

Peroxo and Ferryl Intermediates Detected by ^1H NMR Spectroscopy during the Oxygenation of Iron(II) Porphycene

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The iron(III) 2,7,12,17-tetra-*n*-propylporphycene (TPrPc)Fe^{III}Cl is reduced using aqueous sodium dithionite or zinc amalgam to produce (TPrPc)Fe^{II}. The ^1H NMR spectrum of (TPrPc)Fe^{II} (293 K; δ (ppm): pyrrole, -37.52; meso, 71.56; α -CH₂, 27.47; β -CH₂, 8.92; γ -CH₃, 5.55) can be accounted for by the planar unligated iron(II) porphycene with an $S = 1$ ground electronic state. Introduction of dioxygen into a toluene-*d*₈ solution of (TPrPc)Fe^{II} at 203 K results in the formation of the (μ -peroxo)diiron(III) porphycene (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc). The value of the chemical shift of the pyrrole resonances (17.99 ppm at 203 K) of this species and its distinct non-Curie behavior imply strong antiferromagnetic iron(III)-iron(III) coupling via a μ -peroxo bridge. The (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) intermediate is stable at 203 K, but it converts into the (μ -oxo)diiron complex (TPrPc)Fe^{III}-O-Fe^{III}(TPrPc) upon warming above 203 K. Reaction of (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) with a nitrogen bases (B: pyridine-*d*₅, 1-methylimidazole) results in a homolytic cleavage of the μ -peroxo bridge to form the ferryl porphycene complex B(TPrPc)Fe^{IV}O (^1H NMR (223 K), δ (ppm): pyrrole, -1.32; meso, 11.80). B(TPrPc)Fe^{IV}O reacts with triphenylphosphine at 223 K to yield triphenylphosphine oxide.

Introduction

Alteration of a coordination core is an effective way to control the properties of metalloporphyrins, including their catalytic activity.^{1–5} Porphyrin isomers that have emerged in the past decade, e.g., porphycene,⁶ corrrhycene,^{7,8} hemiporphycene,^{9,10} isoporphycene,¹¹ and inverted porphyrin (2-aza-21-carbaporphyrin),^{12,13} offer particularly interesting opportunities in this respect if one takes into account the notable variety of their coordinating tetragonal geometries.^{1,4,5}

Previously, some similarities between metalloporphycenes and the corresponding metalloporphyrins have been established.^{1,4,5}

In the field of iron(III) porphycene chemistry, the following complexes have been characterized: (TPrPc)Fe^{III}X (X = Cl⁻, Br⁻, N₃⁻, CH₃COO⁻, CF₃COO⁻, C₆H₅O⁻),^{14,15} [(TPrPc)Fe^{III}]₂O,^{15,16} and (TPrPc)Fe^{III}R, where TPrPc = 2,7,12,17-tetrapropylporphycene and R = aryl ligands.^{17,19} By the use of electrochemistry and spectroelectrochemistry, it has been demonstrated that porphycene stabilizes high oxidation states of iron in the following systems: [(TPrPc)Fe^{III}]₂²⁺,¹⁸ [(TPrPc)Fe^{IV}R]⁺,¹⁹ and {[(TPrPc)Fe^{IV}]₂O}₂²⁺.^{16,18} As shown by the formation of the interesting complex (TPrPc)Os^{VI}(O)₂, porphycene coordination allows for the osmium ion to be stabilized in the formal oxidation state VI.²⁰ Iron(II) porphycene, when generated electrochemically, also reacts spontaneously with dioxygen to give a μ -oxo-bridged diiron(III) species (eq 1).¹⁸



As an extension of the previous work on the interactions of dioxygen with iron(II) porphyrins, which resulted in the detection of a number of fundamental intermediates, including (μ -peroxo)diiron(III) and ferrylporphyrins,^{21–32} we explore here the mechanism of the reaction between iron(II) porphycene and dioxygen.

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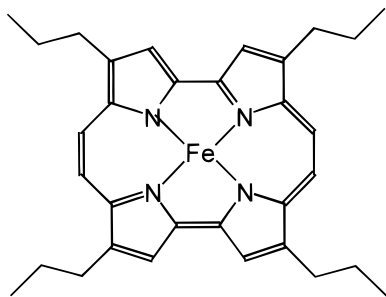
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Since ^1H NMR spectra of paramagnetic metalloporphyrins^{33,34} and core-modified metalloporphyrins² offer a sensitive probe for distinguishing among the various spin, ligation, and oxidation states of formed species, we use NMR spectroscopy as our principal method to monitor the oxygenation of iron(II) porphyrine in toluene- d_8 under low-temperature conditions.



Results and Discussion

The iron(II) 2,7,12,17-tetra-*n*-propylporphyrine, (TPrPc)Fe^{II}, utilized in this study was prepared by in situ reduction of (TPrPc)Fe^{III}Cl or (TPrPc)Fe^{III}Br in toluene- d_8 . Two of the reducing reagents tried, aqueous sodium dithionite and zinc amalgam, produced the navy blue compound (TPrPc)Fe^{II}. Two reductions, each using one of the starting materials, gave species showing identical spectral characteristics. The ^1H NMR spectrum of (TPrPc)Fe^{II} (δ (ppm): pyrrole, -37.52 ; meso, 71.56 ; $\alpha\text{-CH}_2$, 27.47 ; $\beta\text{-CH}_2$, 8.92 ; $\gamma\text{-CH}_3$, 5.55 ppm) at 293 K in toluene- d_8 , shown in traces A and A' of Figure 1 resembles the spectra of planar unligated iron(II) porphyrins with $S = 1$ electronic ground states.^{23,24,33,34} The identity of the pyrrole resonances in these and all other spectra has been confirmed by specific deuteration of the pyrrole positions. The meso and alkyl resonances have been assigned according to their characteristic hyperfine shifts, intensities, and relative line widths. The single resonance for the $\alpha\text{-CH}_2$ protons of the *n*-propyl groups is consistent with the four-coordinate structure. Characteristically, the porphyrine pyrrole resonance is found at a

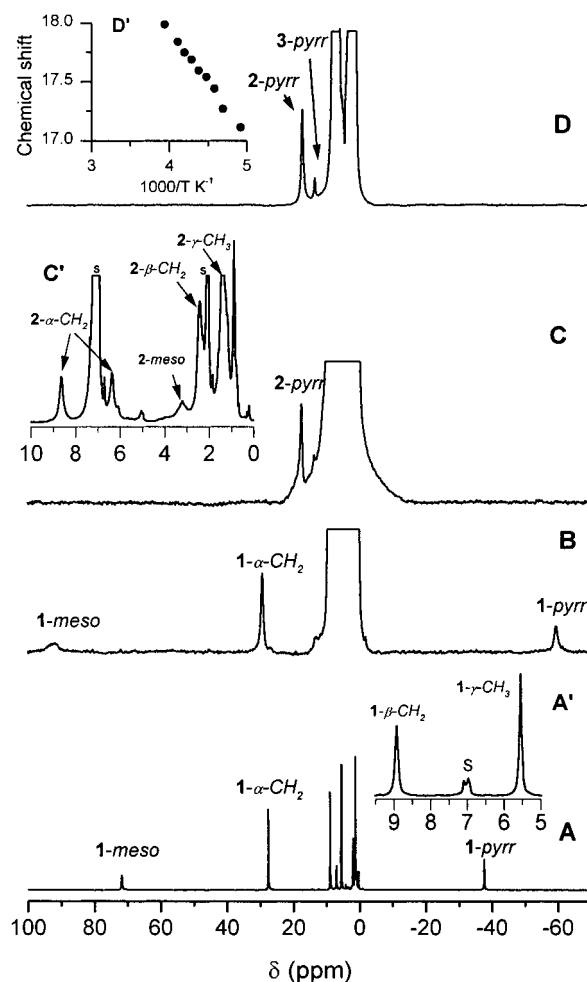


Figure 1. 300 MHz ^1H NMR spectra of (A) (TPrPc)Fe^{II} in toluene- d_8 solution (8.7 mM) at 293 K, (B) (TPrPc)Fe^{II} in toluene- d_8 solution at 203 K, (C) the sample in (B) after the addition of dioxygen at 203 K, and (D) the sample in (C) after warming to 253 K. Insets A' and C' present in detail the respective 10–0 ppm regions. Inset D' shows the temperature dependence of the chemical shifts for pyrrole resonances of **2**. Resonances are denoted by consecutive numbers: **1**, (TPrPc)Fe^{II}; **2**, (TPrPc)Fe^{III}–O–O–Fe^{III} (TPrPc); **3**, (TPrPc)Fe^{III}–O–Fe^{III} (TPrPc). Specific assignments: pyr, pyrrole protons; meso, bridge protons; α , $\alpha\text{-CH}_2$; β , $\beta\text{-CH}_2$; γ , $\gamma\text{-CH}_3$ of the *n*-propyl group.

higher upfield position than those of the corresponding iron(II) tetraarylporphyrins.^{23,24,33,34}

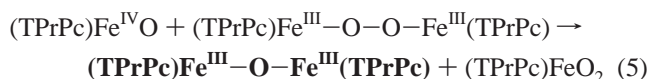
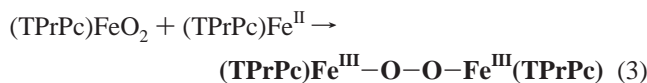
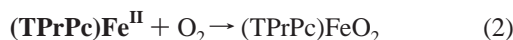
Carbon monoxide adds readily to (TPrPc)Fe^{II} in toluene- d_8 at 298 K to produce diamagnetic (TPrPc)Fe^{II}(CO) with typical positions of the porphyrine resonances (δ (ppm): meso, 9.51 ; pyrrole, 8.85 ; $\alpha\text{-CH}_2$, 3.93 ; $\beta\text{-CH}_2$, 2.32 ; $\gamma\text{-CH}_3$, 1.33 ppm). (TPrPc)Fe^{II}(CO) was previously identified in the course of electrochemical investigations.¹⁸

Introduction of dioxygen into a toluene- d_8 solution of (TPrPc)Fe^{II} at 203 K results in the spectral changes that are readily seen by comparing traces B and C of Figure 1. The resonances of (TPrPc)Fe^{II} have been replaced by those of an intermediate that can confidently be identified as the (μ -peroxy)-diiron(III) porphyrine (TPrPc)Fe^{III}–O–O–Fe^{III}(TPrPc). The chemical shift of the pyrrole protons of the new species is similar to that observed previously for μ -peroxy-bridged diiron(III) porphyrins, such as (TPP)Fe^{III}–O–O–Fe^{III}(TPP).^{21–24} In addition, the chemical shift of the porphyrine pyrrole protons shows a distinct non-Curie behavior as it changes from 17.11 ppm at 203 K to 17.99 ppm at 253 K. The direction and

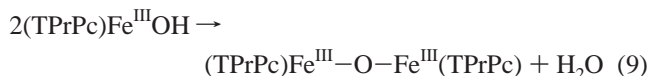
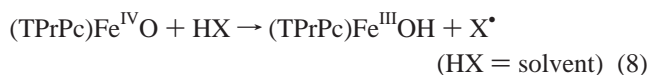
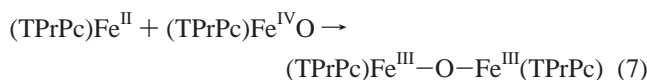
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magnitude of this shift are consistent with corresponding data for μ -peroxy-bridged iron(III) porphyrins.^{21–24} The (TPrPc)-Fe^{III}-O-O-Fe^{III}(TPrPc) intermediate is stable at 203 K, but it is eventually converted into (TPrPc)Fe^{III}-O-Fe^{III}(TPrPc) upon warming above 203 K, as reflected by the increase in intensity of the characteristic pyrrole resonance at 13.32 ppm (at 203 K).¹⁵ The (μ -oxo)diiron(III) complex was previously synthesized by an independent procedure, allowing unambiguous assignments of the diagnostic resonances.^{15,16}

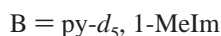
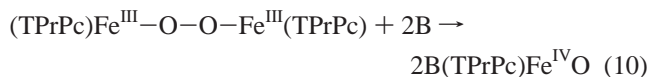
On the basis of the above findings, the autoxidation of iron(II) porphycene appears to follow the route previously established for sterically nonhindered iron(II) porphyrins.^{21–24} Reactions 2–5 present feasible steps for the process. At the crucial



stage, the homolytic cleavage of (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) results in the formation of the intermediate five-coordinate ferryl species (TPrPc)Fe^{IV}O (eq 4), which has remained undetectable because of its high reactivity. Additional reactions (eq 6–9) that reflect the particular reactivity of the ferrylporphycene with iron(II) porphycene or with the solvent can be operative as well.



Trace B in Figure 2 shows the effect of adding pyridine-*d*₅ to the sample containing (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) (trace A, Figure 2) at 223 K. The pyrrole resonance of the (μ -peroxy)diiron(III) species has disappeared from the spectrum while two new resonances at 11.80 and -1.32 ppm have appeared. These new resonances are readily assigned to the meso (11.80 ppm) and pyrrole protons (-1.32 ppm) of the six-coordinate ferrylporphycene species (py-*d*₅)(TPrPc)Fe^{IV}O, which is formed from the (μ -peroxy)diiron complex according to eq 10.



The analogous addition of 1-methylimidazole resulted in the formation of (1-MeIm)(TPrPc)Fe^{IV}O (eq 10). The pyrrole resonance assignment was verified by comparison of (py-*d*₅)(TPrPc)Fe^{IV}O and (py-*d*₅)(TPrPc-*d*₄)Fe^{IV}O (deuterated at pyrrole positions) spectra. By default, the second resonance (11.80 ppm), demonstrating four-proton intensity, corresponds to the meso position. The 1:1 relative intensity ratio of resonances identified

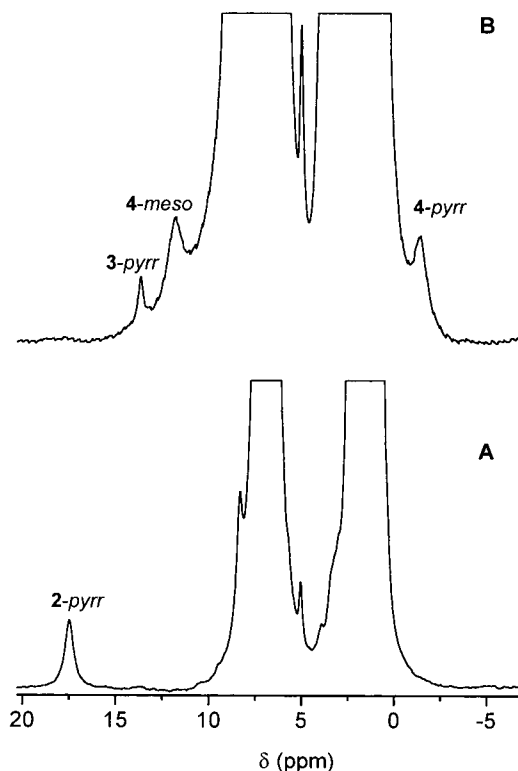


Figure 2. 300 MHz ¹H NMR spectra of toluene-*d*₈ solutions at 223 K of (A) (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) and (B) the sample in (A) after addition of 2 equiv of pyridine-*d*₅. Resonances of (py-*d*₅)(TPrPc)Fe^{IV}O are labeled as 4.

as corresponding to the pyrrole and meso positions was carefully determined at several different temperatures using the line deconvolution approach.

Previously, it was found that PFe^{III}-O-O-Fe^{III}P (P = porphyrin) reacts with py-*d*₅ or 1-MeIm to form six-coordinate BPF^{IV}O.^{35–37} The small hyperfine shifts of B(TPrPc)Fe^{IV}O are similar to those observed for BPF^{IV}O^{35–38} and (CH₃O)(*N*-MeTPP)Fe^{IV}O (*N*-MeTPPH = *N*-methyl-5,10,15,20-tetraphenylporphyrin),³⁹ for which a triplet electronic state has been firmly established. These shifts can be considered as indicative of a high degree of localization of the unpaired spin density on iron and oxygen with negligible delocalization on porphycene (porphyrin). The pyrrole and meso resonances of (py-*d*₅)(TPrPc)Fe^{IV}O follow the Curie law with appropriate intercepts near the known diamagnetic positions for the corresponding functional groups. Both ferryl species, i.e., (py-*d*₅)(TPrPc)Fe^{IV}O and (1-MeIm)(TPrPc)Fe^{IV}O, are observable only in a limited temperature range (193–240 K). Ultimately they decompose to (μ -oxo)diiron(III) porphycene supposedly via reactions with the solvents.^{40,41} In the course of our investigation, we did not observe any formation of a low-spin iron(III) porphycene complex which could be stabilized by the coordination of the

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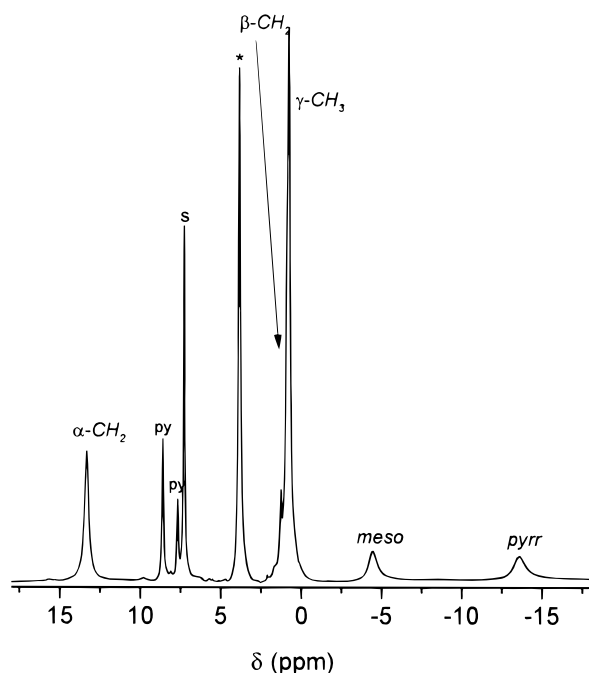


Figure 3. 300 MHz ^1H NMR spectrum of a chloroform- d_1 solution at 293 K of $[(\text{TPrPc})\text{Fe}^{\text{III}}(\text{py}-d_5)_2]^+$. The specific labeling is as in Figure 1. Other assignments: py, residual resonances of pyridine- d_5 ; *, HDO; s, solvent.

two nitrogen bases (py- d_5 , 1-MeIm). added. The representative ^1H NMR pattern for low-spin $[(\text{TPrPc})\text{Fe}(\text{py}-d_5)_2]^+$ (293 K; δ (ppm): meso, -4.51 ; pyrrole, -13.67 ; α - CH_2 , 13.32 ; β - CH_2 , 0.95 ; γ - CH_3 , 0.73) obtained in a separate experiment by titration of $(\text{TrPc})\text{Fe}^{\text{III}}$ I with py- d_5 is shown in Figure 3.

Additionally, $(\text{py}-d_5)(\text{TPrPc})\text{Fe}^{\text{IV}}\text{O}$ has been demonstrated to react with triphenylphosphine finally to yield $(\mu$ -oxo)diiron(III) porphycene. ^{31}P NMR spectroscopy shows that triphenylphosphine is converted to triphenylphosphine oxide. This fact provides additional support for the presence of the ferryl group in the new intermediate. The analogous reactivity of ferrylporphyrin toward oxygen atom acceptors, including triphenylphosphine, was previously observed.^{24,42}

Introduction of dioxygen into a toluene- d_8 solution of $(\text{TPrPc})\text{Fe}^{\text{II}}(\text{CO})$ at 298 K gave $(\mu$ -oxo)diiron(III) porphycene as identified by ^1H NMR spectroscopy.

The transformation sequence observed by ^1H NMR spectroscopy was also detected by UV-vis absorption spectroscopy.

In conclusion, the present work provides ^1H NMR spectroscopic evidence for the existence of two intermediates formed during the interaction of dioxygen with iron(II) porphycene, namely, $(\text{TPrPc})\text{Fe}^{\text{III}}-\text{O}-\text{O}-\text{Fe}^{\text{III}}(\text{TPrPc})$ and $\text{B}(\text{TPrPc})\text{Fe}^{\text{IV}}\text{O}$. Of particular importance is the finding that the porphycene ligand can stabilize a high-valent iron(IV)-oxo species. To the best of our knowledge, (nitrogen base)($\text{TPrPc})\text{Fe}^{\text{IV}}\text{O}$ and the previously described $(\text{CH}_3\text{O})(N\text{-MeTPP})\text{Fe}^{\text{IV}}\text{O}$ ³⁹ represent the only two cases where the ferryl moiety has been trapped in the environment of a core-modified porphyrin.

Ferrylporphyrin complexes are widely accepted as important constituents of the reactive forms of a variety of heme proteins, including the peroxidases and cytochrome P-450.⁴³⁻⁴⁵ Highly oxidized metalloporphyrins are generated in the activation and

transfer of oxygen, including catalytic epoxidation or hydroxylation.⁴⁶ Ferrylporphyrin³⁵⁻³⁷ or ferrylporphyrin π cation radicals^{47,48} were intensively investigated to construct structural/functional models of active states of hemoproteins. The present investigation emphasizes the parallel between iron porphycenes and iron porphyrins observed at the ferryl level. Thus, it is very likely that iron porphycenates, constructed with steric protection in their molecular architecture, would also be capable of carrying out the oxygen atom or dioxygen molecule transfer chemistry.

Experimental Section

Reagents. Free 2,7,12,17-tetra-*n*-propylporphycene, TPrPcH_2 , was prepared using the reported method.⁵ Its deuterated-pyrrole form, $(\text{TPrPc}-d_4)\text{H}_2$, was obtained by dissolving 40 mg of TPrPcH_2 in 1 mL of D_2SO_4 - D_2O (9:1 w/v) and keeping the solution at room temperature for 24 h. The solution was then poured into ice-cold water (60 mL) and the porphycene extracted with CH_2Cl_2 (60 mL). The organic layer was washed with aqueous NaHCO_3 and water and then dried. The ^1H NMR spectra indicated that the protons on the pyrrole rings were replaced by deuterium almost quantitatively.

Insertion of Iron. A solution of 0.5 mL (3.8 mmol) of $\text{Fe}(\text{CO})_5$ was added to a solution of 30 mg (0.0625 mmol) of $(\text{TPrPc})\text{H}_2$ or $(\text{TPrPc}-d_4)\text{H}_2$ in 15 mL of dry toluene. About 10 mg of I_2 was then added to the reaction mixture. The resulting mixture was heated under reflux for 5 h and then cooled and filtered. The solution was evaporated to dryness. After filtration, the solid residue was extracted with chloroform (about 50 mL) mixed with previously obtained solid and the resulting solution was stirred with a 10% sodium hydroxide solution (15 mL) for 4 h. The organic layer was evaporated to dryness, the crude product was dissolved in dichloromethane, and the solution was chromatographed on a basic alumina column. A trace of unreacted TPrPcH_2 was eluted with hexane-dichloromethane (4:1 w/v) as the first band. The second band eluted with dichloromethane was $[(\text{TPrPc})\text{Fe}^{\text{III}}]_2\text{O}$. The yield of the insertion process was found to be 99%. $[(\text{TPrPc})\text{Fe}^{\text{III}}]_2\text{O}$ was cleaved with HX acids to produce $(\text{TPrPc})\text{Fe}^{\text{III}}\text{X}$ (X = Cl, Br). The identity of the products was confirmed by spectroscopic data for analogous species obtained by a different route.^{14,15}

$(\text{TPrPc})\text{Fe}^{\text{II}}$ Preparation and Low-Temperature Studies. Iron(II) porphycene was prepared by reduction of $(\text{TPrPc})\text{Fe}^{\text{III}}\text{Cl}$ (6 mg) in toluene- d_8 (1.2 cm^3) with zinc amalgam under purified nitrogen in a glovebox. The solution was filtered to remove the solid, and the filtrate was placed directly into an NMR tube, which was then sealed with a septum cap. The sample was removed from the box and cooled to 195 K in an ethanol bath that was chilled by the addition of a sufficient amount of liquid nitrogen to reach 195 K. Dioxygen was introduced into the sample through a syringe needle. The sample was shaken in the cold bath and then transferred to the precooled NMR probe, and the progress of the reaction was followed by ^1H NMR spectroscopy. A toluene- d_8 solution of the appropriate nitrogen base was added to the sample through a microsyringe while the sample was maintained at 198 K.

The samples for measurements of electronic spectra were prepared similarly in long-necked cuvettes sealed with septum caps. The cuvettes were cooled by immersion in the ethanol bath. A sample was then transferred to a diode array spectrometer, and the spectrum was immediately recorded. The experiment was repeated several times on different samples to confirm reproducibility. The reproducibility was

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also confirmed for the same sample, as the spectral pattern remained unchanged after several ethanol bath–spectrometer transfers. The sample transfer times in both spectroscopic experiments were similar.

Alternatively, 1 mg of (TPrPc)Fe^{III}X in 1 mL of toluene and 5 mg of sodium dithionite in water (1 mL) were mixed together in the glovebox. After the reduction was complete and the color had changed from green to navy blue, the toluene layer was removed by pipet and evaporated to dryness and the sample was dried under vacuum for 12 h.

(TPrPc)Fe^{II} was characterized by means of ¹H NMR spectroscopy as previously described.

Instrumentation. ¹H NMR (300 MHz) spectra were measured on a Bruker AMX 300 spectrometer. The peaks were referenced against the

residual resonances of the deuterated solvents. Absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer.

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Supporting Information Available: Figure S1, showing the electronic spectral changes during the successive additions of dioxygen and py-*d*₅ to (TPrPc)Fe^{II} at ca. 200 K and the effect of warming to 298 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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