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Synthesis and Hydrogenation of Bis(imino)pyridine Iron Imides

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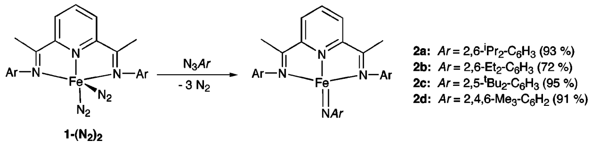
Spectroscopically well-characterized or isolable complexes containing iron−nitrogen multiple bonds are of interest given their role in enzymatic transformations and potential to mediate atom- and group-transfer processes.[1] Iron amides (Fe−NR_2),[2] imides (Fe═NR), and nitrides (Fe≡N)[3] have special relevance given their potential intermediacy in nitrogen fixation schemes.[4] While rare, terminal iron imides in mixed-valent, 3Fe(III), Fe(IV) cubane structures,[5] monomeric Fe(III) compounds,[6] and a diamagnetic, four-coordinate anion[7] are known. Addition of H_2 to the tris(phosphino)borate iron(III) imido yields a ferrous iron amido, Fe-NHR.[8] Heterolytic dihydrogen activation to form diiron imide hydride products has also been observed from a related bridging nitride.[9] More recently, Borovik has reported the synthesis of iron amido compounds from H-atom abstraction reactions involving putative iron(IV) imido compounds.[10] In this communication, we describe the synthesis, structural elucidation, and spectral features of bis(imino)pyridine iron imides and their reactivity toward CO and H_2. These compounds have been identified as key intermediates in the catalytic hydrogenation of aryl azides to the corresponding anilines.[11]

The bis(imino)pyridine iron bis(dinitrogen) complex, (^{iPr}PDI)Fe$(N_2)_2$ (**1-(N$_2$)$_2$**; ^{iPr}PDI = (2,6-^{i}Pr$_2$C$_6$H$_3$N═CMe)$_2$C$_5$H$_3$N) contains one labile N_2 ligand, which readily dissociates in solution at ambient temperature.[12] Inspired by this observation, we reasoned that N_2 displacement may serve as an effective strategy for the synthesis of iron−nitrogen multiple bonds. Treatment of **1-(N$_2$)$_2$** with a stoichiometric quantity of a series of aryl azides induced loss of 3 equiv of N_2, affording the deep-blue or purple iron imides, **2a**−**2d**, in excellent yields (eq 1).



(1)

The ^{1}H NMR spectra of **2b** and **2d** exhibit the number of peaks expected for C_{2v} symmetric molecules over a 400 ppm chemical shift range. For **2a**, only four broadened resonances are observed at 23 °C; cooling the sample in toluene-d_8 to −80 °C resulted in observation of additional peaks. The benzene-d_6 ^{1}H NMR spectrum of **2c** displays the number of peaks for a C_s symmetric compound, a result of the asymmetry imparted by the imido aryl substituents. The electronic structure of **2a** was further interrogated by SQUID magnetometry and Mössbauer spectroscopy (Figure 1). The magnetic moment of 2.8 μ_B from 20 to 300 K clearly establishes an $S = 1$ ground state with $D = -8.7(5)$ cm^{-1}. The zero-field Mössbauer parameters (δ = 0.302 mm/s; ΔE = 1.083 mm/s, 80 K) are consistent with *either* an intermediate spin ferrous or ferric ion.[13]

Two of the bis(imino)pyridine iron imides have been further characterized by X-ray diffraction (Figure 2, Table 1). In both cases, the molecular geometry is significantly deviated from planarity with the Fe═N*Ar* linkage being the most severely distorted. This is most pronounced in **2a**, where a contracted N(2)−Fe(1)−N(4) bond angle of 138.79(7)° is observed, compared to the more open value of 154.75(7)° found in **2d**. The distortion from planarity[14,15] is similar to that observed in Ru(0) and Ru(II) carbonyl complexes[16] and is likely a result of alleviation of σ^* character in d_{z^2} arising from interaction of the taurus with an sp hybrid of the imido nitrogen. Reduction of a four-electron repulsion between d_{xy} and N p_x and steric effects also contribute to the distortion.

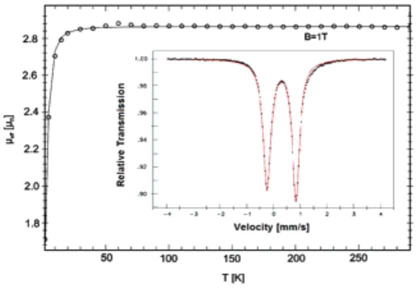


Figure 1. Variable-temperature SQUID magnetic data and zero-field Mössbauer spectrum (inset) of **2a** at 80 K.

Table 1. Selected Bond Lengths (Å) and Angles (deg)

	2a	2d	(^{iPr}PDI)FeCl$_2$
Fe(1)−N(4)	1.7048(16)	1.7165(15)	
Fe(1)−N(2)	1.8403(15)	1.8718(14)	2.091(4)
Fe(1)−N(1)	2.0343(16)	2.0105(14)	2.222(4)
N(1)−C(2)	1.320(2)	1.321(2)	1.301(7)
C(2)−C(3)	1.437(3)	1.436(2)	1.482(8)
N(4)−C(10)	1.346(2)	1.348(2)	
N(2)−C(3)	1.377(3)	1.373(2)	2.091(4)
Fe(1)−N(4)−C(10)	165.68(15)	159.00(13)	
N(1)−Fe(1)−N(3)	149.86(6)	152.37(6)	140.23(16)
N(2)−Fe(1)−N(4)	138.79(7)	154.75(7)	147.90(13)
Fe(dev) N(1),N(2),N(3) plane	0.4456	0.3386	0.5585

The Fe(1)−N(4) bond distances of 1.7048(16) and 1.7165(15) Å are elongated relative to the values of 1.651(3) and 1.6578(2) Å found in Peters' tris(phosphino)borate iron(II) and (III) imides, respectively.[7] The metrical parameters of the bis(imino)pyridine chelate in **2a** and **2d** indicate one-electron ligand reduction.[17] The C(2)−C(3), Fe(1)−N(1), and Fe(1)−N(2) bond distances are contracted with respect to (^{iPr}PDI)FeCl$_2$,[18] where the terdentate chelate is clearly a neutral, L$_3$-donor.[17] Accordingly, the N(1)−C(2) distances are slightly elongated. To account for the overall $S = 1$ magnetic ground state, the solid state and Mössbauer data are most consistent with an intermediate spin iron(III) center ($S = {}^3/_2$), antiferromagnetically coupled to a PDI-ligand centered radical ($S = -{}^1/_2$). The small, negative zero field splitting determined from the SQUID experiment also supports a ferric rather than ferrous ion. DFT calculations are in progress to support this view of the electronic structure.

The reactivity of the four-coordinate iron imides has also been evaluated. Addition of 1 atm of CO to **2a**−**2d** induced facile nitrene group transfer, forming the aryl isocyanate, *Ar*NCO, and the iron

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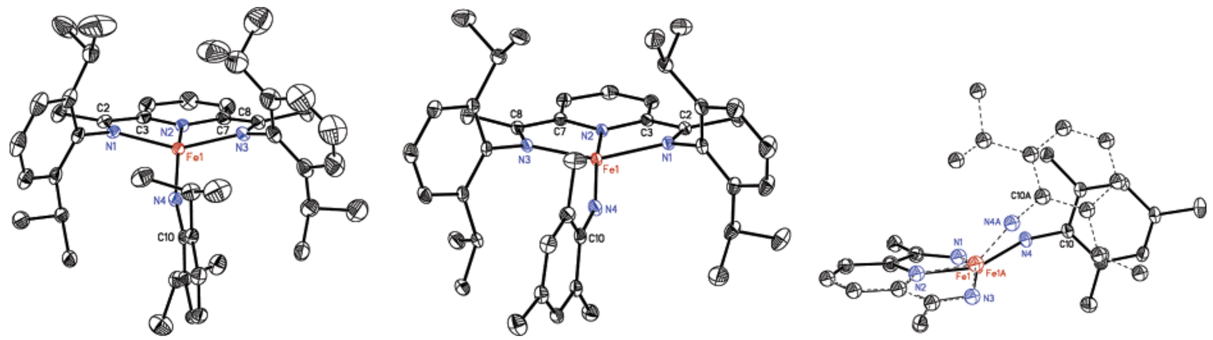
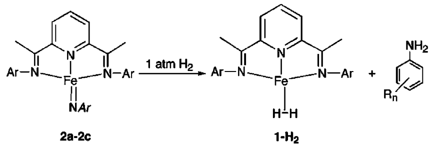


Figure 2. Molecular structure of **2a** (left) and **2d** (middle) at 30% probability ellipsoids. Overlay (right) of the cores of **2a** (dashed) and **2d** (solid).

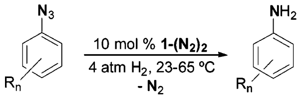
dicarbonyl complex, **1-(CO)$_2$**.[12] Similar observations have been reported for other ferric,[7] cobalt,[19] and nickel imides.[20] In more unique chemistry, exposure of benzene-d_6 solutions of **2a**−**2c** to 1 atm of H_2 at 23 °C resulted in hydrogenation of the Fe═N*Ar* linkage to yield the iron dihydrogen complex, **1-H$_2$**, along with free aniline (eq 2).



(2)

Because **1-H$_2$** rapidly converts to **1-(N$_2$)$_2$** upon exposure to N_2, **1-(N$_2$)$_2$** seemed an ideal candidate for the catalytic hydrogenation of aryl azides to the corresponding anilines. To further explore this possibility, addition of each of the anilines to **1-(N$_2$)$_2$** under either N_2 or vacuum at 23 °C produced no reaction, demonstrating that product inhibition would not be a limitation for catalytic turnover.

Gratifyingly, hydrogenation of the series of aryl azides used to prepare **2a**−**2c** at 23 °C and 1 atm of H_2 in the presence of 10 mol % (unoptimized) of **1-(N$_2$)$_2$** yielded the desired anilines in quantitative yield (eq 3). Notably, the relative rates of catalytic hydrogenation increased as the size of the aryl azide substituents closest to the iron increased. Thus, 2,6-^{i}Pr$_2$-$C_6H_3N_3$ was the fastest in the series, reaching completion in 6 h at 23 °C, while 2,6-Et_2-$C_6H_3N_3$ was the slowest, hydrogenating over the course of 96 h at 65 °C. 2,5-^{t}Bu$_2$-$C_6H_3N_3$ proceeded at an intermediate rate, requiring 16 h for complete conversion at 65 °C. No catalytic hydrogenation of 2,4,6-Me_3-$C_6H_2N_3$ was observed, even upon heating to 65 °C for 24 h.



(3)

R_n: 2,6-^{i}Pr$_2$ > 2,5-^{t}Bu$_2$ > 2,6-Et$_2$ >>> 2,4,6-Me$_3$

To gain additional insight into the course of the catalytic aryl azide hydrogenation, deuteration studies were performed. Treatment of **2a**−**2c** with 1 atm of D_2 gas afforded the *N*-deuterated aniline, *Ar*ND$_2$, and the iron dideuterium complex, **1-D$_2$**. Analysis of the product mixture by ^{2}H NMR spectroscopy revealed isotopic incorporation into the isopropyl aryl methyl groups in the terdentate ligand and the aniline, arising from methyl group cyclometalation. Competition experiments (H_2 vs D_2) with **2a** at 65 °C established a normal, primary kinetic isotope effect of 1.7(2) for hydrogenation (deuteration).

Based on these findings, the mechanism for catalytic aryl azide hydrogenation most likely involves 1,2-addition of H_2 across the iron−nitrogen bond ultimately resulting in reductive elimination of aniline. The lack of catalytic turnover with the smallest aryl azide, 2,4,6-Me_3-$C_6H_2N_3$, suggests N−H reductive coupling as the rate-determining step[21] although additional kinetic and mechanistic experiments must be performed to support this conclusion. The combined synthetic, spectroscopic, and structural studies described here once again highlight the “redox non-innocence”[17] of the bis(imino)pyridine ligand and its importance in stabilizing catalytically active iron centers.[12]

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Supporting Information Available: Experimental procedures and crystallographic data for **2a** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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