Coordination Chemistry

An Iron Nitride Complex**

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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.[1] 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.[2] 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≡N species,[3–6] X-ray crystallographic characterization of a complex with a terminal Fe≡N functionality has not been accomplished.[7, 8]

The first mononuclear $Fe^{IV}=O$ 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 Fe^{V} and Fe^{VI} nitride complexes in unusually high oxidation states.[3, 4, 10]

Recently, Peters and Betley developed a stunningly redox-rich iron system employing the tripodal tris(phosphino)borate ligand system $(PhB^{R}P_3^{-})$, which stabilizes tetrahedral $L_3Fe=N_x$ species in oxidation states ranging from $+I$ to $+IV$.[7] Remarkably, this ligand system enabled the first room-temperature spectroscopic characterization of a terminal Fe^{IV} nitride species. Concentration-dependent coupling to the $Fe^{I}-N_2-Fe^{I}$ 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-ylidene)ethyl]amine ($TIMEN^{R}$, R = xylyl (xyl), mesityl (mes)).[11] Structurally and electronically related to the tetrahedral phosphinoborate ligand system by Peters and Betley,[7] this tripodal N-heterocyclic carbene (NHC) system coordinates a high-spin Fe^{II} center in a trigonal-planar fashion, thus forming four-coordinate complexes with the metal ion in trigonal-pyramidal environments.

Under inert atmosphere, treatment of $TIMEN^{R}$ with one equivalent of anhydrous ferrous chloride in pyridine at room temperature yields the four-coordinate Fe^{II} complexes $[(TIMEN^{R})Fe(Cl)]Cl$ ($\mathbf{1^{mes}}$, $\mathbf{1^{xyl}}$) as analytically pure, white powders in 80% yield (Scheme 1).
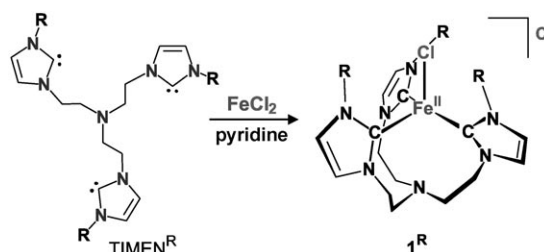
Scheme 1. Synthesis of $[(TIMEN^{R})Fe(Cl)]Cl$ complexes $\mathbf{1^{R}}$.

Reduction of the Fe^{II} complexes $\mathbf{1^{mes}}$ and $\mathbf{1^{xyl}}$ over sodium amalgam in a solution of $NaBPh_4$ 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 Fe^{I} complexes $[(TIMEN^{R})Fe]BPh_4$ ($\mathbf{2^{mes}}$, $\mathbf{2^{xyl}}$). Complexes $\mathbf{1^{R}}$ and $\mathbf{2^{R}}$ 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 Fe^{I} complexes $\mathbf{2^{R}}$ in THF results in elimination of Me_6Si_2 and formation of light yellow solutions, containing pale yellow precipitates of divalent $[(TIMEN^{R})Fe(N_3)]BPh_4$ ($\mathbf{3^{R}}$, Scheme 2).

Both azide complexes are easily identified by the intense and very characteristic $\nu_{as}(N_3)$ IR vibrational band at $2094\ cm^{-1}$. The crystal structures of compounds $\mathbf{3^{R}}$ ($\mathbf{3^{mes}}$ see Figure 1) show the unusual, close to linear azide coordination ($\angle(Fe-N_\alpha-N_\beta) = 174.5(2)°$ in $\mathbf{3^{mes}}$, $166.9(2)°$ in $\mathbf{3^{xyl}}$) at the Fe^{II} tris(carbene) complex.[12] Such linear azide coordination to a metal center is rare but has been observed before in sterically encumbering ligand environments, in which similar cylindrical cavities are generated around the metal center.[13] The Fe–N_α azide distances in $\mathbf{3^{mes}}$ and $\mathbf{3^{xyl}}$ were determined to be $1.947(2)$ and $1.955(2)$ Å, respectively. In both complexes, the amine anchor is not bound ($\mathbf{3^{mes}}$: $d(Fe-N1) = 3.244(2)$; $\mathbf{3^{xyl}}$:

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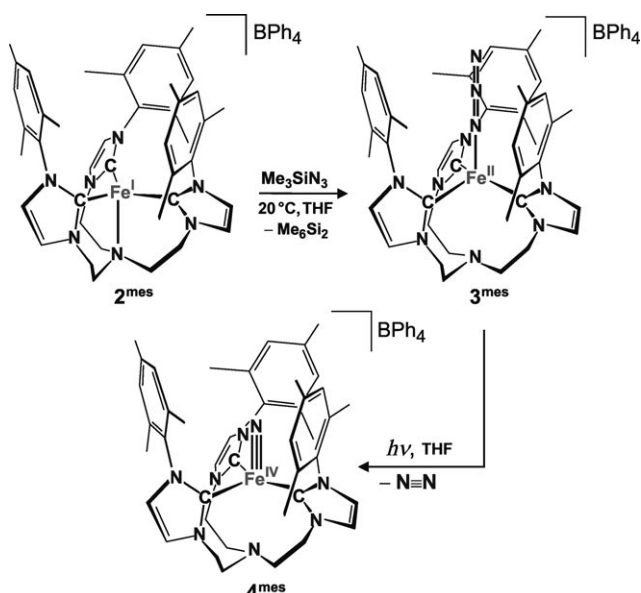
Scheme 2. Synthesis of Fe^{IV} nitride complex **4**^{mes}.
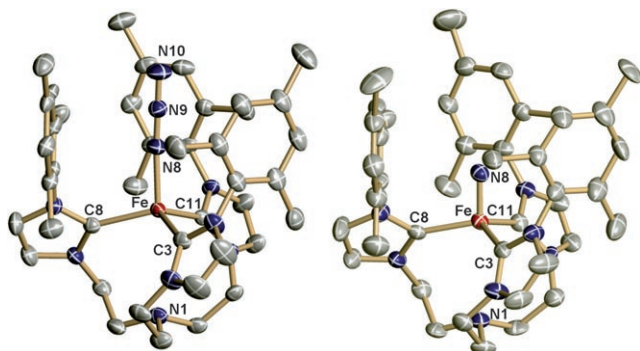
Figure 1. Molecular structures of complex cations of [(TIMEN^{mes})-Fe(N$_3$)]BPh$_4$ (**3**^{mes}, left) and [(TIMEN^{mes})Fe(N)]BPh$_4$ (**4**^{mes}, right) in crystals of **3**^{mes}·2.5 THF and **4**^{mes}·Et$_2$O. Hydrogen atoms and co-crystal-lized solvent molecules are omitted for clarity.

d(Fe−N1) = 3.197(2) Å), leaving the Fe^{II} ion coordinated in a trigonal-pyramidal coordination environment, in which the metal center is located 0.554(2) Å (**3**^{mes}) and 0.536(2) Å (**3**^{xyl}) above the trigonal plane of the three NHC ligands.

Azide compounds **3**^{R} are light sensitive and readily release dinitrogen to form deeply colored products **4**^{R} (Scheme 2). Accordingly, exposure of pale yellow solutions of **3**^{R} in THF to light of a Xenon arc lamp at room temperature results in gradual formation of a purple solution and N$_2$ gas evolution. Whereas the electronic absorption spectra of colorless azide complexes **3**^{R} are transparent in the visible region, the spectra of the photolysis products **4**^{R} (Scheme 2) show an intense absorption band centered at λ_{max} 520 nm ($\varepsilon = 1980$ M^{-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 ν(Fe≡^{14}N). Samples of the ^{15}N-labeled isotopomer, 50% ^{15}N labeled at the terminal nitride, show an additional band at 982 cm^{-1} (see the Supporting Information). This 26 cm^{-1} shift of the ν(Fe≡^{15}N) stretch to lower frequency is predicted from the reduced mass calculation for a harmonic oscillator (calcd: 28 cm^{-1}). In the ^{1}H 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 **4**^{R}. Additionally, the ^{15}N NMR spectrum of ^{15}N-labeled **4**^{mes} exhibits a resonance signal at $\delta = 1121$ ppm (referenced to NH$_3$, see the Supporting Information). Slow diffusion of diethyl ether into THF solutions of **4**^{R} yields purple crystals that are air stable at room temperature and suitable for an X-ray structure analysis. The molecular structures of [(TIME-N^R)Fe≡N]BPh$_4$ (Figure 1, **4**^{mes}; for **4**^{xyl} 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) (**4**^{mes}) and 1.527(3) Å (**4**^{xyl}). 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 **4**^{R} are also very similar to the XAS spectroscopically determined distances of the Fe^{IV} complex [(PhB^{R}P$_3$)Fe(N)] (d(Fe≡N) = 1.51–1.55(2) Å, R = iPr, CH$_2$-Cy)[8] by Peters and co-workers, and the octahedral Fe^{VI} nitrido species [(Me$_3$cy-ac)Fe(N)] (d(Fe≡N) = 1.57 Å) reported by Wieghardt and co-workers.[4]

Like the Fe^{II} ions in azide precursors **3**^{R}, the iron centers in nitrido complexes **4**^{R} are coordinated in trigonal-pyramidal fashion but with the Fe^{IV} ion located at only 0.427(3) (**4**^{mes}) and 0.384(2) Å (**4**^{xyl}) above the trigonal tris(carbene) plane. Evidently, this smaller displacement from the trigonal coordination plane in **3**^{R} is a consequence of increased interaction of the anchoring amine nitrogen (**4**^{mes}: d(Fe−N1) = 3.120(2); **4**^{xyl}: d(Fe−N1) = 2.984(2) Å) and the carbene ligands with the high-valent Fe^{IV} ions. This stronger coordination of the carbenes in **4**^{mes} and **4**^{xyl} 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 Fe^{II} azide precursors of d(Fe−C)$_{av}$ = 2.108(2) in **3**^{mes} and 2.101(2) Å in **3**^{xyl}.

The zero-field Mössbauer spectra of **3**^{mes} and **4**^{mes} are shown in Figure 2. The spectra of crystalline samples of **3**^{mes} at 77 K display a quadrupole doublet with an isomer shift $\delta = 0.69(1)$ mm s^{-1}, a quadrupole splitting parameter $\Delta E_Q = 2.27(1)$ mm s^{-1}, and a line width $\Gamma_{FWHM} = 0.48(1)$ mm s^{-1}. These parameters are characteristic of four-coordinate d^6 high-spin ($S = 2$) Fe^{II} 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 (e^{3}a$_1$^{1}e^2). In contrast, spectra of **4**^{mes} show a sharp quadrupole doublet ($\Gamma_{FWHM} = 0.26(1)$ mm s^{-1}) with very unusual Mössbauer parameters of $\delta = -0.27(1)$ mm s^{-1} and $\Delta E_Q = 6.04(1)$ mm s^{-1}.

The negative isomer shift and remarkably large quadrupole splitting are consistent with values expected for a d^4, $S = 0$ Fe^{IV}≡N species. In fact, the observed $\Delta E_Q = 6.04(1)$ mm s^{-1} for **4**^{mes} is very similar to that determined for the [(PhB^{iPr}P$_3$)Fe(N)] system ($\Delta E_Q = 6.01(1)$ mm s^{-1}).[5] In both cases, the valence and covalency contributions from the dominating Fe≡N moiety affect the unusually large quadru-
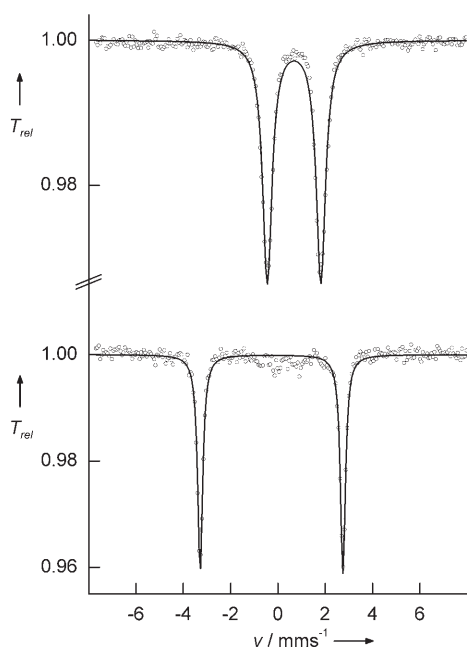
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Figure 2. Mössbauer spectra of complexes **3**[mes] (top) and **4**[mes] (bottom). Spectra were recorded on solid samples at 77 K without an applied magnetic field; solid lines are fits resulting in the parameters given in the text.

pole splitting parameter ΔE_Q of the complexes in accordance with the observed and calculated diamagnetic $\{(d_{xy})^2(d_{x^2-y^2})^2\}$ $\{(d_{z^2})^0(d_{xz})^0(d_{yz})^0\}$ electron ground state configuration (Figure 3).
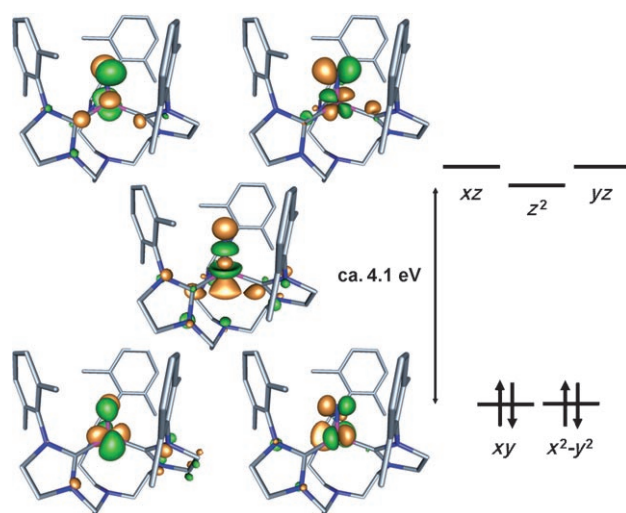

Figure 3. Electronic structure of **4**[R], $S = 0$ (DFT, ORCA, B3LYP). Computed structural parameters (BP86): Fe—N1 3.278, Fe—N8 1.517, Fe—C_{av} 1.949 Å; ∢(N8-Fe-C) 103.1°.

In contrast to this striking similarity in ΔE_Q values, the isomer shift $\delta = -0.27(1)$ mm s^{-1} of **4**[mes] differs significantly from that reported for [(PhB^{iPr}P$_3$)Fe(N)] ($\delta = -0.34$ mm s^{-1}). 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 δ indicates that the iron ion in **4**[mes] is less oxidized than the tetrahedral iron center in [(PhB^{iPr}P$_3$)Fe(N)]. This is likely a consequence of a certain degree of ligand-to-metal back bonding from the NHC ligand π system to empty iron d orbitals in trigonal-pyramidal **4**[mes]. While it is intuitive that the electronic structure of four-coordinate iron nitride complexes is dominated by the strong Fe≡N 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 tetradentate 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 [(TIMEN^R)Fe≡N]$^+$ and the tan-colored, more tetrahedral, [(PhB^{iPr}P$_3$)Fe≡N] complex prone to dimerization. To gain a better understanding of the intricate electronic structure of **4**[R], 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≡N bonds are short at 1.53 Å, and the high-valent Fe^{IV} centers in these molecules possess trigonal-pyramidal coordination environments. The molecular structures of iron nitride complexes **4**[R] 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**[R] 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**[R] 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.

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[12] Data were collected at 100 K on a Bruker Nonius KappaCCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, graphite monochromator). Structures were solved by direct methods and refined on F^2 using full-matrix least-squares techniques. For **3mes**·2.5 THF: triclinic, $P\bar{1}$, $a = 11.3035(5)$, $b = 17.725(2)$, $c = 17.831(2)$ Å, $\alpha = 88.056(10)$, $\beta = 76.821(6)$, $\gamma = 78.047(7)°$, $V = 3402.7(6)$ Å^3, $Z = 2$, $R_1 = 0.0516$ [$I > 2\sigma(I)$], $wR_2 = 0.1292$ (all data). For **4mes**·Et$_2$O: triclinic, $P\bar{1}$, $a = 12.432(2)$, $b = 12.632(2)$, $c = 22.614(3)$ Å, $\alpha = 80.104(13)$, $\beta = 84.734(9)$, $\gamma = 61.303(7)°$, $V = 3068.6(8)$ Å^3, $Z = 2$, $R_1 = 0.0450$ [$I > 2\sigma(I)$], $wR_2 = 0.0938$ (all data). CCDC-676549 (for **3mes**·2.5 THF), CCDC-676550 (for **4mes**·Et$_2$O), CCDC-676551 (for **3^{xyl}**·MeCN), and CCDC-676552 (for **4^{xyl}**·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.

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