{AB'} = 0.55$ Hz, *o*-PhH, 4H), 7.33 (AA'BB'C, $J_{AB} = 7.79$ Hz, $J_{BC} = 7.42$ Hz, $J_{BB'} = 1.48$ Hz, $J_{AB'} = 0.55$ Hz, *m*-PhH, 4H), 7.17 (AA'BB'C, $J_{BC} = 7.42$ Hz, $J_{AC} = 1.29$ Hz, *m*-PhH, 2H), 7.13 (AB₂, 4-pyH, 1H), 6.97 (AB₂, $J = 7.9$ Hz, 3-pyH, 2H), 6.79 (s, *m*-MesH, 4H), 5.51 (s, pyrroleH, 2H), 2.24 (s, *p*-MesCH₃, 6H), 2.18 (s, *o*-MesCH₃, 12H), 1.98 (s, 6H), 1.83 (s, 3H), 1.80 (s, 12H), 1.59 ($J = 12.4$ Hz, 6H), 1.54 (m, $J = 12.4$ Hz, 6H), 1.52 (m, $J = 12.4$ Hz 3H), 1.45 (m, $J = 12.4$, 3H), 1.04 (s, 6H). ^{13}C NMR (151 MHz, dichloromethane- d_2 ; δ , ppm): 163.75 (C23), 163.55 (C18), 157.00 (C3), 147.79 (C4), 140.17 (C6), 138.78 (C13), 137.97 (C12), 136.83 (C11), 135.91 (C15), 134.70 (C1), 129.52 (C7), 128.77 (C5), 128.50 (C8), 127.97 (C14), 125.30 (C9), 116.36 (C10), 108.54 (C2), 57.07 (C24), 56.82 (C19), 43.98 (C25), 42.29 (C20), 35.87 (C27), 35.79 (C22), 29.55 (C21), 29.46 (C26), 21.90 (C16), 21.32 (C17). IR (KBr pellet): 2123 cm^{-1} ($C\equiv N$, broad).

Anal. Calcd for (^{Mes}PDP^{Ph})Fe(C≡N-¹Ad)₃, C₇₆H₈₂FeN₆: C, 80.40; H, 7.28; N, 7.40. Found: C, 80.00; H, 7.29; N, 7.08.

Figure 6.30. ¹³C NMR labeling scheme for (^{Mes}PDP^{Ph})Fe(C≡N-¹Ad)₃.

Preparation of (^{Mes}PDP^{Ph})Fe(CPh₂)(C≡N-¹Ad).

To a 20 mL scintillation vial equipped with a magnetic stirrer was added 100 mg (0.122 mmol) of (^{Mes}PDP^{Ph})Fe(CPh₂) and 2 mL of benzene. Vigorous stirring of the mixture afforded a dark green solution. In a separate vial, 20 mg (0.124 mmol, 1.02 eq.) of 1-adamantylisocyanide was dissolved in 1 mL of pentane. The solution of 1-adamantylisocyanide was added dropwise to the stirring solution of (^{Mes}PDP^{Ph})Fe(CPh₂), resulting in an immediate color change from olive green to dark red/brown. The solvent was immediately removed in vacuo affording a dark solid. Crystallization of the product was accomplished via evaporation of a diethyl ether solution at -35°C. Yield: 19 mg, 0.019 mmols, 16%. ¹H NMR (600 MHz, benzene-*d*₆; δ, ppm): 7.66 (d, *J* = 7.4 Hz, 4H, *ortho*-Ph), 7.21 (t, *J* = 7.6 Hz, 4H, *meta*-Ph), 7.10 (t, *J* = 7.4 Hz, 2H, *para*-Ph), 7.00 (m, 10H, Ar), 6.81 (s, 2H, *meta*-Mesityl), 6.74 (s, 2H, *meta*-Mesityl), 6.55 (d, *J* = 7.9 Hz, 2H, 3-pyridine), 6.37 (s, 2H, pyrrole-H), 6.20 (t, *J* = 7.9 Hz, 1H, 4-pyridine), 2.78 (s, 6H, Mesityl-

CH_3), 2.53 (s, 6H, Mesityl- CH_3), 2.14 (s, 6H, Mesityl- CH_3), 1.60 (s, 3H, ^1Ad), 1.25 (m, $J = 12.3$ Hz, 6H, ^1Ad), 0.76 (s, 6H, ^1Ad). ^{13}C NMR (151 MHz, benzene- d_6 ; δ , ppm): 354.13 (CPh_2). Red single crystals suitable for X-ray crystallography were grown from slow evaporation of a diethyl ether solution of ($^{\text{Mes}}\text{PDP}^{\text{Ph}}$) $\text{Fe}(\text{CPh}_2)(\text{C}\equiv\text{N}-^1\text{Ad})$ at -35°C .

Physical Measurements.

^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were acquired at 25°C on a Varian Unity INOVA 600 MHz spectrometer equipped with a 5 mm inverse broadband PFG probe, on an Agilent 400 MHz DD2 spectrometer equipped with a 5 mm One NMR probe, or a JNM-ECZ400S/L1 spectrometer equipped with a 5 mm ROYAL NMR probe. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Room temperature magnetic susceptibility measurements were performed with a Johnson Matthey Mark 1 instrument that was calibrated with $\text{HgCo}(\text{SCN})_4$. Zero-field ^{57}Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a $^{57}\text{Co}/\text{Rh}$ radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/ N_2 cryostat within an accuracy of ± 0.3 K. The data were calibrated relative to α -iron at 298 K. The fitting procedure to extract quantitative spectral parameters uses a least-squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co. Variable-temperature applied-field ^{57}Fe Mössbauer spectra were performed on samples prepared by mixing a powder sample with mineral oil and then frozen in liquid nitrogen. A second sample was prepared in dilute frozen toluene solution. The spectroscopic results measured on the powder sample and frozen solution sample were consistent, suggesting that potential “powder effects” (such as intermolecular magnetic interactions) could be excluded

from consideration in spectral analysis. The data presented in this chapter is that of the spectroscopic analysis of the sample of solid powder frozen mineral oil.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)⁷⁶ was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.⁷⁷

Density Functional Theory Calculations.

All DFT calculations were performed with the ORCA program package.⁷⁸ Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.⁷⁹⁻⁸¹ The all-electron Gaussian basis sets were those

developed by the Ahlrichs group.⁸²⁻⁸⁴ Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SVP basis sets were used that were of double- ζ quality in the valence region and contained a polarizing set of d functions on the nonhydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)⁸⁵⁻⁸⁷ approach were chosen to match the orbital basis.⁸⁸⁻⁹⁰ Throughout this chapter computational results are described by using the broken-symmetry (BS) approach by Ginsberg⁹¹ and Noodleman.⁹² Because several broken symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation BS(m,n) has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. All molecular orbital and spin density plots were generated using the program Gabedit.⁹³ Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.⁹⁴ Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{95,96}

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CHAPTER VII: CONCLUDING REMARKS AND FUTURE OUTLOOKS

This dissertation has presented the synthesis, characterization, and reactivity studies of a variety of homogenous pyridine dipyrrolide (PDP) ligated iron complexes. An emerging theme in this area is the propensity for the $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ ligand to support iron complexes with unusual coordination environments and electronic structures, which arise from the planarity enforced by the meridional $^{\text{Mes}}\text{PDP}^{\text{Ph}}$ pincer ligand. Notable advances include the first examples of neutral square-planar high-spin Fe^{II} complexes, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (Figure 7.1 and Chapter 2), reactive paramagnetic PDP Fe nitrene adducts such as $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ and $(^{\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{NMes})$ (Figure 7.2 and Chapters 3 and 5), and the first example of a square-planar iron carbene complex, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{CPh}_2)$ (Figure 7.2 and Chapter 6).

Figure 7.1. Neutral square-planar high-spin Fe^{II} complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ (left) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)$ (right).

Figure 7.2. Paramagnetic PDP Fe nitrene complex ($^{Cl_2Ph}PDP^{Ph}$)Fe(NMes) (left) and square-planar iron carbene complex ($^{Mes}PDP^{Ph}$)Fe(CPh₂) (right).

Chapter 2 has presented a thorough electronic structure study of ($^{Mes}PDP^{Ph}$)Fe(OEt₂) and ($^{Mes}PDP^{Ph}$)Fe(thf). These species are the first reported examples of neutral square-planar high-spin Fe^{II} coordination compounds. Both complexes feature a doubly occupied d_{z^2} orbital, accompanied by four singly occupied d orbitals, which account for the observed $S = 2$ ground states. Key consequences of the planar coordination environment imposed by the dianionic $^{Mes}PDP^{Ph}$ ligand are the stabilization of the $d_{x^2-y^2}$ orbital via geometric distortion, destabilization of the d_{xy} orbital via σ donation, and stabilization of the d_{xy}/d_{yz} orbitals via π donation. In combination, these elements result in a compressed ligand field with an energetically accessible $d_{x^2-y^2}$ orbital. This phenomena is in contrast to canonical square-planar coordination compounds which are characterized by a significantly destabilized $d_{x^2-y^2}$ orbital and consequently, intermediate-spin $S = 1$ ground states for Fe^{II} ions.

($^{Mes}PDP^{Ph}$)Fe(NMes) and other related PDP iron nitrene adducts have been implicated as reactive intermediates in the stoichiometric intramolecular C-H amination of the supporting ligand scaffold (Chapter 3). These observations serve as a foundation for future investigations concerning productive intramolecular or intermolecular C-H amination reactivity, or furthermore, the development of catalytic methodologies for C-N bond formation. It is

anticipated that judicious selection of appropriate azides as nitrene sources in conjunction with robust PDP iron complexes lacking weak C-H bonds on the ligand periphery will be key design elements of such systems. Furthermore, successful development of these methodologies may perhaps find application in the synthesis of elaborate N-heterocycles, which are ubiquitous in biologically relevant molecules. For example, Figure 7.3 demonstrates a possible stoichiometric synthesis of iron-bound 2,2-dimethyl-5-phenyl-pyrrolidine, from (4-azido-4-methylpentyl)benzene via a proposed intermediate ($^{Cl_2Ph}PDP^{Ph}$) iron nitrene complex.

Figure 7.3. Stoichiometric synthesis of iron-bound 2,2-dimethyl-5-phenyl-pyrrolidine from 4-azido-4-methylpentylbenzene via a proposed intermediate ($^{Cl_2Ph}PDP^{Ph}$) iron nitrene intermediate.

The synthesis of a coordinatively unsaturated four-coordinate pincer ligand supported iron carbene complex, ($^{Mes}PDP^{Ph}$)Fe(CPh₂), is an important advancement in the chemistry of iron carbenes. Despite decades of study, previously reported examples of iron carbene complexes have largely been limited to systems featuring saturated coordination spheres, or macrocyclic

supporting ligands. Importantly, these coordination motifs disallow the cis-coordination of substrate molecules, a necessity for many catalytic mechanisms. Despite the known stability of iron carbenes supporting the diphenyl carbene fragment, it is anticipated that elaboration of the identity of the carbene substituents in other PDP iron carbene complexes will lead to increased activity in carbene transfer reactions. Moreover, the existence of discrete PDP iron carbene complexes suggests that high-spin Fe^{II} PDP complexes may be utilized as precatalysts in conjunction with diazo reagents to generate PDP iron carbene intermediates in a catalytic fashion. Leveraging such intermediates in cyclopropanation or C-H insertion reactions would offer attractive alternatives to popular precious metal catalyst based methodologies. A proposed catalytic cyclopropanation of styrene using methyl phenyldiazoacetate and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ as precatalyst is depicted below in Figure 7.4.

Figure 7.4. Proposed $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ catalyzed cyclopropanation of styrene using methyl phenyldiazoacetate. Note, stereochemistry of the cyclopropane product is ambiguous.

Note that a 4-methoxyphenyl substituted analogue to the carbene intermediate in this proposed catalytic cycle has been synthesized by the reaction of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ with the corresponding diazo reagent, methyl 4-methoxyphenyldiazoacetate (Scheme 7.1). This species, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}(\text{CO}_2\text{Me})(4\text{-MeOPh}))$, was characterized by X-ray crystallography and an ORTEP diagram is presented in Figure A.2.11. (Appendix II). This result offers an exciting entry into future carbene group transfer reactivity studies of PDP iron complexes carrying donor-acceptor carbene fragments, of which, $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}(\text{CO}_2\text{Me})(4\text{-MeOPh}))$ is the first known crystallographically characterized example.

Scheme 7.1. Synthesis of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{C}(\text{CO}_2\text{Me})(4\text{-MeOPh}))$ from $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{thf})$ and methyl 4-methoxyphenyldiazoacetate.

APPENDIX I: SYNTHESIS AND CHARACTERIZATION OF A REDUCED PYRIDINE DIPYRROLIDE IRON TETRAZENE COMPLEX

A.1.1 Abstract

The pyridine bispyrrolide iron tetrazene complexes, of general formula $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Ar}_2)$ or $(^{2,6\text{Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Ar}_2)$ obtained from the reaction of $(^{\text{R}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{L})$, where L is a diethyl ether or tetrahydrofuran ligand and R' is 2,6-Cl₂Ph or 2,4,6-trimethylphenyl (Mes), with two equivalents of an aryl azide, have been found to possess a complex electronic structure. The proposed ground state configuration of a low-spin iron (III) iron antiferromagnetically coupled to a tetrazene based radical monoanion, $(\text{N}_4\text{Ar}^{\bullet})$, has been adopted based on high resolution X-ray crystallographic analysis, ^{57}Fe Mössbauer spectroscopy, and a density functional theory study performed on the representative complex $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$. Access to a representative reduced pyridine dipyrrolide iron tetrazene species was permitted via chemical reduction of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ with cobaltocene, yielding the separated ion-pair $[\text{CoCp}_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$. ^1H NMR obviated the paramagnetic ground state of this complex, while a combination of magnetic measurements, X-ray crystallography, and ^{57}Fe Mössbauer spectroscopy suggest an electronic structure formulation of a high-spin iron(III) ion and closed-shell dianionic tetrazene ligand, $(\text{N}_4\text{Tol}_2^{2-})$.

A.1.2 Introduction

Iron tetrazene complexes, once rare, have become more frequently encountered due to the surge of research in the area of iron imido chemistry. This type of compound is believed to arise from the [2+3] cycloaddition of an iron imide intermediate with an organic azide. Recently, iron tetrazene complexes have become an attractive target of synthetic chemists, due to their complex

electronic structures and applications in catalysis.¹⁻⁷ Similar to the alpha-diimine class of ligands, tetrazenes possess an extended pi system, and thus have been identified as potentially redox-active. Accordingly, to date, iron complexes have been isolated carrying neutral, radical anionic, and dianionic forms of tetrazeno ligands (Scheme Scheme A.1.1. and Figure A.1.1.).

Scheme A.1.1. Possible formal electronic configurations of a tetrazeno ligand complexed to a metal center.

Figure A.1.1. Examples of Fe^{II} complexes carrying neutral, radical anion, and dianionic tetrazeno ligands. Note: Mes = mesityl, Bn = benzyl, Dipp = 2,6-diisopropylphenyl, Ad = 1-adamantyl.

In chapters 3 and 5 of this dissertation, the synthesis and characterization of (^{Mes}PDP^{Ph})Fe(N₄pTol₂), (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(pFPh)₂), and (^{2,6-Cl₂Ph}PDP^{Ph})Fe(N₄(p^tBuPh)₂), has been described. A combination of X-ray crystallography, ¹H NMR, ⁵⁷Fe Mössbauer spectroscopy, and density functional theory calculations have elucidated the electronic structures of these complexes, best described as low-spin ferric ions antiferromagnetically coupled to

tetrazene radical monoanions. Such an electronic structure has previously been unknown within the context of iron tetrazene coordination chemistry. In an effort to probe the redox-chemistry of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$, its reductive chemistry was explored, resulting in the isolation of $[\text{Co}(\text{Cp})_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$. This appendix describes the synthesis and characterization of $[\text{Co}(\text{Cp})_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$.

A.1.3 Synthesis and Characterization of $[\text{CoCp}_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$

The addition of one equivalent of cobaltocene to stirring solutions of $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)$ in dichloromethane solvent was found to immediately induce a color change from dark red/brown to dark brown/green with concomitant precipitation of a black powder. Removal of volatiles *in vacuo* and subsequent washing of the resulting solid material with benzene and hexanes affording a black powder. Despite poor solubility in hydrocarbon solvents, low-quality ^1H NMR spectra in dichloromethane- d_2 clearly established the paramagnetic nature of the product. Single crystals suitable for X-ray diffraction were obtained from the same solvent and established the identity of the product as the separated ion pair $[\text{CoCp}_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$.

Scheme A.1.2. Synthesis of $[\text{Co}(\text{Cp})_2][(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$. R denotes para-tolyl.

Figure A.1.2. ORTEP of $[\text{Co}(\text{Cp})_2][(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$ depicted at 30% probability ellipsoids. Hydrogen atoms were removed for clarity.

$[\text{CoCp}_2][(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$ crystallizes in the monoclinic space group C2/c and adopts a trigonal bipyramidal structure in the solid state, with the $[(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$ anion lying on a two-fold rotation axis that passes through the Fe(1), N(2), and C(7) atoms. Similarly, the $[\text{Co}(\text{Cp})_2]$ cation is constrained by a two-fold rotation axis that passes through the Co(1) atom. Notable bond lengths include 2.119 (2) Å and 2.111 (3) Å to the pyrrolide and pyridine nitrogens from the iron center and 1.962 (2) Å to the apical tetrazene nitrogen, N4. The relatively long iron pyridine and iron pyrrole bonds are consistent with a high-spin state for the iron center. Importantly, the N3-N4 bond length of 1.375 (3) Å and N4-N4' bond length of 1.283 (5) Å. The N3-N4 bond length is consistent with the N-N single bond in 1,2-diphenylhydrazine (1.394 (7) Å)⁸, while the N4-N4' bond length is similar to the N=N bond in cis azobenzene (1.251 Å)⁹ and is consistent with a double bond. These structural metrics are consistent with a description of the tetrazene ligand as a dianion, as evidenced by the alternating long, short, and long N-N bonds

within the N₄ chelate ligand.² The combination of a dianionic tetrazene and dianionic pyridine dipyrrolide ligand infers a formal oxidation state of +3 for the iron center. The room-temperature solid-state magnetic moment of 6.1 μ_B is consistent with a high-spin ferric center ($S = 5/2$).

Table A.1.1. Selected bond lengths (Å) and angles (deg) for [CoCp₂][(^{Mes}PDP^{Ph})Fe(N₄Tol₂)]

[CoCp ₂][(^{Mes} PDP ^{Ph})Fe(N ₄ Tol ₂)]	
Fe1–N1	2.119 (2)
Fe1–N2	2.111 (3)
Fe1–N3	1.962 (2)
N3–N4	1.375 (3)
N4–N4'	1.283 (5)
N1–Fe1–N2	75.53 (6)
N1–Fe1–N3	106.60 (9)
N2–Fe1–N3	141.35 (7)
Fe1–N3–N4	116.23 (17)
N3–N4–N4'	115.12 (14)

Note: The [(^{Mes}PDP^{Ph})Fe(N₄Tol₂)] anion lies on a two-fold rotation axis that passes through the Fe(1), N(2), and C(7) atoms.

To further interrogate the electronic structure of [Co(Cp)₂][(^{Mes}PDP^{Ph})Fe(N₄Tol₂)] a zero-field Mössbauer spectrum (Figure A.1.3.) was acquired of a powder sample of at 80 K. The resulting spectrum is contains a broad asymmetric feature which was fitted with $\delta = 0.45 \text{ mms}^{-1}$ and $|\Delta E_Q| = 2.83 \text{ mms}^{-1}$. The isomer shift of 0.45 mms^{-1} is consistent with the isomer shift value of $0.39(1) \text{ mms}^{-1}$ for (^tBuPDP^tBu)Fe(Cl), the only previously reported example of a high-spin Fe^{III} PDP iron complex. Notably, (^tBuPDP^tBu)Fe(Cl) also displays an asymmetric Mossbauer spectrum at 77 K, as indicated by linewidths (Γ_{FWHM}) of $0.74(1)$ and $1.24(1) \text{ mms}^{-1}$, however, these linewidths are not nearly as extreme as the linewidths of $\Gamma_L = 1.86 \text{ mms}^{-1}$ and $\Gamma_R = 3.95 \text{ mms}^{-1}$

obtained from the fit of the 80 K spectrum of $[\text{Co}(\text{Cp})_2][(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$.¹⁰ Furthermore, asymmetric Mössbauer spectra have been well documented within the context of similar high-spin Fe^{III} ($S = 5/2$) porphyrin complexes. The manifestation of asymmetry in the Mössbauer spectra of these species has been explained theoretically as resulting from a slowing of temperature dependent spin-spin relaxation times.¹¹⁻¹⁴ Thus, the appearance of a broad and asymmetric feature in the Mössbauer spectrum of $[\text{Co}(\text{Cp})_2][(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$ provides additional evidence for the assignment of a high-spin ferric state for the iron center of this complex.

Figure A.1.3. Zero-field ^{57}Fe Mössbauer spectrum of $[\text{Co}(\text{Cp})_2][(\text{MesPDP}^{\text{Ph}})\text{Fe}(\text{N}_4\text{Tol}_2)]$ acquired at 80 K.

A.1.4 Experimental Procedures

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard Schlenk line and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves. All solids were dried under high vacuum; all liquids were dried over CaH₂ and vacuum transferred into oven-dried glassware in order to bring into the glovebox. Co(Cp)₂ was obtained from commercial sources and used as received. Deuterated benzene (benzene-*d*₆) and dichloromethane (dichloromethane-*d*₂) for NMR spectroscopy were distilled from sodium metal and calcium hydride, respectively. (^{Mes}PDP^{Ph})Fe(N₄Tol₂) was prepared according to the previously reported procedure.¹⁵

Preparation of [Co(Cp)₂][(^{Mes}PDP^{Ph})Fe(N₄Tol₂)].

In the glovebox, 100 mg (0.112 mmol) of (^{Mes}PDP^{Ph})Fe(N₄Tol₂) was dissolved in 5 mL of dichloromethane in a 20 mL scintillation vial equipped with a magnetic stirrer. In a separate vial, 21 mg (0.111 mmol) of cobaltocene was dissolved in 1 mL of dichloromethane. The cobaltocene solution was added dropwise to the stirring solution of (^{Mes}PDP^{Ph})Fe(N₄Tol₂), inducing an immediate color change from dark red/brown to brown/green. The reaction mixture was stirred for one hour and the solvent was then removed *in vacuo*, affording a dark powder. The resulting powder was transferred to a medium porosity glass frit and washed with 20 mL of benzene and 20 mL of hexanes and dried *in vacuo*. Yield: 91 mg, 0.084 mmol, 76 %. $\mu_{\text{eff}} = 6.1 \mu_{\text{B}}$ (298 K, magnetic susceptibility balance). A crystal suitable for study via X-ray diffraction was obtained from a concentrated solution of dichloromethane.

Physical Measurements.

^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were acquired at 25 °C on a Varian Unity INOVA 600 MHz spectrometer equipped with a 5 mm inverse broadband PFG probe, on an Agilent 400 MHz DD2 spectrometer equipped with a 5 mm One NMR probe, or a JNM-ECZ400S/L1 spectrometer equipped with a 5 mm ROYAL NMR probe. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. Room temperature magnetic susceptibility measurements were performed with a Johnson Matthey Mark 1 instrument that was calibrated with $\text{HgCo}(\text{SCN})_4$. Zero-field ^{57}Fe Mössbauer spectra were collected on a SEE Co. Mössbauer spectrometer (MS4) with a $^{57}\text{Co}/\text{Rh}$ radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/N₂ cryostat within an accuracy of ± 0.3 K. The data were calibrated relative to α -iron at 298 K. The fitting procedure to extract quantitative spectral parameters uses a least-squares Lorentzian fitting method implemented in the WMOSS software developed by SEE Co.

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, mounted on a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo K α radiation source ($\lambda = 0.71073$ Å), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned. The APEX3 software program (version 2016.9-0)¹⁶ was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Three sets of 12 frames each were

collected using the omega scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the crystal lattice that was used for the structural analysis. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.¹⁷

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APPENDIX II: MISCELLANEOUS STRUCTURES OBTAINED FROM X-RAY
CRYSTALLOGRAPHIC ANALYSIS

cm31cms: [^{Me}PDP^{Ph})Fe(OEt₂)]₂

Figure A.2.1. ORTEP depictions of $[(^{\text{Me}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)]_2$ and the asymmetric unit of $[(^{\text{Me}}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)]_2$ displayed at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

cm40cms: (^{Me}PDP^{Ph})Fe(py)₃

Figure A.2.2. ORTEP of (^{Me}PDP^{Ph})Fe(py)₃ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized fluorobenzene are omitted for clarity.

cm114cms: (^{Mes}PDP^{Ph})Fe(NH₂Bn)₃

Figure A.2.3. ORTEP of (^{Mes}PDP^{Ph})Fe(NH₂Bn)₃ displayed at 30% probability ellipsoids. Hydrogen atoms, excluding amine protons are excluded for clarity. Only the *ipso* carbon of one mesityl substituent of the ^{Mes}PDP^{Ph} is depicted.

cm141cms: (^{Ph}PDP^{Ph})Fe(thf)₃

Figure A.2.4. ORTEP of (^{Ph}PDP^{Ph})Fe(thf)₃ displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized THF solvent are omitted for clarity. Only the *ipso* carbon of one ^{Ph}PDP^{Ph} phenyl substituent is depicted.

cm158cms: (^{Mes}PDP^{Ph})Fe(Cl)(py)

Figure A.2.5. ORTEP of (^{Mes}PDP^{Ph})Fe(Cl)(py) displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized THF are omitted for clarity.

cm181cms: (^{Mes}PDP^{Ph})Fe(N₃)(py)(thf)

Figure A.2.6. ORTEP of (^{Mes}PDP^{Ph})Fe(N₃)(py)(thf) displayed at 30% probability ellipsoids. A cocrystallized molecule of pentane and hydrogen atoms have been omitted for clarity. Only the *ipso* carbon of one mesityl substituent of the ^{Mes}PDP^{Ph} ligand has been depicted.

cm188cms: (^{Mes}PDP^{Ph})Fe(pyrr)(py)

Figure A.2.7. ORTEP of (^{Mes}PDP^{Ph})Fe(pyrr)(py) displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized diethyl ether have been omitted for clarity. Only the *ipso* carbon of one mesityl group of the ^{Mes}PDP^{Ph} has been depicted.

cm189cms: (^{Mes}PDP^{Ph})Fe(NH₂Mes)

Figure A.2.8. ORTEP of (^{Mes}PDP^{Ph})Fe(NH₂Mes) displayed at 30% probability ellipsoids. Hydrogen atoms (excluding amine protons) and cocrystallized (^{Mes}PDP^{Ph})Fe(NH₂Mes)₂ and toluene are removed for clarity. Only the *ipso* carbon of one ^{Mes}PDP^{Ph} mesityl group is depicted.

cm189cms: (^{Mes}PDP^{Ph})Fe(NH₂Mes)₂

Figure A.2.9. ORTEP of (^{Mes}PDP^{Ph})Fe(NH₂Mes)₂ displayed at 30% probability ellipsoids. Hydrogen atoms (excluding amine protons) and cocrystallized (^{Mes}PDP^{Ph})Fe(NH₂Mes) and toluene are removed for clarity. Only the *ipso* carbon of one ^{Mes}PDP^{Ph} mesityl group is depicted.

cm239cms: (^{2,6-Cl₂Ph}PDP^{Ph})Fe(OEt₂)

Figure A.2.10. ORTEP of (^{2,6-Cl₂Ph}PDP^{Ph})Fe(OEt₂) displayed at 30% probability ellipsoids. Hydrogen atoms and cocrystallized toluene are removed for clarity.

cm254cms: (^{Mes}PDP^{Ph})Fe(C(CO₂Me)(4-MeOPh))

Figure A.2.11. ORTEP of (^{Mes}PDP^{Ph})Fe(C(CO₂Me)(4-MeOPh)) displayed at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

cm272cms: $\text{Co}(\text{}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})$

Figure A.2.12. ORTEP of $\text{Co}(\text{}^{2,6\text{-Cl}_2\text{Ph}}\text{PDP}^{\text{Ph}})$ displayed at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

cm281cms: $(\text{}^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)_2$

Figure A.2.13. ORTEP of $(\text{}^{\text{C}_6\text{F}_5}\text{PDP}^{\text{Ph}})\text{Fe}(\text{OEt}_2)_2$ displayed at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

cm260cms: (H₂^{pTol}PDP^{Ph})•DMSO

Figure A.2.14. ORTEP of H₂^{pTol}PDP^{Ph}•DMSO displayed at 30% probability ellipsoids. Hydrogen atoms (with exception of pyrrole NH hydrogens) and a second cocrystallized molecule of DMSO is excluded for clarity.

cm298cms: (C₆F₅PDP^{Ph})Fe(py)₂•(py)

Figure A.2.15. ORTEP of (C₆F₅PDP^{Ph})Fe(py)₂•(C₆H₅N) displayed at 30% probability ellipsoids. Hydrogen atoms and one C₆F₅ pyrrole substituent (with exception of the *ipso* carbon) have been excluded for clarity.