

## The Remarkable Axial Lability of Iron(III) Corrole Complexes

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**Abstract:** Flash photolysis of nitrosyl tris(aryl)corrolate complexes of iron(III),  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  ( $\text{Ar}_3\text{C}^{3-} = 5,10,15\text{-tris(4-nitro-phenyl)corrolate (TNPC}^{3-})$ ,  $5,10,15\text{-tris(phenyl)corrolate (TPC}^{3-})$  or  $5,10,15\text{-tris(4-tolyl)corrolate (H}_3\text{TTC}^{3-})$ ) leads to NO labilization. This is followed by the rapid reaction of NO with  $\text{Fe}^{\text{III}}(\text{C})$  to regenerate the starting complex. The second-order rate constants for the back reactions ( $k_{\text{NO}}$ ) were determined to be many orders of magnitude faster than the corresponding reactions of ferric porphyrin complexes and indeed are reminiscent of the very large values seen for those of the corresponding ferrous porphyrin analogues. These data are interpreted in terms of the strongly electron-donating character of the trianionic corrolate ligand and the likely triplet electronic configuration of the iron(III) complex. These reduce the affinity of the metal centers to Lewis bases to the extent that axial ligands bind very weakly or not at all. This property is illustrated by the nearly identical  $k_{\text{NO}}$  values ( $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at 295 K) recorded for the back reaction of  $\text{Fe}^{\text{III}}(\text{TNPC})$  with NO after flash photolysis of  $\text{Fe}(\text{TNPC})(\text{NO})$  in toluene solution and in THF solution. Softer Lewis bases have a somewhat greater effect; for example, studies in 1:9 (v:v) acetonitrile:toluene and 1:9 pyridine:toluene gave  $k_{\text{NO}}$  values decreased  $\sim 33\%$  and  $\sim 85\%$ , respectively, but these both remain  $> 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The potential roles of Lewis bases in controlling the dynamics of NO addition to  $\text{Fe}(\text{TNPC})$  in toluene was investigated in greater detail by determining the rates as a function of pyridine concentration over a wide range ( $10^{-4}$  to  $2.5 \text{ M}$ ). These data suggest that, while a monopyridine complex, presumably  $\text{Fe}(\text{TNPC})(\text{py})$ , is readily formed ( $K \approx 10^4 \text{ M}$ ), this species is about one-sixth as reactive as  $\text{Fe}(\text{TNPC})$  itself. It appears that a much less reactive bis(pyridine) complex also is formed at high [py] but the equilibrium constant is quite small ( $< 1 \text{ M}^{-1}$ ).

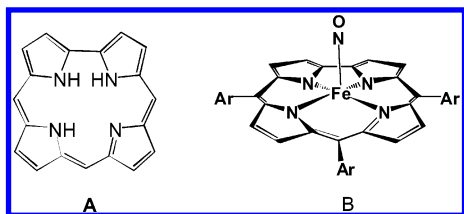
## Introduction

Nitric oxide (NO, nitrogen monoxide) has an established repertoire in mammalian biology with well-known roles in the cardiovascular, neurological, and immune response systems.<sup>1</sup> A key component of the mammalian biochemistry of nitric oxide involves the interactions between NO and metal centers.<sup>2</sup> The photochemical and thermal reactions of metal nitrosyl complexes also draw interest from the possibilities that such species may prove useful in strategies for the therapeutic delivery of NO to specific tissue sites.<sup>3</sup> Accordingly, this laboratory has been systematically investigating the reactions controlling the formation of metal nitrosyl complexes, as well as the subsequent redox, nitrosation, and other reactions in which these species participate. Among such studies, we<sup>4</sup> and others<sup>5</sup> have exten-

sively studied the formation and reactivities of the nitrosyl complexes of various metallo-porphyrins including several ferri- and ferro-heme proteins and models. In the present investigation, we turn to the NO reactivity with an iron(III) center in a related  $\pi$ -unsaturated macrocyclic tetrapyrrole ligand, namely, the corrole complexes,  $\text{Fe}^{\text{III}}(\text{C})$ ,

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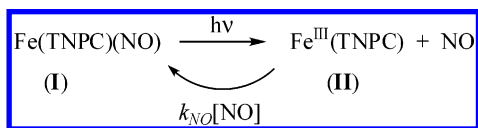
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**Figure 1.** A. Free base corrole. B.  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  ( $\text{Ar}$  = phenyl, 4-nitrophenyl, or 4-methylphenyl).

Corroles differ from the porphyrin analogues by the absence of a meso methine carbon (Figure 1A), a skeletal perturbation that has a significant impact on the ligand properties of these macrocycles.<sup>6</sup> The most obvious difference is that a corrole has three ionizable N–H protons; thus, when coordinated to metal centers, the corrolate ligand is tri-anionic ( $\text{C}^{3-}$ ), while the analogous porphyrinato ligand is dianionic ( $\text{P}^{2-}$ ). The higher ionic charge and the smaller cavity of the corrolate macrocycle stabilizes metals in higher oxidation states; thus, stable tri- and tetravalent metal complexes are common.<sup>7</sup> These “contracted porphyrins”<sup>8</sup> are receiving renewed interest owing to more accessible synthetic procedures;<sup>9</sup> however, reactivity studies remain limited. The present study probes the kinetics of the formation of ferric nitrosyl complexes of the type  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  (Figure 1B) from  $\text{Fe}(\text{Ar}_3\text{C})$  and NO in several different solvent systems.

Described here is a flash photolysis investigation of a representative ferric corrolate complex of nitric oxide,  $\text{Fe}(\text{TNPC})(\text{NO})$  (**I**) (Figure 1B,  $\text{TNPC}^{3-}$  is the 5,10,15-tris(4-nitro-phenyl)-corrolate ligand), in various solutions containing excess NO (in most cases). Photolysis of **I** leads to NO labilization and the formation of  $\text{Fe}(\text{TNPC})$  (**II**), which subsequently undergoes reaction with NO to regenerate **I** as the system relaxes back to equilibrium. The dynamics of this process were investigated in various media using time-resolved optical spectroscopy. A key observation is that the back reaction of NO with **II** (eq 1) is many orders of magnitude faster than the analogous reaction with ferric porphyrinato analogues  $\text{Fe}^{\text{III}}(\text{P})$  with NO. These results and their possible interpretations are presented here.



## Experimental Section

**Materials.** Solvents were distilled under nitrogen. Spectrochemical grade toluene (Burdick & Jackson) was distilled from sodium, tetrahydrofuran (THF) from benzophenone and sodium, and acetonitrile from calcium hydride. Pyridine was stored over molecular sieves. Other organic compounds (Aldrich) were used as purchased without any

further purification. Nitric oxide (99%, Aire Liquide) was purified by passage through a stainless steel column containing Ascarite II (Thomas Scientific), attached via O-ring seal (Viton) to a greaseless vacuum line.

The free base tris(aryl)corroles 5,10,15-tris(4-nitro-phenyl)corrole- ( $\text{H}_3\text{TNPC}$ ), 5,10,15-tris(phenyl)corrole ( $\text{H}_3\text{TPC}$ ), and 5,10,15-tris(4-tolyl)corrole ( $\text{H}_3\text{TTC}$ ) were prepared via the reaction of freshly distilled pyrrole (Aldrich) with the appropriate substituted benzaldehyde in refluxing acetic acid according to published procedures for the synthesis of corroles.<sup>9</sup> These compounds were purified by chromatography of the crude reaction mixtures on an initial silica column using  $\text{CH}_2\text{Cl}_2$  as the elutant and then a second silica column using  $\text{CH}_2\text{Cl}_2$ :hexanes (10:1) as the elutant. The ligands were characterized and shown to be pure by  $^1\text{H}$ NMR and mass spectroscopic techniques. The iron complexes  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  were formed via procedures reported previously for the preparation of other  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  complexes.<sup>7a</sup> A mixture of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (300 mg, 1.5 mmol) and the free base corrole (50 mg,  $\sim 76 \mu\text{mol}$ ) in pyridine:methanol (1:2) was refluxed for 3 h under dinitrogen, after which a 1.0 mL aliquot of saturated aqueous solution of  $\text{NaNO}_2$  was added to the hot solution, and the system was refluxed for an additional 30 min. The solution was then cooled to  $0^\circ\text{C}$ , and the resulting solid was collected by filtration and washed with water. This solid product was then dissolved in dichloromethane and then purified by chromatography on an alumina column (Brockman Activity III) using  $\text{CH}_2\text{Cl}_2$ :hexane (1:3) as the elutant. The procedure leading to formation of  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  complexes typically gave yields of  $\sim 80\%$  after recrystallization from  $\text{CH}_2\text{Cl}_2$ :hexane (1:2). These were characterized and shown to be pure by IR,  $^1\text{H}$  NMR, and mass spectrometry techniques.<sup>11</sup> The detailed syntheses of these compounds will be reported elsewhere.

**Flash Photolysis Experiments.** Solutions of known concentrations of NO and of  $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$  were prepared by vacuum transfer techniques on all-glass vacuum lines using flasks of known volume and procedures designed to prevent contamination of the solution with other  $\text{NO}_x$  impurities. The “pump-probe” flash photolysis apparatus has been described previously.<sup>4d</sup> The excitation source (“pump”) was a Continuum NY-61 Nd:YAG pulse laser operating in either the frequency tripled (355 nm) or frequency doubled mode (532 nm) with an energy of  $\sim 10$  mJ/pulse. Transient absorption changes were monitored with monochromatic probe light beam focused into the sample (at a right angle to the excitation beam) through a double grating monochromator (SPEX model 1680) and onto a photomultiplier tube (RCA IP28). The temporal response (25 shot averages) was recorded using a digital oscilloscope (Tektronix TDS 540) linked to a desktop computer. Plots of intensity versus time were converted to absorbance, and these curves were fit using Igor Pro Carbon software (Wavemetrics).

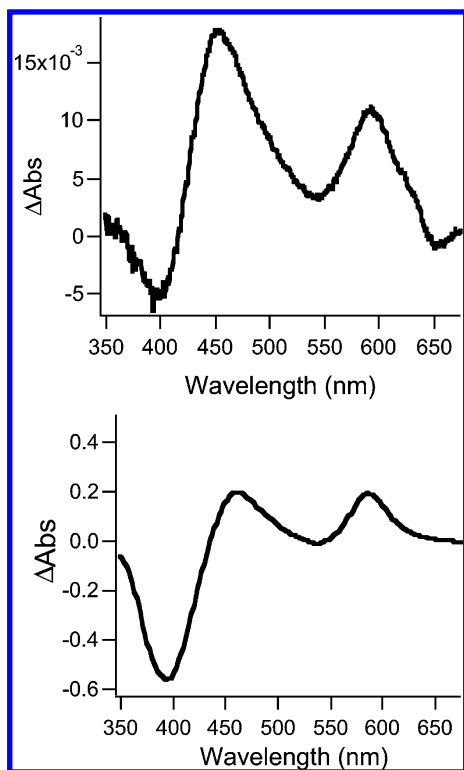
UV–vis spectra were recorded using a Hewlett-Packard model 8452A diode array spectrophotometer. The solutions were prepared and contained in a custom-made glass flask of measured volume fused to a quartz spectrophotometer cuvette and equipped with a coldfinger and with a high-vacuum stopcock for connection to a vacuum line.

## Results and Discussion

The optical absorption spectrum of  $\text{Fe}(\text{TNPC})(\text{NO})$  (**I**) in toluene solution displays a broad band at  $\lambda_{\text{max}}$  392 nm ( $\log \epsilon =$

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- (11) For example the spectroscopic properties for  $\text{Fe}(\text{TNPC})(\text{NO})$  are:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.37 (d, 2H,  $J = 5$  Hz), 7.55 (d, 2H, 5 Hz), 7.76 (d, 2H, 4 Hz), 7.85 (dd, 1H, 8 Hz), 7.90 (dd, 1H, 8 Hz), 8.04 (d, 4H, 8 Hz), 8.11 (d, 2H, 4 Hz), 8.45 (dd, 2H, 8 Hz), 8.51 (d, 4H, 8 Hz). MS(FAB):  $m/z$  744 ( $\text{M}^+$ ); 714 ( $\text{M}^+ - \text{NO}$ ). FTIR:  $\nu_{\text{NO}}$  = 1778  $\text{cm}^{-1}$  (KBr), 1785  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ). UV–vis (toluene):  $\lambda_{\text{max}}$  392 nm ( $\epsilon = 6.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ); 538 nm ( $7.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).



**Figure 2.** (a) Transient difference spectrum recorded using a CCD detector at a time delay of 30 ns from the flash and a 50 ns gate following 532 nm flash photolysis of a toluene solution of Fe(TNPC)(NO). (b) Difference spectra between **I** and Fe(TNPC) (generated in situ, see text) both at  $1.8 \times 10^{-5}$  M in toluene.

4.78) and another band centered at 538 nm (3.89). The spectra of Fe(TPC)(NO) (**III**) (strong bands at 390 nm (4.85) and 534 nm (3.97)) and Fe(TTC)(NO) (**IV**) (390 nm (4.86) and 532 nm (3.97)) are quite similar. These bands can be assigned to  $\pi\pi^*$  transitions largely localized on the corrole macrocycle and are analogous to the Soret and Q-bands seen in the optical spectra of porphyrinato complexes.<sup>10</sup> In the infrared spectra, the NO stretching frequencies ( $\nu_{\text{NO}}$ ) of **I**, **III**, and **IV** are 1778, 1766, and  $1762\text{ cm}^{-1}$ , respectively, in KBr with the trend in accord with the expected electron donor properties of the ring substituents ( $-\text{NO}_2 < -\text{H} < -\text{CH}_3$ ).

Flash photolysis of toluene solutions of each of these Fe(C)(NO) complexes using the excitation wavelengths ( $\lambda_{\text{ex}}$ ) 355 or 532 nm led to transient bleaching of bands corresponding to the parent compounds and the appearance of strong transient absorbances. These transient spectral changes underwent rapid [NO]-dependent decay back to the original spectra as described in more detail below. Figure 2a displays the difference spectrum recorded with a CCD detector and displaying transient absorbances at 460 and 593 nm following 532 nm flash photolysis of **I** in toluene solution.

Experience with similar behavior of the Fe(P)(NO) analogues<sup>4a,h,12</sup> as well as the observation of [NO]-dependent decay rates suggests that the flash photolysis experiment induces reversible NO labilization as indicated in eq 1. This could be confirmed by comparing the spectral differences between the nitrosyl reactant Fe(C)(NO) and the presumed Fe(C) product to the difference spectrum recorded; however, we have as yet

been unsuccessful in preparing analytically pure samples of the NO-free Fe(C) complexes owing to the ready oxidation of these species. To address this question, a species believed to be Fe(TNPC) was prepared in situ as follows in a glass apparatus equipped with vacuum line adaptors and fused to a 1-cm path length quartz spectrophotometer cell.

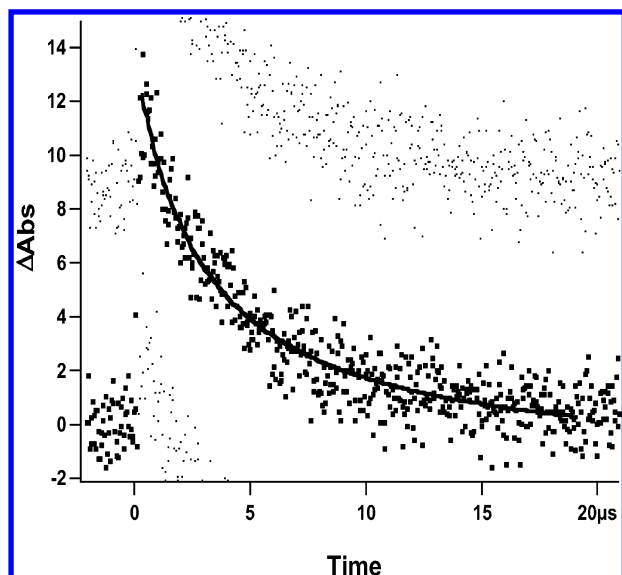
Initially, a solution of **I** ( $1.8 \times 10^{-5}$  M) was prepared in toluene (5.0 mL) at a concentration where the visible range absorption bands are appropriately on-scale and the spectrum was recorded (Supporting Information Figure S-1a). We had noted previously that solutions of **I** in pyridine slowly undergo loss of the coordinated NO when exposed to room light. To exploit this, the toluene was removed from the above solution under vacuum carefully to avoid the loss of any of the resulting solid **I**, which was then redissolved in pyridine (5.0 mL). The resulting solution was then exposed to room light and the spectrum periodically recorded until no further change was noted, and then the spectrum was recorded again (Figure S-1b). The liquid pyridine was then removed by evacuating the flask to give a dry, solid residue. The latter was redissolved in toluene (5.0 mL) to give the same concentration as that of the original solution, and the optical spectrum was recorded (Figure S-1b). The difference between the two is given in Figure 2b. To confirm that there was no loss of the Fe(TNPC) from the system, the resulting toluene solution was then exposed to NO ( $\sim 200$  Torr) and the optical spectrum recorded again. This spectrum (Figure S-1a) is identical to the one recorded initially; thus, there was no significant loss of material resulting from the sequential manipulations.

Notably, the difference spectrum shown in Figure 2b is qualitatively very similar to that in Figure 2a, the major perturbation being the much larger negative peak corresponding to the Soret type band of **I** at 392 nm. However, the latter difference can be attributed to the decreased sensitivity of the CCD camera at the shorter wavelengths since the spectrograph grating is blazed at 500 nm. Thus, a linear correspondence between the intensities of the positive and negative peaks in the difference spectra would not be expected. However, when temporal spectral studies were carried out using the point-by-point mode (decay curves measured at 5 nm intervals), the transient bleaching at 392 nm matched that expected according to Figure 2b).

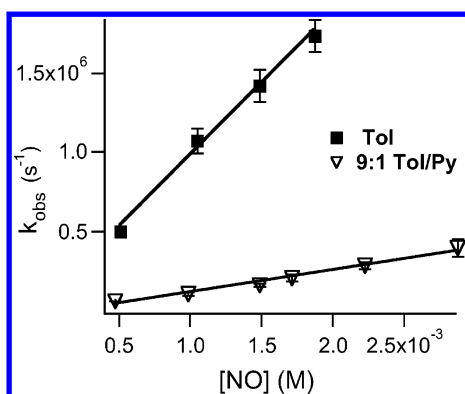
Figure 3 illustrates the temporal decay of the transient absorbance at 470 nm following 355 nm excitation of a deaerated toluene solution of Fe(TNPC)(NO). These  $\Delta\text{Abs}$  vs time data fit well to a second-order process consistent with NO photolabilization from **I** followed by the back reaction of **II** with NO to reform **I** indicated by eq 1. Similar transient decays were seen following 532 nm excitation. When the reaction was carried out under various NO partial pressures  $P_{\text{NO}}$ , the decay traces were faster and could be fit as simple exponentials to give the pseudo-first-order rate constants  $k_{\text{obs}}$ . Plots of  $k_{\text{obs}}$  vs [NO] (Figure 4) over the concentration range 0.5–3.0 mM proved to be linear with y-intercepts near zero according to the expected rate law expressed in eq 2. The slope of this line is therefore the second-order rate constant of recombination,  $k_{\text{NO}}$ , and the value in toluene solution is  $9.0 (\pm 0.5) \times 10^8\text{ M}^{-1}\text{ s}^{-1}$  at 295 K.

$$\left(\frac{d[\text{II}]}{dt}\right) = -k_{\text{NO}}[\text{NO}][\text{II}] \quad (2)$$

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**Figure 3.** Transient absorbance decay at 470 nm following 355 nm flash photolysis of **I** in toluene. The illustrated fit is to a second-order process.

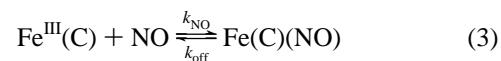


**Figure 4.** Plots of  $k_{\text{obs}}$  values (under excess NO) vs [NO] in pyridine and in 9:1 (v:v) toluene:pyridine following 532 nm excitation.

Analogous flash experiments were also carried out with the corrolate complexes  $\text{Fe}(\text{TTC})(\text{NO})$  (**III**) and  $\text{Fe}(\text{TPC})(\text{NO})$  (**IV**) in 295 K toluene solutions with a range of concentrations of added NO up to  $3 \times 10^{-3}$  M. In each case, transient absorption generated by the 532 nm flash photolysis decayed back to baseline exponentially, and plots of the resulting  $k_{\text{obs}}$  vs [NO] were linear. The  $k_{\text{NO}}$  values determined from these plots for the flash photolyses of **III** and **IV** were  $5.9 (\pm 1.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.8 (\pm 0.9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, similar to the  $k_{\text{NO}}$  determined in the flash photolysis of **I** under similar conditions.

These values for  $k_{\text{NO}}$  seem surprisingly large. They are several orders of magnitude larger than that ( $4.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) recorded for an analogous  $\text{Fe}(\text{III})$  porphyrinate species,  $\text{Fe}(\text{TPP})(\text{NO}_2)$ , formed by flash photolabilization of NO from  $\text{Fe}(\text{TPP})(\text{NO}_2)(\text{NO})$  (TPP = tetraphenylporphyrinato) in ambient temperature toluene solution.<sup>11</sup> Indeed, the much higher  $k_{\text{NO}}$  for NO reaction with **II**,  $\text{Fe}(\text{TTC})$ , and  $\text{Fe}(\text{TPC})$  are much closer to those recorded for the ferrous porphyrinato complex  $\text{Fe}(\text{TPP})$  ( $k_{\text{NO}} = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in benzene).<sup>13</sup> Furthermore, the nitrosyl complexes  $\text{Fe}(\text{TNPC})(\text{NO})$ ,  $\text{Fe}(\text{TTC})(\text{NO})$ , and  $\text{Fe}(\text{TPC})(\text{NO})$  are all moderately stable in the solid state and in aerated solution, and there are no observable changes in their optical spectra when solutions are deaerated by entraining with

argon or by subjecting to a vacuum. Thus, it is obvious that the rate constants of spontaneous NO dissociation ( $k_{\text{off}}$ ) are very small and that the equilibrium constant for eq 3 is quite large. Again, this behavior is much more analogous to that seen for ferro-hemes than for the ferri-heme analogues.<sup>3h</sup>



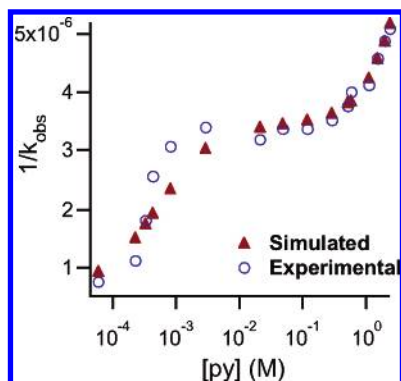
The marked reactivity of **II** toward NO is further demonstrated by probing the back reaction after 532 nm flash photolysis of **I** in 295 K tetrahydrofuran over a range of [NO]. Our expectation was that in a stronger donor solvent, the reaction of **II** with NO would be slowed owing to the occupation of the axial sites of  $\text{Fe}^{\text{III}}(\text{TNPC})$  by the THF. For comparison, the activation parameters measured for the reaction of NO with the ferric porphyrinato complex  $\text{Fe}^{\text{III}}(\text{TPPS})$  (TPPS = tetra(4-sulfonato-phenyl)porphyrinato) in aqueous solution clearly demonstrated that formation rate of the metal nitrosyl complex was dominated by the lability of the axial ligands (in that case, waters).<sup>3c,h</sup> However, this expectation was not met; the  $k_{\text{NO}}$  determined for the NO reaction with **II** in THF was  $10 (\pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , a value essentially identical to that determined in toluene solution.

In the same context, flash photolysis studies of **I** were also carried out in the mixed solvents 9:1 (v:v) toluene:acetonitrile and 9:1 (v:v) toluene:pyridine at 295 K over a range of  $P_{\text{NO}}$ . In the former case, the effect of the added acetonitrile on the rate of NO recombination with **II** was relatively small with  $k_{\text{NO}} = 6.0 (\pm 0.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , about 33% smaller than in toluene. (This value may be an underestimate, given that it was determined with the assumption that NO solubility in the mixed solvent is the same as that in toluene. Since NO solubility in neat  $\text{CH}_3\text{CN}$  is about 50% that in toluene, NO solubility in the mixed solvent might be somewhat lower than that in neat toluene.) On the other hand, the effect of 10% added pyridine was more significant. In that case, the  $k_{\text{NO}}$  is a factor of 6 smaller ( $1.4 (\pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) than that found in neat toluene under these conditions (Figure 4). Thus, of these various donor solvents, only pyridine seems to have a significant effect, although this value of  $k_{\text{NO}}$  remains dramatically larger than that found with the ferri-heme analogue.

An interesting comparison can be drawn to the solvent effects on the  $k_{\text{NO}}$  values determined in a kinetics study of the NO reaction with the Ru(III) complexes  $\text{Ru}(\text{salen})(\text{Cl})(\text{Sol})$  (salen = *N,N'*-bis(salicylidine)ethylenediamine dianion) generated by flash photolysis of  $\text{Ru}(\text{salen})(\text{Cl})(\text{NO})$  in different solvents (Sol) at ambient temperature.<sup>14</sup> In that study, the respective rates in THF and in  $\text{CH}_3\text{CN}$  were found to be  $\sim 8$  orders of magnitude smaller and  $\sim 11$  orders of magnitude smaller than those found in toluene ( $k_{\text{NO}} = 0.22, 4.7 \times 10^{-4}$ , and  $3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively). Although, like  $\text{Fe}(\text{III})$ , the Ru(III) complexes have  $d^5$  electronic configurations, a key difference is that the electronic configuration of the  $\text{Ru}^{\text{III}}(\text{salen})(\text{Cl})(\text{Sol})$  intermediate is low spin and the complex is hexacoordinate; thus, the reactivity with NO is dominated by the lability of the coordinated solvent.

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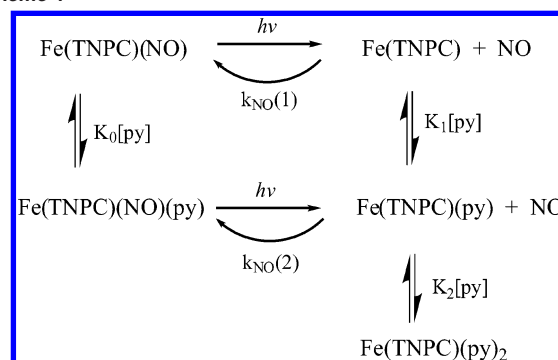


**Figure 5.** Plot of  $k_{\text{obs}}^{-1}$  vs  $\log [\text{py}]$  for the relaxation rates following 532 nm excitation of **I** in 295 K toluene:pyridine solutions under a constant  $P_{\text{NO}}$  of 110 Torr. The squares are the experimental points, while the circles are simulated data based on the model described by Scheme 1 with the following values  $K_0 = 0$ ,  $K_1 = 1 \times 10^4 \text{ M}$ ,  $K_2 = 0.2 \text{ M}$ ,  $k_{\text{NO}}(1) = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{NO}}(2) = 1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

To explore further the effect of pyridine on NO recombination, flash photolysis experiments were conducted with toluene solutions of  $\text{Fe}(\text{TNPC})(\text{NO})$  under various pyridine concentrations ranging from  $8 \times 10^{-5} \text{ M}$  to  $2.5 \text{ M}$  while maintaining a fixed  $P_{\text{NO}}$  at 110 Torr. (This would give a constant  $[\text{NO}]$  of  $1.77 \pm 0.01 \text{ mM}$ , if the nitric oxide solubility in the toluene/pyridine mixture remains the same as that in neat toluene). The decay curves of the transient absorbances detected after 532 nm excitation appeared to fit exponential functions (but see below) and give  $k_{\text{obs}}(\text{ap})$  values (the parenthetical “ap” is introduced to indicate these to be “apparent”  $k_{\text{obs}}$  values) that decreased as the pyridine concentration was increased. For example, under these conditions  $k_{\text{obs}}(\text{ap}) = 1.59 \times 10^6 \text{ s}^{-1}$  at  $[\text{py}] = 0 \text{ M}$ ,  $3.27 \times 10^5 \text{ s}^{-1}$  at  $[\text{py}] = 8.0 \times 10^{-4} \text{ M}$  and  $2.42 \times 10^5 \text{ s}^{-1}$  at  $[\text{py}] = 1.1 \text{ M}$ . However, the behavior is not a simple function of  $[\text{py}]$ . This is illustrated by Figure 5, which is a plot of  $k_{\text{obs}}(\text{ap})^{-1}$  vs  $\log [\text{py}]$ . In general terms, the  $k_{\text{obs}}(\text{ap})$  are little affected up to  $\sim 2 \times 10^{-4} \text{ M}$   $[\text{py}]$ , then decrease somewhat sharply up to  $\sim 10^{-3} \text{ M}$   $[\text{py}]$  with an overall change of about a factor of 5. The  $k_{\text{obs}}(\text{ap})$  values then essentially plateau at  $\sim 3 \times 10^5 \text{ s}^{-1}$  over the  $[\text{py}]$  range  $10^{-3}$  to  $10^{-1} \text{ M}$  before dropping again with further increases in  $[\text{py}]$ .

Notably, there is virtually no change in the optical spectrum of **I** under these conditions ( $<5\%$  reduction in the intensity of the band at 392 nm) between neat toluene and 9:1 (v:v) toluene:pyridine). Indeed, the spectrum of **I** in neat pyridine is virtually the same as that in neat toluene if measured under an NO atmosphere (see Supporting Information Figure S-2). This was demonstrated by an experiment where a solution of **I** ( $1.8 \times 10^{-5} \text{ M}$ ) was prepared in toluene and the spectrum recorded; then the solvent was removed under vacuum and the solid redissolved in the same volume of pyridine. Under argon, there were moderate changes in the optical spectrum as the solutions were being prepared and handled in room light, but once NO (200 Torr) was introduced to the closed vessel, the optical spectrum attributed to **I** was fully restored. Furthermore, in the infrared spectrum there is but a very modest shift of the frequency of the NO stretching band ( $\nu_{\text{NO}}$ ) for **I** between solutions in neat chloroform ( $1785 \text{ cm}^{-1}$ ) and in neat pyridine ( $1778 \text{ cm}^{-1}$ , broader). Thus, coordination of pyridine to  $\text{Fe}(\text{TNPC})(\text{NO})$  either has a very small equilibrium constant  $K_0$  or is not manifested by significant changes in the electronic

**Scheme 1**



and IR spectra. The apparently low value of  $K_0$  indicates that the metal center in the  $\text{Fe}(\text{III})$  corrolate complexes  $\text{Fe}(\text{C})(\text{NO})$  is much less electrophilic than in analogous  $\text{Fe}(\text{III})$  porphyrinate complexes as evidenced by the typically hexacoordinate nature of  $\text{Fe}(\text{P})(\text{L})(\text{NO})$  compounds. This difference is also consistent with the measurably lower frequency of  $\nu_{\text{NO}}$  ( $1778 \text{ cm}^{-1}$  in KBr) for **I** relative to that of a porphyrinato compound such as  $\text{Fe}(\text{TPP})(\text{NO}_2)(\text{NO})$  ( $1872 \text{ cm}^{-1}$  in benzene,<sup>15</sup>  $1868 \text{ cm}^{-1}$  in KBr<sup>16</sup>). The reluctance for **I** to coordinate an axial ligand would also be suggested by the structure of the tris(pentafluorophenyl)-corrolate complex  $\text{Fe}(\text{TFPC})(\text{NO})$  reported by Gross and co-workers,<sup>7a</sup> which shows the metal ion deviating from the  $\text{N}_4$  plane of the corrolate ligand by  $0.45 \text{ \AA}$  toward the nitrosyl.

On the other hand, the dynamics of the reactive intermediate **II** are indeed affected by the added pyridine in a manner that suggests the formation of both mono- and bis(pyridine) adducts of this species. Logical equilibria and NO addition reactions are mapped in Scheme 1 to provide the framework for discussion. In this scenario, the equilibrium constant  $K_0$  for the reaction of **I** with pyridine is considered to be quite small as indicated by the failure to observe significant changes in either the optical or IR spectra of **I** when toluene was replaced by pyridine as the solvent. Flash photolysis of **I** in the toluene/pyridine mixed solvents is proposed to lead to NO labilization to form  $\text{Fe}(\text{TNPC})$ . Once **II** is formed via NO labilization from **I**, reaction with py would also give  $\text{Fe}(\text{TNPC})(\text{py})$  and presumably  $\text{Fe}(\text{TNPC})(\text{py})_2$  in concentrations depending on the py concentration. If it is assumed that these steps are fast relative to relaxation to the nitrosyl species (however, see below) and that there is no direct reaction of NO with  $\text{Fe}(\text{TNPC})(\text{py})_2$ ,  $k_{\text{obs}}$  is predicted by eq 4, where  $k_{\text{NO}}(1)$  is the rate constant for the reaction of NO with **II** and  $k_{\text{NO}}(2)$  is that for the reaction of NO with  $\text{Fe}(\text{TNPC})(\text{py})$ . Notably the value of  $k_{\text{NO}}(1)$  ( $9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 295 K) is already known from the experiments in toluene solution under various NO pressures (Figure 4).

$$k_{\text{obs}} = \frac{(k_{\text{NO}}(1) + k_{\text{NO}}(2)K_1[\text{py}])[\text{NO}]}{1 + K_1[\text{py}] + K_1K_2[\text{py}]^2} \quad (4)$$

On the basis of this model, inspection of the experimental data presented in Figure 5 suggested that  $K_1$  should fall into the range  $\sim 10^3$ – $10^4 \text{ M}$  and that the product  $k_{\text{NO}}(2)[\text{NO}]$  should have a value of about  $3.0 \times 10^5 \text{ s}^{-1}$  (the plateau) under these conditions. The latter conclusion would give a  $k_{\text{NO}}(2)$  value of  $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of NO with  $\text{Fe}(\text{TNPC})(\text{py})$ , about 5-fold

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smaller than  $k_{\text{NO}}(1)$  for the analogous reaction of **II**. Since the second stage of reaction inhibition does not come into play until  $[\text{py}]$  is nearly 1 M, the association constant  $K_2$  for formation of  $\text{Fe}(\text{TNPC})(\text{py})_2$  must be 0.5 M or smaller. Attempts to fit the  $k_{\text{obs}}(\text{ap})$  values to this model give the curve displayed in Figure 5 based on values of  $k_{\text{NO}}(1)$  and  $k_{\text{NO}}(2)$  noted above plus  $K_1 = 1.0 \times 10^4 \text{ M}$  and  $K_2 = 0.2 \text{ M}$ . Notably, this fit is quite good at the higher pyridine concentrations but marginal (at best) for low  $[\text{py}]$ . Nonetheless, the concept that, coordination of **I** to one pyridine is facile but coordination to two pyridines is much less so, is consistent with earlier work by Vogel et al.<sup>6a</sup> who reported the isolation and structure of the monopyridine iron(III) complex  $\text{Fe}(\text{OEC})(\text{py})$  ( $\text{OEC}$  = octaethylcorrolate) under conditions that would have yielded bis(pyridine) adducts for porphyrin analogues.<sup>17</sup> It should be noted, however, that the bis(pyridine) ferric corrolate  $\text{Fe}(\text{TDCC})(\text{py})_2$  ( $\text{TDCC}$  = tris-(2,6-dichlorophenyl)corrolate) has been isolated from pyridine/hexane/benzene solutions and structurally characterized.<sup>7a</sup>

The fundamental problem in attempting to analyze the reaction dynamics of the relaxation processes after the flash photolysis of **I** in mixed pyridine/toluene solutions in terms of this model is the stated assumption that the equilibria between **II** and the mono- and bis(pyridyl) adducts are established rapidly relative to the decay of the transients by reaction with NO. Since it is likely that the reaction of py with **II** will have a rate constant no greater than  $k_{\text{NO}}(1)$ , the relaxation of the systems will involve several competing and sequential processes on comparable time scales at the lowest concentrations of pyridine. At higher  $[\text{py}]$ , the original assumption will have greater validity. For example, the rate constant for the relaxation of **II** and the monopyridine adduct to come into equilibrium will be  $k_{\text{rel}} = k_2[\text{py}] + k_{-2}$ . If  $k_2 = \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , i.e., comparable to  $k_{\text{NO}}(1)$ , this system will approach equilibrium significantly faster than the reaction of **II** with NO only when  $[\text{py}] > [\text{NO}]$ , which is fixed in these experiments at 1.77 mM.

In this context, a closer examination of the apparent single-exponential fits of the transient decays following flash photolysis of **I** revealed the following. The single-exponential fits are excellent at very low  $[\text{py}]$  ( $< 10^{-4} \text{ M}$ ), where decay is dominated simply by the reaction of **II** with NO, and at high  $[\text{py}]$  ( $> 10^{-2} \text{ M}$ ), where the equilibration between **II** and the pyridine complexes is faster than regeneration of **I**. Better fits of the decay curves at intermediate pyridine concentrations were obtained when a dual exponential function ( $\text{Abs}(t) = A_a e^{-k_a t} + A_b e^{-k_b t} + B$ ) was used with  $k_a$  fixed at a value equal to  $k_{\text{NO}}(1)[\text{NO}]$  and with  $A_a$ ,  $A_b$ , and  $k_b$  allowed to iterate to find the best fits. A key observation is that the weighting factor  $A_b$  for the second term increases significantly with increasing pyridine concentration while the rate constant diminishes. For examples, for  $[\text{py}] = 2.3 \times 10^{-4} \text{ M}$ , the ratio  $A_b/A_a$  was  $\sim 0.4$ , but at  $7.9 \times 10^{-4} \text{ M}$ , that ratio has shifted to  $\sim 2.5$ . This behavior is qualitatively consistent with the model described by eq 4, with the proviso that the dynamics at low  $[\text{py}]$  reflect the competition for **I** among the various reactive species present, including NO and py.

Based on this analysis, **II** binds to py to form mono- and bis(pyridine) complexes with equilibrium constants  $\sim 10^4 \text{ M}$  and 0.2 M, respectively. The mono(pyridine) adduct is only 5-fold

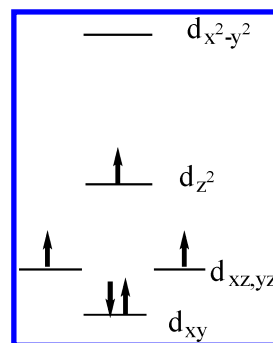


Figure 6. Proposed splitting of d-orbitals in  $\text{Fe}^{\text{III}}(\text{C})$ .

less reactive toward NO than is **II**, but the latter apparently does not react with NO on the time scale of these experiments. For comparison, the iron(II) porphyrinato analogue  $\text{Fe}(\text{TPP})$  binds to pyridine to form  $\text{Fe}(\text{TPP})(\text{py})$  and  $\text{Fe}(\text{TPP})(\text{py})_2$  with respective  $K_1$  and  $K_2$  values of  $1.1 \times 10^3$  and  $3.3 \times 10^4 \text{ M}^{-1}$ , and  $\text{Fe}(\text{TPP})(\text{py})_2$  is not reactive with NO.<sup>13</sup> With the much larger  $K_2$  value, the rate of NO recombination with  $\text{Fe}(\text{TPP})$  in 10% pyridine would be reduced by more than 4 orders of magnitude (relative to pure toluene). The much smaller effect seen here for **II** demonstrates quantitatively that ligands in the sixth coordination site of ferric corrolates are but weakly bound, an attractive feature in catalyst design. Such an impact on axial ligand binding has been noted by Mohammed et al.<sup>9c</sup> in a proposed mechanism for aerobic oxidations catalyzed by chromium(III) corrolates  $\text{Cr}(\text{Ar}_3\text{C})$ , where the first step was suggested to be a fast preequilibrium between hexa- and pentacoordinate  $\text{Cr}(\text{III})$ , allowing the latter to react with  $\text{O}_2$ .

Thus, the present flash photolysis kinetics studies demonstrate that the exceptional electron-donor nature of the  $\text{TNPC}^{3-}$  ligand suppresses the formation of strongly bound hexacoordinate complexes. Although  $^1\text{H}$  NMR studies clearly show **I** to be diamagnetic (whether best represented as  $\text{Fe}^{\text{II}}(\text{NO}^+)$ ,  $\text{Fe}^{\text{IV}}(\text{NO}^-)$ , or ferromagnetically coupled  $\text{Fe}^{\text{III}}(\text{NO})$  will be left for future debate),  $\text{Fe}(\text{III})$  corrolato complexes analogous to **II** have been described as having a  $^3/2$  spin state.<sup>6a,18</sup> While there is undoubtedly electronic delocalization and covalency between the macrocycle  $\sigma$ - and  $\pi$ - and the metal d-orbitals, meaningful insight can be drawn from a simple d-orbital diagram of a tetragonal complex with a very strong equatorial ligand field and a weak axial field (Figure 6). According to this diagram, the  $^3/2$  spin state would give a half-occupied,  $\sigma$ -antibonding  $d_{z^2}$  orbital. Electronic configurations such as high-spin  $d^4$  or low-spin  $d^7$  metal complexes and the ligand field excited states of  $d^6$  metal complexes with a single electron in a  $d_{z^2}$  orbital invariably are extremely labile to axial ligand substitution, owing to the resulting strong Jahn–Teller distortion.<sup>19</sup> Given that  $\text{Fe}(\text{TPP})$  has been reported to have a triplet spin state,<sup>20</sup> this  $d^6$   $\text{Fe}(\text{II})$  species would also display a singly occupied  $d_{z^2}$  orbital, while analogous ferric complexes such as  $\text{Fe}(\text{TPP})(\text{Cl})$  have sextet, high-spin configurations.<sup>21</sup> We attribute that the

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lower reactivity of the ferric porphyrins toward NO, relative to Fe<sup>II</sup>(P) and Fe<sup>III</sup>(C), to the greater Lewis acidity of the Fe<sup>III</sup>(P) center, leading to stronger solvent coordination at the axial sites. The low-spin 4d<sup>5</sup> Ru(salen)(Cl)(sol) complexes formed after flash photolysis of the nitrosyl complex Ru(salen)(Cl)(NO) in different solvents described above would be expected to bind axial donor ligands even more strongly and thus would be much less reactive in donor solvents than are any of the Fe(II) or Fe(III) compounds discussed here.

Notably, the bis(pyridine) complex Fe(TFPC)(py)<sub>2</sub> has been reported<sup>7a</sup> to have a low-spin ( $S = 1/2$ ) electronic configuration, consistent with the apparent low reactivity of Fe(TNPC)(py)<sub>2</sub> toward NO as represented in Scheme 1.

In summary, we have used flash photolysis studies to generate ferric corrolate complexes of the type Fe<sup>III</sup>(Ar<sub>3</sub>C) and to probe for the first time the quantitative dynamics of such species in ligand addition, in this case, reaction with nitric oxide. The corrolate complex Fe(TNPC) (**II**) is much more reactive toward NO than is an analogous ferric porphyrinato complex Fe(TPP)(NO<sub>2</sub>) in toluene solution. Indeed **II** shows a  $k_{\text{NO}}$  for reactivity toward NO similar to that seen for the ferrous porphyrin analogue Fe(TPP) under comparable conditions. This suggests that **II** is pentacoordinate or only very weakly

coordinated in the axial positions not only in hydrocarbon solvents such as toluene but also in stronger Lewis base solvents such as THF and acetonitrile. Furthermore, unlike Fe(TPP), which has been shown to form a bis(pyridine) complex Fe(TPP)(py)<sub>2</sub>,<sup>13</sup> the reactivity of **II** toward NO is only modestly suppressed by high concentrations of pyridine, since formation of the hexacoordinate analogue Fe(TNPC)(py)<sub>2</sub> has a much smaller equilibrium constant.

Ongoing studies in this laboratory with the iron corrolate complexes are focused on evaluating quantitatively how the electronic and steric properties of representative corrolate ligands define the reactivities of coordinated metal centers and how these compare to the representative porphyrinato complexes.

**Acknowledgment.** This research was supported by the National Science Foundation (CHE-0352650).

**Supporting Information Available:** Figures S-1 and S-2 showing spectra of Fe(TNPC)(NO) in different solvents before and after photolysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA044090+