Inorganic Chemistry Communication

Inorg. Chem. **2009**, *48*, 5587–5589 **5587**
DOI: 10.1021/ic9003017

Synthesis of Bis(imino)pyridine Iron Amide and Ammonia Compounds from an N−H Transfer Agent

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Received February 17, 2009

Addition of the [NH] transfer reagent Hdbabh (dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene) to the bis(imino)pyridine iron bis(dinitrogen) complex, $(^{iPr}PDI)Fe(N_2)_2$ (^{iPr}PDI = 2,6-$(2,6\text{-}^{i}Pr_2C_6H_3N{=}CMe)_2C_5H_3N$), furnished the corresponding iron amide and ammonia compounds, resulting from cleavage of the strained amine. Isotopic labeling studies support N−H bond activation by a transient, parent imide, $[(^{iPr}PDI)FeNH]$.

Iron imido and nitrido compounds $L_nFe{=}NR$ and $L_nFe{\equiv}N$, respectively, continue to attract attention because of their potential intermediacy in nitrogen fixation and catalytic group and atom transfer reactions.[1,2] Structurally characterized, terminal iron imides are now known for oxidation states 2+ to 5+.[3,4] One notable recent addition is Power's iron(V) bis(imide), $Ar^*Fe(N^1Ad)_2$ (Ar^* = $C_6H\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3)_2\text{-}3,5\text{-}^{i}Pr_2$), prepared by addition of 1-adamantyl azide to $Ar^*Fe(\eta^6\text{-}C_6H_6)$.[3] Our laboratory reported that the addition of aryl azides to the bis(imino)pyridine iron bis(dinitrogen) complex, $(^{iPr}PDI)Fe(N_2)_2$ (^{iPr}PDI = 2,6-$(2,6\text{-}^{i}Pr_2C_6H_3N{=}CMe)_2C_5H_3N$, **1-(N$_2$)$_2$**), furnished the corresponding iron arylimide complexes, $(^{iPr}PDI)Fe{=}NAr$ (**1=N*Ar***).[5] The metrical parameters from X-ray diffraction, in combination with the zero-field ^{57}Fe Mössbauer (MB) parameters and magnetic susceptibility data, establish an iron(III) complex with a redox-active, one-electron-reduced bis(imino)pyridine chelate. Notably, these compounds undergo complete hydrogenation of the Fe−N bond to yield the corresponding iron dihydrogen complex and the free aniline. In fact, catalytic azide hydrogenation to amines was observed in cases where the imide substituents were sufficiently large to inhibit aniline coordination.[5]

Inspired by these observations, we sought to prepare other examples of bis(imino)pyridine iron imides and explore their reactivity in hydrogenation and related processes. The parent iron imide, $(^{iPr}PDI)FeNH$, is an attractive target given the paucity of such compounds in the literature as well as possible relevance to biological and industrial ammonia synthesis. Because of the dangers associated with the preparation and handling of HN_3, we chose to study the chemistry of Hdbabh (dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene)[6] as an [NH] group transfer agent (Scheme 1).[7]

The addition of 1 equiv of Hdbabh to a diethyl ether solution of **1-(N$_2$)$_2$** yielded two new iron products identified as the paramagnetic iron amide compound, **1-dbabh**, and the diamagnetic iron ammonia derivative, **1-NH$_3$**. Free anthracene, equal to the amount of **1-NH$_3$**, was also detected by ^{1}H NMR spectroscopy. **1-NH$_3$** was previously reported and independently prepared by the treatment of **1-(N$_2$)$_2$** with anhydrous ammonia.[8]

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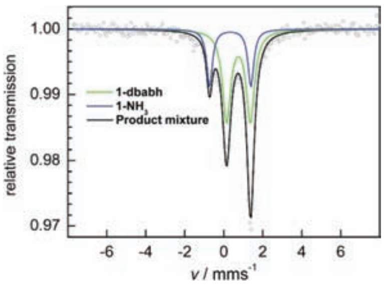
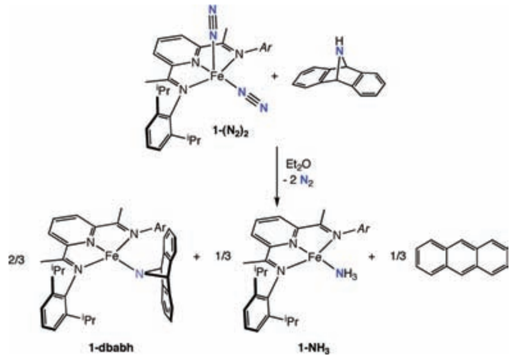


Figure 1. Zero-field ^{57}Fe MB spectrum of the products from the addition of Hdbabh to **1-(N$_2$)$_2$** recorded at 80 K.

Scheme 1



Because of the complications of quantifying paramagnetic versus diamagnetic compounds by ^{1}H NMR spectroscopy, the product mixture from the addition of Hdbabh to **1-(N$_2$)$_2$** was analyzed by zero-field MB spectroscopy. This spectroscopic technique was also used to ensure that no other NMR-silent iron species were formed. A representative zero-field ^{57}Fe MB spectrum, recorded at 80 K, is presented in Figure 1 and establishes clean and reproducible formation of only two iron products in an approximately 80:20 ratio. This ratio deviates from the idealized 2:1 likely due to recrystallization of the sample prior to spectroscopic analysis. The independent preparation of the ammonia compound established **1-NH$_3$** (δ = 0.33 mm s^{-1}; ΔE_Q = 2.22 mm s^{-1}) as the minor product in the MB spectrum (Figure S1).[8]

Attempts to induce a loss of anthracene from **1-dbabh** were unsuccessful. No change was observed upon letting the compound stand at 23 °C in benzene-d_6 for 1 week. Warming benzene-d_6 solutions of **1-dbabh** to 45 °C resulted in decomposition after 24 h. No anthracene was observed from the decomposition. Changing the order of the addition, Hdbabh to **1-(N$_2$)$_2$** or vice versa, has no measurable effect on the ratio of the products.

Both **1-dbabh** and **1-NH$_3$** were characterized by X-ray diffraction (Figure 2). In both cases, essentially square-planar molecules are observed, with the sum of the angles around iron equal to 362.17(13)° (**1-dbabh**) and 360.01(16)° (**1-NH$_3$**). The larger deviation observed for **1-dbabh** is a result of the slight lifting of the iron−amide bond out of the idealized square plane [N2−Fe−N4 = 169.92(7)°]. The iron is also raised by 0.3880(17) Å out of the idealized plane of the chelate. The amide substituents lie above and below the plane of the iron and the chelate, likely to avoid steric interactions with the large aryl groups.

As is well-established in bis(imino)pyridine chemistry,[9−11] distortions to the chelate are diagnostic of ligand reduction and redox activity. The metrical parameters of the bis(imino) pyridine chelate in **1-NH$_3$** are consistent with two-electron reduction.[9,11] Elongated C═N imine bond distances of 1.358 (3) and 1.371(3) Å and contracted C$_{\text{imine}}$−C$_{\text{ipso}}$ lengths 1.420 (3) and 1.436(3) Å are typical of [PDI]$^{2-}$.[9−11] The bond distance changes for **1-dbabh** are less pronounced than those for **1-NH$_3$** and are consistent with those of [PDI]$^-$.[9,11] The C═N distances of 1.318(3) and 1.301(2) Å are only slightly elongated from the free ligand values, while the C−C distances of 1.441(3) and 1.457(3) Å show a minor contraction.

Variable-temperature SQUID measurements on solid samples of **1-dbabh** over the temperature range of 5−300 K (Figure S2 in the Supporting Information) established that the effective magnetic moment, μ_{eff}, undergoes a steady decline as the temperature is lowered, decreasing from 3.90 μ_B at 300 K to 2.90 μ_B at 5 K. These data are consistent with an $S = {}^3/_2$ ground state and are similar to those reported for **1-Cl**[9] and **1-Br**.[12] The zero-field ^{57}Fe MB isomer shift, δ, of 0.75 mm s^{-1} and the quadrupole splitting, ΔE_Q, of 1.22 mm s^{-1} of **1-dbabh** are similar to the values reported for **1-Cl**[9] and are consistent with high-spin iron(II). Thus, the ground state for **1-dbabh** is best described as an $S = {}^3/_2$ compound with a high-spin ferrous center (S_{Fe} = 2) antiferromagnetically coupled to a chelate radical anion ($S_{\text{PDI}} = {}^1/_2$).

Isolation and characterization of **1-dbabh** from Hdbabh cleavage is striking because previous attempts to synthesize **1-NMe$_2$** or **1-N(SiMe$_3$)$_2$** by salt metathesis with **1-Cl** resulted in unidentified mixtures of products. The treatment of **1-Cl$_2$** with 2 equiv of LiNMe$_2$ resulted in chelate deprotonation and formation of the iron amine complex, ($^{\text{iPr}}$PDEA) FeNHMe$_2$.[13] In contrast, the treatment of **1-Cl** with 1 equiv of Li[dbabh] in diethyl ether cleanly furnished **1-dbabh** with no evidence for competing chelate deprotonation. Attempts to prepare **1-dbabh** by the addition of 2 equiv of Li[dbabh] to **1-Cl$_2$** resulted in a complex mixture of products. Similarly, attempts to synthesize **1-Cl** by the addition of Li[dbabh] to **1-Cl$_2$** were unsuccessful, demonstrating the inability of the amide reagent to serve as a reductant and establishing this step as the origin of decomposition in the 2 equiv procedure.

Inspired by isolation of **1-dbabh** from salt metathesis, **1-Cl** was treated with lithium pyrrolidide, Li[NC$_4$H$_8$]. Unfortunately, a mixture of paramagnetic iron products was observed by ^{1}H NMR spectroscopy. As was observed with LiNMe$_2$,[13] the addition of 2 equiv of Li[NC$_4$H$_8$] to **1-Cl$_2$** resulted in clean chelate deprotonation and formation of the iron pyrrolidine complex ($^{\text{iPr}}$PDEA)FeNHC$_4$H$_8$.

Additional experiments were conducted to gain insight into the scope and mechanism of Hdbabh cleavage. The generality of the reaction was explored with other cyclic amines and aziridines. The addition of 1 equiv of pyrrolidine (HNC$_4$H$_8$) to **1-(N$_2$)$_2$** resulted in the loss of N$_2$ and formation of the corresponding bis(imino)pyridine iron pyrrolidine compound, **1-(NHC$_4$H$_8$)**. The absence of significant ring

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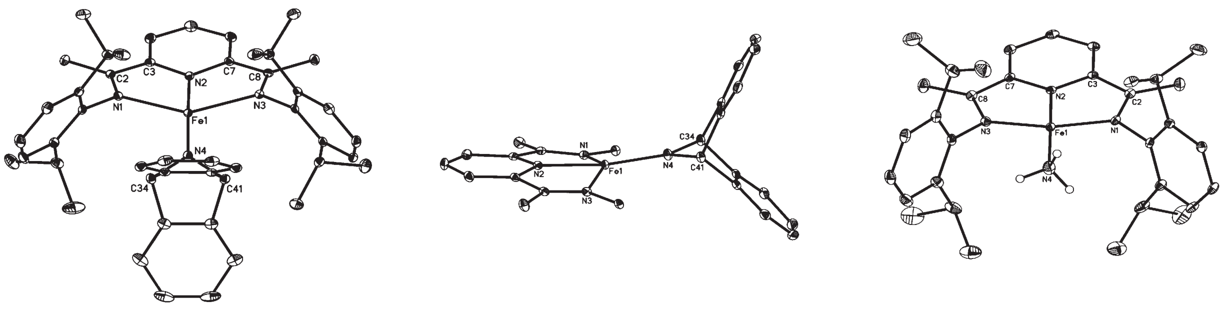
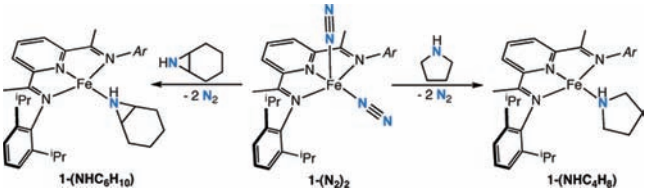


Figure 2. Molecular structures of **1-dbabh** (left and center) and **1-NH_3** (right). Each structure is shown at 30% probability ellipsoids. H atoms, except those on the ammonia in **1-NH_3**, are omitted for clarity. Aryl groups are omitted on the central structure of **1-dbabh**.

Scheme 2



strain and hence a potential driving force for pyrrolidine to act as an [NH] transfer agent prompted exploration of the chemistry of aziridines. The addition of 1 equiv of cyclohexene imine[14] to a benzene-d_6 solution of **1-(N_2)$_2$** cleanly yielded the corresponding bis(imino)pyridine iron aziridine complex, **1-(NHC_6H_{10})**, with no evidence for [NH] group transfer (Scheme 2). Heating a benzene-d_6 solution of **1-(NHC_6H_{10})** at 65 °C for 24 h resulted in a mixture of iron compounds; however, analysis of the volatile products of the reaction mixture established the formation of cyclohexene and ammonia in a 1:0.75 ratio. These results indicate that cleavage chemistry similar to that of Hdbabh may be possible at elevated temperatures, but the resulting iron products are not thermally stable.

The coordination of pyrrolidine and aziridine to **1-(N_2)$_2$** over [NH] group transfer highlights the unique reactivity of Hdbabh. Assuming strain similar to that of cyclohexene imine, the observation of group transfer from Hdbabh is likely a consequence of the gain in aromaticity arising from the elimination of anthracene, an effect noted by Cummins and others[7] in the application of the dbabh anion in the synthesis of metal nitrides.

Isotopic labeling studies were also conducted to determine the course of the H atoms in the formation of **1-NH_3** from Hdbabh. Potential involvement of the imine methyl groups of the bis(imino)pyridine ligand was assayed by treatment of the deuterated dinitrogen complex **1**-(N_2)$_2$** (** indicates deuterated imine methyl groups) with Hdbabh. Analysis of the ammonia product by ^1H and ^2H NMR spectroscopy established the exclusive formation of **1**-NH_3**, eliminating imine methyl group participation. In a complementary experiment, Ddbabh (the ^2H isotopologue of Hdbabh) was added to **1-(N_2)$_2$**. Analysis of the resulting iron ammonia compound by ^1H and ^2H NMR spectroscopy as well as by solid-state (KBr) IR spectroscopy established the exclusive formation of **1-ND_3**, identifying Ddbabh (or Hdbabh) as the sole source of the H atoms in ammonia formation.

On the basis of these observations, Hdbabh cleavage by **1-(N_2)$_2$** likely proceeds via initial [NH] group transfer to form the desired parent iron imide **[1=NH]** and free anthracene. This transient species likely promotes H-atom abstraction from the remaining Hdbabh to yield the observed ammonia complex **1-NH_3**. Capture of the amide radical [dbabh] by **1-(N_2)$_2$** yields the amide complex **1-dbabh**. Because of the potential intermediacy of **[1=NH]**, attempts were made to observe or trap it with other reagents. The addition of Hdbabh to **1-(N_2)$_2$** under an H_2 or D_2 atmosphere produced no change to the product or isotopic distribution. The cleavage reaction was also conducted in the presence of styrene, 1,4-cyclohexadiene, 9,10-dihydroanthracene, fluorene, and mesitylaniline, all with no effect. Performing the addition of Hdbabh to **1-(N_2)$_2$** in diethyl ether at −78 °C for 12 h increased the amount of anthracene produced from 33 to 46% and yielded a new, unidentified paramagnetic iron product (in addition to **1-dbabh** and **1-NH_3**). Hydrolysis of this mixture yielded a modified bis(imino)pyridine ligand, suggestive of C−H activation by putative **[1=NH]**. Studies are ongoing to gain additional information about this process.

In summary, the addition of the [NH] group transfer agent, Hdbabh, to a bis(imino)pyridine iron bis(dinitrogen) compound formed the corresponding amide and ammonia derivatives, likely through a transient parent imide. Additional reactivity of the iron amide complex **1-dbabh**, particularly toward anthracene loss and nitride formation, is currently under investigation in our laboratory.

Acknowledgment. P.J.C. thanks the Packard Foundation and K.M. thanks the University of Erlangen-Nürnberg and DFG (SFB 583) for financial support. S.C.B. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship. We also thank Jörg Sutter for collecting MB data.

Supporting Information Available: Experimental procedures, the zero-field MB spectrum of **1-NH_3**, SQUID data for **1-dbabh**, and crystallographic data for **1-dbabh** and **1-NH_3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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