Iron Diazoalkane Chemistry: N−N Bond Hydrogenation and Intramolecular C−H Activation

Suzanne C. Bart, Amanda C. Bowman, Emil Lobkovsky, and Paul J. Chirik*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received January 4, 2007; E-mail: pc92@cornell.edu

The interaction of diazoalkanes and transition metal compounds is of interest given the utility of these transformations in the generation of alkylidene complexes that are active for the catalytic cyclopropanation of alkenes[1] and olefin metathesis.[2] Often times, however, N_2 loss is not observed and stable diazoalkane complexes are isolated.[3] Iron diazoalkane chemistry is particularly attractive for the aforementioned catalytic reactions due to the low cost and environmental compatibility of the first row metal. Woo and others have previously reported the preparation and catalytic cyclopropanation activity of porphyrin[4,5] and tetraazo macrocycle-ligated[6] iron alkylidenes. In contrast, insertion of diazoalkanes into the Fe−P bonds of tetrahedral $(R_3P)_2FeCl_2$ compounds has been reported to yield the corresponding, catalytically inactive phosphazine derivatives.[7]

The bis(imino)pyridine iron bis(dinitrogen) complex, $(^{i}PrPDI)$-$Fe(N_2)_2$ ($1\text{-}(N_2)_2$; $^{i}PrPDI = 2,6\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3N=CMe)_2C_5H_3N$),[8] has been characterized as an intermediate spin ferrous compound with a two electron reduced chelate.[9] The ability to store electron density in a redox-active supporting ligand[10] has interesting consequences on chemical reactivity. For example, treatment of $1\text{-}(N_2)_2$ with aryl azides furnished the corresponding imide compounds, $(^{i}PrPDI)Fe=NAr$ (Ar = aryl), that undergo hydrogenation of the Fe−N bond.[11] Magnetic, spectroscopic, and structural data support an iron(III) center with a one electron reduced chelate demonstrating that the formal two-electron oxidation occurs by two separate one-electron events: one at the ligand and one at the metal. This behavior, reminiscent of iron porphyrins, inspired exploration of the corresponding diazoalkane compounds. In this communication, we describe the synthesis of a bis(imino)pyridine iron diazoalkane complex and its unusual N−N, N−C, and C−H bond cleavage chemistry.

Addition of 1 equiv of Me_3SiCHN_2 to a pentane solution of $1\text{-}(N_2)_2$ followed by recrystallization at −35 °C furnished $1\text{-}N_2CHSiMe_3$ as a diamagnetic, purple-brown solid (eq 1).
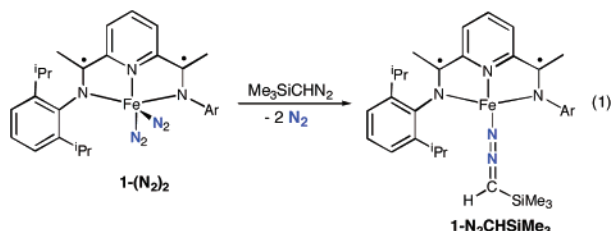
As expected for a bis(imino)pyridine iron compound with a weak field ligand completing the coordination sphere, $1\text{-}N_2CHSiMe_3$ exhibits temperature-independent paramagnetism, whereby an energetically similar $S = 1$ excited state mixes with an $S = 0$ ground state via spin orbit coupling.[9] Notably, the imine methyl resonance shifts significantly upfield to −1.55 ppm, and the *meta*-pyridine peak shifts downfield to 9.00 ppm. These chemical shifts do not change upon cooling to −80 °C.

The solid-state structure of $1\text{-}N_2CHSiMe_3$ (Figure 1) establishes an essentially square planar iron complex with the isopropyl aryl substituents orthogonal to the idealized plane. Observation of elongated $C_{imine}-N_{imine}$ and $C_{ortho}-N_{pyr}$ bonds in conjunction with contracted $C_{imine}-C_{ipso}$ distances (Figure 1) supports a two electron reduced chelate and an intermediate spin ferrous center.[9] Accordingly, the diazoalkane ligand is unperturbed, consistent with little reduction from the d^6, Fe(II) ion. Short N(4)−N(5) and N(5)−C(10) distances of 1.1669(17) and 1.282(2) Å, respectively, and N(4)−N(5)−C(10) (176.26(16)°) and Fe(1)−N(4)−N(5) (169.89(12)°) angles approaching linearity are observed.

The iron diazoalkane compound, $1\text{-}N_2CHSiMe_3$, is thermally unstable in benzene-d_6 solution at 23 °C, slowly and quantitatively converting to an NMR-silent product, **2**, with concomitant loss of $SiMe_4$ (^1H NMR). Recrystallization of green **2** from a diethyl ether/pentane mixture at −35 °C under a N_2 atmosphere deposited a small quantity of brown crystals. Analysis of this minor product by solid state (KBr) IR spectroscopy established a new N≡N stretch centered at 2090 cm^{-1}, consistent with formation of an iron dinitrogen complex, $2\text{-}N_2$.

X-ray diffraction studies established the identity of $2\text{-}N_2$ as the iron−olefin complex, arising from dehydrogenation of one of the isopropyl aryl substituents (Figure 2). NMR-silent **2** is therefore formulated as the iron olefin complex without the dinitrogen ligand. This formulation has been corroborated by magnetic susceptibility, elemental analysis, infrared spectroscopy (lack of an N≡N band), and reactivity studies. The bond distances of the bis(imino)pyridine ligand in $2\text{-}N_2$ (Figure 2) are consistent with two-electron reduction of the chelate.[9] As was observed with $1\text{-}N_2CHSiMe_3$, there is little back-bonding with the olefin as the C(16)−C(17) bond distance of 1.389(3) Å is only slightly perturbed from a typical C=C bond.

Exposure of either **2** or $2\text{-}N_2$ to D_2 gas followed by removal of the D_2 atmosphere and addition of excess N_2 regenerated $1\text{-}(N_2)_2$ (Figure 3). Analysis of the product by ^2H NMR spectroscopy established a 1:1 incorporation of deuterium into the isopropyl methine and methyl positions, consistent with olefin deuteration. This result is unique from previous cyclometalation chemistry observed with $1\text{-}(N_2)_2$ where only the isopropyl methyl group undergoes isotopic exchange upon addition of D_2.[8] Alkane dehydrogenation, while well-established with precious metals such as iridium[12] and platinum,[13] is to our knowledge unknown for iron. While mechanistic data are limited, one possible pathway for dehydrogenation of $1\text{-}N_2CHSiMe_3$ is formation of a transient iron alkylidene followed by 1,2-addition of an isopropyl aryl C−H bond. The putative iron dialkyl then undergoes β-hydrogen and reductive eliminations to yield the observed products. Consistent with this pathway is the failure of $1\text{-}(N_2)_2$ to yield either **2** or $2\text{-}N_2$ upon thermolysis under vacuum.

The unique hydrogenation chemistry observed with $(^{i}PrPDI)Fe=NAr$ to yield free anilines[11] prompted investigation into the reactivity of $1\text{-}N_2CHSiMe_3$ with H_2. Addition of 1 atm of dihydrogen to a

N(1)-C(8): 1.3466(17)
N(3)-C(2): 1.3413(18)
C(7)-C(8): 1.410(2)
C(2)-C(3): 1.418(2)
N(2)-C(7): 1.3767(17)
N(2)-C(3): 1.3777(18)

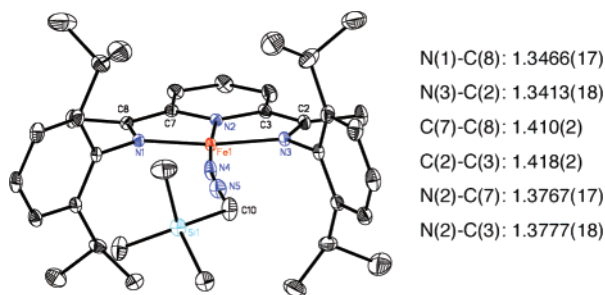**Figure 1.** Molecular structure of **1-N₂CHSiMe₃** at 30% probability ellipsoids with selected bond distances (Å). Hydrogen atoms omitted.

N(1)-C(2): 1.338(2)
N(3)-C(8): 1.342(2)
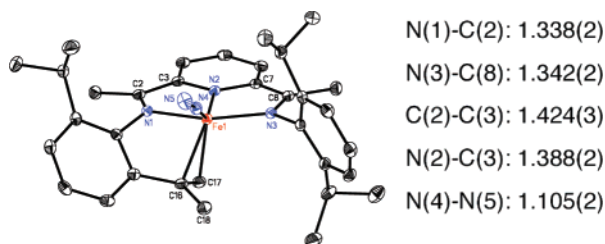C(2)-C(3): 1.424(3)
N(2)-C(3): 1.388(2)
N(4)-N(5): 1.105(2)

Figure 2. Molecular structure of **2-N₂** at 30% probability ellipsoids with selected bond distances (Å). Hydrogen atoms omitted.
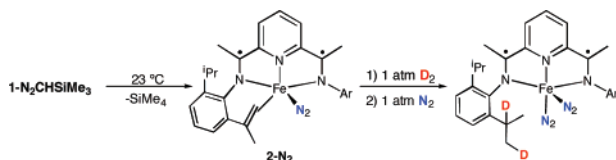

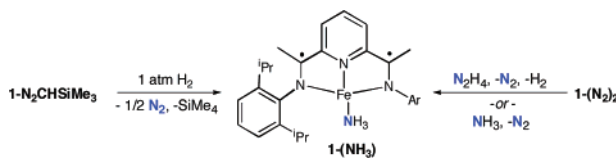**Figure 3.** Intramolecular C–H activation with **1-N₂CHSiMe₃**.

Figure 4. N–N bond cleavage with **1-N₂CHSiMe₃** and **1-(N₂)₂**.

benzene-d_6 solution of **1-N₂CHSiMe₃** at 23 °C resulted in liberation of SiMe₄ along with formation of a diamagnetic, C_{2v}-symmetric (¹H NMR) compound identified as the iron ammonia complex, **1-NH₃** (Figure 4), arising from N–N and N–C hydrogenative cleavage.[14] Repeating the experiment with D₂ gas yielded Me₃SiCHD₂ and **1-ND₃** as judged by ¹H and ²H NMR spectroscopy. N–N bond cleavage in coordinated diazoalkanes is rare, having been observed at elevated temperatures in bi- and multi-metallic compounds and in only a handful of mononuclear species.[3,15] The hydrogenative N–N and N–C bond cleavage observed with **1-N₂CHSiMe₃** at 23 °C is therefore noteworthy and appears to be a new transformation for diazoalkane ligands.

Several experiments were conducted to explore the origin of ammonia formation. **1-NH₃** was independently prepared by addition of NH₃ to **1-(N₂)₂** and exhibits shifted ¹H NMR resonances due to temperature-independent paramagnetism.[9] Because 1,2-addition of H₂ to **1-N₂CHSiMe₃**[16] is a likely first step in N–N bond cleavage and may ultimately yield N₂H₄, the chemistry of **1-(N₂)₂** with hydrazine was explored.

Treatment of a benzene-d_6 solution of **1-(N₂)₂** with 1 equiv of N₂H₄ and monitoring the reaction by ¹H NMR spectroscopy in the presence of a ferrocene standard demonstrated quantitative formation of **1-NH₃**. Performing the reaction on a preparative scale with 2 equiv of hydrazine and collecting the liberated gas with a Toepler pump confirmed evolution of N₂ and H₂, consistent with N₂H₄ disproportionation.[17] Addition of 0.25 and 0.50 equiv of N₂H₄ to **1-(N₂)₂** yielded 35 and 75% **1-NH₃**, demonstrating that 1.4 equiv of NH₃ is produced from N₂H₄ cleavage. Previous studies with various metal salts both in the gas phase and in solution have demonstrated the complexities of N₂H₄ decomposition, and several competing reactions to form NH₃, N₂, and H₂ are known.[17]

New transformations for iron diazoalkane complexes, intramolecular C–H activation and N–N and N–C hydrogenative cleavage, have been discovered. While not definitive, the intermediacy of N₂H₄ is plausible in diazoalkane hydrogenation to ammonia. These transformations, along with those associated with the corresponding iron imides,[11] motivate continued study of the role in redox-active ligands in cleavage and hydrogenation of N–N and Fe–N bonds.

Supporting Information Available: Experimental procedures and crystallographic data for **1-N₂CHSiMe₃** and **2-N₂**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Doyle. M. P. *Chem. Rev.* **1996**, *86*, 919.
(2) (a) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003. (b) Trnka, T.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *21*, 18.
(3) (a) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *178–180*, 623. (b) Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281. (c) Park, S.-B.; Nishiyama, H.; Itoh, Y.; Itoh, K. *Chem. Commun.* **1994**, 1315. (d) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532.
(4) Artaud, I.; Gregoire, N.; Leduc, P.; Mansuy, D. *J. Am. Chem. Soc.* **1990**, *112*, 6899.
(5) (a) Guilong, G.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2003**, *22*, 1468. (b) Hamaker, C. G.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2001**, *20*, 5171.
(6) Du, G.; Andrioletti, B.; Rose, E.; Woo, L. K. *Organometallics* **2002**, *21*, 4490.
(7) Louie, J.; Grubbs, R. H. *Organometallics* **2001**, *20*, 481.
(8) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.
(9) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.
(10) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.
(11) Bart, S. C.; Lobkovsky, E.; Bill, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 5302.
(12) (a) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257. (b) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
(13) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286.
(14) Complete experimental details are reported in the Supporting Information.
(15) Kaplan, A. W.; Polse, J. L.; Ball, G. E.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11649.
(16) Hanna, T. E.; Keresztes, I.; Lobkovsky, E.; Bernskoetter, W. H.; Chirik, P. J. *Organometallics* **2004**, *23*, 3448.
(17) Schmidt, E. *Hydrazine and its Derivatives: Preparation, Properties and Applications*; Wiley-Interscience: New York, 1984; pp 681–696.

JA070056U