

thus accounting for some reduction in the catalysis of decarboxylation. An additional pathway for the inductive effect of the pyridine nitrogen involves the α' -carbon directly. The inductive effect of the pyridine nitrogen is partially distributed around the aromatic ring, so that the azomethine nitrogen is separated from this effect by only a single aliphatic carbon atom. It has been suggested by a reviewer of this paper that deprotonation of the pyridine nitrogen may favor a shift of the azomethine proton to the phenolate oxygen resulting in the formation of a new microspecies, **17a**. This change in bonding would have a considerable influence on the rates, over a wide range of **17** \rightleftharpoons **17a** equilibrium quotient. In other words even a small contribution from **17a** would have a pronounced effect.

As the pH is increased above **11**, the major ketimine initially present is **18**. In this species the azomethine nitrogen is now deprotonated, thus accounting for the observed large decrease in catalytic activity. Species **19** and **20** ketonize rapidly to **21** and **22** and dissociate almost quantitatively into AKBA and pyridoxamine since the Schiff base formation constant is small, as are the concentrations of AKBA and PM. α -Ketobutyric acid was identified as the product by NMR measurement on more concentrated solutions and this product was verified earlier by Sakkab and Martell.³²

It should be possible to estimate the pK_a 's of the OPA: pyridoxamine Schiff bases involved in decarboxylation from the inflection points in the pH-rate constant profile of k_{SB} in Figure 4. Not enough data have been collected below the first inflection and beyond the second inflection, for reasons previously mentioned, to carry out a precise determination of the dissociation constants of the Schiff base. However, an estimate of the K_a 's defined by

eq 6 and 7 observed inflection regions in Figure 4. Thus, the

$$K_{a_1} = \frac{[17][H^+]}{[14]} \quad (6)$$

$$K_{a_2} = \frac{[18][H^+]}{[17]} \quad (7)$$

mathematical expression for pyridoxamine catalysis over the entire pH range is

$$k_{SB} = k_{H_2A} \alpha_{H_2A} + k_{HA} \alpha_{HA} + k_A \alpha_A \quad (8)$$

with H_2A , HA , and A representing species **14**, **17**, and **18**, respectively. The fraction of each species and the specific rate constant of decarboxylation for each species are α_i and k_i , respectively. Banks et al.³³ have reported 6.9 and 10.3 for the analogous pK_a 's in the pyridoxamine:pyruvate ketimine Schiff base system. The specific rate constants indicated in eq 8 were found to be 41.6 s^{-1} , 19.2 s^{-1} , and 0.3 s^{-1} for species **14**, **17**, and **18**, respectively, with an error of $\pm 0.6 s^{-1}$.

The catalytic effects on OPA decarboxylation by pyridoxamine are dependent on two factors: (1) the extent of Schiff base formation and (2) the protonation of the Schiff base species present. On the basis of the specific rate constants determined above, it is proposed that the fully protonated Schiff base is more active toward decarboxylation than the monoprotonated species while the fully deprotonated species is relatively inactive.

Registry No. 1, 85-87-0; 2, 642-93-3; 3, 84065-57-6; vitamin B₆, 8059-24-3.

Nitrosoalkane Complexes of Iron-Porphyrins: Analogy between the Bonding Properties of Nitrosoalkanes and Dioxygen

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Abstract: Various iron-porphyrin complexes involving an iron-nitrosoalkane bond, $Fe^{II}(\text{porphyrin})(RNO)(L)$, with porphyrin = TPP, TpCIPP, TTP, or DPDME, $R = i\text{-Pr}$ or Me , and $L = \text{MeOH}$, $i\text{-PrNHOH}$, $i\text{-PrNH}_2$, pyridine, N -methylimidazole, or PPhMe_2 ,¹ have been prepared either by reaction of $Fe^{II}(\text{porphyrin})$ with the RNO dimer or of $Fe^{III}(\text{porphyrin})(Cl)$ with $RNHOH$, in the presence of the L ligand. These hexacoordinate complexes and the pentacoordinate $Fe(\text{porphyrin})(RNO)$ complexes are in the low-spin state and exhibit IR ν_{NO} frequencies ranging from 1400 to 1445 cm^{-1} . Their trans ligands L are in fast exchange, vs. the 1H NMR time scale, at 20 $^\circ\text{C}$, and bind to the pentacoordinate complex $Fe(\text{porphyrin})(RNO)$ with rather high affinities (for porphyrin = TPP and $R = i\text{-Pr}$, the binding equilibrium constants are respectively 350 , 6×10^4 , and 15×10^4 L mol^{-1} for $L = \text{MeOH}$, pyridine, and N -methylimidazole at 27 $^\circ\text{C}$). The X-ray structure of $Fe(\text{TPP})(i\text{-PrNO})(i\text{-PrNH}_2)$ shows that $i\text{-PrNO}$ is bound to the iron by its nitrogen atom, the $Fe-N(O)i\text{-Pr}$ distance (1.865 (14) \AA) being considerably shorter than the $Fe-NH_2i\text{-Pr}$ distance (2.100 (14) \AA). The $Fe-N(O)R$ bond is much stronger than the $Fe-N$ bonds formed with usual amino ligands of iron-porphyrins such as amines, pyridines, or imidazoles. A comparison of some structural, IR, resonance Raman, and Mössbauer data of the $Fe(\text{TPP})(i\text{-PrNO})(N\text{-methylimidazole})$ and $Fe(\text{"picket fence"}\text{-TPP})(O_2)(N\text{-methylimidazole})$ complexes indicates a great similarity in the bonding properties of the $i\text{-PrNO}$ and O_2 ligands. These results explain various aspects concerning the formation and properties of hemoglobin- or cytochrome P-450-nitrosoalkane complexes.

There is a considerable current interest in the structural and chemical properties of hemoprotein-iron(II) complexes and in particular in the dioxygen complexes which are the key intermediates in various hemoprotein-dependent enzymatic systems.² Recently, evidence has been obtained in favor of the formation of nitrosoalkane complexes of hemoglobin, myoglobin,³ and cy-

tochrome P-450.⁴ In fact, nitrosoalkanes constitute a new class of ligands exhibiting a very high affinity for hemoprotein-iron(II).⁵

(1) Abbreviations: TPP, *meso*-tetraphenylporphyrinate; TpCIPP, *meso*-tetra(4-chlorophenyl)porphyrinate; TTP, *meso*-tetratolylporphyrinate; DPDME, deuteroporphyrinate dimethyl ester; P, porphyrinate; $i\text{-PrNH}_2$, 2-aminopropane; $i\text{-PrNHOH}$, 2-(hydroxyamino)propane; $i\text{-PrNO}$, 2-nitroso-propane; py, pyridine; $N\text{-MeIm}$, N -methylimidazole; PPhMe_2 , dimethylphenylphosphine; Me, methyl; Pyr, pyrrole; Ph, phenyl; MeOH, methanol; s, singlet; d, doublet; t, triplet; h, heptuplet.

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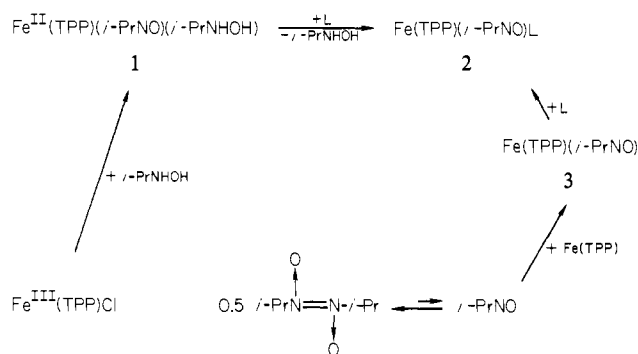
They are interesting ligands for two main reasons. First, they are formed during the oxidative metabolism of several drugs or exogenous compounds containing an amine or hydroxylamine function^{4c,6} or during the reduction of the corresponding nitroalkanes,^{4b} and they bind tightly to the iron(II) of the hepatic detoxifying cytochromes P-450, causing a severe inhibition of the catalytic functions of these cytochromes.^{6a,c} Secondly, they display common features with dioxygen: their nitroso group is isoelectronic with dioxygen and involves a low-lying π^* system readily available for back-bonding,⁷ and they present two possible binding modes, either "end on" or "side on".

Only a few transition-metal complexes having nitrosoalkane ligands have been reported.^{8,9} Nitrosoalkanes, particularly those which are not hindered around their nitrogen atom, are especially unstable, leading almost irreversibly to the corresponding dimers or tautomers.⁷ On the contrary, nitrosoarenes exist predominantly as monomers in solution, allowing an easy study of their interactions with transition-metal complexes.⁹

Among the few described transition-metal-nitrosoalkane complexes, three types of coordination have been indicated. In the particular case of chelate nitrosoalkyl ligands, nitrogen coordination has been established from X-ray data for a cobalt(I) bidentate dinitrosoalkyl complex^{8a,b} and for tris(violurato)iron(III)^{8c} and -ruthenium(II)^{8d} complexes and is very probable for a tris-(3-nitroso-2,4-pentanedionato)cobalt(III) complex.^{8e} A side-on η^2 coordination has been proposed for nitrosomethane bridging the two metal atoms of a cobalt(I) dinuclear complex.^{8f} Finally, the monodentate N-bonding mode has been established from an X-ray study for the $\text{PtCl}_2(t\text{-BuNO})_2$ complex,^{8g} proposed for a ruthenium(II) complex on the basis of IR results,^{8h} and seems possible for some ferrocyanide complexes.^{8i,j}

In order to prove definitely the involvement of an $\text{Fe}^{\text{II}}\text{-N(O)R}$ bond in the hemoprotein-nitrosoalkane complexes previously described⁴ and to get an insight into the mode of binding of the nitrosoalkane ligand in these complexes, we have prepared "model" $\text{Fe}(\text{porphyrin})(\text{RNO})$ complexes. The preparation of such complexes from reaction of iron(III)-porphyrins with aliphatic hydroxylamines has been reported in a preliminary communication.¹⁰

Scheme I



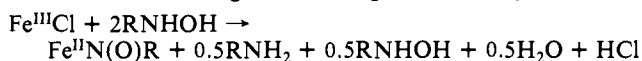
2a, L = py; 2b, L = *i*-PrNH₂; 2c, L = *N*-MeIm; 2d, L = MeOH; 2e, L = PPhMe₂

One of them, $\text{Fe}(\text{protoporphyrin IX})(N\text{-methylimidazole})(i\text{-PrNO})$, exhibited an electronic spectrum in benzene-DMF almost superimposable to that of myoglobin- $\text{Fe}^{\text{II}}(i\text{-PrNO})$ complex. The present paper describes different preparations of iron-porphyrin-nitrosoalkane complexes and their study by various spectroscopic methods including an X-ray analysis. This study definitely proves the existence of the $\text{Fe}^{\text{II}}\text{-RNO}$ bond, establishes the end-on N-binding mode of nitrosoalkanes in these ferroporphyrin complexes and gives information on the electronic structure of the $\text{Fe}\text{-RNO}$ bond. Moreover, it points out a striking similarity between the bonding properties of nitrosoalkanes and dioxygen as ligands of iron(II)-porphyrins.

Results

Preparation of *i*-PrNO-Iron-Porphyrin Complexes. Reaction of chloro(*meso*-tetraphenylporphyrinato)iron(III), $\text{Fe}(\text{TPP})(\text{Cl})$, with an excess of 2-(hydroxyamino)propane (*i*-PrNHOH), for a few hours at room temperature, under argon, followed by crystallization upon addition of MeOH, affords a nearly quantitative yield of the hexacoordinate complex $\text{Fe}(\text{TPP})(i\text{-PrNO})(i\text{-PrNHOH})$ (1). For preparation of other hexacoordinate complexes $\text{Fe}(\text{TPP})(i\text{-PrNO})(\text{L})$ (2), with L ligands such as 2-aminopropane (*i*-PrNH₂), pyridine (py), or *N*-methylimidazole (*N*-MeIm), the same procedure can be used with the addition of a few equivalents of L before the crystallization step. In the case where L is a weak ligand such as an alcohol, the preparation of the corresponding complex has to be carried out with only 2 mol of *i*-PrNHOH per mol of $\text{Fe}(\text{TPP})(\text{Cl})$ in a 1:1 alcohol- CH_2Cl_2 solvent mixture. The yields obtained for the preparation of complexes 1, 2a, 2b, 2c, and 2d (Scheme I) are always higher than 90%. These complexes have been fully characterized in the solid state by elemental analysis, mass spectrometry, and IR spectroscopy. The hexacoordinate complex 2e, $\text{Fe}(\text{TPP})(i\text{-PrNO})(\text{PPhMe}_2)$, has been obtained from the $\text{Fe}(\text{TPP})(i\text{-PrNO})(\text{MeOH})$ complex, by displacement of the weak ligand MeOH, upon addition of about 1 equiv of PPhMe₂. It is noteworthy that this strong ligand has been found able to partially displace the nitrosoalkane ligand, leading also to the formation of about 10% of the hemochrome $\text{Fe}(\text{TPP})(\text{PPhMe}_2)_2$. Complex 2e has been characterized in solution by IR, visible, and ¹H NMR spectroscopy (Tables I, III, and IV).

For a better understanding of the stoichiometry of the reaction between $\text{Fe}(\text{TPP})(\text{Cl})$ and *i*-PrNHOH, experiments were done with a $\text{Fe}(\text{TPP})(\text{Cl}):i\text{-PrNHOH}$ 1:2 molar ratio. In the absence of oxygen, a mixture of iron complexes is obtained; after treatment of this mixture by pyridine, one observes by ¹H NMR the quantitative formation of complex 2a. Moreover, *i*-PrNH₂ is formed in this reaction with a 24% yield (in mole per mole of starting *i*-PrNHOH) and about 23% of unreacted *i*-PrNHOH is recovered, indicating the following stoichiometry:



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Table I. IR and UV-Visible Spectroscopy Characteristics of Fe(P)(*i*-PrNO)(L) Complexes

Fe(P)(RNO)L		IR, ^a ν_{NO} , cm^{-1}	UV and visible, ^b λ , nm (ϵ , $\text{mM}^{-1} \text{cm}^{-1}$)		K , ^{b,c} L M^{-1}
P = TPP, R = <i>i</i> -Pr					
L = <i>i</i> -PrNHOH	1	1432	422 (270)	535 (12)	
= py	2a	1432	424 (256)	536 (11)	60 000
= <i>i</i> -PrNH ₂	2b	1432	425 (255)	539 (12)	125 000
= <i>N</i> -MeIm	2c	1432	426 (262)	540 (12)	150 000
= MeOH	2d	1445	420 (264)	536 (12)	350
= PPhMe ₂	2e ^d	1433	417-444	556-600	
Fe(TPP)(<i>i</i> -PrNO)	3	1445	413 (219)	525 (11)	
L = Py, R = <i>i</i> -Pr					
P = TpClPP	4	1438	424 (233)	535 (11)	
= TTP	5	1432	424 (243)	535 (15)	
= DPDME	6	1430	408 (218)	523 (12), 552 (12)	
Fe(TPP)(MeNO)py		¹⁴ N 1400; ¹⁵ N, 1390	423 (285)	536 (12)	
free MeNO ⁷		1564			
free C ₅ H ₁₁ NO ⁷		1558			

^a KBr pellets, cm^{-1} (± 2). ^b Deaerated benzene solutions at 27 °C. ^c Equilibrium 1 constant (see text). ^d 2e was obtained as a mixture with 6% Fe(TPP)(PPhMe₂)₂, ϵ was not determined in this case.

The Fe(TPP)(*i*-PrNO)(L) complexes have been also prepared by direct interaction of Fe(TPP) with the *i*-PrNO dimer. 2-Nitrosopropane exists as a dimer in the solid state and is mostly dimeric in solution.⁷ However, the affinity of *i*-PrNO for Fe(TPP) is so high that one can observe the fast and quantitative formation of the Fe(TPP)(*i*-PrNO)(MeOH) complex, after reaction of Fe(TPP) with 5 excess of (*i*-PrNO)₂ in benzene at 70 °C followed by MeOH addition (Scheme I).

The above described methods are general and have been used for the preparation of the Fe(porphyrin)(*i*-PrNO)(py) complexes 4, 5, and 6, respectively, with porphyrin = *meso*-tetra(4-chlorophenyl)porphyrin (TpClPP), *meso*-tetratolylporphyrin (TTP), and deuterioporphyrin dimethyl ester (DPDME). These complexes have been identified by mass spectrometry and IR, visible, and ¹H NMR spectroscopy (Tables I, III, and IV).

Characteristics of the Crystalline Complexes. Mass Spectrometry. Upon direct introduction of the complexes at 25–100 °C (70 eV), one observes the peaks corresponding to the two axial ligands, *i*-PrNO and L. When the temperature reaches 200 °C, the peaks corresponding to Fe(TPP) appear. Because of the fast decomposition of the complexes under the mass spectrometry conditions, we never observed the molecular peaks corresponding to Fe(TPP)(*i*-PrNO)(L), either with a lower energy source (30 eV) or by using field desorption and ionization techniques.

IR Spectroscopy. The IR spectra of complexes 1 and 2 are very similar to those of Fe(TPP)(py)₂ or Fe(TPP)(Cl) but they all exhibit an intense additional band between 1400 and 1450 cm^{-1} . For definite assignment of this band to the N–O stretching vibration, a complex containing a nitrogen-15-labeled R¹⁵NO ligand was synthesized. Preparation of a Me¹⁵NO complex was preferred to that of an *i*-Pr¹⁵NO complex, since MeNHOH is easier to prepare than *i*-PrNHOH from commercially available ¹⁵N-labeled precursors. Me¹⁵NHOH was prepared by reaction of Na¹⁵NO₂ with ClCH₂COOH¹¹ followed by reduction of Me¹⁵NO₂ by zinc and NH₄Cl.¹² The Fe(TPP)(Me¹⁵NO)(py) complex was then obtained by reaction of Fe(TPP)(Cl) with Me¹⁵NHOH in the presence of pyridine. In the IR spectrum of the Fe(TPP)(Me¹⁴NO)(py) complex, the band assigned to the N–O vibration is at 1400 cm^{-1} . In agreement with this assignment, this band exhibits a 10- cm^{-1} shift to lower frequencies upon replacement of Me¹⁴NO by Me¹⁵NO (Figure 1). This is the only significant difference between the IR spectra of Fe(TPP)(Me¹⁴NO)(py) and Fe(TPP)(Me¹⁵NO)(py) complexes, apart from a shift of a weak band from 930 to 918 cm^{-1} .¹³

As shown in Table I, the N–O stretching frequency of RNO is greatly lowered upon coordination to iron-porphyrins (from 1558

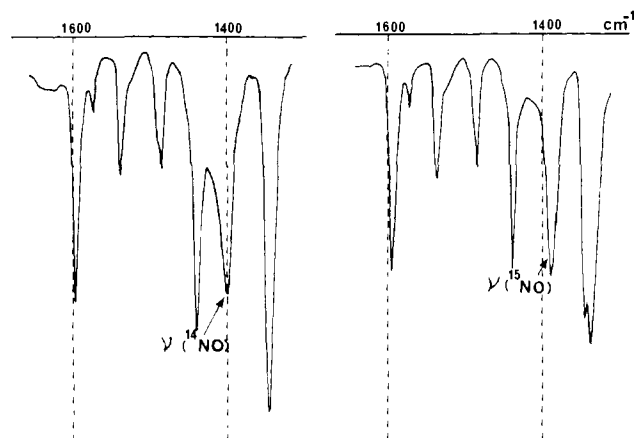


Figure 1. Infrared spectra of (a) Fe^{II}(TPP)(Me¹⁴NO)(py) and (b) Fe^{II}(TPP)(Me¹⁵NO)(py) (KBr pellet, $\pm 2 \text{ cm}^{-1}$). Bands due to the bound nitrosomethane are indicated by arrows.

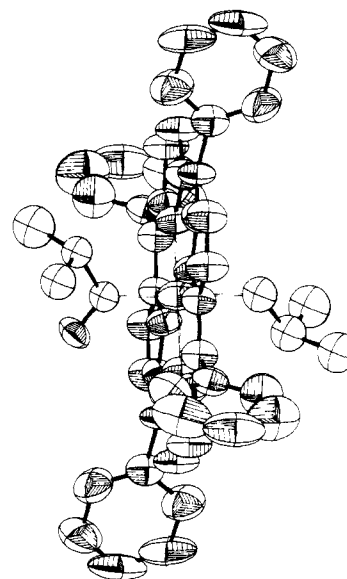


Figure 2. General view of the molecule—50% probability ellipsoids are used for anisotropic atoms. The darker ellipsoids and the centered light spheres represent, respectively, the anisotropically and isotropically refined atoms.

cm^{-1} for the free ligand⁷ to about 1430 cm^{-1}). This shift to lower frequencies depends significantly upon the electron-donor ability of the trans L ligand (1445 cm^{-1} for L = MeOH to 1432 cm^{-1} for L = *N*-MeIm) and upon that of the porphyrin (1438 cm^{-1} for

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(13) A similar band, also present in the IR spectrum of Ru[bpy]₂[N-(O)C₆H₄NMe₂]Cl at 875 cm^{-1} (¹⁴N) and 866 cm^{-1} (¹⁵N) was tentatively assigned to a $\nu_{\text{N-C}}$ rock.^{9b}

Table III. ^1H NMR Data of $\text{Fe}(\text{P})(i\text{-PrNO})\text{L}$ Complexes^a

	porphyrin			<i>i</i> -PrNO		L	
	H _{Pyr}	H _{Ph}		CH (h, 6.5)	CH ₃ (d, 6.5)		
		<i>o</i>	<i>o'</i>	<i>m,p</i>			
1	8.73	8.09		7.71	-1.09	-2.15	<i>c</i>
2a	8.65	8.10	8.01	7.69	-0.82	-2.02	1.53 (d, 6.5), 5.23 (t, 6.5), 6.11 (t, 6.5)
2b	8.65	8.09	8.06	7.72	-0.94	-2.03	-3.16 (h, 6.5), -1.84 (d, 6.5), -4.64
2c	8.61	8.08	8.02	7.67	-0.84	-2.01	0.70 (s), 1.23 (s), 2.18 (s), 4.8 (s)
2d	8.72	8.12	8.06	7.70	-1.19	-2.10	<i>c</i>
2e	8.54	8.07	7.95	7.71	-0.54	-2.01	4.09 (t, 7.5), 6.53 (t, 7.5), 6.85 (t, 7.5), -2.57 (d, 8.5)
3	8.72	8.10		7.72	-0.46	-2.26	
4	8.61	7.98	7.92	7.64	-0.86	-2.07	1.52 (d, 6.5), 5.21 (t, 6.5), 6.13 (t, 6.5)
5 ^d	8.64	7.96	7.86	7.46	-0.86	-2.04	1.58 (d, 6.5), 5.19 (t, 6.5), 6.10 (t, 6.5)
6	8.86	<i>b</i>	<i>b</i>	<i>b</i>	-1.71	-2.45	0.89 (d, 6.5), 4.96 (t, 6.5), 5.88 (t, 6.5)

^a 0.1 M in deaerated CDCl_3 , at -63°C , 250 MHz, δ (ppm/Me₄Si) (multiplicity, ¹J in Hz). ^b H meso δ 9.79, 9.68, 9.66, 9.57; CH_2 : 4.26, 3.17; CH_3 3.61, 3.58, 3.52, 3.47. ^c An excess of L is required in order to get the spectra of the hexacoordinate species. ^d CH_3 of TTP δ 2.66.

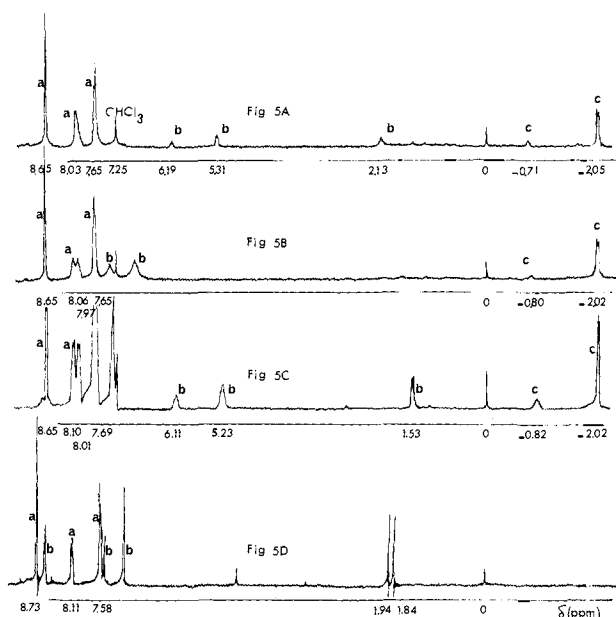


Figure 5. ^1H NMR study of complex **2a**: $\text{Fe}^{\text{II}}(\text{TPP})(i\text{-PrNO})(\text{py})$. Signals: a (porphyrin), b (pyridine), c (*i*-PrNO). (A) **2a**, 2.4×10^{-2} M in CDCl_3 at 20°C ; (B) addition of $2 \mu\text{L}$ of pyridine- d_5 at 20°C ; (C) conditions as in (B) but at -63°C ; (D) decomposition of **2a** in neat $\text{C}_5\text{D}_5\text{N}$ giving $\text{Fe}(\text{TPP})(\text{C}_5\text{D}_5\text{N})_2$.

complexes. The other signals, corresponding to the protons of the axial ligands py and *i*-PrNO are well separated because of the large ring current-induced shifts which depend on the distance of these protons to the porphyrin plane.

Upon addition of 2 equiv of pyridine to the solution (Figure 5B), one observes average signals for pyridine which are indicative of a rapid exchange of this ligand (vs. NMR time scale) under these conditions. This exchange becomes slow upon cooling to -63°C as shown by the appearance of both signals of free and bound pyridine (Figure 5C), allowing the determination of the NMR characteristics of complex **2a** itself. Therefore, from the chemical shifts of the pyridine protons of complex **2a** at 20°C (Figure 5A), one can estimate that about 93% of starting complex

involved in equilibrium 1 is in the hexacoordinate form **2a**, under the ^1H NMR recording conditions at 20°C . When the solution of complex **2a** without any excess of pyridine is cooled to -63°C , two sets of signals appear corresponding respectively to complexes **2a** (δ -2.02 and -0.82 for *i*-PrNO) and **3** (-2.26 and -0.41) which are in slow equilibrium. Under these conditions, the solution contains no more than 5% of complex **3**.

Similar results have been obtained with the other nitrosoalkane complexes, the ^1H NMR data of which are compared in Table III. It is noteworthy that in the case of complexes **1** and **2d**, the exchange rate between free and bound L ($\text{L} = i\text{-PrNHOH}$ or MeOH) is fast even at -63°C .

From its ^1H NMR characteristics, one can conclude that the pentacoordinate complex **3** is diamagnetic and, at least formally, a Fe(II) low-spin complex, like other previously described pentacoordinate complexes involving a strong axial ligand such as $\text{Fe}(\text{TPP})(\text{CO})$,¹⁶ $\text{Fe}(\text{TPP})(\text{CS})$,¹⁷ $\text{Fe}(\text{TPP})(\text{CCl}_2)$,¹⁸ $\text{Fe}(\text{TPP})(\text{C}=\text{C}\text{Ar}_2)$,¹⁹ or $\text{Fe}(\text{"capped porphyrin"}) (\text{PnBu}_3)$.²⁰ It is different from Fe(II) pentacoordinate complexes involving axial ligands such as alcohols, ethers, or the sterically hindered 2-methylimidazole ligand, which are in the high-spin ($S = 2$) state.²¹

^1H NMR spectroscopy allows an easy determination of the nature of the axial ligands present in the iron-porphyrin-nitrosoalkane complexes obtained as crystalline solids by the aforementioned techniques. Accordingly, upon dissolution of a Fe-(porphyrin)(R_2CHNO)(L) complex in neat pyridine- d_5 , the L ligand is immediately replaced by pyridine- d_5 and the signals of free L appear. Then, reaction 2 slowly occurs (within a few hours for a 8×10^{-2} M complex), with appearance of the signals corresponding to the oxime $\text{R}_2\text{C}=\text{NOH}$ and $\text{Fe}(\text{TPP})(\text{pyridine-}d_5)_2$ (Figure 5D). The only exception to this general behavior is the reaction of complex **1** in neat pyridine- d_5 , since in this case, the liberated L ligand, *i*-PrNHOH, is able to further react with $\text{Fe}(\text{TPP})(\text{py-}d_5)_2$ transiently generating complex **2b**, presumably via dismutation of *i*-PrNHOH in the medium.⁸¹

¹³C NMR Spectroscopy. The ^{13}C NMR spectrum of complex **2a** (0.2 M in CDCl_3 at 20°C) displays seven signals, corresponding to the porphyrin carbons, whose shape and chemical shifts are very similar to those of TPPH_2 ,²² $\text{Zn}(\text{TPP})$,²³ $\text{Cd}(\text{TPP})$,²⁴ or $\text{Fe}(\text{TPP})(\text{CCl}_2)$.¹⁸ This is a further argument in favor of the diamagnetism of complex **2a**. The signals corresponding to bound *i*-PrNO are at 82.1 and 16.4 ppm. These porphyrin and *i*-PrNO resonances are not modified upon addition of 1 equiv of pyridine, whereas the pyridine resonances are shifted in a position intermediate between those of free and bound pyridine. This indicates

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Table IV. ^{13}C NMR Data of $\text{Fe}(\text{P})(i\text{-PrNO})\text{L}$ Complexes^{a,b}

	$\delta^{13}\text{C}(\text{porphyrin})$			$\delta^{13}\text{C}(\text{phenyl ring})$				$\delta^{13}\text{C}(i\text{-PrNO})$	
	α	β	meso	Cq	<i>o</i>	<i>m</i>	<i>p</i>	CH	CH ₃
1 ^c	145.4	132.8	119.7	142.2	133.7	126.3	127.2	82.0	16.4
2a	145.0	132.3	119.1	142.2	133.5	126.1	127.0	82.0	16.3
2b	145.6	132.9	120.0	142.1	133.7	126.3	127.2	82.7	16.4
2c	145.0	132.2	119.2	142.8	133.8	126.0	126.9	80.9	16.4
2d ^c	145.0	132.0	119.3	142.0	133.3	125.8	126.7	82.2	15.8
2e	145.3	132.6	119.2	142.5	133.7	126.1	126.9	80.4	16.3
4	144.9	132.6	118.2	140.6	134.7	126.5	133.5	82.3	16.4
5 ^e	145.0	131.9	119.3	139.5	132.3	126.7	136.3	81.9	16.3
6	<i>d</i>							80.9	15.7

^a 0.2 M in deaerated CDCl_3 at 33 °C, δ (ppm/ Me_4Si); the assignments given for the porphyrin ^{13}C signals were done according to ref 22–25. ^b ^{13}C NMR signals for the ligand L are given in the Experimental Section. ^c Spectrum obtained with an excess of L. ^d δ 173.3, 143.8, 143.5, 143.2, 141.2, 139.6, 139.4, 137.8, 130.6, 99.9, 99.3, 97.0, 95.5, 51.5, 37.4, 22.1, 13.9, 11.9. ^e CH₃ of TTP δ 21.6.

that equilibrium 1 is completely shifted toward the hexacoordinate species in both conditions, as expected if one takes into account the high concentration of complex 2a used, the results of ^1H NMR studies, and the high affinity constant of pyridine for complex 3 determined previously (Table I). The ^{13}C NMR characteristics of various nitrosoalkane–iron–porphyrin complexes have been similarly determined except for complexes 1 and 2d for which addition of an excess of L was needed in order to get the spectra of the hexacoordinate species (Table IV).

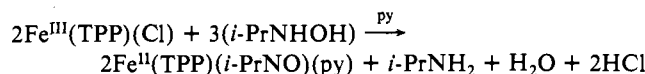
Stability of the Fe–RNO Bond. In deoxygenated solvents like CHCl_3 , C_6H_6 , or alcohols, complexes 1 and 2 are stable indefinitely. No dissociation of the Fe–RNO bond could be detected even after an important dilution ($[\text{complex}] \approx 10^{-7}$ M). This indicates a very high affinity of the nitrosoalkanes for iron(II)–porphyrins. This high affinity is confirmed by (i) the lack of displacement of the RNO ligand by carbon monoxide (1 atm, even at -63 °C), as already observed for the nitrosoalkane–hemoprotein complexes,^{3,4} and (ii) the easy formation of complex 2d upon interaction of $\text{Fe}(\text{TPP})$ with the dimer $(i\text{-PrNO})_2$ which is dissociated to $i\text{-PrNO}$ to only a minor extent at 70 °C.

In aerated solution, the $\text{Fe}(\text{porphyrin})(i\text{-PrNO})(\text{L})$ complexes are irreversibly oxidized to the μ -oxo dimer $[\text{Fe}^{\text{III}}(\text{porphyrin})]_2\text{O}$. The half-lives of the $\text{Fe}(\text{TPP})(i\text{-PrNO})(\text{L})$ complexes, 10^{-4} M in aerated benzene, depend on the nature of the L ligand. They decrease from 48 to 5.3 and 1.6 h when going from L = *N*-MeIm to L = py and MeOH, respectively. The stability of the complexes increases with the binding constant of L (Table I), suggesting that the oxidation proceeds through interaction of dioxygen with the pentacoordinate species 3. The nature of the solvent also influences the oxidation rate of complexes 2; for instance, the half-lives of 2a (10^{-4} M at 27 °C) are respectively 14, 5.3, and 0.3 h in MeOH, benzene, and DMF. In comparison, the $\text{Fe}^{\text{II}}(\text{TPP})(\text{L})(\text{L}')$ complexes known to give reversible dissociation of both iron–axial ligand bonds in solution, such as $\text{Fe}(\text{TPP})(\text{py})_2$ and $\text{Fe}(\text{TPP})(\text{py})(\text{CO})$ are considerably more sensitive to dioxygen in identical conditions ($t_{1/2}$) for the oxidation of these complexes 10^{-4} M in benzene at 27 °C: 0.01 and 0.5 h, respectively). On the contrary, $\text{Fe}^{\text{II}}(\text{TPP})(\text{L})(\text{L}')$ complexes containing one iron–axial ligand bond which is not reversibly dissociated in solution such as the Fe–RNO bond, are more stable to oxygen; for instance, the $\text{Fe}(\text{TPP})(\text{CCl}_2)$ complex is half-oxidized under identical conditions after 4 h,¹⁸ and the $\text{Fe}(\text{TPP})(\text{CS})$ ¹⁷ and $\text{Fe}(\text{TPP})(\text{C}=\text{CAR}_2)$ ¹⁹ complexes appear indefinitely stable to oxygen in solution.

Discussion

The aforementioned results show that the formation of very stable iron–porphyrin–nitrosoalkane complexes is a general phenomenon, which allows to understand the previously reported formation and great stability of hemoglobin-, myoglobin-, and (cytochrome P-450)–nitrosoalkane complexes.^{3–5} For instance, these results explain the mechanism of formation of the $\text{Fe}^{\text{II}}\text{–RNO}$ bond upon reaction of iron(III)–porphyrin and RNHOH. This reaction implies a two-electron oxidation of RNHOH to RNO. The results of the reaction performed with the $\text{Fe}(\text{TPP})(\text{Cl})\text{:}i\text{-PrNH}_2$ 1:2 molar ratio indicate that the starting iron(III)–porphyrin acts as a one-electron oxidant and that, under anaerobic

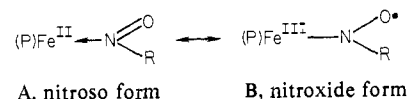
conditions, the second one-electron oxidant is $i\text{-PrNH}_2$ itself. The stoichiometry of the reaction, which involves a dismutation of RNHOH, is as follows:



Concerning the binding mode of the nitrosoalkanes in the iron–porphyrin complexes, the end-on binding by nitrogen is demonstrated by X-ray crystallography in the case of complex 2b. It should be involved in the other described $\text{Fe}(\text{porphyrin})(\text{RNO})(\text{L})$ complexes because of the close similarity of their spectral data with those of complex 2b. This binding mode is also very likely in the hemoprotein–nitrosoalkane complexes since the electronic spectra of $\text{Fe}(\text{protoporphyrin IX})(i\text{-PrNO})(\text{N-MeIm})$ and myoglobin–Fe– $i\text{-PrNO}$ are almost identical.¹⁰

When compared to other nitrogenous ligands such as amines, pyridines, or imidazoles, nitrosoalkanes appear as particularly strong ligands of iron(II) porphyrins. The great strength of the Fe–RNO bond is underlined by the following results: (i) it does not dissociate at room temperature even upon great dilution of the complexes, (ii) the RNO ligand is not displaced by CO, while one L ligand of the hemochromes $\text{Fe}(\text{TPP})(\text{L})_2$ with L = amine or pyridine is readily displaced by CO under these conditions, (iii) the Fe–N(O)R distance of complex 2b (1.865 (14) Å) is considerably shorter than the Fe–NH₂ $i\text{-Pr}$ distance (2.100 (14) Å) or than the Fe–N distances found in various hemochromes $\text{Fe}(\text{TPP})(\text{amine})_2$ (≈ 2.1 Å).¹⁵ In agreement with a strong Fe–RNO bond, the pentacoordinate $\text{Fe}(\text{TPP})(i\text{-PrNO})$ complex 3 is low spin as $\text{Fe}^{\text{II}}(\text{TPP})(\text{NO})$, while pentacoordinate $\text{Fe}^{\text{II}}(\text{TPP})(\text{L})(\text{L}')$ complexes containing weak nitrogen-bound axial ligands (L = amine) are high spin ($S = 2$).²¹ In this respect, nitrosoalkanes are closer to strong π -acid ligands such as NO,²⁶ CO,¹⁶ CS,¹⁷ CCl_2 ,¹⁸ or $\text{C}=\text{CAR}_2$,¹⁹ the formation of low-spin complexes upon coordination of a π -acid ligand to an iron(II)porphyrin having been related to a destabilization of the iron d_{z^2} orbital.¹⁶

The extent of back-bonding from iron to RNO in complexes 2 and of the contribution of resonance form B to the description



of the Fe–RNO bond is emphasized by (i) the $\approx 100\text{-cm}^{-1}$ decrease of the ν_{NO} frequency upon coordination of $i\text{-PrNO}$ (Table V) to iron(II)–porphyrins, (ii) the N–O distance of complex 2b (1.260 (20) Å) which is longer than the N–O distance assumed for free CH_3NO (1.18 Å)⁷ but close to that of the cis and trans nitrosodimers $\text{CH}_3\text{N}(\text{O})=\text{N}(\text{O})\text{CH}_3$ (respectively 1.31 and 1.25 Å).⁷

Back-donation from the metal to the nitrosoalkane ligand in complex 2b seems larger than in the $\text{PtCl}_2(t\text{-BuNO})_2$ complex, for which ν_{NO} (1555 cm^{-1}) and $d_{\text{N-O}}$ (1.21 Å)^{7c} are very close to ν_{NO} (1546 cm^{-1}) and $d_{\text{N-O}}$ (≈ 1.2 Å) of free $t\text{-BuNO}$, but smaller

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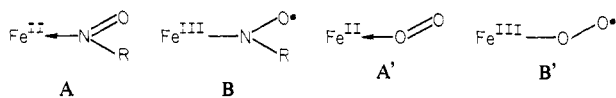
Table V. Comparison of Some Characteristics of RNO- and O₂-Fe^{II}(Porphyrin) Complexes

	IR ν_{X-O} , cm ⁻¹ (X = O or N)	resonance Raman, cm ⁻¹		Mössbauer				ref
				T, K	δ , mm/s	ΔE_q , mm/s	η	
Fe(TPP)(<i>i</i> -PrNO)(<i>i</i> -PrNH ₂)	1432	1365 ^a	1565	300 4.2	0.22 0.29	1.19 -1.23	0.6	32
Fe(TPP)(<i>i</i> -PrNO)(<i>N</i> -MeIm)	1432			300 4.2	0.20 0.29	1.15 -1.15	0.5	32
C ₆ H ₁₁ NO (<i>t</i> -Bu) ₂ N-O·	1558 ^b 1345 ^c							
Fe(TpivPP)(<i>N</i> -MeIm)(O ₂)	1159 ^d	1366 ^e	1563	295 4.2	0.19 0.28	1.28 -2.10	0.1-0.3	31
O ₂	1580 ^f							
O ₂	1097 ^f							

^a Reference 30. ^b Reference 7. ^c Reference 27. ^d Reference 28. ^e Reference 29. ^f Reference 39.

than in the (Ru(NH₃)₅[HOC(CH₃)₂CH₂NO])²⁺ complex^{9h} for which $\nu_{NO} = 1370$ cm⁻¹ is close to the $\nu_{NO} = 1345$ cm⁻¹ of the nitroxide (*t*-Bu)₂N-O·.²⁷

Since the NO group of nitrosoalkanes is isoelectronic with dioxygen and since both O₂²⁸ and *i*-PrNO are bound in a bent end-on fashion to the iron of *meso*-tetraphenylporphyrins, it is interesting to compare the characteristics of the Fe-N(O)R and Fe-O₂ bonds. For this purpose, some characteristic spectroscopic data of the Fe(TPP)(*i*-PrNO)(*N*-MeIm) and Fe("picket fence"-TPP)(O₂)(*N*-MeIm)²⁸ complexes are indicated in Table V. For the data concerning the RNO or O₂ ligands, one notes that for both complexes, the ν_{X-O} (X = N or O) frequency is closer to those of related species involving an X-O simple bond, (*t*-Bu)₂N-O· and O₂⁻, respectively, than to those involving an X=O double bond, CH₃NO and O₂. The effects of the RNO or O₂ ligands on the porphyrin ring are similar, as shown by the close resemblance of the electronic and resonance Raman spectral data of the two complexes. Of particular interest are the two strong resonance Raman bands, called A and D, around 1360 and 1560 cm⁻¹ which are present in all Fe(TPP) complexes and correspond to porphyrin vibrational modes.^{29,30} These bands are sensitive to changes in spin and oxidation state of the iron.²⁹ For the low-spin Fe(II) complexes, they were shown to be particularly sensitive to $d\pi(\text{Fe})-\pi^*(\text{TPP})$ interactions. Band A frequency is more specifically dependent on π acidity of the axial ligands, and band D frequency more specifically reflects the stereochemistry around the iron atom.³⁰ The nearly identical position of the 1365- and 1565-cm⁻¹ bands in the *i*-PrNO and O₂ complexes (Table V), which are both low spin with the iron in the mean plane of the porphyrin ring, indicate very similar π -accepting ability of these two ligands. The positions of these bands are quite different in low-spin Fe^{II}(TPP)(L)₂ complexes with L = py or Im (ca. 1359 and 1560 cm⁻¹) but closer in low-spin Fe(III) complexes like Fe^{III}(TPP)(Im)₂(Cl) (1370 and 1568 cm⁻¹), suggesting, in agreement with IR data, an important contribution of resonance forms B or B' to the description of the Fe-N(O)R and Fe-O₂ bonds.



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The similarity of the π -accepting abilities of *i*-PrNO and O₂ is confirmed by the striking similarity of Mössbauer data of their complexes^{31,32} (Table V): (i) nearly identical isomer shift δ and quadrupole interaction ΔE_q values at 300 K, (ii) identical isomer shift value at 4.2 K, (iii) a negative sign of the quadrupole interaction and the existence of a significant asymmetry parameter η for both complexes. The only difference is the variation of the ΔE_q value with temperature in the case of the O₂ complex. When comparing these Mössbauer parameters to those of various hexacoordinate Fe^{II}, or Fe^{III}(TPP)(L)(L') complexes, with L = imidazole, CO, or amine, such a complete similarity is never observed.³² These data led us to propose³² that the Fe(TPP)(*i*-PrNO)(*N*-MeIm) complex has 3d orbital populations close to those calculated by Kirchner and Loew,³³ for model oxyferroporphyrin complexes.

Taken altogether, the data collected in Table V point to a great similarity between the coordinating properties of the O₂ and RNO ligands, at least in Fe(TPP) complexes.⁴⁰ It is noteworthy that an analogous similarity of the binding properties of nitroso-compounds and dioxygen has been reported in the case of molybdenum complexes.^{9b,c}

As far as the hemoprotein complexes of O₂ or RNO are concerned, it is noteworthy that the resonance Raman spectra of hemoglobin (Hb)O₂ and -CH₃NO complexes exhibit nearly identical positions of the porphyrin bands considered as markers of the spin and formal oxidation state of the iron (respectively 1377, 1584³ and 1376, 1585 cm⁻¹³). This is a first indication in

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(40) NO is not isoelectronic with O₂ or RNO, and the Fe^{II}-NO complexes are paramagnetic ($S = 1/2$), contrary to Fe^{II}-O₂ or -RNO complexes which are diamagnetic. However, there is a good parallel between the structural parameters of the Fe-N(O) bond in Fe(TPP)(*i*-PrNO)(*i*-PrNH₂) and Fe(TPP)(NO)(4-methylpiperidine).⁴¹ In particular, both complexes involve a bent Fe-NO bond with short Fe-N(O) distances and relatively long Fe-N (trans amine) distances. Moreover, some Mössbauer parameters (ΔE_q) of Fe^{II}-*i*-PrNO³² and Fe^{II}-NO⁴² complexes are similar. One must, however, note that the Fe-N(O) distance in Fe(TPP)(NO)(4-methylpiperidine) is shorter (1.73 Å) than in Fe(TPP)(*i*-PrNO)(*i*-PrNH₂) (1.86 Å) and that the Fe-N (trans amine) distance is long (2.33 or 2.46 Å) in the former, whereas it is nearly normal (2.1 Å) in the latter.

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favor of similar bonding properties of O₂ and RNO to the iron(II) of hemoproteins.

Nitrosoalkanes thus appear as attractive dioxygen analogues which mimic quite well the bonding properties of dioxygen but which lead to considerably more stable Fe(II) complexes. This could be of interest for "model" studies of the properties of very unstable hemoprotein- or iron-porphyrin-dioxygen complexes. Nitrosoalkanes, which can be formed in vivo by various routes, i.e., oxidation of an amine or an hydroxylamine or reduction of a nitroalkane, and which bind strongly to the iron of hemoproteins,³⁻⁶ leading to the inhibition of their functions,⁶ should also play an important role in pharmacology and toxicology.⁵

Experimental Section

Physical Measurements. All experimental operations with Fe(II) complexes were performed on a vacuum line. UV and visible spectra were obtained, at 27 °C, on a Varian Super Scan 418 spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 221 spectrometer. Varian EM 390, Bruker 90, and Cameca 250 instruments were used for the ¹H NMR spectra and Bruker 90 for ¹³C NMR spectra. Mass spectra were performed on a Varian CH7, Rieber spectrometer (70 eV) at temperatures ca. 220 °C. Elemental analyses were performed by the Service de Microanalyse du CNRS at Gif-sur-Yvette.

Reagents and Solvents. All solvents were deaerated before use by argon bubbling for 0.25 h. MeOH was distilled from (MeO)₂Mg in an argon atmosphere. CH₂Cl₂, CHCl₃, and all other reagents were used as supplied (puriss. grade). Fe(TPP)(Cl), Fe(TTP)(Cl), Fe(TpClPP)(Cl), and Fe(DPDME)(Cl) were prepared according to literature procedures.^{34,35} 2-(Hydroxyamino)propane, mp 87 °C (lit.³⁶ mp 87 °C) was obtained by reduction of 2-nitropropane by Zn-NH₄Cl. *trans*-2-Nitrosopropane dimer, mp 52 °C (lit.³⁷ mp 50–52 °C) was prepared by oxidation of the corresponding hydroxylamine with silver carbonate.³⁷

Crystallographic Study. Prismatic dark crystals of C₅₀H₄₄N₆OFe·C·HCl₃ (*M_r* = 920.185) were grown by slow evaporation from a CHCl₃-CH₃OH solution under argon atmosphere. A well-formed crystal of about 0.3 × 0.4 × 0.4 mm was used for data collection and determination of the unit cell on a Philips PW 1100 diffractometer, using graphite monochromated Mo Kα radiation (λ 0.7107 Å).

Crystals were triclinic, space group *P1* or *P1̄* with two molecules in the unit cell of the following dimensions: *a* = 10.885 (11) Å, *b* = 15.247 (19) Å, *c* = 15.516 (24) Å, α = 114.67 (10)°, β = 94.73 (13)°, γ = 89.25 (19)°, *V* = 2331.4 Å³, *d_c* = 1.314.

Parameter values were determined by the least-squares refinement of the *θ* values of 32 well-centered reflections.

The data were collected using the (*θ*-2*θ*) scan technique with a speed of 0.1° s⁻¹, a constant width of 2.0° up to five scans depending on the intensity of each reflection. The measurement of the background was performed during 10 s on both sides of each reflection. From 5690 independent intensities (2° < *θ* < 22°), 2614 were considered as observed, their value being greater than twice *σ*(*I*) calculated from counting statistics. During the course of the intensity data collection, the crystal showed no loss in intensity due to exposure.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier methods in space group *P1̄*. Initially, it was assumed that the Fe atom was in general position. All the atoms of the porphyrin ring could be located but not refined (*R* = 0.040).

Two independent molecules with iron atoms on centers of symmetry were then considered. The position of the atoms of the porphyrin ring and those of axial 2-nitrosopropane ligand with "N-end-on" geometry were developed by Fourier and difference Fourier syntheses. In addition, a molecule of CHCl₃ solvent was found in the asymmetric unit. The structure was refined by least-squares techniques. The quantity minimized was Σw(|*F_o*| - |*F_c*|)² where *w* was taken as *σ*⁻²(*F_o*). Atomic scattering factors were taken from ref 38, and the effects of anomalous dispersion for iron were included in *F_c*. A least-squares refinement involving anisotropic thermal parameters for the Fe atoms and isotropic thermal parameters for the TPP, the solvent molecule, and the centrosymmetric axial 2-nitrosopropane ligands led to the values of *R* and *R_w* of 0.109 and 0.110.

At this stage, the *B* value for the oxygen atom of the 2-nitrosopropane group was 14.7 Å (14 for the second molecule of the asymmetric unit) while *B* values for the N and C atoms were respectively 4.9 (4.8) and 7.0 (4.2), the Fe-N distance being 1.997 Å (2.002). These results were consistent with the presence of 2-nitrosopropane and 2-aminopropane as axial ligands. It was assumed that the correct space group was the centrosymmetric one, *P1̄* rather than the noncentrosymmetric one *P1*. With this assumption, the two ligands *i*-PrNO and *i*-PrNH₂ are superimposed (because of *I* symmetry). In the next cycles of refinement the disordered groups were included with occupancy factors of 0.5 and Fe-N

distances of 1.74 (nitroso) and 2.14 (amine) Å.

Hydrogen positions were calculated for the porphyrin ring, CHCl₃, and the phenyl rings [*d_{C-H}* = 1.00 Å, *B*(H) = *B*(C)] and added as fixed contributions. Temperature factors were anisotropic for TPP, CHCl₃, and the oxygen atom of *i*-PrNO group, and isotropic for the atoms of the ligands which were superimposed. Parameters were refined in three large blocks including alternatively the porphyrin core, the *i*-PrNO and *i*-PrNH₂ groups. Refinement converged to the final *R* and *R_w* values of 0.059 and 0.060. The maximum deviations in the last cycles were 0.1σ for the atoms of TPP and 0.5σ for atoms of the disordered ligands.

The disordered space group *P1̄* has been assumed in our calculations although the *i*-PrNO and *i*-PrNH₂ ligands do not need to be disordered in space group *P1*. Several factors suggested that the space group *P1̄* is correct. The last difference syntheses showed no peak greater than 0.4 e/Å³ and 28 of the 29 H atoms were located on difference maps. The vibrational ellipsoids of Fe(TPP) portions seemed quite normal. The strongest evidence that the space group is correct is the fact that the two molecules in the asymmetric unit are quite identical.

[2-(Hydroxyamino)propane](2-nitrosopropane) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*i*-PrNHOH) (1). Fe^{III}(TPP)(Cl) (1 g) in CHCl₃ (30 mL) was added, under argon, to *i*-PrNHOH (0.5 g) in CHCl₃ (10 mL). After the mixture was stirred 6 h, the solvent was removed under vacuum. Recrystallization from CHCl₃-MeOH at -15 °C afforded 1: 1.1 g (95%); mass spectrum, *M⁺* *m/e* 668 [Fe(TPP)], 75 (*i*-PrNHOH), 73 (*i*-PrNO). Anal. Calcd for C₅₀H₄₄N₆O₂Fe (816.8 g/mol): C, 73.52; H, 5.43; N, 10.28. Found: C, 73.92; H, 5.45; N, 10.54.

General Procedure for Preparation of Complexes 2a, 2b, 2c, 2d, 4, 5, 6. Fe^{III}(TPP)(Cl) was treated by *i*-PrNHOH in CHCl₃ (40 mL) at 20 °C, under an argon atmosphere in the presence of the L ligand. The volume of the solution was reduced by argon bubbling. Two recrystallizations from CHCl₃, MeOH, and L give the expected complexes. Most of their spectral data are indicated in the tables.

(2-Nitrosopropane)(pyridine) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(py) (2a). Fe^{III}(TPP)(Cl) (0.6 g), *i*-PrNHOH (0.3 g), pyridine (0.1 mL), reaction time 15 h, recrystallization from CHCl₃ (5 mL), MeOH (8 mL), pyridine (0.1 mL): yield 0.7 g (100%); ¹³C NMR of 6th ligand (py) δ 146, 133, 120.6; mass spectrum, *M⁺* *m/e* 668 [Fe(TPP)], 79 (py), 73 (*i*-PrNO). Anal. Calcd for C₅₂H₄₀N₆OFe (820.2 g/mol): C, 76.07; H, 4.92; N, 10.25. Found: C, 75.92; H, 5.00; N, 9.91.

Complex 2a has been also prepared by reaction of Fe^{II}(TPP) with (*i*-PrNO)₂. Fe^{II}(TPP) in benzenic solution (100 mL) was obtained by reduction of Fe^{III}(TPP)(Cl) (0.07 g) by an aqueous solution of Na₂S₂O₄. The organic layer was decanted, dried, and added to a deaerated benzenic solution of (*i*-PrNO)₂ (0.062 g) at 70 °C. The mixture was kept at 70 °C for 0.5 h. Then 0.01 mL of pyridine was introduced at room temperature. The solvent was removed by argon bubbling. Recrystallization from CH₂Cl₂-MeOH afforded 2a, 0.067 g (85%).

(2-Aminopropane) (2-nitrosopropane) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*i*-PrNH₂) (2b). Fe^{III}(TPP)(Cl) (0.2 g), *i*-PrNHOH (0.1 g), *i*-PrNH₂ (0.04 mL), reaction time 15 h, recrystallization from CHCl₃ (2 mL), MeOH (3 mL), *i*-PrNH₂ (0.1 mL) at -15 °C: yield 0.2 g (89%); ¹³C NMR of 6th ligand (*i*-PrNH₂) δ 48.7, 16.0; mass spectrum, *M⁺* *m/e* 688 [Fe(TPP)], 73 (*i*-PrNO), 59, 58 (*i*-PrNH₂). Anal. Calcd for C₅₀H₄₄N₆OFe (800.8 g/mol): C, 74.99; H, 5.53; N, 10.49. Found: C, 74.99; H, 5.40; N, 10.24.

(*N*-Methylimidazole) (2-nitrosopropane) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*N*-MeIm) (2c). Fe^{III}(TPP)(Cl) (0.22 g), *i*-PrNHOH (0.1 g), *N*-MeIm (0.04 mL), reaction time 15 h, recrystallization from CHCl₃, MeOH (3 mL): yield 0.19 g (73%); ¹³C NMR of 6th ligand (*N*-MeIm) δ 132.5, 124.4, 117.4, 33.2; mass spectrum, *M⁺* *m/e* 668 [Fe(TPP)], 82 (*N*-MeIm), 73 (*i*-PrNO). Anal. Calcd for C₅₁H₄₁N₄OFe (823.8 g/mol): C, 74.35; H, 5.01; N, 11.90. Found: C, 74.46; H, 5.00; N, 11.81.

(Methanol) (2-nitrosopropane) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(MeOH) (2d). Fe^{III}(TPP)(Cl) (0.45 g), *i*-PrNHOH (0.1 g), MeOH (20 mL), reaction time 6 h, recrystallization from CH₂Cl₂-MeOH: yield 0.45 g (90%); mass spectrum, *M⁺* *m/e* 668 [Fe(TPP)], 73 (*i*-PrNO). Anal. Calcd for C₄₈H₃₉N₅O₂Fe (773.2 g/mol): C, 74.56; H, 5.08; N, 9.05. Found: C, 74.61; H, 4.64; N, 8.87.

(Dimethylphenylphosphine) (2-nitrosopropane) (meso-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(PPhMe₂) (2e). Fe(TPP)(*i*-PrNO)(MeOH) (0.15 g) was treated by PPhMe₂ (0.023 g, 0.8 equiv) in deaerated CH₂Cl₂ during 2 min. MeOH (10 mL) was added, and purple crystals were filtered and washed with MeOH, yield 0.152 g (88%). As shown by ¹H NMR spectroscopy, these crystals contain a mixture of Fe(TPP)(*i*-PrNO)(PPhMe₂) (94%) and Fe(TPP)(PPhMe₂)₂ (6%): ³¹P NMR (CDCl₃) δ 5.35 (from H₃PO₄); mass spectrum, *M⁺* *m/e* 668 [Fe(TPP)], 138 (PPhMe₂), 73 (*i*-PrNO).

(2-Nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO) (3). Fe(TPP)(*i*-PrNO)(*i*-PrNHOH) (0.08 g) in C₆H₆ (5 mL) was treated by HCl (0.1 N, 5 mL), under an argon atmosphere, during 5 min. The organic layer was washed twice with water (5 mL) and dried (deacrated Na₂SO₄), and the solvent removed by argon bubbling. The resulting crystalline complex has been heated (60–70 °C) under vacuum (0.1 mmHg) for 4 h: yield 0.07 g (94%); mass spectrum, M⁺ *m/e* 668 [Fe(TPP)], 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(*meso*-tetra(4-chlorophenyl)-porphyrinato)iron(II), Fe(TpClPP)(*i*-PrNO)(py) (4). Fe^{III}(TpClPP)(Cl) (0.33 g), *i*-PrNHOH (0.12 g), pyridine (0.01 mL), reaction time 4 h, recrystallization from CHCl₃ (2 mL), MeOH (6 mL), pyridine (0.01 mL): yield 0.34 g (90%); ¹³C NMR of 6th ligand (py) δ 146, 133.5, 120.8; mass spectrum, M⁺ *m/e* 806 [Fe(TpClPP)], 79 (py), 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(*meso*-tetratolylporphyrinato)iron(II), Fe(TTP)(*i*-PrNO)(py) (5). Fe^{III}(TTP)(Cl) (0.3 g), *i*-PrNHOH (0.12 g), pyridine (0.01 mL), reaction time 4 h, recrystallization from CHCl₃ (2 mL), MeOH (6 mL), pyridine (0.01 mL): yield 0.32 g (93%); ¹³C NMR of 6th ligand (py) δ 146.2, 132, 120.7; mass spectrum, M⁺ *m/e* 724 [Fe(TTP)], 79 (py), 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(deuteroporphyrinato dimethyl ester)-iron(II), Fe(DPDME)(*i*-PrNO)(py) (6). Fe^{III}(DPDME)(Cl) (0.077 g), *i*-PrNHOH (0.5 g), pyridine (0.05 mL), reaction time 6 h, recrystallization from CHCl₃ (1 mL), MeOH (7 mL), pyridine (0.01 mL) at 5 °C: yield 0.07 g (67%); ¹³C NMR of the 6th ligand (py) δ 145.8, 133, 120; mass spectrum, M⁺ *m/e* 586 [Fe(DPDME)], 79 (py), 73 (*i*-PrNO).

Labeled [¹⁵N]Nitromethane, Me¹⁵NO₂. To a stirred mixture of 2.63 g of ClCH₂COOH and 50 g of cracked ice was added cold 1 M NaOH just enough to make the solution alkaline to phenolphthalein. The solution was mixed with 1.4 g of ¹⁵NO₂Na in 10 mL of water and with 1.3 g of boric acid. The solution was heated slowly until bubbles of carbon dioxide appeared. Nitromethane and water were then distilled and nitromethane extracted with ether and dried (Na₂SO₄). Careful distillation of ether gave a 0.62-g residue which was found by ¹H NMR to contain a 70:30 mixture of Me¹⁵NO₂ and Et₂O: IR (neat) ν_{15NO} 1515 cm⁻¹; ¹H NMR δ 4.29 (d, J_{15N-CH₃} = 2.5 Hz).

(Hydroxy[¹⁵N]amino)methane Chlorohydrate, Me¹⁵NHOH·HCl. Me¹⁵NO₂ (0.35 g) in 20 mL of MeOH was added to a solution of NH₄Cl (1 g) in 25 mL of cold water. To the vigorously stirred mixture was added 1 g of Zn powder slowly. After the mixture was stirred for 0.3 h, the solid was filtrated and washed with MeOH. The solution was made acidic with concentrated HCl. Water was distilled off and MeOH added in order to precipitate NH₄Cl. Upon removal of MeOH, the

resulting colorless oil crystallized upon cooling to -15 °C and was used without any further purification.

([¹⁵N]Nitrosomethane)(pyridine)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(Me¹⁵NO)(py). Fe^{III}(TPP)(Cl) (0.14 g) was treated by Me¹⁵NHOH, HCl (0.4 g) in MeOH-CH₂Cl₂ (1:1) (25 mL), under an argon atmosphere, in the presence of 0.15 mL of pyridine during 4 h. The volume of the solution was reduced by argon bubbling. The purple crystals were recrystallized from CH₂Cl₂, MeOH, and pyridine: yield 0.11 g (70%); visible spectrum (CH₂Cl₂) 424, 536 nm; IR 1390, 918 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 8.66 (s, 8 H, pyrrole), 8.08 (m, 8 H, *o*-Ph), 7.70 (m, 12 H, *m*-, *p*-Ph), 6.17 (t, J = 6.5 Hz, 1 H, *p*-py), 5.30 (t, J = 6.5 Hz, 2 H, *m*-py), 2.05 (d, J = 6.5 Hz, 2 H, *o*-py), -1.29 (d, J_{15N-CH₃} = 3 Hz, MeNO); mass spectrum, M⁺ *m/e* 688 [Fe(TPP)], 79 (py), 46 (Me¹⁵NO).

Stoichiometry of the Reaction between Fe^{III}(TPP)(Cl) and *i*-PrNHOH. To a deacrated solution of Fe^{III}(TPP)(Cl) in CH₂Cl₂ (0.35 g, 0.5 mmol) under argon was added a solution of *i*-PrNHOH (0.075 g, 1 mmol) in CH₂Cl₂. The argon bubbling was kept for 6 h. The solvents were removed by argon bubbling, giving 0.42 g of a crude mixture. This crude mixture (0.020 g) was dissolved in deacrated CDCl₃ and analyzed by ¹H NMR spectroscopy. After addition of 5 μL of C₃D₃N, the chemical shifts (8.60, 8.00, 7.65, -0.74, -2.00 ppm) were those of the Fe(TPP)(*i*-PrNO)(py) complex 2a. Additional signals at 1.42 and 1.34 ppm were attributed to *i*-PrNH₂, HCl, and *i*-PrNHOH·HCl by comparison with those of authentic samples added to the NMR tube.

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Supplementary Material Available: Tables of the final atomic coordinates for the non-hydrogen and hydrogen atoms, atomic thermal parameters, comparative bond distances and angles, and a list of the observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.