

Chapter 2

TIMEN^{mes}: An Iron Nitride Complex

2.1 Introduction

Coordination compounds of iron in high oxidation states have been invoked as reactive intermediates in biocatalyses. Iron(IV) ferryl species are examples of highly reactive compounds 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 and electronic 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 $\equiv$ N species [3–10], X-ray crystallographic characterization of a complex with a terminal Fe $\equiv$ N functionality has not been accomplished [11, 12]. The first mononuclear Fe(IV)=O entity crystallographically characterized was stabilized in an octahedral environment provided by a macrocyclic *tetra*-N-methylated cyclam ligand [13]. 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 [4, 5, 8]. Recently, Peters and Betley developed a stunningly redox-rich iron system employing the tripodal *tris*(phosphino)borate ligand system (PhB^RP₃[−]), which stabilizes tetrahedral L₃Fe=N_x species in oxidation states ranging from +I to +IV [11]. 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)–N₂–Fe(I) dinuclear product, however, prevents crystallization of this nitride species.

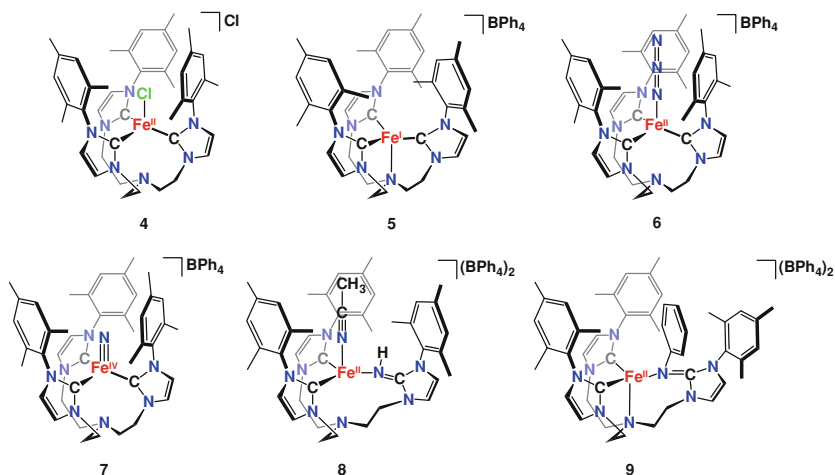


Chart 2.1 Overview of the iron complexes derived from the tripodal TIMEN^{mes} ligand

Inspired by this work, we sought to prepare an iron nitride by employing the sterically more encumbering N-anchored *tris*(carbene) ligand, *tris*[2-(3-mesityl-imidazol-2-ylidene)ethyl]amine (TIMEN^{mes}, mesityl (mes)) [14].

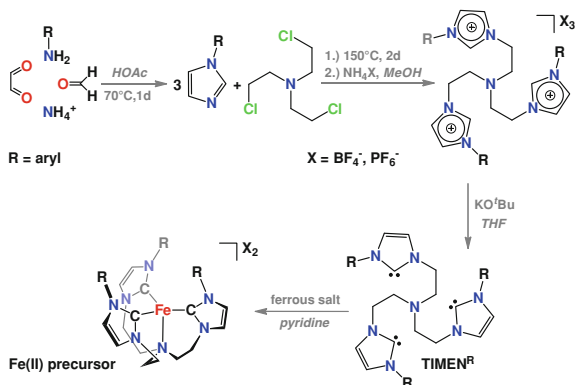
This chapter deals with the synthesis, spectroscopy, and most significantly, the X-ray diffraction analysis of a discrete iron nitride complex. Chart 2.1 gives an overview of the series of iron complexes bearing the TIMEN^{mes} ligand, which were synthesized and characterized in this context.

2.2 Results and Discussion

2.2.1 General Synthetic Procedure for the Precursors of the TIMEN^R System

Only a few N-substituted imidazoles such as the N-methyl and N-benzyl imidazoles are commercially available. For custom-tailored ligand environments with varying steric demand, it is therefore inevitable to synthesize the desired imidazoles by one-pot condensation reactions of aryl amine, formaldehyde, glyoxal, and ammonium acetate [15]. In the course of this work, the imidazolium precursors, *tris*-[2-(3-arylimidazolium)ethyl]amine [H₃TIMEN^R]³⁺ (R = mesityl (mes), tolyl (tol), 3,5-xylyl (3,5xyl) 3,5-trifluoromethylphenyl (3,5CF₃)) were prepared by quaternization of the functionalized N-arylimidazoles with *tris*(chloroethyl)amine (Scheme 2.1) [16]. Chart 2.2 gives an overview of all TIMEN^R ligands available to date.

Scheme 2.1 Synthesis of TIMEN^R and the Fe(II) precursor complexes



Treatment of [H₃TIMEN^R](Cl)₃ in methanol with ammonium hexafluorophosphate results in complete substitution of chloride and formation of [H₃TIMEN^R](PF₆)₃. Deprotonation of the imidazolium precursors with a strong base, like potassium *tert*-butoxide, yields the free *tris*(carbene) ligands TIMEN^R (*tris*-[2-(3-*aryl*-imidazol-2-ylidene)-ethyl]-amine), which can be isolated and stored under nitrogen. However, it is difficult to remove the deprotonation byproduct *tert*-butanol. The free carbenes are highly soluble in Et₂O and THF and even slightly soluble in hexane and *n*-pentane. Thus, there is no possibility to remove the alcohol by washing and because of the high boiling point it is difficult to remove *tert*-butanol *in vacuo*. This is also the reason why there is no exact yield of the carbene specified in the experimental section. The free *tris*(carbene) ligands were characterized by ¹H- and ¹³C-NMR spectroscopy. The characteristic ¹³C-NMR signals for the deprotonated carbene carbon atoms can be found between 210 and 215 ppm. After deprotonation of the imidazolium salt, the free carbene can be treated with ferrous chloride which yields an iron(II) complex. Depending on the solvent used in the synthesis, the remaining *tert*-butanol can cause further problems. Using pyridine, which acts as a mild base, coordination of the iron ion by the carbene ligand occurs smoothly. By changing the solvent from pyridine to Et₂O and THF, the mixture of *tert*-butanol and ferrous chloride creates acidic conditions, which result in protonation of the carbene. This back reaction reforms the imidazolium precursor faster than the free carbene is able to chelate to the iron center.

2.2.2 The TIMEN^{mes} Ligand and its Coordination to Iron: Synthesis Towards an Elusive Iron Nitride Complex

Under inert atmosphere, treatment of TIMEN^{mes} (2.3) with one equivalent of anhydrous ferrous chloride in pyridine at room temperature yields the four-coordinate Fe(II) complex [(TIMEN^{mes})Fe(Cl)]Cl (2.4) as analytically pure,

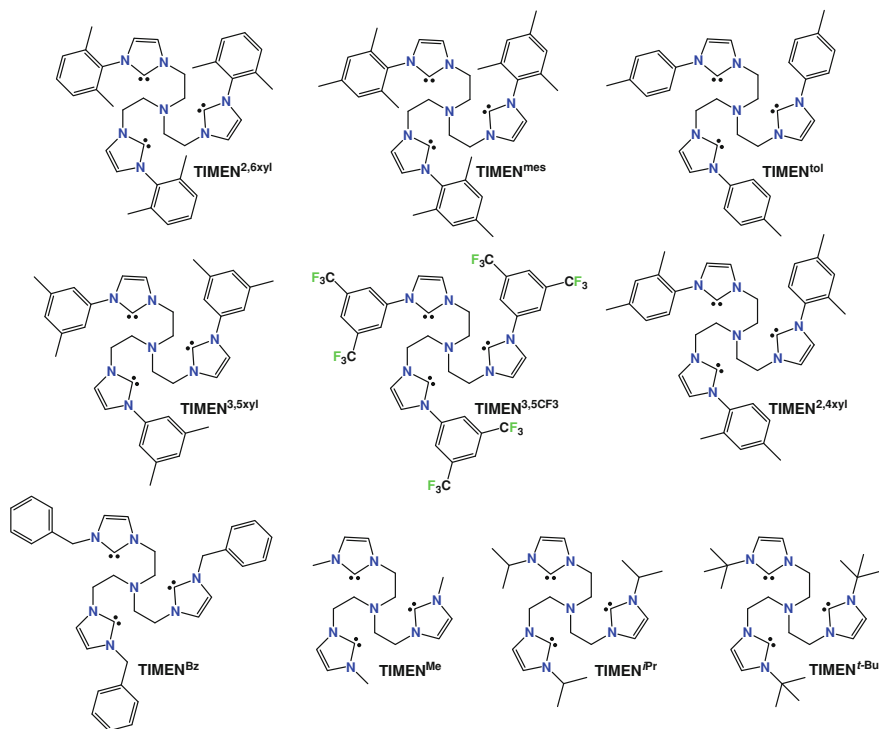


Chart 2.2 Overview of the tripodal TIMEN^R ligand family

white powder in 80% yield (Scheme 2.1). The ¹H-NMR spectrum of **4** in solution is consistent with a paramagnetic high-spin iron(II) complex. It shows eleven paramagnetically shifted resonances in the range between −6 and 78 ppm. Only three signals at 5.14, −0.32 and −5.90 ppm, which belong to the methyl groups at the aryl rings, can be clearly assigned due to peak integration (Fig. 2.1).

The zero-field Mößbauer spectrum of **4** is shown in Fig. 2.2. This spectrum recorded from a crystalline sample of **4** at 77 K displays a quadrupole doublet with an isomer shift $\delta = 0.71(1) \text{ mm s}^{-1}$, a quadrupole splitting parameter $\Delta E_Q = 1.78(1) \text{ mm s}^{-1}$, and a line width $\Gamma_{\text{FWHM}} = 0.32(1) \text{ mm s}^{-1}$. These parameters are characteristic of a four-coordinate d^6 high-spin ($S = 2$) Fe(II) complex [17]. The SQUID magnetization measurements of **4** also confirm an $S = 2$ ground state for this high-spin Fe(II) complex (see Fig. 2.3).

The molecular structure shows the iron center to coordinate in a distorted trigonal pyramidal fashion. A long Fe1...N1 distance of 3.008(3) Å indicates that the nitrogen anchor is non-coordinating, while the three carbene carbon atoms bind with a mean bond distance of 2.135 Å. The iron center is 0.439(2) Å above the trigonal plane, defined by the three carbene carbon atoms. For the deviation of the iron center from the carbene plane the term out-of-plane (oop) shift, $d_{\text{Fe oop}}$ has

Fig. 2.1 ^1H -NMR spectrum of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) (recorded in $\text{DMSO}-d_6$ at RT)

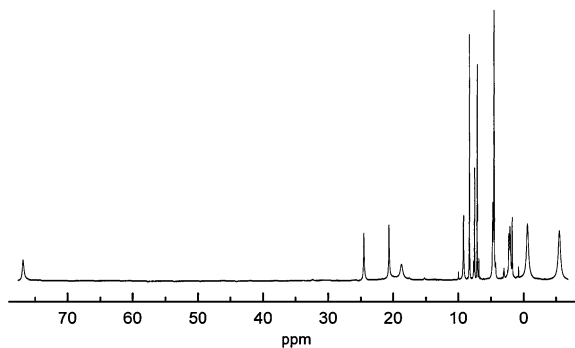


Fig. 2.2 Zero-field Mößbauer spectrum of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) (recorded in solid state at 77 K; $\delta = 0.71(1) \text{ mm s}^{-1}$, $\Delta E_Q = 1.78(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.32(1) \text{ mm s}^{-1}$)

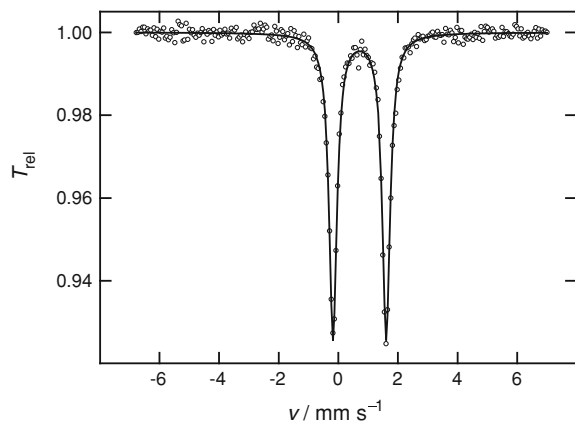
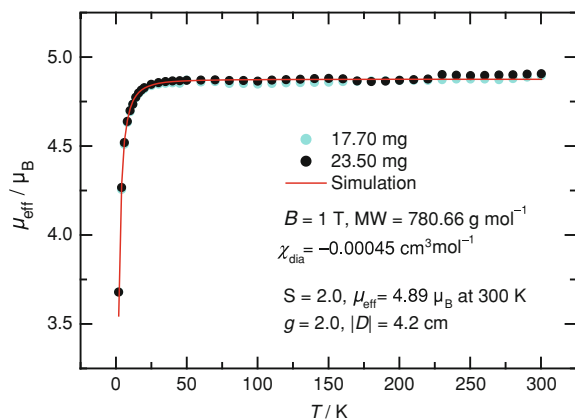


Fig. 2.3 Plot of the effective magnetic moment, μ_{eff} , versus temperature from SQUID magnetization measurements for two independently prepared samples of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) ($\mu_{\text{eff}} = 4.89 \mu_{\text{B}}$ at 300 K, simulated parameters: $g = 2.0$, $|D| = 4.2 \text{ cm}^{-1}$, diamagnetic impurity = 1.0%)



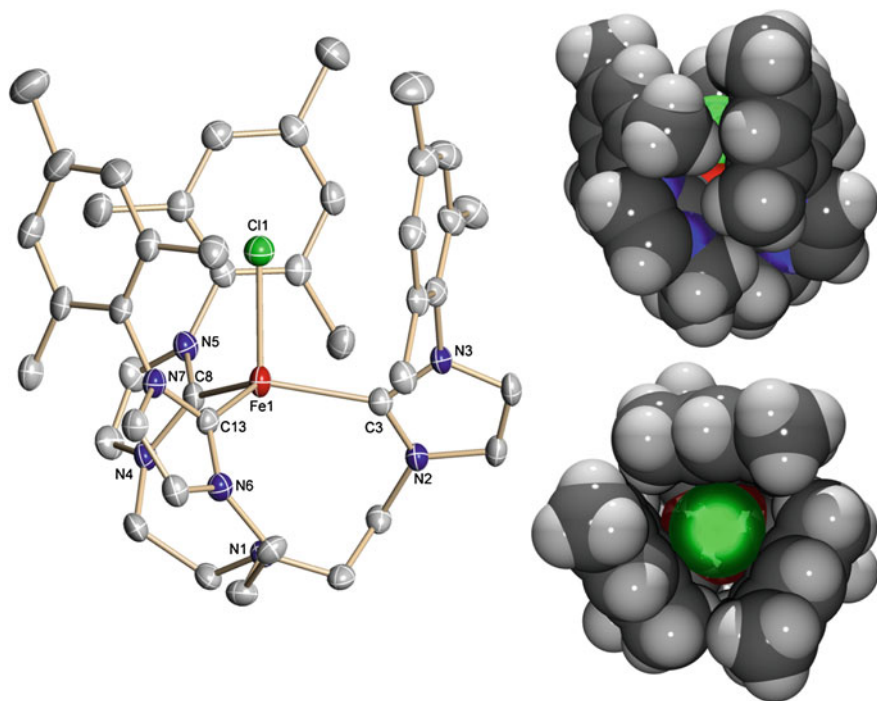
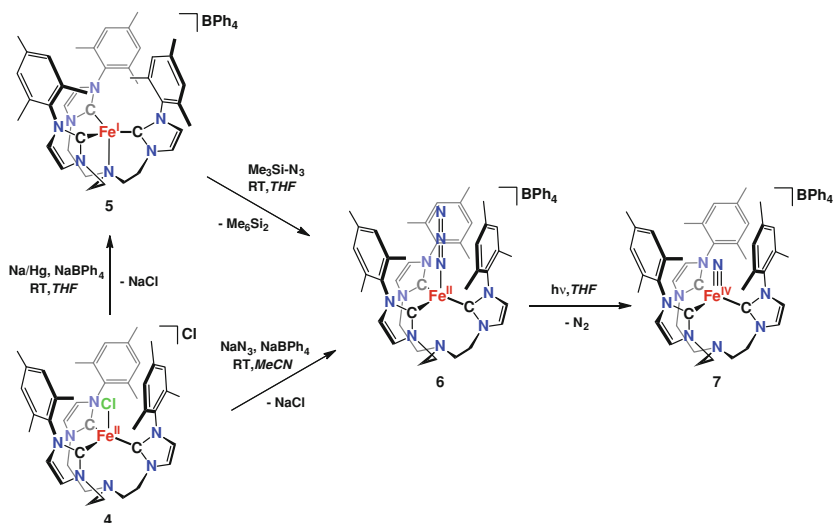


Fig. 2.4 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) in crystals of $4 \cdot 3$ MeCN (50% probability ellipsoids). Hydrogen atoms, Cl^- anion, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **4** *side view* (right, top) and *top view* (right, bottom). Selected bond distances ($\text{\AA}$): Fe1–Cl1 2.2768(8), Fe1–C3 2.128(3), Fe1–C8 2.138(3), Fe1–C13 2.138(2), Fe1 $\cdots$ N1 3.008(3), $d_{\text{Fe oop}}$ 0.439(2)

been established. The axial chloro ligand occupies the protective cavity formed by the three mesityl substituents (for principle bond distances see Fig. 2.4).

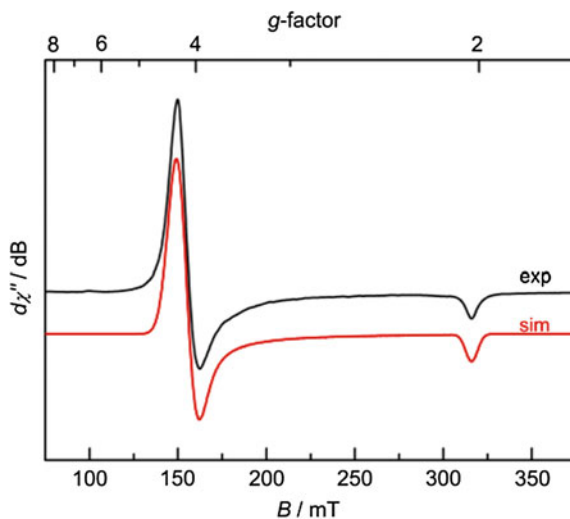
Reduction of the Fe(II) precursor complex **4** over sodium amalgam in a solution of NaBPh_4 in THF leads to the formation of deep red solutions of the reduced compound. The reaction mixture was stirred over night, the solution was filtered, concentrated, and cooled to -35°C to yield dark red crystals of the Fe(I) complex $[(\text{TIMEN}^{\text{mes}})\text{Fe}]\text{BPh}_4$ (**5**, Scheme 2.2). Compound **5** is NMR silent but EPR active. An axial EPR spectrum with g -values of 4.20 and 2.025 confirms the $S = 3/2$ ground state of this molecule (Fig. 2.5).

The zero-field Mößbauer spectrum of **5** is shown in Fig. 2.6. The spectrum of a crystalline sample of **5** at 77 K displays a quadrupole doublet with an isomer shift $\delta = 0.64(1) \text{ mm s}^{-1}$, a quadrupole splitting parameter $\Delta E_{\text{Q}} = 2.34(1) \text{ mm s}^{-1}$, and a line width $\Gamma_{\text{FWHM}} = 0.29(1) \text{ mm s}^{-1}$. The results of a single crystal X-ray analysis show that the molecular structure of the core-complex of the $[(\text{TIMEN}^{\text{mes}}\text{Fe})^+]$ system is barely changed upon reduction (Fig. 2.7).



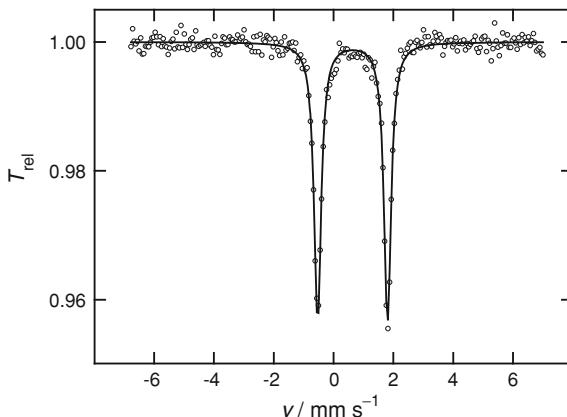
Scheme 2.2 Synthetic routes towards the iron(IV) nitride complex $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (**7**)

Fig. 2.5 X-band EPR spectrum of $[(\text{TIMEN}^{\text{mes}})\text{Fe}]\text{BPh}_4$ (**5**) recorded in frozen acetonitrile solution at 14 K, $\nu = 8.962$ GHz, $P = 0.998$ mW, $S = 3/2$, $g_{\perp} = 4.2$, $g_{\parallel} = 2.025$, $\Delta H_{1/2\perp} = 6.7$ mT, $\Delta H_{1/2\parallel} = 4.0$ mT [18]



However, upon chloride removal the nitrogen anchor binds to the iron center. This is indicated by the shortened Fe1–N1 bond distance of 2.275(2) Å. Also interesting to mention is the observation that the mean value of the iron carbene distances shortens significantly upon reduction from 2.135(3) Å in the Fe(II) complex **5** to 2.023(2) Å in the Fe(I) species **4**. This can be accounted to strong π -backbonding within the iron carbene bond. A similar trend is observed in the

Fig. 2.6 Zero-field Mößbauer spectrum of [(TIMEN^{mes})Fe]BPh₄ (**5**) (recorded in solid state at 77 K; $\delta = 0.64(1) \text{ mm s}^{-1}$, $\Delta E_Q = 2.34(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.29(1) \text{ mm s}^{-1}$)



Mößbauer spectrum, where the isomer shift changes in an opposite direction to what is expected. The isomer shift allows conclusions on possible oxidation states of the examined compounds. It is generally applicable that with increasing electron density at the ^{57}Fe nucleus the isomer shift, δ , becomes more negative. Going from elemental iron with an $[\text{Ar}]3d^64s^2$ electron configuration to Fe(IV), first of all the $4s$ electrons are removed. Fe(II) compounds with an $[\text{Ar}]3d^6$ electron configuration have no $4s$ electrons left. Upon further oxidation the $3d$ electrons, which predominantly influence the electron density at the nucleus, are removed. The closer the outer electron can get to the nucleus, the more it can penetrate the density distribution of the inner shell electrons and the atomic nucleus. For many purposes, atomic nuclei can be treated as mathematical point charges. But when electrons penetrate the nuclear volume the shape and size of the nucleus does play a role. The usual “far-field” approximation is then invalid and these “near-field” effects lead to small corrections to all terms in the multipole expansion for the electrostatic interaction between nuclei and electrons. The correction to the monopole term corresponds to experimentally well-known phenomena: the isotope shift in atomic spectroscopy and of particular interest here, the isomer shift in Mößbauer spectroscopy [19]. Because of the possibility that electrons, mainly s electrons, can penetrate into the nucleus one could speak of an electron density at the nucleus, expressed by the square wave function at the position $r = 0$, $\psi(0)^2$. The electrostatic interaction between nucleus and electron (electric monopole interaction) changes the energy level of the nucleus. The volume of the nucleus in the excited state is different from that in the ground state, and therefore, also the strength of the electric monopole interaction differs in both states. The consequence is a different shift of the energy level of the ground state and the excited state. The virtual transition energy E_0 (the required energy for the nuclear transition between the ground state and the excited state, without any perturbation and interaction), is then exchanged by the real transition energies E_S (emitting nucleus, excited state; radiation source) and E_A (absorber nucleus, ground state; sample).

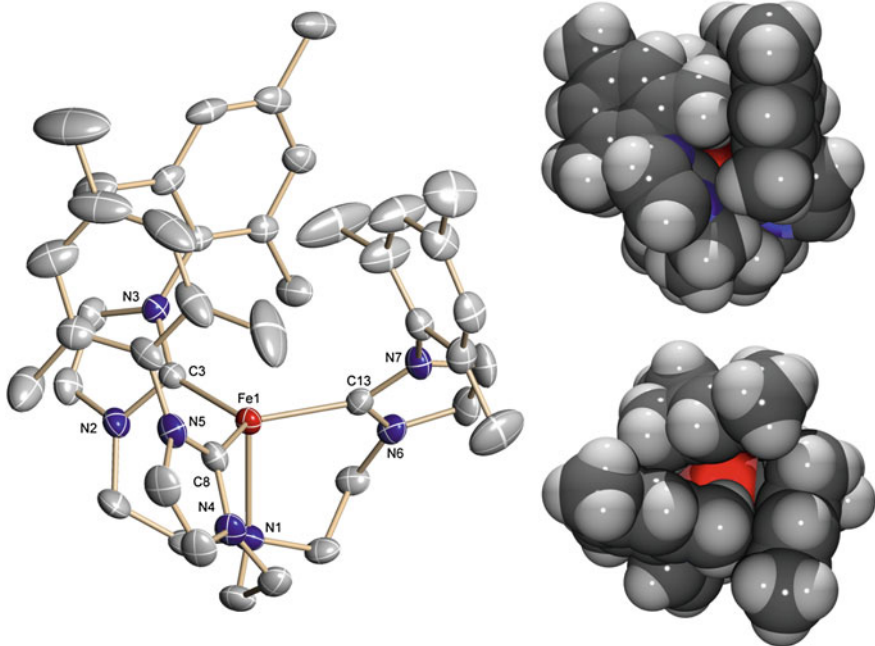


Fig. 2.7 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}})\text{Fe}]\text{BPh}_4$ (**5**) in crystals of $5 \cdot 2 \text{ THF} \cdot 0.5 \text{ Et}_2\text{O}$ (50% probability ellipsoids). Hydrogen atoms, BPh_4^- anion, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **5** *side view* (right, top) and *top view* (right, bottom). Selected bond distances (Å): Fe1–C3 2.032(2), Fe1–C8 2.024(2), Fe1–C13 2.012(2), Fe1–N1 2.275(2), $d_{\text{Fe oop}}$ 0.191(2)

The differences

$$\Delta E(\text{S}) = E_{\text{S}} - E_0 = \text{const} \cdot |\psi(0)|_{\text{E}}^2 \cdot \left(R_{\text{e}}^2 - R_{\text{g}}^2 \right) \quad (2.1)$$

$$\text{and } \Delta E(\text{A}) = E_{\text{A}} - E_0 = \text{const} \cdot |\psi(0)|_{\text{A}}^2 \cdot \left(R_{\text{e}}^2 - R_{\text{g}}^2 \right) \quad (2.2)$$

are determined by two factors, the electron density at the nucleus and the different spatial dimensions of the nucleus in the excited and the ground state (expressed by the difference of the mean square nuclear radii: $R_{\text{e}}^2 - R_{\text{g}}^2$). If the environment of the Mößbauer nucleus differs in the radiation source and the absorber, the electron density at the nuclei are different ($|\psi(0)|_{\text{E}}^2 \neq |\psi(0)|_{\text{e}}^2$); thus the energy differences $\Delta E(\text{S})$ and $\Delta E(\text{A})$ are unequal aswell. The difference is the isomer shift, δ , which can be measured.

$$\delta = \Delta E(\text{A}) - \Delta E(\text{S}) = E_{\text{A}} - E_{\text{S}} \quad (2.3)$$

$$\delta = \text{const} \cdot \left\{ |\psi(0)|_{\text{A}}^2 - |\psi(0)|_{\text{S}}^2 \right\} \cdot \left(R_{\text{e}}^2 - R_{\text{g}}^2 \right) \quad (2.4)$$

The factor ($R_e^2 - R_g^2$) in (2.4) of the isomer shift is a negative term in case of the Mößbauer nucleus ^{57}Fe . Accordingly, the shift values for Fe(IV) species with high oxidation state are at the negative end of the scale, whereas low-valent iron compounds have more positive isomer shifts [20, 21]. As a result, it can be expected when going from Fe(II) to Fe(I) the isomer shift should increase with decreasing oxidation state; however, the reverse is observed. Again, π -backbonding within the iron carbene bond causes this effect. The more electron density is withdrawn by π -backbonding out of the 3d orbitals the less is the shielding of the nucleus. This explains the more negative isomer shift of the Fe(I) species **5** compared to its Fe(II) counterpart **4**.

The Fe(I) compound **5** is highly reactive towards oxygen and moisture. Complex **5** can easily be oxidized, even by chlorinated solvents like chloroform and methylene chloride. Addition of excess trimethylsilyl azide to the Fe(I) complex **5** in THF results in elimination of Me_6Si_2 and formation of a light yellow solution, from which pale yellow crystals of divalent [(TIMEN^{mes})Fe(N₃)]BPh₄ (**6**, Scheme 2.2) can be isolated in 79% yield.

In search of an alternative synthetic route for the preparation of the ^{15}N labeled azide complex, it turned out that a salt metathesis reaction between the Fe(II) chloro precursor **4** and an excess of sodium azide also yields **6**. The azide complex is easily identified by the intense and very characteristic $\nu_{\text{as}}(\text{N}_3)$ IR vibrational band at $2,094\text{ cm}^{-1}$. The crystal structure of compound **6** (see Fig. 2.8) features an unusual, close to linear azide coordination ($\angle(\text{Fe}-\text{N}_\alpha-\text{N}_\beta) = 174.5(2)^\circ$ in **6**) at the Fe(II) *tris*(carbene) complex. Such linear azide coordination to a metal center is rare but has been observed before in sterically demanding ligand environments, in which similar cylindrical cavities are generated around the metal center [22]. The Fe–N_α azide distance in **6** is determined to be $1.947(2)\text{ Å}$. The amine anchor is not bound [$d(\text{Fe}\cdots\text{N1}) = 3.244(2)\text{ Å}$] leaving the Fe(II) ion in a trigonal-pyramidal coordination environment, in which the metal center is located $0.554(2)\text{ Å}$ above the trigonal plane formed by the three carbene carbon donor atoms of the NHC ligand.

The azide compound **6** is light sensitive and readily releases dinitrogen to form the deeply purple colored product [(TIMEN^{mes})Fe(N)]BPh₄ (**7**, Scheme 2.2). Accordingly, exposure of a pale yellow solution of **6** in THF to the light of a Xenon arc lamp at room temperature results in gradual formation of a purple solution and N₂ gas evolution. While the electronic absorption spectrum of the colorless azide complex **6** is featureless in the visible region, the spectrum of the photolysis product **7** (Fig. 2.9) shows an intense absorption band centered at $\lambda_{\text{max}} 520\text{ nm}$ ($\varepsilon = 1,980\text{ M}^{-1}\text{ cm}^{-1}$) and given rise to the purple color.

Photolysis of the iron azide **6** was continued until no more gas evolution was observed and the azide vibrational band could no longer be observed by IR spectroscopy (see Fig. 2.10). Instead, in the spectrum of the purple photolysis product a new band appeared at $1,008\text{ cm}^{-1}$, which is assigned to the iron nitride band $\nu(\text{Fe}\equiv^{14}\text{N})$.

Samples of the ^{15}N -labeled isotopomer (50% ^{15}N -labeled at the terminal nitride) show an additional band at 982 cm^{-1} (Fig. 2.10). This 26 cm^{-1} shift of

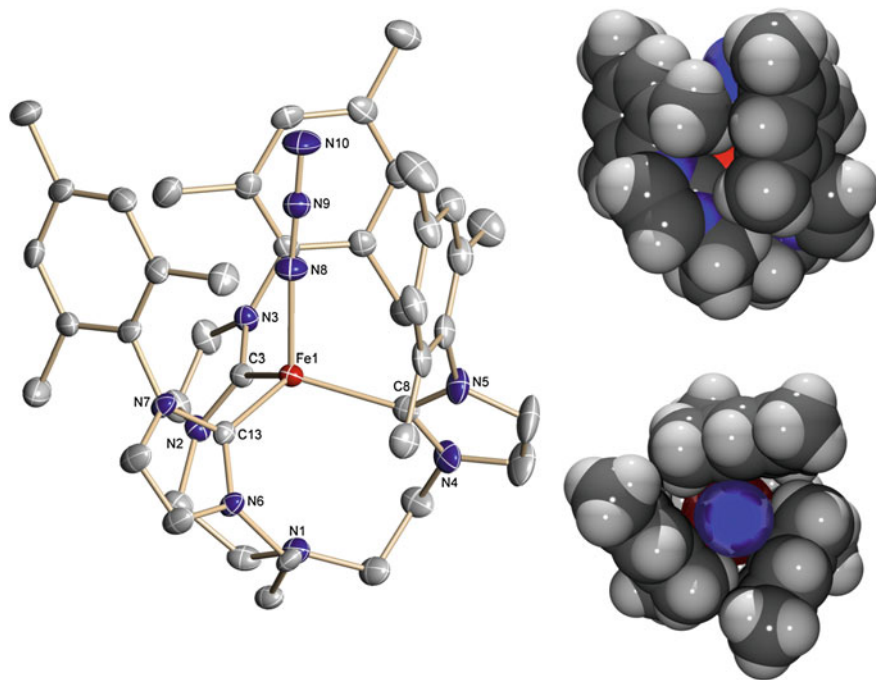


Fig. 2.8 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N}_3)]\text{BPh}_4$ (**6**) in crystals of $6 \cdot 2.5$ THF (50% probability ellipsoids). Hydrogen atoms, BPh_4^- anion, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **6** *side view* (right, *top*) and *top view* (right, *bottom*). Selected bond distances and angles ($\text{\AA}$, $^\circ$): Fe1–N8 1.947(2), Fe1–C3 2.104(2), Fe1–C8 2.110(3), Fe1–C13 2.111(2), Fe1...N1 3.244(2), $d_{\text{Fe oop}}$ 0.554(2), Fe1–N8–N9 174.5(2), N8–N9–N10 179.6(3)

Fig. 2.9 Electronic absorption spectra of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N}_3)]\text{BPh}_4$ (**6**) (black) and $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (**7**) (magenta), recorded in THF

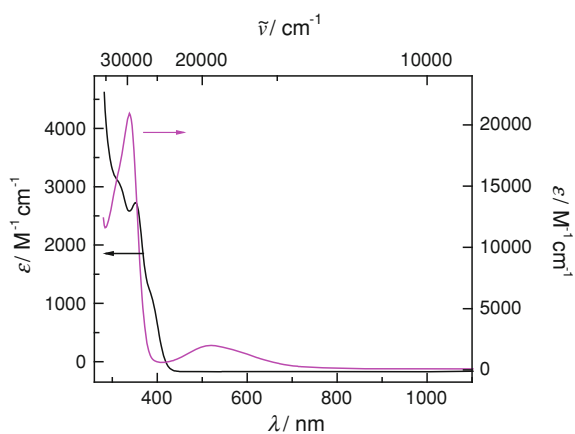
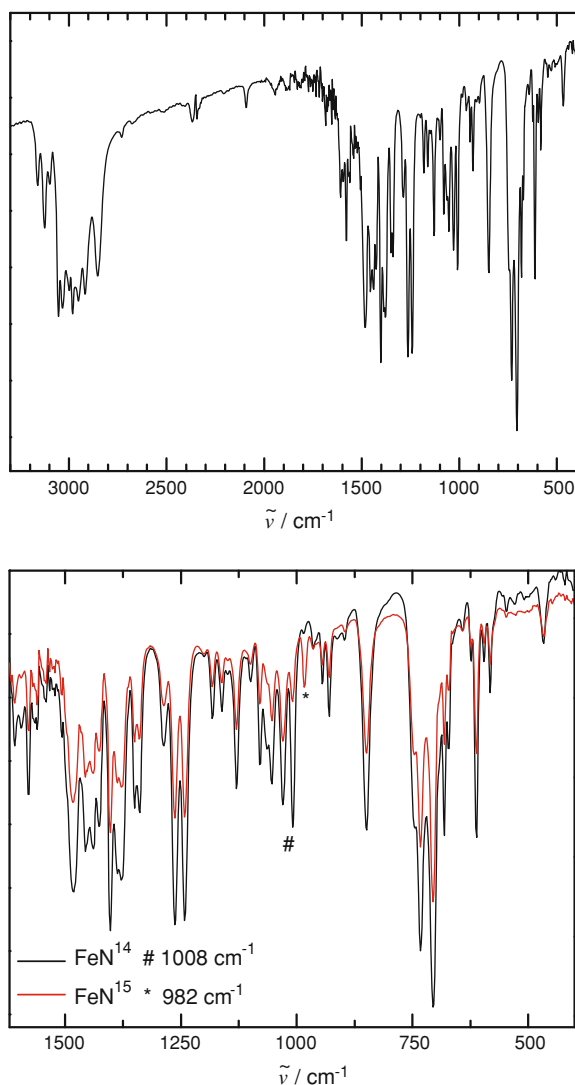


Fig. 2.10 *Top*: IR spectrum of [(TIMEN^{mes})Fe(N)]BPh₄ (**7**) (KBr pellet); *bottom*: IR spectrum of [(TIMEN^{mes})Fe(¹⁴N)]BPh₄ (black) and ¹⁵N-labeled isotopomer [(TIMEN^{mes})Fe(¹⁵N)]BPh₄ (red, 50% ¹⁵N-labeled at the terminal nitride)



the $\nu(\text{Fe}\equiv^{15}\text{N})$ stretch to lower frequency is predicted from the reduced mass calculation for a harmonic oscillator (calcd: 28 cm⁻¹). In the ¹H-NMR spectrum (Fig. 2.11) the purple, diamagnetic reaction product shows the expected resonances for the functionalized *tris*(carbene) chelator coordinated to the iron center of **7**. Additionally, the ¹⁵N-NMR spectrum of ¹⁵N-labeled **7** (Fig. 2.12) exhibits a resonance signal at $\delta = 1,121$ ppm (referenced to NH₃). Slow diffusion of diethyl ether into a THF solution of **7** yields purple crystals that are air stable at room temperature and suitable for an X-ray structure analysis.

Fig. 2.11 ^1H -NMR spectrum of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (**7**) (recorded in $\text{DMSO}-d_6$ at RT)

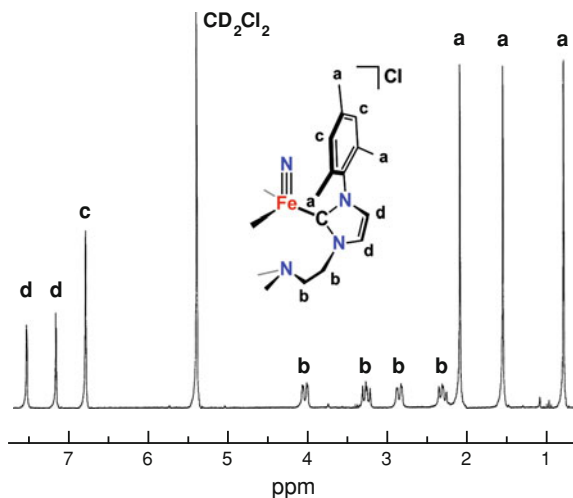
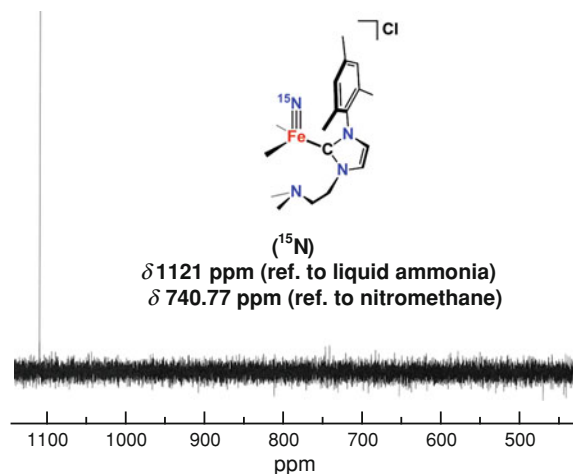


Fig. 2.12 ^{15}N -NMR spectrum of ^{15}N -labeled isotopomer $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (**7**) (recorded in $\text{DMSO}-d_6$ at RT)



The molecular structure of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (Fig. 2.13) confirms the light-induced transformation of the axial azide to a terminal nitride ligand with a short $\text{Fe}\equiv\text{N}$ bond of 1.526(2) Å. Such short $\text{M}\equiv\text{N}$ distances are typically observed for transition-metal complexes with triply bonded nitride ligands ($\text{M}=\text{Cr}$, Mn) [8, 23–26]. The $\text{Fe}\equiv\text{N}$ distance in **7** is also very similar to the XAS spectroscopically determined distances of the $\text{Fe}(\text{IV})$ complexes $[(\text{PhB}^{\text{R}}\text{P}_3)\text{Fe}(\text{N})]$ [$d(\text{Fe}\equiv\text{N}) = 1.51\text{--}1.55(2)$ Å, $\text{R} = i\text{-Pr}$, $\text{CH}_2\text{-Cy}$] by Peters and co-workers, and of the octahedral $\text{Fe}(\text{VI})$ nitrido species $[(\text{Me}_3\text{cy-ac})\text{Fe}(\text{N})]$ [$d(\text{Fe}\equiv\text{N}) = 1.57$ Å] reported by Wieghardt and co-workers [4]. As observed for the $\text{Fe}(\text{II})$ azide precursor **6**, the iron center in the nitrido complex **7** is coordinated in a trigonal-pyramidal fashion but with the $\text{Fe}(\text{IV})$ ion located at only 0.427(3) Å above the

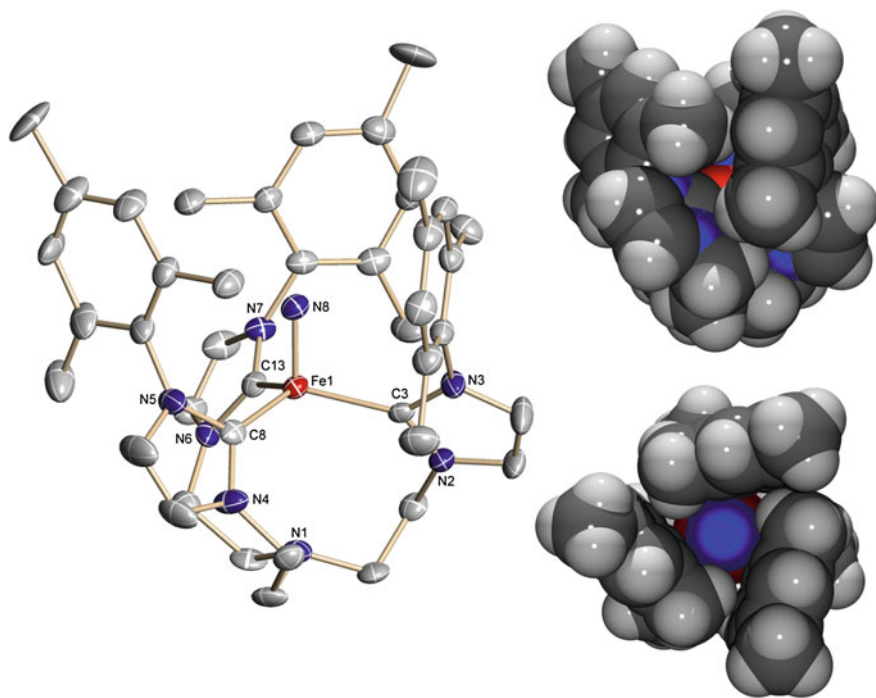


Fig. 2.13 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N})]\text{BPh}_4$ (**7**) in crystals of **7** · Et₂O (50% probability ellipsoids). Hydrogen atoms, BPh₄[−] anion, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **7** *side view* (right, top) and *top view* (right, bottom). Selected bond distances (Å): Fe1–N8 1.526(2), Fe1–C3 1.987(3), Fe1–C8 1.955(5), Fe1–C13 1.946(4), Fe1···N1 3.120(2), $d_{\text{Fe oop}}$ 0.427(3)

trigonal *tris*(carbene) plane [in **6**: 0.554(2) Å]. Evidently, this smaller displacement from the trigonal coordination plane in **7** is a consequence of increased interaction of the anchoring amine nitrogen [$d(\text{Fe1} \cdots \text{N1}) = 3.120(2)$ Å in **7** versus 3.244(2) Å in **6**] and the carbene ligand with the high-valent Fe(IV) ion. This stronger coordination of the carbene in **7** is also reflected by a significantly shorter average Fe–C distance of 1.941(5) Å compared to the weaker binding in the Fe(II) azide precursor **6** with a $d(\text{Fe}–\text{C})_{\text{av}} = 2.108(2)$ Å.

The zero-field Mößbauer spectra of **6** and **7** are shown in Figs. 2.14 and 2.15.

The spectra of crystalline samples of **6** at 77 K display a quadrupole doublet with an isomer shift $\delta = 0.69(1)$ mm s^{−1}, a quadrupole splitting parameter $\Delta E_{\text{Q}} = 2.27(1)$ mm s^{−1}, and a line width $\Gamma_{\text{FWHM}} = 0.48(1)$ mm s^{−1}. These parameters are characteristic of four-coordinate d^6 high-spin ($S = 2$) Fe(II) complexes [17]. 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, the spectrum of **7** shows a sharp quadrupole doublet ($\Gamma_{\text{FWHM}} = 0.26(1)$ mm s^{−1}) with very unusual Mößbauer parameters of

Fig. 2.14 Zero-field Mößbauer spectrum of [(TIMEN^{mes})Fe(N₃)]BPh₄ (**6**) (recorded in solid state at 77 K; $\delta = 0.69(1) \text{ mm s}^{-1}$, $\Delta E_Q = 2.27(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.48(1) \text{ mm s}^{-1}$)

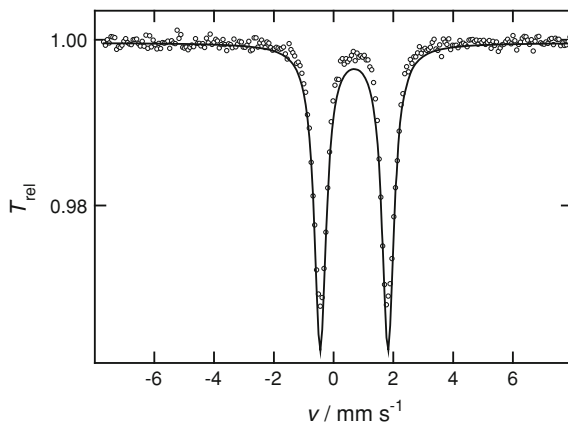
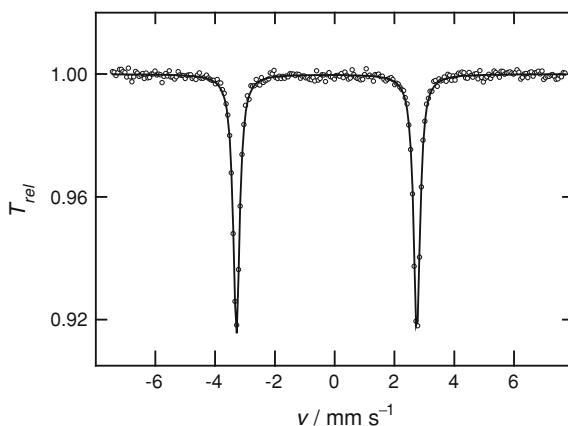


Fig. 2.15 Zero-field Mößbauer spectrum of [(TIMEN^{mes})Fe(N)]BPh₄ (**7**) (recorded in solid state at 77 K; $\delta = -0.27(1) \text{ mm s}^{-1}$, $\Delta E_Q = 6.04(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.26(1) \text{ mm s}^{-1}$)



$\delta = -0.27(1) \text{ mm s}^{-1}$ and $\Delta E_Q = 6.04(1) \text{ mm s}^{-1}$. The negative isomer shift and the remarkably large quadrupole splitting are consistent with values expected for a d^4 , $S = 0$ Fe(IV) $\equiv$ N species. In fact, the observed $\Delta E_Q = 6.04(1) \text{ mm s}^{-1}$ for **7** is very similar to that determined for the [(PhBⁱPrP₃)Fe(N)] system ($\Delta E_Q = 6.01(1) \text{ mm s}^{-1}$) [3]. In both cases, the valence and covalency contributions from the dominating Fe $\equiv$ N moiety affect the unusually large quadrupole splitting parameter ΔE_Q of the complexes in accordance with the observed and calculated diamagnetic $\{(d_{xy})^2(d_{x^2-y^2})^2\} \{(d_{z^2})^0(d_{xz})^0(d_{yz})^0\}$ ground state electronic configuration that has been computed exemplarily for the 2,6-xylyl derivative (Fig. 2.16).

The positive electron field gradient (EFG) derived from the applied field Mößbauer spectrum (Fig. 2.17) confirms the $\{(d_{xy})^2(d_{x^2-y^2})^2\}$ electron configuration and the asymmetry parameter $\eta = 0$, a measure of deviations from axial symmetry (e.g. towards tetragonal), confirms the three fold symmetry of the

Fig. 2.16 Electronic structure of [(TIMEN)^{2.6xy1}Fe(N)]BPh₄, $S = 0$ (DFT, ORCA, B3LYP). Computed structural parameters (BP86): Fe–N1 3.278 Å, Fe–N8 1.517 Å, Fe–C_{av} 1.949 Å; $\angle(\text{N8–Fe–C})$ 103.18°

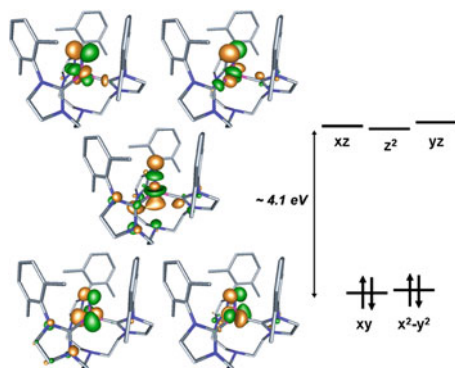
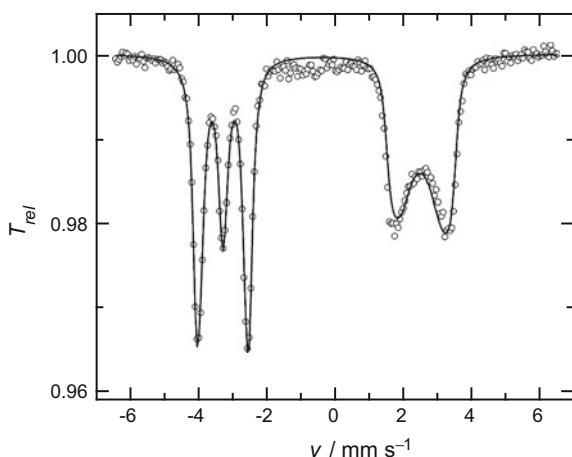


Fig. 2.17 Applied Field Mößbauer spectrum of [(TIMEN)^{mes}Fe(N)]BPh₄ (**7**) (recorded in solid state at 20 K, 6.5 T; $\eta = 0$)

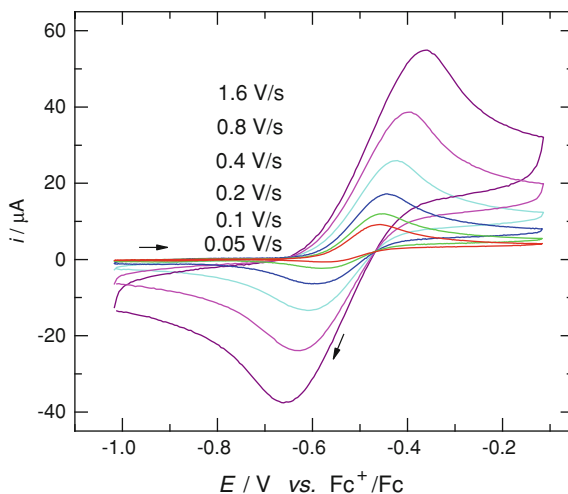


molecule. In contrast to the striking similarity of the ΔE_Q values, the isomer shift $\delta = -0.27(1) \text{ mm s}^{-1}$ of **7** differs significantly from that reported for [(PhB^{iPr}P₃)Fe(N)] ($\delta = -0.34 \text{ mm s}^{-1}$). Table 2.1 gives an overview of Mößbauer parameters obtained from the TIMEN^{mes} iron complex series.

The isomer shift determined by ⁵⁷Fe 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 **7** is less oxidized than the tetrahedrally coordinated iron center in [(PhB^{iPr}P₃)Fe(N)]. This is likely a consequence of a certain degree of ligand-to-metal back bonding from the NHC ligand's π -system to empty iron *d* orbitals in trigonal-pyramidal **7**. While it is intuitive that the electronic structure of the four-coordinate iron nitride complex is dominated by the strong Fe $\equiv$ N interaction, the different isomer shift clearly demonstrates that other factors, such as ligand-donor set and coordination geometry, ultimately determine the detailed electronic structure and the reactivity of high-valent iron nitride

Table 2.1 Mößbauer parameters of [(TIMEN^{mes})Fe(Cl)]Cl (**4**), [(TIMEN^{mes})Fe]BPh₄ (**5**), [(TIMEN^{mes})Fe(N₃)]BPh₄ (**6**), [(TIMEN^{mes})Fe(N)]BPh₄ (**7**)

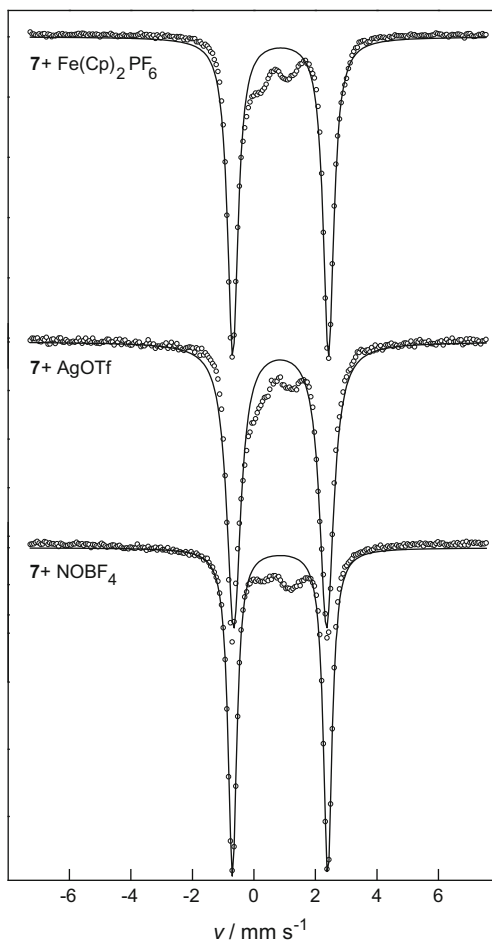
	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ_{FWHM} (mm s ⁻¹)
[(TIMEN ^{mes})Fe(Cl)]Cl (4)	0.71(1)	1.78(1)	0.32(1)
[(TIMEN ^{mes})Fe]BPh ₄ (5)	0.64(1)	2.34(1)	0.29(1)
[(TIMEN ^{mes})Fe(N ₃)]BPh ₄ (6)	0.69(1)	2.27(1)	0.48(1)
[(TIMEN ^{mes})Fe(N)]BPh ₄ (7)	-0.27(1)	6.04(1)	0.26(1)

Fig. 2.18 Cyclic voltammogram of [(TIMEN^{mes})Fe(N)]BPh₄ (**7**) recorded in THF solution containing 0.1 M TBAPF₆ electrolyte under N₂; working: glassy carbon, counter: Pt, pseudo-reference: Pt; internal standard: Fc⁺/Fc; $E(\text{Fc}^+/\text{Fc}) = 0.41$ V versus NHE

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 amino-carbene Fe(IV) nitride [(TIMEN^{mes})Fe(N)]⁺ (**7**) and the tan-colored, more tetrahedral, [(PhB^{iPr}P₃)Fe≡N] complex prone to dimerization. The high stability, not least due to steric shielding of the iron center in **7**, illustrated by the space filling model of the complex (Fig. 2.13), prevents reactivity studies of this molecule. The [FeN] moiety is well protected in the deep cylindrical cavity, thereby completely inhibiting a side access towards the axial ligand. By this means an atom transfer to a substrate is almost entirely prohibited or is only conceivable *via* an axial approach. On the basis of these considerations there are two starting points of increasing the reactivity. On one hand the steric demand of the ligand can be reduced; on the other hand the reactivity can be enhanced *via* manipulating its electronic properties. The redox behaviour of **7** was examined by electrochemical methods.

The cyclic voltammogram of a solution of **7** in THF exhibits a reversible one-electron oxidation at a potential of -0.515 V versus Fc/Fc⁺ (Fig. 2.18). Fe(IV) nitride complex **7**, dissolved in acetonitrile, was oxidized using different oxidizing agents such as [Fe(Cp)₂]₂PF₆, AgOTf and NOBF₄ at temperatures below -40 °C.

Fig. 2.19 Zero-field Mößbauer spectra of oxidation reaction products of [(TIMEN^{mes})Fe(N)]BPh₄ (**7**) with [Fe(Cp)₂]PF₆, AgOTf and NOBF₄ (⁵⁷Fe-enriched samples in acetonitrile solution, 77 K; $\delta = 0.85(1) \text{ mm s}^{-1}$, $\Delta E_Q = 3.10(1) \text{ mm s}^{-1}$)



All oxidizers were able to induce an immediate reaction indicated by a spontaneous color change from purple to light green. The reaction mixtures were cooled down to liquid nitrogen temperature after completion of the reaction. Figure 2.19 shows the zero-field Mößbauer spectra of the resulting compounds.

The spectra of the ⁵⁷Fe enriched samples in acetonitrile at 77 K display a quadrupole doublet with an isomer shift $\delta = 0.85(1) \text{ mm s}^{-1}$ and a quadrupole splitting parameter $\Delta E_Q = 3.10(1) \text{ mm s}^{-1}$. These parameters would match best to a four-coordinate *d*⁶ high-spin (*S* = 2) Fe(II) complex. The solutions of the obtained compounds are temperature sensitive and change color from light green to deep brown when stored at RT. Storage of the solutions at -35°C slows down the color change but can not prevent the process. According to NMR measurements of the solutions of the resulting products these compounds seem to be NMR silent. After several crystallization attempts, single crystals suitable for an X-ray

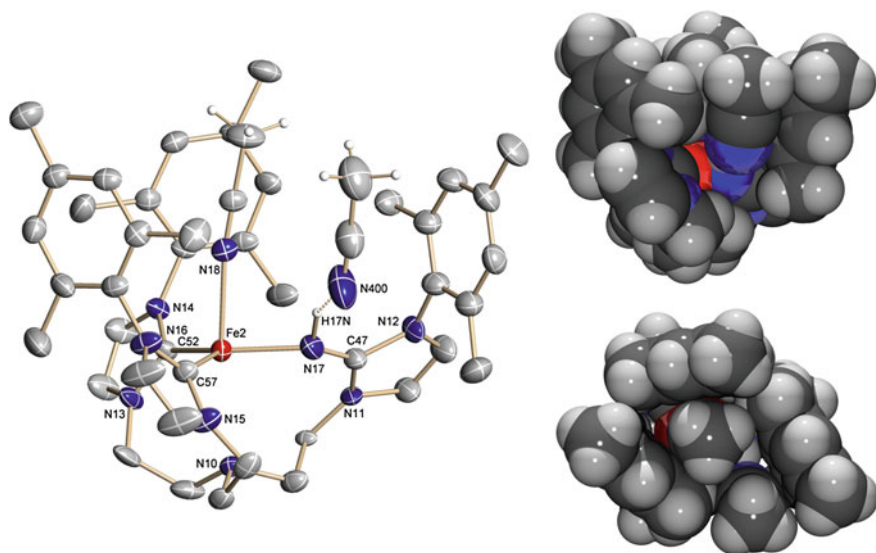
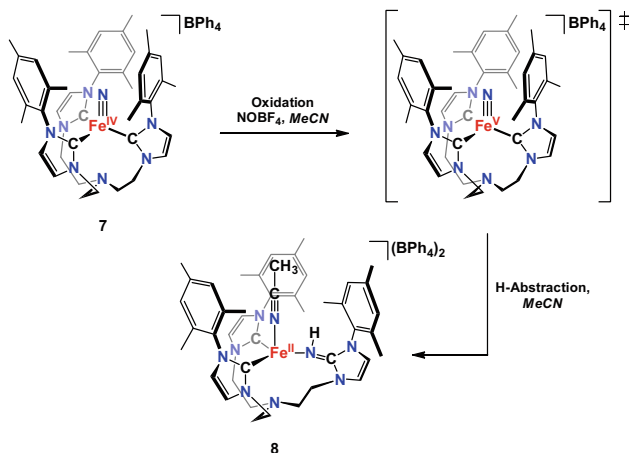


Fig. 2.20 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{H}})\text{Fe}(\text{MeCN})]\text{BPh}_4$ (**8**) in crystals of $[(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{H}})\text{Fe}(\text{MeCN})](\text{BPh}_4)_2 \cdot [(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{H}})\text{Fe}(\text{MeCN})](\text{BF}_4)(\text{BPh}_4) \cdot \text{Et}_2\text{O} \cdot 1.5 \text{ MeCN}$ (30% probability ellipsoids). Hydrogen atoms of the $\text{TIMEN}^{\text{mes}}$ ligand (except H17A), BPh_4^- anions, BF_4^- anion, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **8** *side view* (right, top) and *top view* (right, bottom). Selected bond distances (Å): Fe2–N18 2.237(3), Fe2–N17 2.005(3), N17–C47 1.341(9), N17–H17 N 1.00, Fe2–C52 2.091(4), Fe2–C57 2.097(4), Fe2–N10 2.585(4), $d_{\text{Fe oop}}$ 0.110(2)

structure analysis could be obtained at RT by slow diffusion of Et_2O into a MeCN solution.

The molecular structure of $[(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{H}})\text{Fe}(\text{MeCN})]\text{BPh}_4$ (**8**, Fig. 2.20) shows that the iron center is still coordinated in a trigonal-pyramidal fashion by the ligand, but a nitride insertion has occurred. The axially coordinated nitride ligand of **7** is inserted into one of the Fe–carbene bonds and the axial position is now occupied by an acetonitrile solvent molecule. After this insertion the original *tris*(carbene) ligand possesses two unaltered carbene ligand arms and one imidazol-2-imine moiety. It can be postulated that the reaction mechanism starts with the oxidation of the Fe(IV) nitride to an Fe(V) nitride species, followed by nitride insertion into one of the Fe–carbene bonds (Scheme 2.3). The immediate reaction product is most likely an iron(III) complex. After abstraction of a hydrogen atom, most probably from decomposition reactions of either the solvent or the iron complex, the compound is isolated as an Fe(II) imine species.

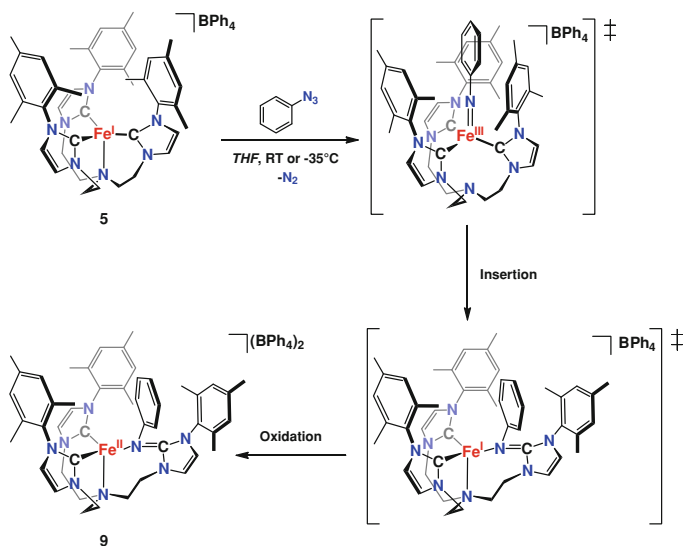
The insertion product could not be isolated in reasonable yields and appears to be formed only in trace amounts. The last step of the proposed mechanism, i.e. the hydrogen abstraction, could be the crucial point. If the hydrogen abstraction is hindered or too slow, the newly formed complex cannot be stabilized and undergoes decomposition. Attempts to facilitate the hydrogen abstraction by



Scheme 2.3 Insertion reaction of [(TIMEN^{mes})Fe(N)]BPh₄ (**7**) under oxidative conditions

addition of a hydrogen source, e.g. 1,4-cyclohexadiene, were unsuccessful and did not improve the yield. Therefore, **8** could only be detected by ESI-MS and characterized by X-ray crystal structure determination. The species observed by mass spectrometry is the insertion product, without the axially coordinated acetonitrile. There are other examples for insertion reactions with transition metal complexes bearing the TIMEN^R system. Treating [(TIMEN^{mes})Fe]BPh₄ (**5**) with an excess of phenyl azide in THF at RT, also yields an insertion product [(TIMEN^{mes}=N^{ph})Fe]BPh₄ (**9**, Scheme 2.4). During the reaction, gas evolution could be monitored, while the red solution, stemming from the Fe(I) species, turned brown. Again, the insertion product **9** was formed in low yield and could solely be characterized by X-ray crystal structure determination. The experiment was redone at -35°C , in order to obtain either the intermediate imido species or to improve the synthesis of the insertion product. Neither the isolation of the intermediate nor the improvement of the insertion reaction was possible by running the experiment at low temperature. Several attempts gave only a few crystals of the compound, thereby precluding an in-depth investigation of the complex. The molecular structure of **9** shows large similarities with **8** (Fig. 2.21; Table 2.2).

As observed for **8**, the TIMEN^{mes}=N^{ph} ligand coordinates to the iron center through two of its remaining carbenoid carbons, the anchoring nitrogen and the newly formed imine nitrogen atom. In contrast to **8**, no axial solvent molecule is bound due to steric hindrance exerted by the phenyl substituent at the imine nitrogen. As a result, when comparing complex **8** and **9** the most significant differences in the molecular structure are visible in the coordination sphere of the iron center. Without axially coordinated acetonitrile, the Fe1–N1 bond in complex **9** is 0.312 Å shorter than in complex **8**. The increase in bond strength is also reflected in the different out-of-plane shifts of **8** and **9**. Whereas in **8** the out-of-plane shift, $d_{\text{Fe oop}}$ is only 0.097(2) Å and directed towards the axially coordinated acetonitrile, the out-of-plane shift in **9** is much more pronounced and oriented in



Scheme 2.4 Spontaneous imido insertion into the iron-carbene bond: $[(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{ph}})\text{Fe}](\text{BPh}_4)_2$ (**9**)

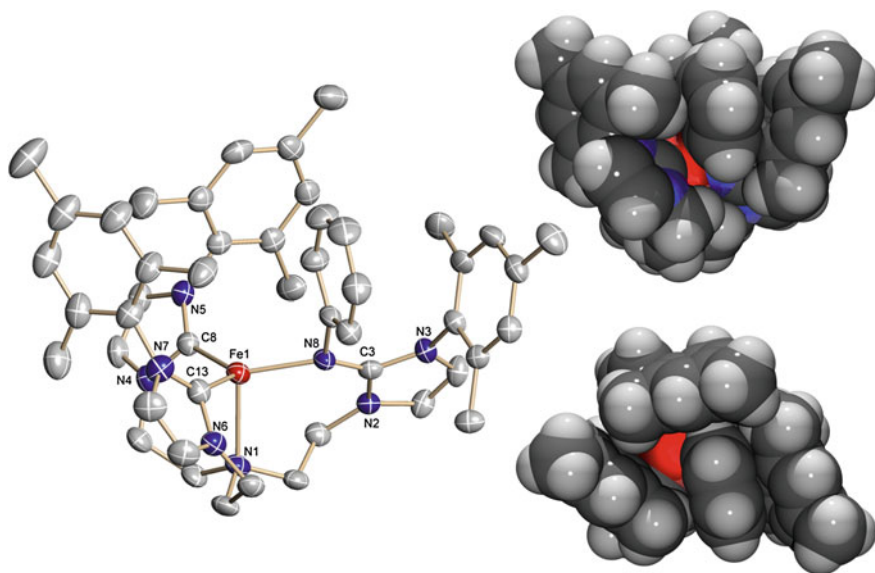


Fig. 2.21 Molecular structure of the complex cation of $[(\text{TIMEN}^{\text{mes}}=\text{N}^{\text{ph}})\text{Fe}](\text{BPh}_4)_2$ (**9**) in crystals of **9** · solv (50% probability ellipsoids). Hydrogen atoms, BPh_4^- anions, and co-crystallized solvents are omitted for clarity. Space-filling representations of the cation **9** side view (right, top) and top view (right, bottom). Selected bond distances (Å): Fe1–N8 2.017(3), N8–C3 1.338(4), N8–C43 1.456(4), Fe1–C8 2.055(3), Fe1–C13 2.092(3), Fe1–N1 2.244(3), $d_{\text{Fe oop}}$ 0.222(2)

Table 2.2 Selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses for [(TIMEN^{mes}=N^H)Fe(MeCN)](BPh₄)₂ · [(TIMEN^{mes}=N^H)Fe(MeCN)](BF₄)(BPh₄) · Et₂O · 1.5 MeCN (**8** · Et₂O · 1.5 MeCN), [(TIMEN^{mes}=N^{ph})Fe](BPh₄)₂ · solv (**9** · solv)

	8 · Et ₂ O · 1.5 MeCN	9 · Solv
Fe1–N1	2.556(3)	2.244(3)
Fe1–N8	2.030(3)	2.017(3)
Fe1–N9	2.237(3)	–
N8–C3	1.317(4)	1.338(4)
N8–H8 N/C43	1.00	1.456(4)
Fe1–C8	2.098(3)	2.055(3)
Fe1–C13	2.106(4)	2.092(3)
N2–C3	1.358(4)	1.366(4)
N3–C3	1.363(5)	1.356(4)
N4–C8	1.354(4)	1.350(4)
N5–C8	1.362(4)	1.364(4)
N6–C13	1.360(4)	1.364(4)
N7–C13	1.353(4)	1.348(4)
N8–Fe1–C8	128.02(12)	123.80(12)
N8–Fe1–C13	111.35(13)	113.77(12)
C8–Fe1–C13	119.98(13)	118.93(13)
C3–N8–Fe1	138.7(3)	136.0(2)
H8 N/C43–N8–Fe1	108.6	104.29(19)
C3–N8–H8 N/C43	108.1	117.7(3)
<i>d</i> _{Fe oop}	0.097(2)	0.222(2)

the opposite direction. Removal of the axial ligand reverses the out-of-plane shift due to a strengthening of the bonding interaction between iron and the nitrogen anchor. In **9**, the remaining iron-carbene bonds, as well as the iron-imine bond are slightly shorter than in **8**. In general, the iron-ligand distances in the four-coordinate complex **9** are shorter than in the five-coordinated complex **8**.

The same type of reaction has been observed before when treating the highly reactive Co(I) complex [(TIMEN^R)Co]Cl with different aryl azides [27]. In this case Co(III) imido complexes [(TIMEN^R)Co(NAr^{R'})]Cl can be isolated at low temperature in near quantitative yields. These complexes are stable in the solid state and in solution at –35 °C. In solution at RT, however, the imido group readily inserts into one of the Co-carbene bonds. Also in these cases, the yields are low and the formation of the insertion products is accompanied by decomposition of a certain amount of the Co(III) imido species.

2.3 Conclusion

In summary, the generation and stabilization of a discrete Fe(IV) nitride complex was accomplished employing a sterically demanding nitrogen-anchored N-heterocyclic *tris*(carbene) ligand (TIMEN^{mes}). The tripodal TIMEN^{mes} ligand was coordinated to iron by treatment with ferrous chloride. The corresponding Fe(II) azide complex **6** could be obtained *via* two different reaction routes: either by reduction of the Fe(II)

chloro precursor **4** to the Fe(I) species **5**, followed by treatment of the resulting complex with TMS-azide. Alternatively, by salt metathesis reaction, stirring the Fe(II) precursor **4** with an excess of sodium azide in acetonitrile. Photolysis of the Fe(II) azide complex **6** generates the Fe(IV) nitride complex **7**. The crystal structure determination of this iron nitride complex **7** reported here is the first structural verification of the [FeN] synthon that has been recognized as the reactive intermediate in the industrial Haber–Bosch process. Complex **7** is remarkably air and moisture stable at room temperature, which can be attributed to the steric protection provided by the TIMEN^{mes} ligand. The X-ray crystallographically determined Fe≡N bond is short at 1.53 Å, and the high-valent Fe(IV) center in this molecule possesses a trigonal-pyramidal coordination environment. Aiming for high-valent iron N-heterocyclic carbene complexes, and especially for iron nitride complexes, we tried to obtain an iron(V) nitride complex, as well. Attempts to oxidize **7** with different oxidizing reagents yielded the insertion product [(TIMEN^{mes}=N^H)Fe(MeCN)]BPh₄ (**8**). Similar reaction behavior can be observed with transition metal imido complexes [(TIMEN^R)M=N^R]⁺ (M=Co(III), Fe(III)).

2.4 Experimental

2.4.1 Methods, Procedures, and Starting Materials

All air- and moisture-sensitive experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. Iron(II) chloride, anhydrous 99.9%, was purchased from Aldrich and used as received. Trimethylsilyl azide 97% and sodium tetraphenylborate were purchased from ACROS and were used without further purification. Phenyl azide was prepared following the literature procedure [28]. Solvents were purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA) and transferred to the glovebox without exposure to air. NMR solvents were obtained packaged under argon and stored over activated molecular sieves and sodium (where appropriate) prior to use.

¹H-NMR spectra were recorded on JEOL 270 and 400 MHz instruments, operating at respective frequencies of 269.714 and 400.178 MHz with a probe temperature of 23 °C.

¹³C-NMR spectra were recorded on JEOL 270 and 400 MHz instruments, operating at respective frequencies of 67.82 and 100.624 MHz with a probe temperature of 23 °C. Chemical shifts were reported relative to the peak for SiMe₄, using ¹H (residual) chemical shifts of the solvent as a secondary standard and are reported in ppm.

¹⁵N-NMR data were acquired on a JEOL 400 MHz instrument, and chemical shifts were referenced to CH₃NO₂ (380.23 ppm relative to liquid ammonia at 0 ppm).

Electronic absorption spectra were recorded from 300 to 2,000 nm with a UV-vis-NIR-Spectrophotometer (Shimadzu UV-3600) in THF.

All infrared spectra were recorded on a Shimadzu IRPrestige-21 system in KBr pellets.

Elemental analysis results were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nuremberg (Erlangen, Germany).

⁵⁷Fe Mößbauer spectra were recorded on a WissEl Mößbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. ⁵⁷Co/Rh was used as the radiation source. WinNormos for Igor Pro software was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.23 mm s⁻¹.

The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N₂ cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Measurements were obtained for a finely ground microcrystalline powder restrained within a polycarbonate gel capsule. Dc susceptibility data were collected in the temperature range 2–300 K under a dc field of 1 T. The data were corrected for core diamagnetism of the sample estimated using Pascal's constants. The program julX written by E. Bill was used for the simulation and analysis of magnetic susceptibility data [18].

EPR measurements were performed in quartz tubes with J. Young valves. Frozen solution EPR spectra were recorded on a JEOL continuous wave spectrometer JESFA200 equipped with an X-band Gunn diode oscillator bridge, a cylindrical mode cavity, and a helium cryostat. All spectra were obtained on freshly prepared solutions of 1–10 mM compound in acetonitrile. The spectra were simulated using the W95EPR program [29].

Samples for mass spectrometry were prepared by dissolving the compound in dry acetonitrile under nitrogen to yield a 10⁻⁴ M solution. Using a syringe pump at a flow rate of 240 mL h⁻¹, the acetonitrile solutions were infused into an orthogonal ESI source of an Esquire 6,000 ion trap mass spectrometer (Bruker, Bremen, Germany). Nitrogen was used as the nebulizing gas. The source voltages for the positive-ion mode were set as follows: capillary at -4.0 kV, end plate offset at -500 V, capillary exit at 151.0 V. The ion trap was optimized for the respective target mass.

2.4.2 Computational Details

The electronic structure and geometry of the iron(IV) nitride complex **7** were investigated with Kohn–Sham DFT calculations using the ORCA package [30]. The B3LYP [31–33] functional was used together with the SV(P) basis set [34] for the main group elements, and the TZV(P) basis for the iron centre [35].

2.4.3 Synthetic Details

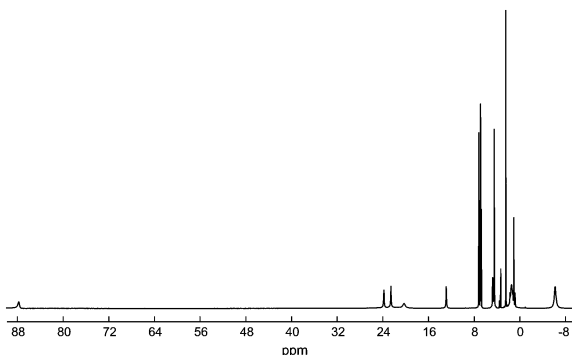
Im^{mes} (1). A solution of ammonium acetate (30.8 g, 0.4 mol) and 2,4,6-trimethylaniline (54.1 g, 51.9 mL, 0.4 mol) dissolved in 100 mL acetic acid was added dropwise to a stirred solution of glyoxal (58.1 g, 45.9 mL, 0.4 mol) and formaldehyde (32.7 g, 30.0 mL, 0.4 mol) in 100 mL acetic acid at 80 °C. The resulting mixture was stirred for 16 h at 80 °C during which the solution turned brown. The reaction mixture was added dropwise to a stirred solution of KOH in distilled water (200 g KOH in 1.25 L), the crude product was extracted with methylene chloride. After drying with sodium sulfate, filtration, and removing of solvent the residue was purified by vacuum distillation (36.8 g; yield 49.4%). ¹H-NMR (270 MHz, chloroform-*d*₁, RT): δ (ppm) = 7.78 (s, 1H), 7.35 (s, 1H), 7.20 (s, 1H), 6.94 (s, 2H), 2.30 (s, 3H), 1.94 (s, 6H). ¹³C{¹H}-NMR (68 MHz, chloroform-*d*₁): δ (ppm) = 137.1, 135.3, 129.0, 128.7, 128.4, 120.0, 20.9, 17.3.

[H₃TIMEN^{mes}](PF₆)₃ (2). A suspension of *tris*(2-chloroethyl)amine-hydrochloride (9.00 g, 37.3 mmol) and potassium hydroxid (3.28 g, 56.7 mmol, ca. 1.5 eq.) was stirred for 30 min until all hydrochloride salt had separated from the aqueous solution. The light yellow oil was extracted with methylene chloride (3 × 20 mL) and the solvent was removed using the rotovap (7.30 g; yield 95.7%). A 100 mL flask was charged with *tris*(2-chloroethyl)amine (7.30 g, 35.7 mmol) and **1** (19.95 g, 0.11 mol), and the mixture was heated to 150 °C for 2 days. During this time, the reaction mixture became a brown solid, to complete the conversion the solidified melt can be redissolved by adding acetonitrile from time to time. After 2 days the resulting solid was dissolved in a minimum amount of hot methanol. The hygroscopic chloride salt [H₃TIMEN^{mes}](Cl)₃ (**2a**) in solution, was converted to the corresponding stable hexafluorophosphate salt, [H₃TIMEN^{mes}](PF₆)₃, by addition of a solution of NH₄PF₆ (20.00 g, 12.27 mol) in a minimum amount of hot methanol. The off-white hexafluorophosphate salt was collected by filtration, washed with methanol and diethyl ether. The resulting solid was dried in vacuo (23.39 g; yield 60%). ¹H-NMR (270 MHz, DMSO-*d*₆, RT): δ (ppm) = 9.37 (s, 3H), 8.01 (d, 6H), 7.16 (s, 6H), 4.36 (t, ³*J*(H,H) 4.45 Hz, 6H), 3.13 (t, ³*J*(H,H) 4.45 Hz, 6H), 2.32 (s, 9 H), 2.00 (s, 18H). ¹³C {¹H}-NMR (68 MHz, DMSO-*d*₆, RT): δ (ppm) = 215.0, 140.4, 137.4, 134.3, 131.1, 124.0, 123.4, 52.1, 46.7, 20.6, 16.9.

[TIMEN^{mes}] (3). A suspension of potassium *tert*-butoxide (0.45 g, 4.04 mmol) and [H₃TIMEN^{mes}](PF₆)₃ (**2**) (1.43 g, 1.30 mmol) in 20 mL Et₂O was stirred for 5 h. The solution was filtered over celite and the filtrate was evaporated to dryness in vacuo. ¹H-NMR (400 MHz, benzene-*d*₆, RT): δ (ppm) = 6.80 (d, ³*J*(H,H) 1.62 Hz, 3H), 6.71 (s, 6H), 6.28 (d, ³*J*(H,H) 1.62 Hz, 3H), 4.02 (t, ³*J*(H,H) 6.53 Hz, 6H), 2.85 (t, ³*J*(H,H) 6.53 Hz, 6H), 2.06 (s, 9H), 2.04 (s, 18H). ¹³C {¹H}-NMR (100 MHz, benzene-*d*₆, RT): δ (ppm) = 213.59, 150.29, 139.11, 137.19, 135.38, 134.88, 123.17, 120.19, 120.07, 56.62, 49.68, 20.95, 18.13.

[(TIMEN^{mes})Fe(Cl)]Cl (4). A solution of FeCl₂ (0.17 g, 1.3 mmol) in 10 mL pyridine was added to a solution of TIMEN^{mes} (**3**) (0.85 g, 1.30 mmol) in 10 mL

Fig. 2.22 ^1H -NMR spectrum of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N}_3)]\text{BPh}_4$ **6** (recorded in $\text{DMSO}-d_6$ at RT)



pyridine. The reaction mixture was allowed to stir overnight, during which an off-white precipitate formed. The precipitate was collected by filtration, washed with pyridine, diethyl ether and n-pentane and dried in vacuo (1.02 g; yield 80%). ^1H -NMR (270 MHz, CD_2Cl_2 , RT): δ (ppm) = 77.14 (s, 3H), 25.45 (s, 3H), 20.12 (s, 3H), 19.53 (s, 3H), 9.99 (s, 3H), 8.55 (s, 3H), 5.14 (s 9H), 4.96 (s, 3H), 1.79 (s, 3H), -0.32 (s, 9H), -5.90 (s, 9H). Elemental analysis (%) for $\text{C}_{42}\text{H}_{51}\text{Cl}_2\text{FeN}_7$ calcd. C 64.62, H 6.58, N 12.56; obsd. C 64.78, H 6.50, N 12.84. Mößbauer (solid state, 80 K) $\delta = 0.71(1) \text{ mm s}^{-1}$, $\Delta E_Q = 1.78(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.32(1) \text{ mm s}^{-1}$. SQUID ($\chi_{\text{dia}} = 4.53 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$, RT) $\mu_{\text{eff}} = 4.89 \mu_B$.

$[(\text{TIMEN}^{\text{mes}})\text{Fe}]\text{BPh}_4$ (5). A mixture of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) (0.50 g, 0.64 mmol) and sodium tetraphenylborate (0.22 g, 0.64 mmol) in 20 mL THF was stirred over sodium amalgam (5.00 g, equates to 22.99 mg, 1.70 mmol sodium) overnight. The solution was filtered over celite, concentrated and cooled to -35°C to yield the product as dark red crystals (0.53 g, yield 80%). Mößbauer parameters (solid state, 80 K) $\delta = 0.64(1) \text{ mm s}^{-1}$, $\Delta E_Q = 2.34(1) \text{ mm s}^{-1}$, $\Gamma_{\text{FWHM}} = 0.29(1) \text{ mm s}^{-1}$. EPR (acetonitrile, 14 K, 8.962 GHz, Mod-Width = 1.0 mT, Power = 0.998 mW, $g_{\perp} = 4.2$, $g_{\parallel} = 2.025$, $\Delta H_{1/2\perp} = 6.7 \text{ mT}$, $\Delta H_{1/2\parallel} = 4.0 \text{ mT}$.

$[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{N}_3)]\text{BPh}_4$ (6). **A:** Excess $\text{TMS}-\text{N}_3$ was added to a solution of $[(\text{TIMEN}^{\text{mes}})\text{Fe}]\text{BPh}_4$ (**5**) (195.50 mg, 0.19 mmol) in 20 mL THF. The reaction mixture was stirred overnight, during which the red solution turned yellow. Half of the solvent was removed and addition of 10 mL of diethyl ether to the solution induced precipitation of a light yellow powder. The precipitate was filtered, washed with diethyl ether and pentane, and dried in a vacuum (161.0 mg; yield: 79%). Light yellow crystals suitable for X-ray diffraction analysis were grown by diffusion of pentane into a saturated solution of **6** in THF at room temperature. **B:** A mixture of $[(\text{TIMEN}^{\text{mes}})\text{Fe}(\text{Cl})]\text{Cl}$ (**4**) (0.40 g, 0.51 mmol), sodium tetraphenylborate (0.17 g, 0.51 mmol) and sodium azide (0.07 g, 1.10 mmol) was stirred in 15 mL THF for 2 days. The solution was filtered over celite and the solvent removed in vacuo. In the ^1H -NMR, eleven signals are expected for the complex, nine are observed, two signals are likely broadened into the baseline. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$, RT): δ (ppm) = 87.50 (s, 3H), 23.80 (s, 3H), 22.58 (s, 3H), 20.28 (s, 3H), 12.89 (s, 3H), 7.18

(m, 8H), 6.94 (m, 8H), 6.92 (m, 4H), 4.80 (s, 3H), 4.52 (s, 9H), 1.50 (s, 9H), -6.11 (s, 9H). Elemental Analysis (%) for $C_{66}H_{71}BFeN_{10}$ calcd. C 74.02, H 6.68, N 13.08; obsd. C 74.13, H 6.73, N 12.66. Mößbauer (solid state, 80 K) $\delta = 0.687(1) \text{ mm s}^{-1}$, $\Delta E_Q = 2.267(3) \text{ mm s}^{-1}$, $\Gamma_{FWHM} = 0.48(1) \text{ mm s}^{-1}$ (Fig. 2.22).

[(TIMEN^{mes})Fe(N)]BPh₄ (7). A stirred solution of **6** (161.0 mg, 0.15 mmol) in 20 mL THF was irradiated for 24 h (Osram XBO 150 W Xenon arc lamp) during which the yellow solution turned purple. The solution was filtered through Celite, concentrated and addition of *n*-pentane to the solution induced precipitation of a purple powder. The precipitate was filtered, washed with *n*-pentane, and dried in a vacuum (101.9 mg; yield: 65%). Purple crystals suitable for X-ray diffraction analysis were grown by diffusion of diethyl ether into a saturated solution of **7** in THF at room temperature. ¹H-NMR (400 MHz, DMSO-*d*₆, RT): δ (ppm) = 7.59 (d, ³*J*(H,H) = 1.8, 3H), 7.20 (d, ³*J*(H,H) = 1.8, 3H), 7.16 (m, 8H), 6.86 (m, 8H), 6.75 (m, 4H), 6.61 (s, 3H), 6.60 (s, 3H), 4.06 (m, 3H), 3.10 (m, 3H), 2.68 (m, 3H), 2.26 (m, 3H), 2.13 (s, 9H), 1.61 (s, 9H), 0.92 (s, 9H). ¹³C-NMR (100 MHz, DMSO-*d*₆, RT): δ (ppm) = 198.29, 163.94, 138.22, 137.49, 137.29, 136.08, 133.27, 128.57, 128.43, 125.82, 124.63, 122.06, 58.38, 50.56, 20.88, 17.36, 16.80. Elemental analysis (%) for $C_{66}H_{71}BFeN_8$ calcd. C 76.00, H 6.86, N 10.74; obsd. C 75.47, H 7.04, N 10.61. Mößbauer (solid state, 80 K) $\delta = -0.27(1) \text{ mm s}^{-1}$, $\Delta E_Q = 6.04(1) \text{ mm s}^{-1}$, $\Gamma_{FWHM} = 0.26(1) \text{ mm s}^{-1}$.

[(TIMEN^{mes}=N^H)Fe(MeCN)]BPh₄ (8). A solution of NOBF₄ (6.1 mg, 0.53 mmol) in 5 mL acetonitrile was added dropwise to a solution of **7** (55.0 mg, 0.53 mmol) in 5 mL of acetonitrile. After complete addition of the oxidizing agent, the solvent was immediately removed in vacuo. Suitable single crystals for X-ray crystal structure determination could be obtained by dissolving the resulting residue in acetonitrile-*d*₃, filtration and slow diffusion of Et₂O into the saturated solution of **8** at RT. ESI-MS (*m/z*) for $C_{42}H_{52}FeN_8$ calcd. 362 [M^{2+}]; obsd. 362 [M^{2+}].

[(TIMEN^{mes}=N^{ph})Fe]BPh₄ (9). An excess of phenyl azide was added to a stirred solution of **5** (50.0 mg, 48.6 μmol) in 10 mL THF. The reaction mixture was stirred for 2 h during which time the red solution became brown and a precipitate was formed, accompanied by gas evolution. Half of the solvent was removed under vacuum and complete precipitation was induced by addition of *n*-pentane to the mixture. The precipitate was collected by filtration and washed with *n*-pentane. Suitable single crystals for X-ray crystal structure determination could be obtained by dissolving the resulting residue in a mixture of THF and acetonitrile, filtration and slow diffusion of *n*-pentane into the saturated solution of **9** at RT.

2.4.4 X-ray Crystal Structure Determination Details

Orange needles of $[H_3TIMEN^{mes}](Cl)_3$ (**2a**) were obtained at RT from a saturated solution of **2a**. Orange blocks of $[(TIMEN^{mes})Fe(Cl)]Cl \cdot 3 \text{ MeCN}$ (**4** $\cdot$ 3 MeCN) were grown at RT by layering a MeCN solution of **4** with Et₂O, ruby red needles of $[(TIMEN^{mes})Fe]BPh_4 \cdot 2 \text{ THF} \cdot 0.5 \text{ Et}_2\text{O}$ (**5** $\cdot$ 2 THF $\cdot$ 0.5 Et₂O) were obtained at

RT by slow diffusion of Et₂O into a THF solution of **5**, pale-yellow needle-shaped crystals of [(TIMEN^{mes})Fe(N₃)]BPh₄ · 2.5 THF (**6** · 2.5 THF), were grown by layering a THF solution of **6** with *n*-pentane, dark-violet prisms of [(TIMEN^{mes})Fe(N)]BPh₄ · Et₂O (**7** · Et₂O) were obtained by slow diffusion of Et₂O into a THF solution of **7** that was layered with *n*-pentane. Green-brown plates of [(TIME-N^{mes}=N^H)Fe(MeCN)](BPh₄)₂ · [(TIMEN^{mes}=N^H)Fe(MeCN)](BF₄)(BPh₄) · Et₂O · 1.5 MeCN (**8** · Et₂O · 1.5 MeCN) were obtained at RT by slow diffusion of Et₂O into a MeCN solution of **8**. Brown plates of [(TIMEN^{mes}=N^{ph})Fe](BPh₄)₂ · solv (**9** · solv; solv = 1.044 *n*-pentane · 1.023 THF) were obtained at RT by slow diffusion of *n*-pentane into a THF/acetonitrile solution of **9**. Suitable single crystals were embedded in protective perfluoropolyalkylether oil and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data were collected either on a Bruker-Nonius KappaCCD diffractometer (**5** · 2 THF · 0.5 Et₂O, **6** · 2.5 THF, **7** · Et₂O, **8** · Et₂O · 1.5 MeCN, **9** · solv and **2a**) using graphite monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) or on a Bruker Kappa APEX2 Duo diffractometer (**4** · 3 MeCN) equipped with an *I* μ S microsource and QUAZAR focusing optics using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using *SADABS* [36]. All structures were solved by direct methods and refined by full-matrix least-squares procedures on *F*² using *SHELXTL NT* 6.12 [37]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. In the crystal structure of **2a** the molecule lies on a crystallographic threefold axis, accordingly the molecule exhibits C₃ symmetry. Compound **4** crystallizes with a total of three molecules of MeCN per formula unit. The residual electron density maximum at the iron center indicates the presence of a small amount of [(TIMEN^{mes})Fe(MeCN)]²⁺ (less than 5%). Adopting the concept of split positions was not successful in this case. Compound **5** crystallizes with a total of two molecules of THF and 0.5 Et₂O per formula unit. One of the THF molecules is disordered. Two alternative orientations were refined in each case resulting in site occupancies of 57.3(5)% for the atoms O200-C204 and 42.7(5)% for the atoms O210-C214, respectively. The half molecule of Et₂O is disordered and situated on a crystallographic inversion center. SIMU and SAME restraints were applied in the refinement of the disordered structure parts. The crystal structure of [(TIMEN^{mes})Fe(N)]BPh₄ · Et₂O (**7** · Et₂O) is subjected to heavy disorder which affects the cationic iron complex exhibiting two different orientations of the chelating ligand around the central atom, the BPh₄ anion having a threefold disorder of the phenyl ring pointing towards the cation as well as the Et₂O solvent molecule that is also threefold disordered. This disorder gives rise to two apparent short contacts between disordered fragments of different parts and orientations, respectively, namely the ligand of the cationic complex and the Et₂O solvent molecules. ISOR and SIMU restraints were used in the refinement of some of the affected atoms. The orientational disorder of the rotor-like arranged ligand leads to two preferred orientations that are occupied by 67.6(2) and 32.4(2)%, respectively, with a few

Table 2.3 Crystallographic data, data collection and refinement details of [(TIMEN^{mes})Fe(CI)]Cl · 3 MeCN (**4** · 3 MeCN), [(TIMEN^{mes})Fe]BPh₄ · 2 THF · 0.5 Et₂O (**5** · 2 THF · 0.5 Et₂O), [(TIMEN^{mes})Fe(N₃)]BPh₄ · 2.5 THF (**6** · 2.5 THF), [(TIMEN^{mes})Fe(N)]BPh₄ · Et₂O (**7** · Et₂O)

	4 · 3 MeCN	5 · 2 THF · 0.5 Et ₂ O	6 · 2.5 THF	7 · Et ₂ O
Empirical formula	C ₄₈ H ₆₀ Cl ₂ FeN ₁₀	C ₇₆ H ₉₂ BF ₆ N ₇ O _{2.5}	C ₇₆ H ₉₁ BF ₆ N ₁₀ O _{2.5}	C ₇₀ H ₈₁ BF ₆ N ₈ O
Mol. weight	903.81	1,210.23	1,251.25	1,117.09
Crystal size (mm)	0.28 × 0.10 × 0.08	0.50 × 0.14 × 0.13	0.58 × 0.14 × 0.11	0.33 × 0.27 × 0.14
Temperature (K)	100	150	100	100
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	10.6405(4)	11.2380(10)	11.3035(5)	12.432(2)
<i>b</i> (Å)	10.6824(4)	17.4660(10)	17.725(2)	12.632(2)
<i>c</i> (Å)	23.9778(11)	17.6820(10)	17.831(2)	22.614(3)
α (°)	93.3580(10)	85.287(5)	88.056(10)	80.104(13)
β (°)	93.8020(10)	79.615(6)	76.821(6)	84.734(9)
γ (°)	118.7900(10)	77.372(5)	78.047(7)	61.303(7)
<i>V</i> (Å ³)	2,370.51(17)	3,327.9(4)	3,402.7(6)	3,068.6(8)
<i>Z</i>	2	2	2	2
ρ (g cm ⁻³) (calc.)	1.266	1.208	1.221	1.209
μ (mm ⁻¹)	0.475	0.279	0.277	0.296
<i>F</i> (000)	956	1,296	1,336	1,192
<i>T</i> _{min} · <i>T</i> _{max}	0.688; 0.746	0.826; 0.960	0.861; 0.970	0.846; 0.960
2 θ interval (°)	5.62 ≤ 2 θ ≤ 54.2	6.24 ≤ 2 θ ≤ 54.2	6.6 ≤ 2 θ ≤ 52.8	6.9 ≤ 2 θ ≤ 54.2
Coll. refl.	46,788	94,905	66,209	69,261
Indep. refl.	10,377	15,670	13,885	13,497
Obs. refl. <i>F</i> ₀ ≥ 4 σ (<i>F</i>)	8,227	10,608	9,649	9,016
No. ref. param.	562	855	847	1,346
<i>wR</i> ₂ (all data)	0.1398	0.1496	0.1292	0.0938
<i>R</i> ₁ (<i>F</i> ₀ ≥ 4 σ (<i>F</i>))	0.0522	0.0560	0.0516	0.0450
Goof on <i>F</i> ²	1.068	1.020	1.021	1.042
Max.; min. residual electron density	1.377; -0.533	1.263; -0.549	0.623; -0.422	0.305; -0.275

Table 2.4 Crystallographic data, data collection and refinement details of [(TIME-N^{mes}=N^H)Fe(MeCN)](BPh₄)₂ · [(TIMEN^{mes}=N^H)Fe(MeCN)](BF₄)(BPh₄) · Et₂O · 1.5 MeCN (**8** · Et₂O · 1.5 MeCN), [(TIMEN^{mes}=N^{ph})Fe](BPh₄)₂ · solv (**9** · solv), [H₃TIMEN^{mes}](Cl)₃ (**2a**)

	8 · Et ₂ O · 1.5 MeCN	9 · solv	2a
Empirical formula	C ₁₆₇ H _{184.5} B ₄ F ₄ Fe ₂ N _{19.5} O _{1.02}	C _{105.31} H _{116.28} B ₂ FeN ₈ O _{1.02}	C ₄₂ H ₅₄ Cl ₃ N ₇
Mol. weight	2,711.78	1,587.92	1,251.25
Crystal size	0.36 × 0.24 × 0.10	0.40 × 0.18 × 0.05	0.62 × 0.18 × 0.18
Temperature (K)	200	100	150
Crystal system	Monoclinic	Monoclinic	Trigonal
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>R</i> $\bar{3}$ (no. 148)
<i>a</i> (Å)	15.570(2)	29.432(2)	21.687(3)
<i>b</i> (Å)	18.196(1)	14.6980(15)	21.687(3)
<i>c</i> (Å)	47.439(9)	21.1561(15)	15.1534(9)
α (°)	90	90	90
β (°)	98.598(10)	107.317(6)	90
γ (°)	90	90	120
<i>V</i> (Å ³)	14,996(3)	8,737.1(12)	6,172.2(13)
<i>Z</i>	4	4	6
ρ (g cm ⁻³) (calc.)	1.201	1.207	1.232
μ (mm ⁻¹)	0.258	0.228	0.261
<i>F</i> (000)	5,756	3,393	2,436
<i>T</i> _{min} ; <i>T</i> _{max}	0.874; 0.980	0.871; 0.990	0.797; 0.950
2 θ interval (°)	6.46 ≤ 2 θ ≤ 50.06	6.42 ≤ 2 θ ≤ 51.36	6.5 ≤ 2 θ ≤ 54.2
Coll. refl.	169,822	119,834	44,209
Indep. refl.	26,372	16,559	3,026
Obs. refl. <i>F</i> ₀ ≥ 4 σ (<i>F</i>)	15,098	10,886	2,374
No. ref. param.	2,025	1,175	160
<i>wR</i> ₂ (all data)	0.1680	0.1871	0.1045
<i>R</i> ₁ (<i>F</i> ₀ ≥ 4 σ (<i>F</i>))	0.0682	0.0684	0.0379
Goof on <i>F</i> ²	1.066	1.040	1.093
Max.; min. residual electron density	0.610; -0.628	1.232; -0.590	0.389; -0.252

atoms belonging to both orientations; most importantly, the amine nitrogen, N1, the iron ion, Fe1, and the nitride, N8, as well as N2, N4, and C1. For the disordered phenyl ring (C61–C66) of the BPh₄ anion three preferred orientations could be refined that are occupied by 36.0(5)% for the atoms C62–C66, 30.5(5)% for the atoms C62A–C66A, and 34.0(5)% for the atoms C62B–C66B. The treatment of the threefold disorder of the Et₂O solvent molecule resulted in site occupancies of 38.0(4)% for C101–C105, 32.0(4)% for C201–C205, and 30.0(4)% for C301–C305. A number of restraints (SIMU, ISOR, and SAME) was applied in the refinement of the disordered regions of the crystal structure of **7** · Et₂O. The crystal structure of [(TIMEN^{mes}=N^H)Fe(MeCN)](BPh₄)₂ · [(TIMEN^{mes}=N^H)Fe(MeCN)](BF₄)(BPh₄) · Et₂O 1.5 MeCN (**8** · Et₂O · 1.5 MeCN) contains two independent molecules of the complex cation in the asymmetric unit, one of which (Fe2) is disordered. Two

Table 2.5 Selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses for [(TIMEN^{mes})Fe(Cl)]Cl · 3 MeCN (**4** · 3 MeCN), [(TIMEN^{mes})Fe]BPh₄ · 2 THF · 0.5 Et₂O (**5** · 2 THF · 0.5 Et₂O), [(TIMEN^{mes})Fe(N₃)]BPh₄ · 2.5 THF (**6** · 2.5 THF), [(TIMEN^{mes})Fe(N)]BPh₄ · Et₂O (**7** · Et₂O)

	4 · 3 MeCN	5 · 2 THF · 0.5 Et ₂ O	6 · 2.5 THF	7 · Et ₂ O (major) ^a	7 · Et ₂ O (minor) ^a
Fe1–N1	3.008(3)	2.275(2)	3.244(2)		3.120(2)
Fe1–Lig _{axial} ^b	2.2768(8)	–	1.947(2)		1.526(2)
Fe1–C3	2.128(3)	2.032(2)	2.104(2)	1.987(3)	1.920(7)
Fe1–C8	2.138(3)	2.024(2)	2.110(3)	1.955(5)	1.982(10)
Fe1–C13	2.138(2)	2.012(2)	2.111(2)	1.946(4)	2.006(8)
N8–N9	–	–	1.183(3)	–	–
N9–N10	–	–	1.157(3)	–	–
N2–C3	1.360(3)	1.378(3)	1.363(3)	1.323(4)	1.391(7)
N3–C3	1.376(3)	1.380(3)	1.365(3)	1.382(4)	1.370(8)
N4–C8	1.365(3)	1.370(3)	1.367(3)	1.361(5)	1.268(10)
N5–C8	1.360(3)	1.374(3)	1.362(3)	1.373(5)	1.359(10)
N6–C13	1.359(3)	1.374(3)	1.356(3)	1.409(9)	1.31(2)
N7–C13	1.371(3)	1.374(3)	1.368(3)	1.374(4)	1.375(9)
Fe1–N8–N9	166.9(2)	–	174.5(2)	–	–
N8–N9–N10	179.1(2)	–	179.6(3)	–	–
C3–Fe1–Lig _{axial}	100.56(7)	–	103.9(1)	115.1(2)	101.5(2)
C8–Fe1– Lig _{axial} ^b	102.41(7)	–	105.2(1)	101.4(2)	103.4(3)
C13–Fe1– Lig _{axial} ^b	102.61(7)	–	106.6(1)	103.8(2)	102.0(2)
<i>d</i> _{Fe oop}	0.439(2)	0.191(2)	0.554(2)	0.427(3)	0.420(5)

^a In its crystal structure the cation **7** exhibits two different orientations of the chelate ligand around the central atom with the major component being occupied by 67.6(2) and the minor component by 32.4(2)%

^b Lig_{axial} corresponds to the respective axial Ligand, for compound **4**: Cl (chloro); for compound **6**: N8 (azide); for compound **7**: N8 (nitride)

alternative positions were refined in the case of the ligand arm which is affected by insertion, each position is refined with occupancies of 50%. The BF₄[–] anion is disordered over two sites with refined occupancies of 62.0(3)% and 38.0(3)% for the atoms B1–F14 and B1A–F14A. The solvent molecule Et₂O is also disordered, whereas the 50:50-occupancy is correlated with the disorder of the cation (Fe2). Also the occupancy of 50% of one of the MeCN molecules is based on the disorder of the cation (Fe2). The crystal structure of [(TIMEN^{mes}=N^{ph})Fe](BPh₄)₂ · solv (**9** · solv; solv = 1.044 *n*-pentane · 1.023 THF) contains several highly disordered solvent molecules (THF and *n*-pentane). In parts different solvent molecules share one crystallographic site, which results in a non-integer sum formula. SIMU, ISOR, DFIX and SAME restraints were applied in the refinement of the disordered solvent molecules (Tables 2.3, 2.4, 2.5).

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