An Iron Nitride Complex**

Carola Vogel, Frank W. Heinemann, Jörg Sutter, Christian Anthon, and Karsten Meyer*

Coordination compounds of iron in high oxidation states have been invoked as reactive intermediates in biocatalyses. Iron(IV) ferryl species are examples of such highly reactive species that have long been known to be at the catalytic centers of oxygenases. Supported by X-ray diffraction studies on nitrogenase, the iron nitride moiety has recently been suggested to be present at the site of biological nitrogen reduction. As a result, well-characterized high-valent iron complexes have been sought as biomimetic models for transformations mediated by iron-containing enzymes.

To gain understanding of iron nitride reactivity and the possible role of such species in biocatalysis, insight into the molecular structure of complexes stabilizing the [FeN] synthon is highly desirable. Whereas significant progress has been made in the synthesis and spectroscopic elucidation of Fe=NR and Fe=NN complexes,[1–6] X-ray crystallographic characterization of a complex with a terminal Fe≡N functionality has not been accomplished.[7,8]

The first mononuclear FeIV=O entity crystallographically characterized was stabilized in an octahedral environment provided by a macrocyclic tetra-N-methylated cyclam ligand.[9] Similar cyclam derivatives also allow the stabilization and detailed spectroscopic characterization of octahedral FeV and FeVI nitride complexes in unusually high oxidation states.[3,4,10]

Recently, Peters and Betley developed a stunningly redox-rich iron system employing the triprolid tris(phosphino)borate ligand system (PhB3P3−), which stabilizes tetrahedral L3Fe=NX species in oxidation states ranging from +I to +IV.[7] Remarkably, this ligand system enabled the first room-temperature spectroscopic characterization of a terminal FeVII nitride species. Concentration-dependent coupling to the FeV-N2-FeII dinuclear product, however, prevents crystallization of this nitride species.

We herein present the synthesis, spectroscopy, and most significantly, the X-ray diffraction analysis of a discrete iron nitride complex stabilized by the sterically encumbering N-anchored tris(carbene) ligand, tris(2-(3-aryl-imidazol-2-ylide)ethyl)amine (TIMENR, R = xyl (xyl), mesityl (mes)).[11] Structurally and electronically related to the tetrahedral phosphinoborate ligand system by Peters and Betley,[7] this triprolid N-heterocyclic carbene (NHC) system coordinates a high-spin FeII center in a trigonal-planar fashion, thus forming four-coordinate complexes with the metal ion in trigonal-pyramidal environments.

Under inert atmosphere, treatment of TIMENR with one equivalent of anhydrous ferrous chloride in pyridine at room temperature yields the four-coordinate FeIII complexes [(TIMENR)Fe(Cl)]Cl (1mes, 1xyl) as analytically pure, white powders in 80% yield (Scheme 1).

![Scheme 1. Synthesis of [(TIMENR)Fe(Cl)]Cl complexes 1e.](image)

Reduction of the FeII complexes 1mes and 1xyl over sodium amalgam in a solution of NaBPh4 in THF leads to the formation of deep red solutions of the reduced compounds. After 2 h, these solutions were filtered, concentrated, and cooled to −35 °C to yield dark red crystals of FeI complexes [(TIMENR)Fe(BPh4)2 (2mes, 2xyl)]. Complexes 1e and 2e were characterized by X-ray crystallography, spectroscopy, and elemental analysis. Detailed spectroscopy and further reactivity of these complexes will be reported in a full paper.

Addition of excess trimethylsilylazide to FeII complexes 2e in THF results in elimination of Me3Si and formation of light yellow solutions, containing pale yellow precipitates of divalent [(TIMENR)Fe(N3)]BPh4 (3e, Scheme 2).

Both azide complexes are easily identified by the intense yellow bands in the IR spectra. The IR vibrational band at 2094 cm−1. The crystal structures of compounds 3e (3mes see Figure 1) show the unusual, close to linear azide coordination (Fe–N3) IR vibrational band at 2094 cm−1. The Fe–N3 azide distances in 3mes and 3xyl were determined to be 1.947(2) and 1.955(2) Å, respectively. In both complexes, the amine anchor is not bound (3mes: d(Fe–N1) = 2.344(2); 3xyl).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
These are the not the final page numbers!

d(Fe–N1) = 3.197(2) Å, leaving the FeII ion coordinated in a trigonal-pyramidal coordination environment, in which the metal center is located 0.554(2) Å (3mes) and 0.536(2) Å (3R) above the trigonal plane of the three NHC ligands.

Azide compounds 3mes are light sensitive and readily release dinitrogen to form deeply colored products 4mes (Scheme 2). Accordingly, exposure of pale yellow solutions of 3mes in THF to light of a Xenon arc lamp at room temperature results in gradual formation of a purple solution and N2 gas evolution. Whereas the electronic absorption spectra of colorless azide complexes 3mes are transparent in the visible region, the spectra of the photolysis products 4mes (Scheme 2) show an intense absorption band centered at 550 nm (ε = 1980 mol⁻¹ cm⁻¹), see the Supporting Information) giving rise to the purple color. Photolysis of iron azides[10] was continued until no gas evolution was observed and the azide vibrational bands could no longer be observed by IR spectroscopy. Instead, in the spectra of both purple photolysis products, a new band appears at 1008 cm⁻¹, which is assigned to the iron nitride band v(Fe=15N). Samples of the 15N-labeled isotopomer, 50% 15N labeled at the terminal nitride, show an additional band at 982 cm⁻¹ (see the Supporting Information). This 26 cm⁻¹ shift of the v(Fe=15N) stretch to lower frequency is predicted from the reduced mass calculation for a harmonic oscillator (calcd: 28 cm⁻¹). In the 1H NMR spectra (see the Supporting Information), the purple, diamagnetic reaction products show the expected resonances for the functionalized tris(carbene) chelator coordinated to the iron centers of 4mes. Additionally, the 15N NMR spectrum of 15N-labeled 4mes exhibits a resonance signal at δ = 1121 ppm (referenced to NH3, see the Supporting Information). Slow diffusion of diethyl ether into THF solutions of 4mes yields purple crystals that are air stable at room temperature and suitable for an X-ray structure analysis. The molecular structures of [(TIMEN3)FeN]BPh4 (Figure 1, 4mes; for 4R see the Supporting Information) confirm the light-induced transformation of the axial azide to a terminal nitride ligand with short Fe–N bonds of 1.526(2) Å (4mes) and 1.527(3) Å (4R). Such short M–N distances are typically observed for transition-metal complexes with triply bonded nitride ligands (M = Cr, Mn).[14–19] The Fe–N distances in 4mes are also very similar to the XAS spectroscopically determined distances of the FeIV complex [(Ph3P)2Fe(N)] (δ(Fe–N) = 1.51–1.55(2) Å, R = iPr, CH2–Cy)[3] by Peters and co-workers, and the octahedral FeVI nitrido species [(Me2cy-ac)Fe(N)] (δ(Fe–N) = 1.57 Å) reported by Wieghardt and co-workers.[4]

Like the FeIV ions in azide precursors 3mes, the iron centers in nitride complexes 4mes are coordinated in trigonal-pyramidal fashion but with the FeIV ion located at only 0.427(3) Å (4mes) and 0.384(2) Å (4R) above the trigonal (tris(carbene) plane. Evidently, this smaller displacement from the trigonal coordination plane in 3mes is a consequence of increased interaction of the anchoring amine nitrogen (4mes; δ(Fe–N1) = 3.120(2); 4mes; δ(Fe–N1) = 2.984(2) Å) and the carbene ligands with the high-valent FeIV ions. This stronger coordination of the carbene in 4mes and 4R is reflected in significantly shorter average Fe–C distances of 1.941(5) and 1.956(4) Å compared to the weaker binding in the FeIII azide precursors of δ(Fe–C)av = 2.108(2) Å in 3mes and 2.101(2) Å in 3R.

The zero-field Mössbauer spectra of 3mes and 4mes are shown in Figure 2. The spectra of crystalline samples of 3mes at 77 K display a quadrupole doublet with an isomer shift δ = 0.691(1) mm s⁻¹, a quadrupole splitting parameter ΔE0 = 2.27(1) mm s⁻¹ and a line width ΓFWHM = 0.49(1) mm s⁻¹. These parameters are characteristic of four-coordinate d⁰ high-spin (S = 2) FeIII complexes.[20] Considering the trigonal coordination of the tris(carbene) chelator we suggest a ligand field, in which the paired electron is in an e orbital (ε4a1, ε2). In contrast, spectra of 4mes show a sharp quadrupole doublet (ΓFWHM = 0.26(1) mm s⁻¹) with very unusual Mössbauer parameters of δ = −0.27(1) mm s⁻¹ and ΔE0 = 6.04(1) mm s⁻¹. The negative isomer shift and remarkably large quadrupole splitting are consistent with values expected for a d², S = 0 FeIV=15N species. In fact, the observed ΔE0 = 6.04(1) mm s⁻¹ for 4mes is very similar to that determined for the [(Ph3P)2Fe(N)] system (ΔE0 = 6.01(1) mm s⁻¹).[21] In both cases, the valence and covalency contributions from the dominating Fe≡N moiety affect the unusually large quadrupole splitting of the terminal nitride.
pole splitting parameter $\Delta E_0$ of the complexes in accordance with the observed and calculated diamagnetic $\left[(d_{xy})^2(d_{xy})^2\right]$ $\left[(d_{x^2})^2(d_{x^2})^2\right]$ electron ground state configuration (Figure 3).

In contrast to this striking similarity in $\Delta E_0$ values, the isomer shift $\delta = -0.27(1)$ mm/s of $4^{\text{mes}}$ differs significantly from that reported for $\left[(\text{PhB}^\text{IP}_3)^\text{Fe}(\text{N})\right]$ ($\delta = -0.34$ mm/s). The isomer shift determined by $^{57}$Fe Mössbauer spectroscopy is directly related to the s electron density at the nucleus, which is shielded by electron density in the shells with nonzero angular momenta (p and d orbitals). Accordingly, the less negative $\delta$ indicates that the iron ion in $4^{\text{mes}}$ is less oxidized than the tetrahedral iron center in $\left[(\text{PhB}^\text{IP}_3)^\text{Fe}(\text{N})\right]$. This is likely a consequence of a certain degree of ligand-to-metal back bonding from the NHC ligand $\pi$ system to empty iron d orbitals in trigonal-pyramidal $4^{\text{mes}}$. While it is intuitive that the electronic structure of four-coordinate iron nitride complexes is dominated by the strong $\text{Fe=NI}$ interaction, the different isomer shifts clearly demonstrate that other factors, such as ligand-donor set and coordination geometry, ultimately determine the detailed electronic structure and complex stability of high-valent iron nitride species. Obviously, the neutral, potentially tetradeionate tris(carbene) ligand and the anionic tridentate tris(phosphino)borate, exhibit not only steric but also significant electronic differences. This could also explain the differences in color and stability of the deep purple aminocarbene Fe IV nitride system $\left[(\text{TIMENR})\text{Fe}(\text{N})\right]^+$ and the tan-colored, more tetrahedral, $\left[(\text{PhB}^\text{IP}_3)^\text{Fe}(\text{N})\right]$ complex prone to dimerization. To gain a better understanding of the intricate electronic structure of $4^{\text{mes}}$, in-depth computational and spectroscopic analysis will be carried out.

In conclusion, photolysis of Fe II azide complexes of sterically encumbering nitrogen-anchored N-heterocyclic tris(carbene) ligands generates discrete, air-stable Fe IV nitride complexes. The X-ray crystallographically determined Fe=NI bonds are short at 1.53 Å, and the high-valent Fe IV nitride centers in these molecules possess trigonal-pyramidal coordination environments. The molecular structures of iron nitride complexes $4^{\text{mes}}$ here reported are the first structural verification of the [FeN] synthon that has been recognized as the reactive intermediate in the industrial Haber–Bosch process.

While iron nitride complexes $4^{\text{mes}}$ are remarkably air and moisture stable at room temperature, they demonstrate promising reactivity with proton sources in preliminary experiments. Detailed reactivity investigations of the iron nitride complexes $4^{\text{mes}}$ are currently underway.

**Experimental Section**

Detailed descriptions of the syntheses as well as spectroscopic and crystallographic details of all compounds are given in the Supporting Information.

Received: February 5, 2008
Published online: 2008

**Keywords:** azides · carbene ligands · iron · Mössbauer spectroscopy · nitrides

Communications


These are not the final page numbers!


[12] Data were collected at 100 K on a Bruker Nonius KappaCCD diffractometer using Mo Ka radiation (λ = 0.71073 Å, graphite monochromator). Structures were solved by direct methods and refined on F2 using full-matrix least-squares techniques. For 3mes·2.5THF: triclinic, P1, a = 11.305(3), b = 17.725(2), c = 17.831(2) Å, α = 88.056(10), β = 76.821(6), γ = 78.047(7), V = 3402.7(6) Å3, Z = 2. R1 = 0.0516 [I > 2σ(I)], wR2 = 0.1292 (all data). For 4mes·Et2O: triclinic, P1, a = 12.432(2), b = 12.632(2), c = 22.614(3) Å, α = 80.104(13), β = 84.734(9), γ = 61.303(7), V = 3068.6(8) Å3, Z = 2. R1 = 0.0450 [I > 2σ(I)], wR2 = 0.0938 (all data). CCDC-676549 (for 3mes·2.5THF), CCDC-676550 (for 4mes·Et2O), CCDC-676551 (for 3xyl·MeCN), and CCDC-676552 (for 4xyl·THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


An Iron Nitride Complex

High on nitride: Discrete iron nitride complexes stabilized by N-anchored tris-(carbene) ligands have been synthesized (see picture). These high-valent Fe=\equiv N complexes are stable at room temperature, which allows their full spectroscopic and—for the first time—crystallographic characterization.