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N−N Bond Cleavage in Diazoalkanes by a Bis(imino)pyridine Iron Complex

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The reactivity of diazoalkanes with first row transition metals is of long-standing interest due to the utility of carbene transfer in organic synthesis[1] and the intermediacy of M=CR_2 species in olefin metathesis.[2] Diazoalkanes have also been used as mimics of dinitrogen to understand N_2 coordination and functionalization.[3] Motivated by the economic and environmental advantages of finding base metal alternatives to established precious metal catalysts[4] coupled with the role of iron in nitrogen-fixing bacteria,[5] the coordination chemistry of diazoalkanes with reduced iron complexes is of fundamental and potentially practical interest.

The diazoalkane chemistry of iron has been dominated by porphyrin and related macrocyclic complexes and catalytic cyclopropanation methods have been developed.[6] Our laboratory has recently reported the unusual chemistry of the bis(imino)pyridine iron diazoalkane complex, (^{iPr}PDI)$FeN_2CHSiMe_3$ (**1-N_2CHSiMe$_3$**; ^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2$−C_6H_3N=CMe_2)$_2C_5H_3N$), which undergoes hydrogenative N−N and N−C bond cleavage to yield the corresponding iron ammonia complex, **1-NH_3**, and $SiMe_4$.[7] Inspired by these observations, we sought to explore the scope of bis(imino)pyridine diazoalkane chemistry. Here we describe a rare example of the cleavage of the N−N bond in a series of monosubstituted diazoalkanes that occurs in the absence of H_2 under mild conditions in solution.

Addition of one equivalent of N_2CHPh to a benzene-d_6 solution of the bis(imino)pyridine iron dinitrogen complex, **1-(N_2)$_2$**, resulted in immediate and quantitative conversion to two new iron products. A combination of ^{1}H NMR, ^{13}C NMR, infrared spectroscopy and combustion analysis identified these compounds as the iron benzonitrile and benzaldimine compounds, **1-NCPh** and **1-NHCHPh**, respectively, arising from N−N bond cleavage of the diazoalkane (Figure 1).

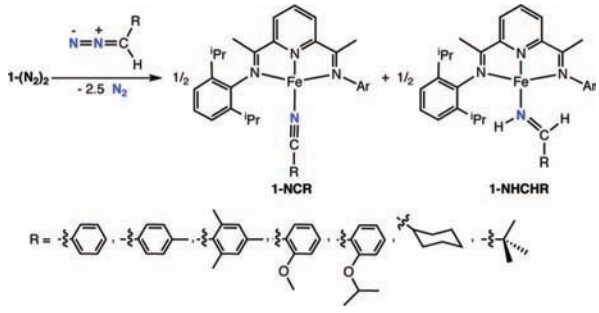

Figure 1. Scope of diazoalkane N−N bond cleavage with **1-(N_2)$_2$**.

Both **1-NCPh** and **1-NHCHPh** exhibit ^{1}H NMR spectroscopic features consistent with temperature independent paramagnetism.[8] For example, the imine methyl groups are shifted upfield to −0.12 and −2.82 ppm in benzene-d_6 and the *m*-pyridine downfield to 11.32 and 11.16 ppm for the nitrile and imine complexes, respectively. These peaks do not shift dramatically upon cooling or warming. **1-NHCHPh** was independently synthesized from addition of 1 atm of H_2 to isolated **1-NCPh**, a rare example of iron-promoted nitrile hydrogenation.[9] Confirmation of the N−H and C−H peak assignments was accomplished by a ^{1}H, ^{13}C HSQC NMR experiment and isotopic labeling with D_2 gas. Continued hydrogenation of **1-NHCHPh** for one week at 23 °C in benzene-d_6 yielded the iron amine complex, **1-NH_2CH_2Ph**.

Green **1-NHCHPh** exhibits signature doublets centered at 3.74 and 17.95 ppm ($^3J_{H-H}$ = 21.6 Hz) for the C−H and N−H of the coordinated imine. Characterization by X-ray diffraction (Figure 2) revealed chelate distortions consistent with two electron reduction.[8] The X-ray data was of sufficient quality such that all of the hydrogens were located in the difference map and established formation of a square planar iron complex with the *trans* isomer of the imine, consistent with the large ^3J coupling constants observed by solution ^{1}H NMR spectroscopy.

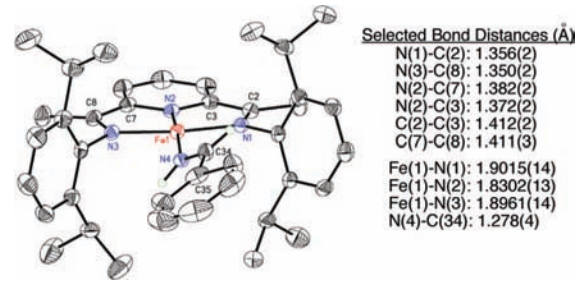

Figure 2. Molecular structure of **1-NHCHPh** at 30% probability ellipsoids. Hydrogen atoms, except those on the imine, omitted for clarity.

The scope of the N−N bond cleavage reaction was assayed with a series of monosubstituted diazoalkanes. In each case, rapid and quantitative conversion to the corresponding bis(imino)pyridine iron nitrile and imine complexes was observed (Figure 1). All of the bis(imino)pyridine iron imine complexes exhibit ^{1}H NMR doublets diagnostic for the NH and CH peaks, similar to those observed for **1-NHCHPh** (see Supporting Information). One notable case is the reaction of **1-(N_2)$_2$** with N_2CH^tBu. In addition to the expected **1-NC^{t}Bu** and **1-NHCH^{t}Bu** compounds, a third product, identified as the iron diazoalkane complex, **1-N_2CH^{t}Bu**, was observed in approximately 60% yield. Importantly, **1-N_2CH^{t}Bu** does not convert to **1-NC^{t}Bu** and **1-NHCH^{t}Bu** over time or upon addition of excess diazoalkane, thereby ruling out its intermediacy on the N−N bond cleavage pathway.

A series of experiments was conducted to gain additional insights into the mechanism of iron-promoted N−N bond cleavage. Addition of 0.5 equiv. of benzalazine, Ph(H)C=N−N=C(H)Ph, to a benzene-d_6 solution of **1-(N_2)$_2$** resulted in immediate formation of **1-NCPh** and **1-NHCHPh**. While symmetric azine cleavage to form two M−N=CR_2 species is well-documented,[10,11] so-called "non-symmetrical" N−N bond breaking to yield metal nitrile and imine complexes remains rare. A seminal example was reported by Milstein and co-workers whereby a pincer-ligated rhodium(I) dinitrogen species cleaves benzalazine to yield the corresponding benzonitrile and imine complexes.[12] In toluene solution at room

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temperature, the latter complex decomposed to unidentified products. No such decomposition was observed for any of the iron imine complexes described in this work.

Performing the reaction of **1-(N_2)$_2$** with 10 equiv. of N_2CHPh yielded the expected cleavage products, **1-NCPh** and **1-NHCHPh**, along with benzalazine, establishing catalytic conversion of diazoalkane to azine. Treatment of this mixture with additional diazoalkane produced more azine, demonstrating the catalytic competency of the products. A crossover experiment was conducted whereby 5 equivalents of each of N_2CHPh and N_2CHTol were added to **1-(N_2)$_2$**. In addition to the four expected iron products, a statistical mixture of the three possible azines was detected by GC-MS and ^{1}H NMR spectroscopy (see Supporting Information).

Finally, an isotopic labeling experiment was conducted. Addition of N_2CDPh to **1-(N_2)$_2$** yielded **1-NCPh** and **1-NDCDPh** with no evidence for isotopic incorporation into the bis(imino)pyridine chelate of either product. Monitoring the reaction by ^{1}H and ^{2}H NMR spectroscopy at 23 °C over the course of minutes allowed observation of a diamagnetic, C_s symmetric intermediate ($t_{1/2} \approx$ 15 min) with a ^{2}H NMR resonance centered at 5.20 ppm in benzene. This species was not detected when the reaction was performed with natural abundance N_2CHPh. Importantly, this compound is indeed an intermediate as it cleanly converts (confirmed by integration versus an internal standard) to **1-NCPh** and **1-NDCDPh** over the course of minutes. Based on these limited data, this intermediate is either the iron alkylidene, **[1=CHPh]**, or the metallacycle, **2**. Because of the isotopic sensitivity and observed diamagnetism, we tentatively favor **2**. In either case, the observation of an intermediate upon isotopic labeling but not with the natural abundance diazoalkane establishes a C−H(D) bond breaking event as the rate determining step during N−N bond cleavage.

A proposed mechanism for N−N bond cleavage in monosubstituted diazoalkanes is presented in Figure 3 using N_2CHPh as a representative substrate. The sequence begins with formation of a putative iron alkylidene complex, **[1=CHPh]**, arising from nucleophilic attack of **1-(N_2)$_2$** on the diazoalkane carbon. Collecting the gas generated during N−N bond cleavage with a Toepler pump provided 97% of the expected N_2 gas (in addition to that arising from **1-(N_2)$_2$**) consistent with this pathway. [4π + 2π] cycloaddition of an additional equivalent of diazoalkane with transient **[1=CHPh]** generates the iron azine complex, **2**[13] which was observed for the deuterated isotopologue. Rate-determining 1,3-hydrogen migration followed by retrocyclization, nitrile and imine linkage isomerization and capture by additional free bis(imino)pyridine iron complexes, either in the form of **1-(N_2)$_2$** or **2**, yields the observed products.

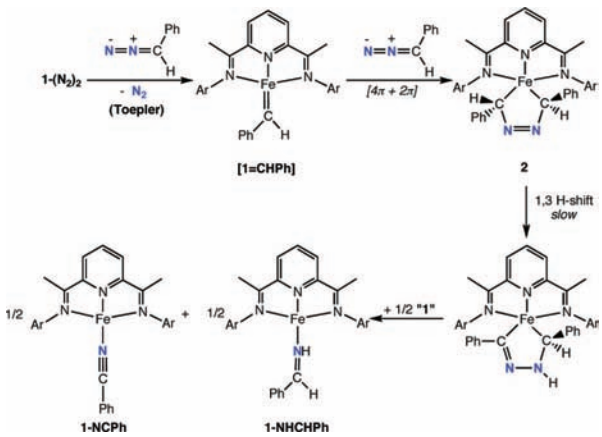

Figure 3. Proposed mechanism for N−N bond cleavage in diazoalkanes promoted by **1-(N_2)$_2$**.

Because **[1=CHPh]** was proposed as an intermediate, several attempts were made to observe or trap it. Slow or inverse addition of diazoalkane to **1-(N_2)$_2$** resulted in rapid N−N cleavage with no evidence for any intermediates. Performing the reaction under dilute conditions or at low temperature also had no effect. Likewise, addition of N_2CHPh in the presence of norbornene, isoprene, styrene, acetophenone, pyridine, or 4 atm of H_2 also produced no change in the product distribution. Attempts were also made to trap a bis(imino)pyridine iron alkylidene by intramolecular Lewis base coordination. *Ortho*-alkoxy substituted diazoalkanes, popularized by Hoveyda and co-workers,[14] also yielded the expected N−N bond cleavage products with no evidence for alkylidene intermediates (Figure 1). Despite the inability to observe the putative iron alkylidene, we favor the pathway in Figure 3 as the observed diazoalkane complex, **1-N_2CH^{t}Bu**, did not yield N−N bond cleavage products upon treatment with excess diazoalkane.

In summary, the reduced bis(imino)pyridine iron dinitrogen complex, **1-(N_2)$_2$** promotes rapid N−N bond cleavage in monosubstituted diazoalkanes in solution under mild conditions, highlighting the utility of electrons stored in the bis(imino)pyridine chelate to affect cleavage of strong bonds.

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Supporting Information Available: Complete experimental procedures, selected NMR spectra, and crystallographic data for **1-NHCHPh**. This material is available free of charge via the Internet at http://pubs.acs.org.

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