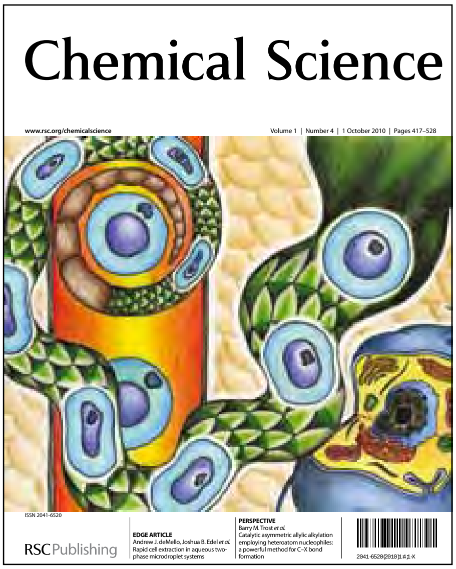
Chemical Science

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSC Publishing

www.rsc.org/chemicalscience

Registered Charity Number 207890

Chemical Science
Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x
www.rsc.org/xxxxxx
Edge Article

Synthesis, Electronic Structure and Reactivity of Bis(imino)pyridine Iron Carbene Complexes: Evidence for a Carbene Radical.

Sarah K. Russell,[a] Jordan M. Hoyt,[a] Suzanne C. Bart,[b] Carsten Milsmann,[a] S. Chantal E. Stieber,[a] Scott P. Semproni,[a] Serena DeBeer[b,c] and Paul J. Chirik[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The reactivity of the disubstituted diazoalkane, N_2CPh_2 with a family of bis(imino)pyridine iron dinitrogen complexes was examined. For the most sterically protected member of the series, $(^{iPr}PDI)Fe(N_2)_2$ (^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2$-C_6H_3-N=CMe)$_2C_5H_3N$), an $S = 1$ iron diazoalkane complex was obtained and structurally characterized. Reducing the size of the 2,6-aryl substituents to ethyl or methyl groups resulted in isolation of bis(imino)pyridine iron carbene complexes. Magnetic measurements established $S = 1$ ground states, demonstrating rare examples of iron carbenes in a weak ligand field. Electronic structure determination using metrical parameters from X-ray diffraction as well as Mössbauer, XAS and computational data established high spin iron(II) compounds engaged in antiferromagnetic coupling with redox-active bis(imino)pyridine and carbene radicals.

Introduction

Metal carbene complexes, L_nMCR_2 have a long-standing history in organometallic chemistry due to their fundamental bonding properties,[1] use as [CR_2] transfer agents for organic synthesis,[2] role in C-H activation processes[3] and as key intermediates in olefin metathesis.[4] Traditionally, metal carbene complexes have been classified as electrophilic (Fischer-type) or nucleophilic (Schrock-type) at carbon.[5] A third, redox active variant has also been identified where the carbon atom has been reduced by one electron forming a carbene radical.[6] This electronic structure translates onto reactivity as carbene radicals have been implicated in C-C and C-H bond forming reactions and also identified as key intermediates in cobalt-catalysed asymmetric alkene cyclopropanation.[7]

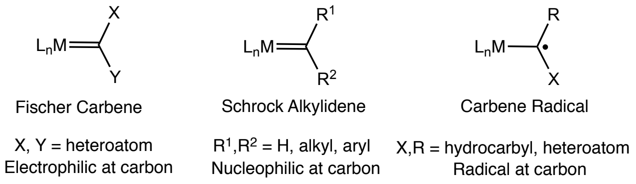


Figure 1. Bonding formalisms in metal carbene complexes.

Continued interest in developing more sustainable catalystic methods that employ base metals[8] inspires the synthesis, characterization and determination of the electronic structure of iron carbene complexes. Early examples of these compounds were dominated by strong field ligand environments, typically piano stool derivatives with supporting phosphine and carbonyl donors.[9,10] As such, highly covalent low spin compounds were obtained and crystallographically characterized examples such as Lapinte's[11] [(η^5-C_5H_5)(dppe)Fe(=CHMe)][OTf] (dppe = 1,2-bis(diphenyl)phosphino ethane) and Guerchais'[12] [(η^5-C_5Me_5)(CO)Fe(η^2-C(OMe)C_6H_4-*o*-Cl)][OTf] exhibited relatively short Fe=C bond distances of 1.787(8) and 1.857(6) Å, respectively.

Catalytic alkene cyclopropanation activity has been observed with a family of in situ generated iron carbene complexes supported by macrocyclic, tetradentate, nitrogen-donor ligands.[13] Interest in these molecules also derives from their relationship to oxoiron poryphrin compounds.[14] Floriani and coworkers reported structural characterization of one such example, (tmtaa)$FeCPh_2$ (tmtaa = tetramethyldibenzotetrazannulene), a diamagnetic compound with a relatively short Fe-C bond distance of 1.794(3) Å.[15] The molecular geometry, magnetic data and extended Hückel calculations resulted in assignment as an Fe(II) compound with a closed-shell, Fischer type carbene ligand. Che and coworkers have subsequently synthesized and crystallographically characterized (TPFPP)$FeCPh_2$ (TPFPP – *meso*-tetrakis(pentafluorophenyl) porphyrin) and its complex with methylimadazole, both of which are diamagnetic and are active for intra- and intermolecular cyclopropanation.[16] The base-free, five coordinate compound exhibits a contracted Fe-C bond distance of 1.763(3) Å which lengthens to 1.827(5) Å upon coordination of methylimidazole. The metrical data, diamagnetism and the low Mössbauer isomer shift (δ = 0.03 mm/s) are consistent with a covalent, low spin Fe(II) compound with a closed-shell carbene ligand.

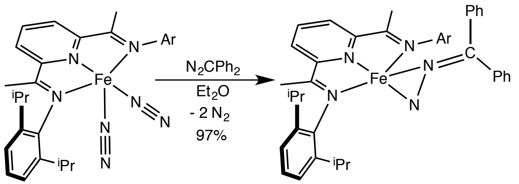
Our laboratory has been studying the chemistry of iron dinitrogen compounds bearing redox-active bis(imino)pyridine (^{R}PDI) ligands. In addition to their rich catalytic chemistry,[17] these compounds serve as convenient entry points to iron complexes with metal-ligand multiple bonds in idealized planar ligand fields. Examples include bis(imino)pyridine iron imide complexes that exhibit spin crossover behavior[18] and compounds that undergo rare examples of complete hydrogenolysis of the Fe=N bond.[19] The oxidation state of the iron and bis(imino)pyridine as well as the nature of the Fe=NR bond was influenced by the identity of the nitrogen substituent. For *N*-alkyl substituents, imidyl radicals were observed while with *N*-aryl groups more traditional $[NAr]^{2-}$ ligands were identified. The variable electronic structures highlight the redox flexibility imparted by the redox-active bis(imino)pyridine chelate.

This behaviour raised the question as to whether similar electronic structure variability and tuning was possible with related bis(imino)pyridine iron carbene complexes. The redox activity of the chelate coupled with its relatively weak ligand field (as compared to cyclopentadienyl complexes, for example) suggested that new types of iron carbenes may be accessible. To our knowledge, high spin compounds or those with carbene radicals have yet to be identified in iron chemistry. In addition to their potentially interesting electronic structures, bis(imino)pyridine iron carbene complexes are of interest to evaluate the theoretical predictions by Musaev and coworkers concerning the ability of these compounds to promote catalytic C-H functionalization chemistry.[20]

Attempts to prepare bis(imino)pyridine iron carbene complexes from monosubstituted diazoalkanes have not yielded observable $(^{R}PDI)Fe{=}C(H)R$ compounds. Treatment of $(^{iPr}PDI)Fe(N_2)_2$ (^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2$-C_6H_3-N=CMe)$_2C_5H_3N$) with $N_2CHSiMe_3$ furnished the iron diazoalkane complex, $(^{iPr}PDI)Fe(N_2CHSiMe_3)$, which undergoes quantitative loss of $SiMe_4$ to form a bis(imino)pyridine iron olefin complex arising from transfer dehydrogenation of an isopropyl aryl substituent.[21] Performing the addition with N_2CHPh resulted in N=N cleavage of the diazoalkane and furnished an equimolar mixture of the iron nitrile and imine complexes, $(^{iPr}PDI)FeNCPh$ and $(^{iPr}PDI)FeNHCHPh$, respectively.[22] In both cases, bis(imino)pyridine iron carbene complexes were invoked as intermediates but the inherent reactivity of these species prohibited observation and electronic structure determination leaving open the question as to the nature of the Fe=C(H)R bonding and the role of the bis(imino)pyridine. Here we describe the synthesis, characterization and preliminary reactivity studies of isolable bis(imino)pyridine iron carbene complexes. Determination of the electronic structure by a combination of structural, magnetic, spectroscopic and computational techniques established formation of iron-carbene radicals.

Results and Discussion

Because of the reactivity of the putative $(^{iPr}PDI)FeC(H)R$ compounds, disubstituted diazoalkanes were explored as carbene transfer agents. Addition of one equivalent of N_2CPh_2 to a diethyl ether solution of $(^{iPr}PDI)Fe(N_2)_2$ at 23 ºC resulted in effervescence of N_2 gas and furnished, following recrystallization from pentane at -35 ºC, blue-green crystals identified as the bis(imino)pyridine diazoalkane complex, $(^{iPr}PDI)Fe(N_2CPh_2)$ in 97% yield (eq 1).



(1)

$(^{iPr}PDI)Fe(N_2CPh_2)$

Both solution (method of Evans, μ_{eff} = 3.1 μB, 22 ºC) magnetic measurements and variable temperature solid-state SQUID data established an S = 1 ground state. The benzene-d_6 ^1H NMR spectrum at 22 ºC is broad, featureless and largely uninformative. A diagnostic stretch was observed at 2042 cm^{-1} in the pentane solution infrared spectrum, consistent with formation of a diazoalkane complex. Unlike $(^{iPr}PDI)Fe(N_2CHSiMe_3)$, $(^{iPr}PDI)Fe(N_2CPh_2)$ proved persistent in both the solid state and in benzene-d_6 solution at 22 ºC.

The solid-state structure of $(^{iPr}PDI)Fe(N_2CPh_2)$ was confirmed by X-ray diffraction (Figure 1). The diazoalkane ligand is side-on coordinated with an N-N bond distance of 1.280(3) Å, indicating only slight elongation from coordination to the iron. The iron atom is lifted by 0.6816(3) Å from the idealized plane of the chelate and the carbon substituents bonded to C(10) are oriented perpendicular to the plane of the ligand.

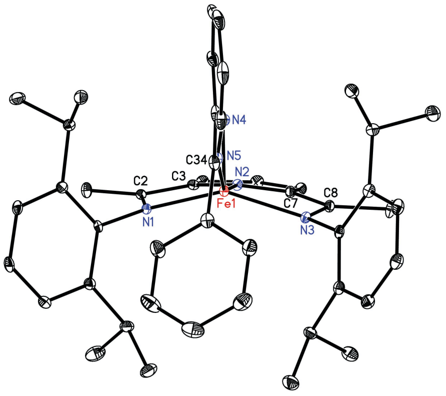
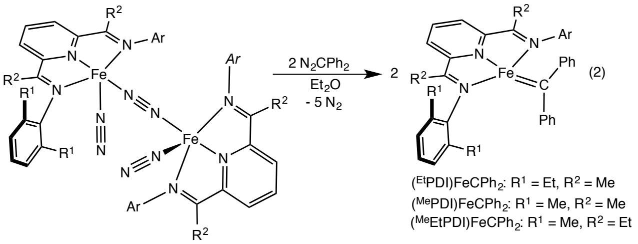


Figure 2. Representation of the solid state molecular structure of $(^{iPr}PDI)Fe(N_2CPh_2)$ at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

It is now well established that perturbations to certain bis(imino)pyridine bond distances are diagnostic of redox-activity.[23,24] In $(^{iPr}PDI)Fe(N_2CPh_2)$, the N_{imine}-C_{imine} distances are elongated to 1.324(3) and 1.315(3) Å while the C_{imine}-C_{ipso} bond lengths are contracted to 1.445(3) and 1.437(3) Å, all consistent with one electron reduction of the chelate. These data, in combination with the observed S = 1 ground state suggest a high spin Fe(I) compound (S_{Fe} = 3/2) antiferromagnetically coupled to a bis(imino)pyridine radical anion (S_{PDI} = 1/2). The relatively long Fe-N_{imine} bond distances of 2.072(2) and 2.063(2) Å are consistent with a high spin iron compound.

The electronic structure of $(^{iPr}PDI)Fe(N_2CPh_2)$ was also interrogated with zero-field ^{57}Fe Mössbauer spectroscopy and broken symmetry DFT calculations. An isomer shift and quadrupole splitting of 0.62 and 2.34 mm/s were measured at 80 K, respectively, consistent with a high spin Fe(I) compound.[17j,25] Computational studies (see SI) also support formation of a high spin iron compound with a bis(imino)pyridine radical anion and little backbonding to the side-on diazoalkane ligand.

The isolation of a diazoalkane complex instead of the desired iron carbene with $(^{iPr}PDI)Fe(N_2)_2$ is likely due to the presence of the large isopropyl aryl substituents that inhibit attack of the iron on the carbon necessary for N_2 loss. To circumvent this issue, bis(imino)pyridine iron dinitrogen complexes with smaller aryl substituents were examined. Addition of N_2CPh_2 to diethyl ether solutions of $[(^{R}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ (R = Me, Et)[17e] or $[(^{Me}EtPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ (^{Me}EtPDI = 2,6-(2,6-Me_2-C_6H_3-N=CEt)$_2C_5H_3N$) furnished green solids identified as the desired bis(imino)pyridine iron carbene complexes, $(^{R}PDI)FeCPh_2$ or $(^{Me}EtPDI)FeCPh_2$ in high isolated (95-97%) yields (eq 2).



A summary of the zero-field ^{57}Fe Mössbauer parameters and solution and solid state magnetic data for the bis(imino)pyridine iron carbene complexes is presented in Table 1. Each example exhibits an effective magnetic moment consistent with an $S = 1$ spin state, establishing isolation of rare paramagnetic iron carbene compounds. SQUID data were collected on $(^{Me}EtPDI)FeCPh_2$ and simple paramagnetic behavior that establishes an $S = 1$ ground state was observed. The benzene-d_6 ^{1}H NMR spectra recorded at 20 ºC exhibit the number of paramagnetically shifted and broadened resonances consistent with C_{2v} symmetric molecules in solution. The resonances for $(^{Et}PDI)FeCPh_2$ span 250 ppm while those for $(^{Me}PDI)FeCPh_2$ appear over a 200 ppm range. In both compounds, one phenyl resonance appears upfield at -27 ppm while the two other peaks were located downfield at 50 and 120 ppm. Importantly, the spectra are readily assigned and useful for identifying the compounds.

Table 1. ^{57}Fe Mössbauer parameters and effective magnetic moments for bis(imino)pyridine iron carbenes.

Compound	**δ (mm/s)**	**δE_Q (mm/s)**	**μ_{eff}[a]**	**μ_{eff}[b]**
$(^{Et}PDI)FeCPh_2$	0.41	1.50	3.2	3.2
	0.45[c]	*1.80*		
$(^{Me}PDI)FeCPh_2$	0.41	1.31	3.0	3.4
$(^{Me}EtPDI)FeCPh_2$	0.40	1.29	2.8	3.0
	0.45	*2.01*		

[a] Recorded in benzene-d_6 at 20 ºC. [b] Recorded in the solid state at 20 ºC. [c] Values in italics are DFT-computed values.

Two examples, $(^{Et}PDI)FeCPh_2$ and $(^{Me}EtPDI)FeCPh_2$ were characterized by X-ray diffraction. The data for the latter compound was of higher quality and will be presented in detail here. In general, iron compounds of the bis(imino)pyridine with ethylated imine backbone tend to be more crystalline. The lower quality structure for $(^{Et}PDI)FeCPh_2$ is reported in the Supporting Information but the two molecules are topologically similar. For $(^{Me}EtPDI)FeCPh_2$, two molecules were present in the asymmetric unit, a representation of one of them is presented in Figure 3. The molecular structure exhibits an overall distorted four-coordinate geometry with the iron atom lifted by 0.7056(3) Å out of the idealized chelate plane. The Fe-CPh_2 vector is also directed away from the plane of the molecule with an N(2)-Fe(1)-C(30) bond angle of 104.49(7)º. This more tetrahedral-like geometry is reminiscent of $(^{iPr}PDI^{1-})Fe^{III}NAr$ complexes.[21] In $(^{Me}EtPDI)FeCPh_2$, the carbene substituents are oriented above and below the iron-chelate plane and are slightly canted, likely to minimize interaction with the 2,6-dimethylaryl substituents.

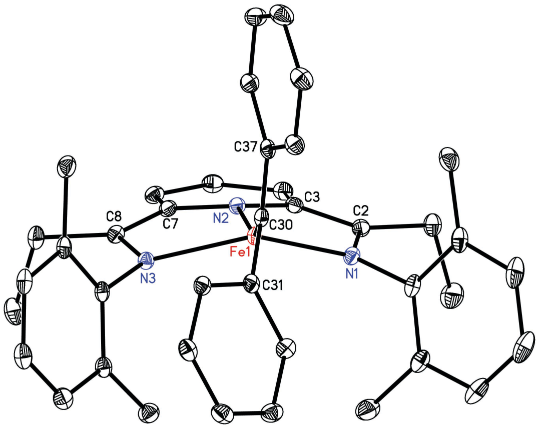


Figure 3. Representation of the solid state molecular structure of $(^{Me}EtPDI)FeCPh_2$ at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

The Fe-N_{imine} distances of 2.082(1) and 2.048(2) Å are relatively long and indicative of a high spin state at the metal. The distortions to the bis(imino)pyridine (N_{imine}-C_{imine}: 1.320(3), 1.328(3) Å; C_{imine}-C_{ipso}: 1.445(3) and 1.440(2) Å) are consistent with one electron reduction.[23,24] Notably, the Fe-C bond distance of 1.936(2) Å is significantly elongated and is only slightly shorter than the values of 2.001(6) and 2.036(4) Å reported for the iron alkyl complexes, $(^{iPr}PDI)FeCH_3$[26] and $(^{Et}PDI)FeCH_2CMe_3$, respectively.[27] This value is also significantly longer the previously structurally characterized iron carbene complexes. The notable exceptions are the iron cycloheptatrienylidene examples, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-}C_7H_6)][PF_6]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-}C_{11}H_8)][PF_6]$, reported by Jones and coworkers with reported Fe-C bond distances of 1.979(3) and 1.996(2) Å, respectively.[10] The bond angles about C(30) in $(^{Me}EtPDI)FeCPh_2$ also indicate an sp^2 hybridized carbon and no electron density attributable to a hydrogen atom was located in the difference maps supporting formulation as a carbene rather than an alkyl complex.

The electronic structure of the bis(imino)pyridine iron carbene complexes was also probed by X-ray absorption spectroscopy (XAS). Spectra highlighting both the rising and pre-edge regions of $(^{Me}PDI)FeCPh_2$ are presented in Figure 4. Also presented in Figure 3 are the spectra for $(^{iPr}PDI^{1-})Fe^{II}CH_2CMe_3$ and $(^{iPr}PDI^{1-})Fe^{III}NAr$, known high spin Fe(II) and intermediate spin Fe(III) complexes respectively. Both reference compounds are also four-coordinate and have one electron reduced bis(imino)pyridine chelates. The pre-edge energy for (^{Me}PDI)FeCPh$_2$ is 7111.8 eV, identical to the value of 7111.8 eV for (^{iPr}PDI^{1-})Fe^{II}CH$_2$CMe$_3$ and indistinguishable from the energy of 7112.0 eV reported for (^{iPr}PDI^{1-})Fe^{III}N*Ar*. Thus, this region of the spectra is largely uninformative for distinguishing the oxidation states of these compounds. By contrast, the rising edge regions of the spectra are distinct with the energy of (^{Me}PDI)FeCPh$_2$ appearing more reduced than (^{iPr}PDI^{1-})Fe^{III}N*Ar* yet less oxidized than (^{iPr}PDI^{1-})Fe^{II}CH$_2$CMe$_3$.

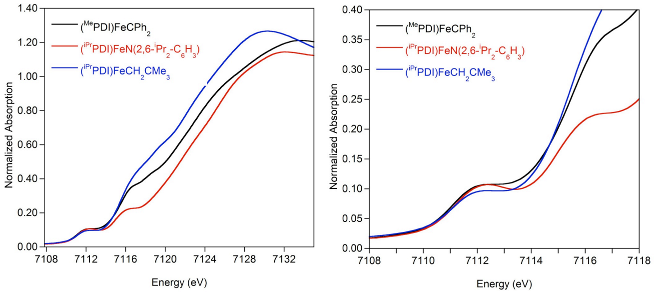


Figure 4. Normalized Fe K-edge X-ray absorption spectra of the rising edge (left) and the pre-edge (right) of (^{Me}PDI)FeCPh$_2$ at 10 K. Also included are the spectra for (^{iPr}PDI)FeN(2,6-^{i}Pr$_2$-C$_6$H$_3$)[18] and (^{iPr}PDI)FeCH$_2$CMe$_3$.

Examination of the bis(imino)pyridine iron carbene complexes by ^{57}Fe Mössbauer spectroscopy established isomer shifts between 0.40-0.41 mm/s for each example. These values are between those previously measured for high spin iron(II) alkyl complexes such as (^{iPr}PDI)FeCH$_2$CMe$_3$ (δ = 0.57 mm/s) and intermediate spin Fe(III) imido compounds such as (^{iPr}PDI^{1-})Fe^{III}N*Ar* (δ = 0.30 mm/s) and consistent with the XAS data. Isomer shifts in this range are consistent with either iron(II) or iron(III) oxidation states.

In an attempt to reconcile the ambiguities from the experimental data, full molecule, broken symmetry density functional theory calculations were carried out at the B3LYP level of theory. In broken symmetry notation, B(*m*, *n*) describes a state in which there are *m* unpaired spin-up electrons and *n* unpaired spin down electrons on separate fragments.[28] Calculations were performed on both structurally characterized bis(imino)pyridine iron carbene complexes, the results for (^{Et}PDI)FeCPh$_2$ will be presented here, the output for (^{Me}EtPDI)FeCPh$_2$ is reported in the Supporting Information. The previous computational study by Varela-Álvarez and Musaev examined the intermediacy of a bis(imino)pyridine parent carbene, (PDI)FeCH$_2$ but the overall electronic structure and oxidation state of the iron compound, bis(imino)pyridine and carbene ligand were not explicitly addressed. For (^{Et}PDI)FeCPh$_2$, a BS(4,2) solution was found to be the lowest in energy and successfully reproduced the experimental metrical parameters (see SI) and ^{57}Fe Mössbauer parameters (computed δ = 0.45, ΔE_Q = 1.80 mm/s). A BS(3,1) input also converged to the BS(4,2) solution. As illustrated in Figure 5, this solution corresponds to a high spin Fe(II) centre with the d_{xz}-d_{z^2} admixed orbital engaged in antiferromagnetic coupling (*S* = 0.45, *S* = spatial overlap of the magnetic orbitals) with the b_2 orbital of the bis(imino)pyridine chelate. A second iron orbital, essentially d_{xy} in character, is engaged in antiferromagnetic coupling (S = 0.50) with the p_y orbital of a carbene radical. Thus, the combined structural, magnetic spectroscopic and computational data support an electronic structure description whereby the observed *S* = 1 bis(imino)pyridine iron carbene is best described as a high spin ferrous compound with both chelate and carbene radical ligands. Note that *both* radicals are not free radicals but antiferromagnetically coupled to iron spins.

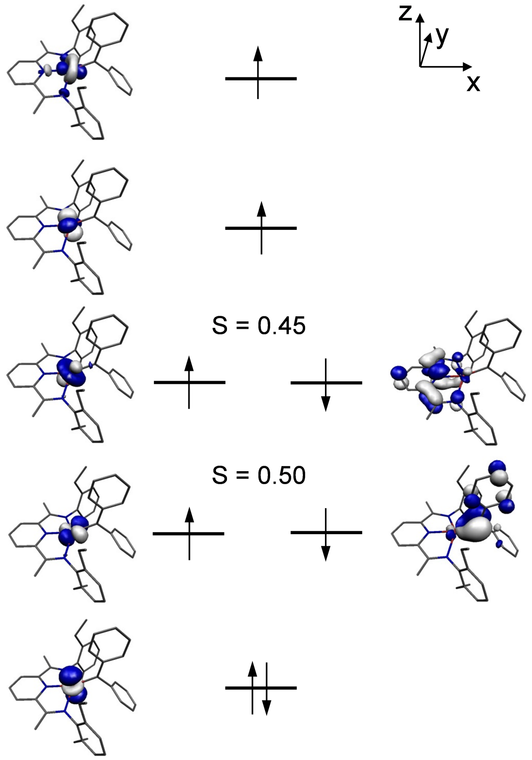


Figure 5. Qualitative molecular orbital diagram for (^{Et}PDI)FeCPh$_2$ from a geometry optimized B3LYP DFT calculation.

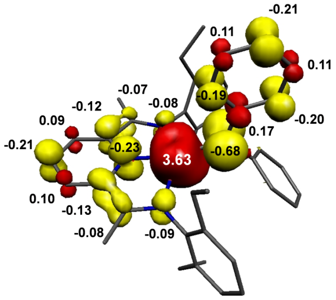
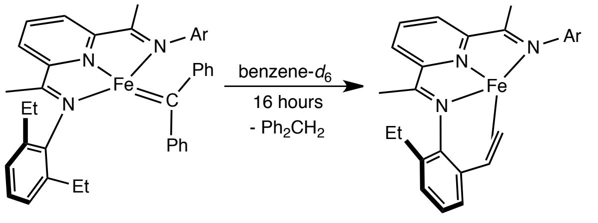


Figure 6. Spin density plot for (^{Et}PDI)FeCPh$_2$ from a Mulliken population analysis.

Time dependant DFT was used calculate XAS spectra as described previously. Calculations were based on the crystal structures of (^{Et}PDI)FeCPh$_2$ and (^{Me}EtPDI)FeCPh$_2$. (^{Me}PDI)FeCPh$_2$ was also calculated using the crystallographic data from (^{Me}EtPDI)FeCPh$_2$ as a starting point, followed by geometry optimization. The calculated spectra for all three compounds are very similar (see SI) and yielded calculated pre-edge energies of 7111.8 eV, 7118.0 eV and 7112.0 eV for

(^{Et}PDI)FeCPh$_2$, (^{Me}EtPDI)FeCPh$_2$ and (^{Me}PDI)FeCPh$_2$, respectively. These values are in excellent agreement with the experimental value of 7118.8 eV for (^{Me}PDI)FeCPh$_2$ and provide additional support the high spin iron(II) oxidation state assignment. For all three compounds, the pre-edge is dominated by transitions to the d_{yz} and $d_{x^2-y^2}$ orbitals.

The reactivity of the bis(imino)pyridine iron carbene complexes was examined. When stored under an inert atmosphere, (^{Me}PDI)FeCPh$_2$ is stable for weeks at 22 ºC in benzene-*d*$_6$ solution. Under the same conditions, (^{Et}PDI)FeCPh$_2$ quantitatively liberates Ph$_2$CH$_2$ over the course of 16 hours with concomitant formation of an NMR silent bis(imino)pyridine iron compound, identified as the intramolecular iron olefin compound based on degradation experiments (eq 3). The observed products likely arise from a transfer hydrogenation sequence similar to that proposed for the putative bis(imino)pyridine iron carbene, (^{iPr}PDI)Fe=CHSiMe$_3$.[21] Support for this hypothesis derives from the stability of (^{Me}PDI)FeCPh$_2$ where the absence of β-hydrogens on the 2,6-aryl substituents prohibits transfer dehydrogenation.



(3)

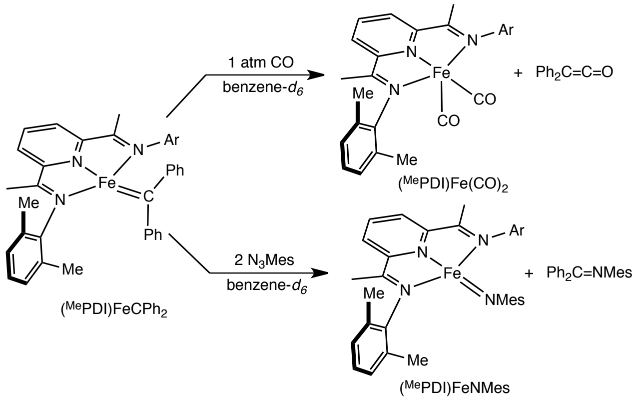
(^{Et}PDI)FeCPh$_2$

Subsequent reactivity studies focused on transfer of the iron-carbene fragment. In most cases, these experiments were conducted with (^{Me}PDI)FeCPh$_2$ in order to circumvent complications associated with the instability of (^{Et}PDI)FeCPh$_2$. Exposure of a benzene-*d*$_6$ solution of (^{Me}PDI)FeCPh$_2$ to a dihydrogen atmosphere rapidly liberated Ph$_2$CH$_2$, similar to the hydrogenolysis reactivity of the bis(imino)pyridine iron compounds with aryl imide ligands.[19] Repeating the procedure with D$_2$ gas furnished Ph$_2$CD$_2$. In both experiments, a brown, NMR silent iron compound was obtained, similar to the material obtained from addition of H$_2$ to [(^{Me}PDI)Fe(N$_2$)]$_2$(μ$_2$-N$_2$).[17e] This compound, likely an iron hydride or dihydrogen complex, has proven challenging to characterize.

Attempts to use (^{Me}PDI)FeCPh$_2$ for olefin metathesis, cyclopropanation and C-H abstraction have been unsuccessful. Stirring a benzene-*d*$_6$ solution with excess (~ 10 equiv) of styrene, norbornene, diethyl diallyl malonate, 1,4-cyclohexadiene, 9,10-dihydroanthracene, methyl methacrylate or ethylene produced no reaction after 24 hours at 22 ºC. Heating these mixtures to 85 ºC resulted in decomposition of the iron compound. Olefination of carbonyl compounds was also probed by the addition of benzaldehyde, acetone and acetophenone to a benzene-*d*$_6$ solution of (^{Me}PDI)FeCPh$_2$. In all three cases, no reaction was observed after 24 hours demonstrating no Schrock-like, alkylidene character in the compound, consistent with a high spin iron(II) formulation.

Carbene group transfer was also explored with carbon monoxide and aryl azides (Scheme 1). Mindiola and Hillhouse have reported carbonylation of (dtbpe)NiCPh$_2$ (dtbpe = di-*tert*-butylphosphino ethane) furnished the nickel dicarbonyl complex and diphenylketene.[30] Addition of 1 atm of CO to a benzene-*d*$_6$ solution of (^{Me}PDI)FeCPh$_2$ resulted in rapid carbene transfer and cleanly and quantitatively yielded (^{Me}PDI)Fe(CO)$_2$ and Ph$_2$CCO. The organic product was identified based on comparison of ^{1}H NMR and IR spectra to an authentic sample. Carbene transfer was also observed upon treatment with an organic azide.[31,32] Stirring a diethyl ether solution of (^{Me}PDI)FeCPh$_2$ with two equivalents of N$_3$Mes (Mes = 1,3,5-Me$_3$-C$_6$H$_2$) furnished a deep blue iron product identified as (^{Me}PDI)FeNMes. The free ketimine, Ph$_2$C=NMes was also detected by ^{1}H NMR and IR spectroscopy.

Scheme 1.



Conclusions

The synthesis and isolation of a series of bis(imino)pyridine iron carbene complexes has been achieved by addition of the disusbtituted diazoalkane, N$_2$CPh to the corresponding iron dinitrogen compounds. Selection of the appropriate aryl substituents is critical to the success of the reaction as addition of N$_2$CPh$_2$ to the more sterically protected iron compound, (^{iPr}PDI)Fe(N$_2$)$_2$ produced an iron(I) complex with a side-on bound diazoalkane ligand. Each of the (^{R}PDI)FeCPh$_2$ derivatives has an *S* = 1 ground state, representing rare examples of open shell iron carbene complexes in a weak ligand field. Further investigation into the electron structure of these compounds by a combination of X-ray diffraction, X-ray absorption, ^{57}Fe Mössbauer and computational techniques, established high spin iron(II) compounds engaged in antiferromagnetic coupling with a redox-active bis(imino)pyridine radical anion and a carbene radical. The reactivity of this unique structural type was examined and intramolecular C-H activation chemistry, Fe-CPh$_2$ hydrogenolysis and carbene transfer to nitrenes and carbon monoxide was observed. Importantly, this electronic structure description must be considered when developing synthetic cycles or developing mechanistic proposals involving iron carbenes.

Acknowledgements.

We thank the U.S. National Science Foundation and the Deutsche Forschungsgemeinschaft for a Cooperative Activities in Chemistry between U. S. and German investigators grant (CHE-1026084). S. P. S thanks the National Science and Engineering Research Council of Canada for a predoctoral fellowship (PGS-

D) and S. C. E. S. thanks the U. S. National Science Foundation for a graduate fellowship (DGE-0646086). We also thank the Air Force Office of Scientific Research (FA9550-11-1-0252), Dr. Emil Lobkovsky (Cornell) for preliminary structural characterization and Prof. Karsten Meyer (Erlangen) for assistance with SQUID measurements. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the DOE, BES. The SSRL SMB Program is supported by DOE, BER and NIH, NCRR, BMTP. Some of the simulations presented in this article were performed on computational resources supported by the Princeton Institute for Computational Science and Engineering (PICSciE) and the Office of Information Technology's High Performance Computing Center and Visualization Laboratory at Princeton University.

Notes and references

[a] *Department of Chemistry, Princeton University, Princeton, NJ 08544 United States. Fax: 609 258 6746; Tel: 609 258 4130; E-mail: pchirik@princeton.edu*
[b] *Department of Chemistry and Chemical Biology, Cornell University Ithaca, NY 14853 United States.*
[c] *Max-Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36. D-45470 Mülheim an der Ruhr, Germany. E-mail: serena.debeer@cec.mpg.de*

† Electronic Supplementary Information (ESI) available: Complete experimental procedures, characterization data for all new compounds and computational results. Crystallographic data: CCDC 957144, 957115 and 957116. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

1. (a) R. R. Schrock, *Acc. Chem. Res.* 1979, **12**, 98. (b) G. Frenking, N. Frohlich, *Chem. Rev.* 2000, **100**, 717. (c) D. J. Mindiola, *Acc. Chem. Res.* 2006, **39**, 813. (d) P. de Fremont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* 2009, **253**, 862.
2. (a) W. Kirmse, *Angew. Chem. Int. Ed. Engl.* 2003, **42**, 1088. (b) H. M. L. Davies, S. J. Hedley, *Chem. Soc. Rev.* 2007, **36**, 1109. (c) M. P. Doyle, *Angew. Chem. Int. Ed.* 2009, **48**, 850.
3. (a) C. B. Pamplin, P. Legzdins, *Acc. Chem. Res.* 2003, **36**, 223. (b) L. Ackerman, *Chem. Rev.* 2011, *111*, 1314. (c) H. M. L. Davies, J. Du Bois, J. –Q. Yu, *Chem. Soc. Rev.* 2011, **40**, 1855. (d) S. –T. Zhang, F. –M. Zhang, Y. –Q. Tu, *Chem. Soc. Rev.* 2011, **40**, 1937. (e) J. Yamaguchi, A. D. Yamaguchi, K. Itami *Angew. Chem. Int. Ed.* 2012, **51**, 8960.
4. a) R. R. Schrock, *Angew. Chem. Int. Ed.* 2006, **45**, 3748. b) R. H. Grubbs, *Angew. Chem. Int. Ed.* 2006, **45**, 3760.
5. J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd Ed. University Science, 1987.
6. W. I. Dzik, X. P. Zheng, B. de Bruin, *Inorg. Chem.* 2011, **50**, 9896.
7. (a) W. I. Dzik, X. Xu, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc* 2010, **132**, 10891. (b) H. J. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin, *J. Am. Chem. Soc.* 2011, **133**, 8518.
8. M. S. Holzwarth, I. Alt, B. Plietker, *Angew. Chem. Int. Ed.* 2012, **51**, 5351.
9. (a) P. W. Jolly, R. Pettit, *J. Am. Chem. Soc.* 1966, **88**, 5044. (b) M. Brookhart, W. B. Studabaker, M. B. Humphrey, *Organometallics* 1989, **8**, 132. (c) V. Guerchais, C. Lapinte, *J. Chem. Soc., Chem. Commun.* 1986, 663. (d) C. P. Casey, W. H. Miles, H. Tukada, J. M. O'Conner, *J. Am. Chem. Soc.* 1982, **104**, 1203. (d) M. Brookhart, J. R. Tucker, T. C. Flood, J. Jensen, *J. Am. Chem. Soc.* 1980, **102**, 1203. (e) M. Brookhart, G. O. Nelson, *J. Am. Chem. Soc.*1977, **99**, 6099.
10. (a) N. T. Allison, Y. Kawada, W. M. Jones, *J. Am. Chem. Soc.* 1978, **100**, 5224. (b) P. E. Riley, R. E. Davies, N. T. Allison, W. M. Jones, *Inorg. Chem.* 1982, **21**, 1321.
11. V. Mahias, S. Cron, L. Toupet, C. Lapinte, *Organometallics* 1996, **15**, 5399.
12. G. Poignant, S. Nlate, V. Geurchais *Organometallics* 1997, **16**, 124.
13. (a) J. R. Wolf, C. G. Hamaker, J. –P. Djukic, T. Kodadek, L. K. Woo, *J. Am. Chem. Soc.* 1995, **117**, 9194. (b) G. C. Hamaker, G. A. Mirafzal, L. K. Woo, *Organometallics* 2001, **20**, 5171. (c) G. Du, B. Andrioletti, E. Rose, L. K. Woo *Organometallics* 2002, **21**, 4490. (d) G. Cheng, G. A. Mirafzal, L. K. Woo, *Organometallics* 2003, **22**, 1468. (e) L. K. Baumann, H. M. Mbuvi, G. Du, L. K. Woo *Organometallics* 2007, *26*, 3995. (f) H. M. Mbuvi, L. K. Woo, *Organometallics* 2008, **27**, 637.
14. (a) D. Mansuy, M. Lange, J-C. Chottard, P. Guerin, P. Morliere, D. Brault, M. Rougee, *J. Chem. Soc., Chem. Commun.* 1977, 648. (b) J. T. Groves, G. E. Avaria-Neisser, K. M. Fish, M. Imachi, R. L. Kuczkowski, *J. Am. Chem. Soc.* 1986, **108**, 3837.
15. A. Klose, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, *Chem. Commun.* 1997, 2297.
16. Y. Li, J.-S. Huang, Z. –Y. Zhou, C. M. Che, X.-Z. You, *J. Am. Chem. Soc.* **2002**, *124*, 13185.
17. (a) S.C. Bart, E. Lobkovsky, *J. Am. Chem. Soc.* 2004, **126**, 13794. (b) M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* 2006, **128**, 13340. (c) A. M. Archer, M. W. Bouwkamp, M. –P. Cortez, E. Lobkovsky, P. J. Chirik, *Organometallics* 2006, **25**, 4269. (d) R. J. Trovitch, E. Lobovsky, E. Bill, P. J. Chirik, *Organometallics* 2008, **27**, 1470. (e) S. K. Russell, J. M. Darmon, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* 2010, **49**, 2782. (f) K. T. Sylvester, P. J. Chirik, *J. Am. Chem. Soc.* 2009, **131**, 8772. (g) Yu, R. P.; J. M. Darmon, J. M. Hoyt, G. W. Margulieux, Z. R. Turner, P. J. Chirik, *ACS Catalysis* 2012, **2**, 1760. (h) Atienza, C. C. H.; A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P. J. Chirik, *ACS Catalysis* 2012, **2**, 2169. (i) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* 2012, **335**, 567. (j) J. M. Hoyt, K. T. Sylvester, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* 2013, **135**, 4862. (k) J. V. Obligacion, P. J. Chirik, *Org. Lett.* 2013, **15**, 2680.
18. A. C. Bowman, C. Milsmann, E. Bill, Z. R. Turner, E. Lobkovsky, S. DeBeer, K. Wieghardt, P. Chirik, *J. Am. Chem. Soc.* 2011, **133**, 17353.
19. S. C. Bart, E. Lobkovsky, E. Bill, P. J. Chirik, *J. Am. Chem. Soc.* 2006, **128**, 5302.
20. A. Varela-Álvarez, D. G. Musaev, *Chem. Sci.* 2013, **4**, 3758.
21. S. C. Bart, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* 2007, **129**, 7212.
22. S. K. Russell, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* 2009, **131**, 36.
23. S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Weighardt, *J. Am. Chem. Soc.* 2006, **128**, 13901.
24. Q. Knijnenburg, S. Gambarotta, P. H. M. Budzelaar, *Dalton Trans.* 2006, 5442.
25. P. Gütlich, E. Bill, A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry, Fundamentals and Applications*, Springer, Heidelberg, 2011.
26. M. W. Bouwkamp, S. C. Bart, E. J. Hawrelak, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* 2005, 3406.
27. I. Fernández, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Organometallics* 2008, **27**, 109.
28. L. Noodleman, C. Y. Peng, D. A. Case, J. M. Mouesca, *Coord. Chem. Rev.* 1995, **144**, 199.
29. S. C. E. Stieber, C. Milsmann, J. M. Hoyt, Z. R. Turner, K. D. Finkelstein, K. Weighardt, S. DeBeer, P. J. Chirik, *Inorg. Chem.* **2012**, *51*, 3770.
30. D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* 2002, **124**, 9976.
31. N. D. Harrold, R. Waterman, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2009**, *131*, 12872.
32. C. A. Laskowski, G. L. Hillhouse *Chem. Sci.*, **2011**, *2*, 321