Iron(IV) Complexes

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A *cis*-Divacant Octahedral and Mononuclear Iron(IV) Imide**

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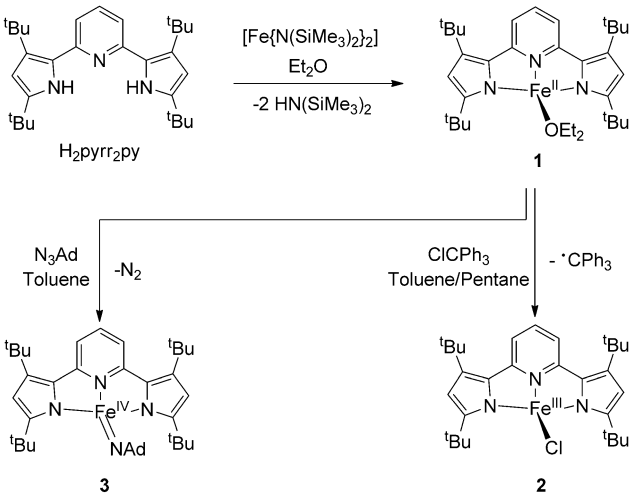
Dedicated to Professor T. Don Tilley on the occasion of his 60th birthday

Abstract: *A rare, low-spin Fe^{IV} imide complex [(pyrr$_2$py)Fe=NAd] (pyrr$_2$py^{2-} = bis(pyrrolyl)pyridine; Ad = 1-adamantyl) confined to a cis-divacant octahedral geometry, was prepared by reduction of N_3Ad by the Fe^{II} precursor [(pyrr$_2$py)Fe(OEt$_2$)]. The imide complex is low-spin with temperature-independent paramagnetism. In comparison to an authentic Fe^{III} complex, such as [(pyrr$_2$py)FeCl], the pyrr$_2$py^{2-} ligand is virtually redox innocent.*

It has been well-established that the catalytic cycles of many heme and non-heme iron metalloenzymes utilize transiently generated, multiply bonded, high-valent iron centers as potent oxidants.[1,2] These iron centers are principally in the +4 oxidation state, such as that found for Fe^{IV}(oxo)(porphyrin π-radical cation) in Cytochrome P450. It has also been shown that the heme-containing terminal oxidase enzymes of the P450 platform can perform nitrene transfer chemistry which is thought to proceed via a putative Fe^{IV} imide intermediate.[1b,3] Thus, the electronic and structural characterization of molecules containing Fe^{IV}=E moieties (E = O, NR) are important for providing better insight into the active species of iron metalloenzymes and developing group-transfer catalysts.[1b,4] However, relatively few Fe^{IV} complexes featuring terminal oxo[5] or imide[6] ligands have been isolated in the solid-state and structurally characterized.

The support of stable Fe^{IV}=E functionalities requires an ancillary ligand that is sufficiently electron donating and resistant to oxidative degradation, while providing a coordination geometry that minimizes filled–filled pπ–dπ orbital repulsions[7] within the multiply bonded Fe^{IV}=E fragment. Interestingly, of the structurally characterized Fe^{IV} imides, only tetrahedral[6a–c] and octahedral[6d] coordination geometries are known, in part because of their low-spin nature and ligand-field stabilization energies. For example, Peters et al. and Smith and co-workers have each successfully utilized tripodal ligands with strongly electron-donating phosphine/pyrazolyl and N-heterocyclic carbene donors, respectively, to stabilize tetrahedral $[LFe^{IV}{=}NAd]^+$ complexes from the one-electron oxidation of $[LFe^{III}{=}NAd]$ precursors (L=bis((di-*tert*-butylphosphino)methyl)(3,5-dimethylpyrazole)phenylborate, or tris(1-mesitylimidazol-2-ylidene)phenylborate; Ad = 1-adamantyl).[6b,c]

Recently, we reported the synthesis of a bulky bis(pyrrolyl)pyridine pincer (H_2pyrr$_2$py, Scheme 1) and its coordination chemistry with a variety of late transition metals, including Fe^{II}.[8] Herein, we describe the synthesis of a novel Fe^{II} complex supported by the dianionic pyrr$_2$py pincer, namely [(pyrr$_2$py)Fe(OEt$_2$)], and discuss its clean and direct conversion into the Fe^{IV} imide [(pyrr$_2$py)Fe=NAd]. The four-coordinate Fe^{IV} imide complex has a coordinatively



Scheme 1. Synthesis of [(pyrr$_2$py)Fe(OEt$_2$)] (**1**), [(pyrr$_2$py)FeCl] (**2**), and [(pyrr$_2$py)Fe=NAd] (**3**).

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unsaturated metal center, whose new and unusual geometry is best described as a *cis*-divacant octahedron. Spectroscopic, magnetic, and theoretical studies have been combined to address the unique electronic structure of this system.

Coordination of a single bis(pyrrolyl)pyridine ligand to iron was accomplished by the slow addition of one equivalent of H_2pyrr_2py to $[Fe\{N(SiMe_3)_2\}_2]$ in Et_2O, which yielded a red solution after stirring for 14 hours. The mononuclear complex $[(pyrr_2py)Fe(OEt_2)]$ (**1**) was obtained in 81% yield and crystallizes as red plates from concentrated Et_2O or pentane solutions stored at −35 °C. The ^{1}H NMR spectrum of **1** recorded in C_6D_6 at room temperature reveals seven broad resonance signals, ranging from $\delta = -2.9$ ppm to 120.5 ppm, attributable to protons of a paramagnetic complex, which are consistent with a C_s symmetric structure in solution. Solution magnetic susceptibility measurements of **1**, determined by the Evans method in C_6D_6 at room temperature, indicate a magnetic susceptibility value of 5.2 μ_B, which is only slightly higher than the calculated spin-only value of 4.9 μ_B for a high-spin Fe^{II} complex ($S = 2$). Variable-temperature SQUID magnetization measurements also indicate a high-spin Fe^{II} complex, which confirms a negligibly temperature-dependent effective magnetic moment (μ_{eff}) ranging from 5.09 to 5.25 μ_B over the temperature range 30–300 K (dc mode).[9]

The solid-state molecular structure of **1** (Figure 1a) reveals a four-coordinate iron center bound by one Et_2O molecule and the tridentate $pyrr_2py$ ligand in a meridional configuration. The $Fe-N_{py}$ (Fe1−N1 = 2.021(2) Å) and $Fe-N_{pyrr}$ (Fe1−N2 = 1.987(1) Å) distances are unexceptional and comparable to those of recently reported $[(Hpyrr_2py)_2Fe]$ (e.g. $Fe-N_{py} = 2.077(2)$ Å, $Fe-N_{pyrr} = 2.012(2)$ Å).[8] Notably, the iron center in **1** exhibits a non-planar coordination geometry, with a deviation of 0.57 Å from the plane defined by the three $pyrr_2py$ nitrogens, and with the coordinated Et_2O found *cis* (N1-Fe1-O1 = 102.37(8)°, N2-Fe1-O1 = 106.03(4)°) to the $pyrr_2py$ ligand. The most valid geometric description of **1** is between trigonal pyramidal and *cis*-divacant octahedral ($\tau_4 = 0.80$),[10] reminiscent of that found for the Zn^{II} analogue $[(pyrr_2py)Zn(DMAP)]$ (DMAP = *para*-(dimethylamino)-pyridine).[8] A space-filling model[9] of **1** suggests that the *tert*-butyl groups of the pyrrole α-carbons effectively block the site trans to the pyridyl nitrogen, preventing adoption of a square-planar geometry.

Intrigued by the idea of stabilizing high-valent iron complexes, we subsequently investigated the one- and two-electron chemical oxidations of complex **1**. Single-electron oxidation was accomplished by the reaction of $ClCPh_3$ (1 equiv) with **1** in a toluene/pentane mixture to afford the mononuclear Fe^{III} complex $[(pyrr_2py)FeCl]$ (**2**) in 72% yield as a dark red/brown microcrystalline material (Scheme 1). Upon separation of Gomberg's radical and dimer, the ^{1}H NMR spectrum of **2**, recorded in C_6D_6 at room temperature, displays five broad resonance signals in the range $\delta =$ 10.4–143.3 ppm, which is consistent with loss of Et_2O from the molecule and the preservation of the C_s symmetry. X-ray diffraction studies were performed on red single crystals, grown by layering a concentrated toluene solution of **2** with pentane stored at −35 °C. The solid-state structure of **2** (Figure 1b) shows that the molecule adopts a geometry between trigonal pyramidal and *cis*-divacant octahedral ($\tau_4 = 0.73$)[10] where the $Fe-N_{py}$ (Fe1−N2 = 1.981(2) Å) and $Fe-N_{pyrr}$ (Fe1−N1 = 1.991(2) Å) distances are comparable to that of the Fe^{II} precursor. Similar to **2**, the iron center is positioned 0.62 Å above the plane defined by the three $pyrr_2py$ nitrogens. It is noteworthy that the N_{py}-Fe-Cl angle (N2-Fe1-Cl1 = 115.02(8)°) is 9° more obtuse when compared to the N_{py}-Fe-OEt_2 angle (N1-Fe1-O1 = 102.37(8)°) of complex **1**. Variable-temperature SQUID magnetization measurements performed on **2** indicate a high-spin Fe^{III} center ($S =$ 5/2), which also shows a negligibly temperature-dependent μ_{eff} value, ranging from 5.83 to 5.73 μ_B over the temperature range 30–300 K (dc mode).[9]

We subsequently investigated the two-electron oxidation of **1** with an alkyl azide in attempts to generate an Fe^{IV} imide complex. Treatment of **1** with 1-adamantyl azide (N_3Ad; 1 equiv) at room temperature, in either toluene or Et_2O, results in the slow formation of a dark red/purple solution over the course of 13 hours from which the product can be isolated in 96% yield. Single-crystal X-ray diffraction studies performed on a dark-red crystal confirmed the formation of the expected $[(pyrr_2py)Fe{=}NAd]$ (**3**) (Figure 1c). Chirik et al. have recently reported a series of Fe imide complexes,[11] which deviate from idealized square-planar geometry. However, the overall *cis*-divacant geometry ($\tau_4 = 0.68$)[10] and oxidation state of complex **3** represents an entirely unprecedented coordination environment in Fe imide chemistry. The imide is positioned *cis* (N1-Fe1-N3 =

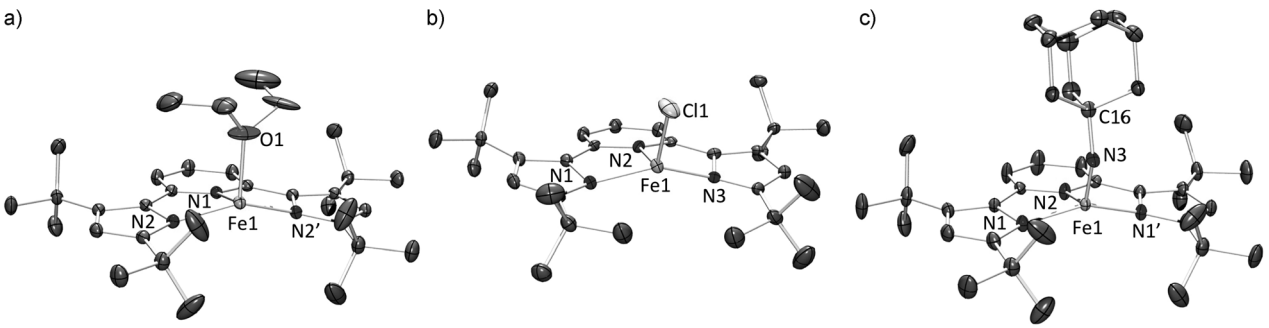

Figure 1. ORTEP drawings of a) $[(pyrr_2py)Fe(OEt_2)]$ (**1**), b) $[(pyrr_2py)FeCl]$ (**2**), and c) $[(pyrr_2py)Fe{=}NAd]$ (**3**), showing selected atom labeling. Thermal ellipsoids are set at 50% probability and hydrogen atoms have been removed for clarity.

106.21(7)°, N2-Fe1-N3 = 116.6(2)°) to the nitrogens of the pyrr$_2$py ligand. The Fe–N_{py} (Fe1–N2 = 1.867(3) Å) and Fe–N_{pyrr} (Fe1–N1 = 1.910(2) Å) bond distances in **3** are noticeably shorter than those of both **1** and **2** and the iron center deviates from the plane of the pyrr$_2$py nitrogens by 0.52 Å. In all, this is consistent with a low-spin, metal-centered, oxidized iron ion. Unlike the few structurally characterized Fe^{IV} imides which have nearly linear Fe-N_{imide}-C_{ipso} angles, the angle measured for **3** is significantly more acute (Fe1-N3-C16 = 140.5(3)°). Furthermore, the Fe–N_{imide} bond length (Fe1–N3 = 1.640(4) Å) is slightly longer when compared to the range of 1.618–1.635 Å for tetrahedral Fe^{IV} imide complexes,[6a–c] but significantly shorter than an octahedral Fe^{IV} imide distance of 1.73 Å determined from EXAFS measurements by Que et al.[6d] Both the ^{1}H and ^{13}C NMR spectra of **3** recorded at room temperature in C_6D_6 exhibit sharp resonance signals with chemical shifts in the normal diamagnetic range, spanning $\delta = 1.14$–6.64 ppm and $\delta = 28.84$–159.90 ppm, respectively. The number of resonance signals is in accord with a C_s symmetric species, and thus is consistent with the solid-state structure being retained in solution. SQUID magnetization measurements were also performed to establish the $S = 0$ state of **3**.[9]

Given that Fe^{IV} imide complexes have been shown to have intermediate spin states,[6] and that Fe^{III} metal centers antiferromagnetically coupled to an imide-based radical have been reported by the research groups of Chirik[11] and Betley,[12] we collected zero-field ^{57}Fe Mössbauer spectra at 77 K on complexes **1**–**3** (Figure 2) in an attempt to further authenticate the iron oxidation state. Accordingly, complexes **1**, **2**, and **3** produced quadrupole doublets with isomer shifts, δ, of +0.86(1), +0.39(1), and −0.09(1) mm s^{-1}, and quadrupole splitting values, ΔE_Q, of 1.12(1), 2.38(1), and 2.78(1) mm s^{-1}, respectively. As the local geometry at the iron center experiences minimal change upon one- and two-electron oxidations of complex **1**, the consistent change in isomer shift of approximately 0.48 mm s^{-1} indicates that iron centers in complexes **1**–**3** are each indeed in different oxidation states. Furthermore, the slightly negative δ value detected for **3** is comparable to that of Lee's tetranuclear Fe^{IV} imide cluster ($\delta = -0.17$ mm s^{-1})[6a] and Que's octahedral Fe^{IV} imide complex ($\delta = +0.02$ mm s^{-1}).[6d]

As a result of the unique electronic configuration of the Fe^{IV} imide complex, complex **3** was further examined by density functional theory (DFT) calculations. A model complex substituting the two *tert*-butyl groups at the 3-position of the pyrrolyl rings with hydrogen atoms in a spin singlet state ($S = 0$) accurately reproduces the metrical parameters determined by X-ray analysis.[9] The subsequent analysis of frontier molecular orbitals (MOs) reveals the electronic configuration of the iron center and the details of bonding in the *cis*-divacant geometry. Within the chosen coordinate system, d_{xy} and d_{xz} orbitals are doubly occupied MOs, whereas d_{yz}, d_{z^2}, and $d_{x^2-y^2}$ orbitals become unoccupied (Figure 3). This configuration is consistent with a low-spin Fe^{IV} center. The $d_{x^2-y^2}$ and d_{z^2} orbitals are substantially destabilized because of strong σ-donation from the three pyyr$_2$py nitrogens and the N_{imide}, respectively. The d_{xz} and d_{yz} orbitals show prevailing π* antibonding character to the N_{imide} but

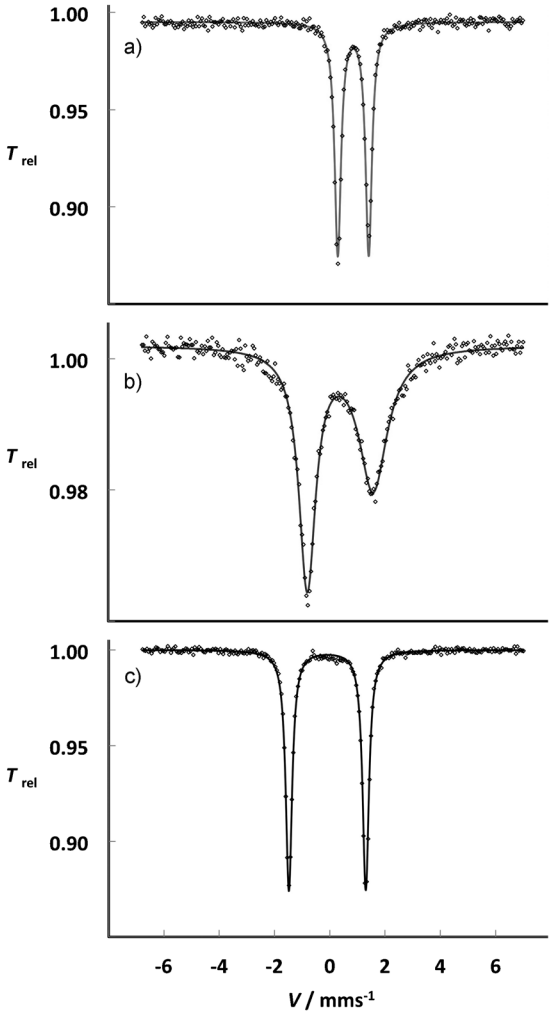

Figure 2. Zero-field ^{57}Fe Mössbauer spectra of a) [(pyrr$_2$py)Fe(OEt$_2$)] (**1**), b) [(pyrr$_2$py)FeCl] (**2**), and c) [(pyrr$_2$py)Fe=NAd] (**3**) recorded at 77 K (see text for simulation parameters). T_{rel} = relative transmission. Open symbols represent experimental data and solid lines represent fitted data.

experience differing degrees of destabilization, resulting in a bent imido group (Fe1-N3-C16: calculated angle = 142.0°, experimental = 140.5°). General considerations indicate that the more acute is the Fe-N-C angle, the more double-bond character the Fe–N_{imide} bond has. In the case of **3** this is supported by Loewdin and Mayer population analysis indicating an Fe–N_{imide} bond order of 2.18 and 2.02, respectively. Finally, the d_{xy} orbital is essentially nonbonding and thus is the lowest energy *d*-orbital.

The accuracy of the calculated $S = 0$ electronic structure for **3** was further validated by calculating Mössbauer parameters. Both the calculated isomer shift (−0.14 mm s^{-1}) and quadrupole splitting (−3.14 mm s^{-1}) are in good agreement with the experimentally obtained values. Interestingly, the largest component of electric field gradient (EFG)[13] $V_{zz} = -1.85$ lies not along Fe–N_{imide} bond as one might expect, but approximately along the Fe–$N_{pyrrolyl}$ vector.[9] We calculated an $S = 1$ state for the model of **3** as well. Both the calculated

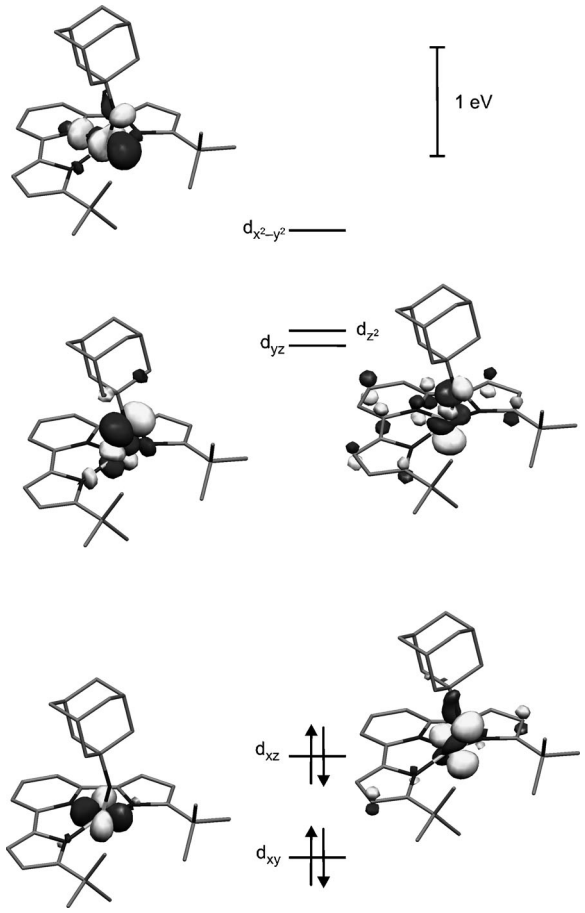

Figure 3. Frontier metal-based molecular orbitals for a model complex of **3** ($S=0$) obtained from spin-unrestricted B3LYP-DFT calculations. The *x* and *y*-axes are placed in the approximate plane of the $pyrr_2py$ ligand and the *z*-axis is approximately along the Fe–N_{imide} bond vector. Kohn–Sham orbitals are shown.

geometry and the Mössbauer parameters for the $S=1$ state do not match the experimentally obtained data,[9] which supports strongly an $S=0$ state for complex **3**.

Finally, we checked the influence of the *tert*-butyl groups at the 5-position of the pyrrolyl rings on the coordination geometry. Thus, all four *tert*-butyl groups of the $pyrr_2py$ ligand were replaced with hydrogens, and the geometry of the truncated complex was optimized for an $S=0$ state. To our surprise, in the absence of bulky *tert*-butyl groups and the geometrical flexibility of the molecule, the unusual *cis*-divacant coordination geometry was preserved.[9] Multiple attempts to obtain any other geometry by varying the starting point all converged to the same structure with $\tau_4=0.62$.[10] Thus, although two bulky *tert*-butyl groups at the 5-position of the pyrrolyl rings prevent formation of a planar geometry for **3**, the electronic factors seem to be a driving force for formation of *cis*-divacant geometry.

Considering all data, we believe that complex **3** can be best described as a low-spin Fe^{IV} imide species ($S=0$). It should also be noted that the direct oxidation of Fe^{II} centers by organic substrates to generate an Fe^{IV} imide derivative is a rare phenomenon[6d] and typically requires low-valent Fe^0 or Fe^I synthons as two-electron reductants.[6b,c,11,14] Furthermore the geometry and low-spin configuration of **3** is unprecedented, indicating that the $pyrr_2py$ pincer ligand is a robust, strongly electron-donating, and most notably, redox-innocent ligand scaffold that enforces an unusual geometry.

In conclusion, we have described the meridional coordination of the bis(pyrrolyl)pyridine ligand ($pyrr_2py$) to a series of iron complexes ranging from Fe^{II}–Fe^{IV}. In all cases, the unusual trigonal pyramidal to *cis*-divacant octahedral geometry is maintained by the $pyrr_2py$ ligand. Additionally, we have shown that the direct two-electron oxidation of [($pyrr_2py$)Fe(OEt_2)] (**1**) results in the unique, and high-yield synthesis of an Fe^{IV} imide complex [($pyrr_2py$)Fe=NAd)] (**3**) which has an $S=0$ state. Calculations also indicate that removal of the *tert*-butyl substituents from the $pyrr_2py$ ligand results in retention of the *cis*-divacant geometry. This opens exciting perspectives in tuning the reactivity of the complex by replacing bulky *tert*-butyl groups with smaller substituents, thus rendering the Fe^{IV} center more available for coordination by substrate molecules. Constraining the Fe^{IV} center to this unusual geometry allows for the stabilization of a terminally bound imido ligand that does not have the expected radical character at the imide nitrogen atom. This opens the possibility to stabilize high-valent metal centers having metal–ligand multiple bonds by manipulating their geometry and coordination number.

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