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Complexes of Ferrous Phthalocyanine with Aromatic Nitroso Compounds, Isocyanides, and Phosphites

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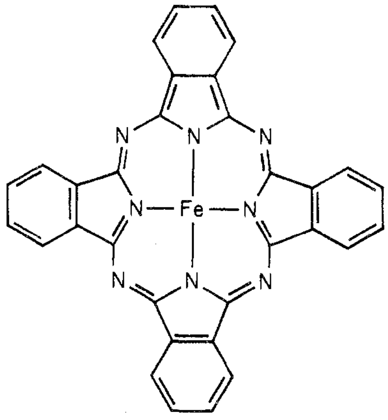
A number of new adducts of ferrous phthalocyanine (FePc) have been isolated. These include mixed-ligand complexes LFePcL' [L = a nitroso aromatic group, L' = *n*-butylamine or *N*-methylimidazole; L = cyclohexyl isocyanide, L' = *N*-methylimidazole; L = a phosphite, L' = *n*-butylamine] and bis adducts L_2FePc [where L is an isocyanide or a phosphite]. The complexes have been characterized by elemental analysis, electronic spectra, infrared spectra, and proton magnetic resonance spectra. The ring-current-induced shifts found for coordinated nitrosobenzene have been analyzed and it is concluded that this ligand coordinates iron through the nitrogen lone pair. The rate of exchange between free and complexed nitrosotoluene in $(CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$ has been determined by observing the ^{1}H NMR spectrum under intermediate exchange conditions. The exchange occurs via a dissociative path and the activation parameters for exchange are $\Delta H^\ddagger = 20.1 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = 14.2 \pm 0.2$ eu.

Introduction

The nitroso group is isoelectronic with two classes of ligands—dioxygen and diazenes—which are of considerable current interest to chemists. However, relatively few examples of metal–nitroso complexes are known, and there is only limited structural work in this area. The substitution product from the reaction of nitrosobenzene and ferrocyanide has been known for some time[1] and it also has been shown that aromatic nitroso compounds will complex ferrous hemoglobin and ferrous myoglobin.[2-6] Although these last two reactions undoubtedly involve axial coordination of the heme iron by nitrosobenzene, little is known in detail about the iron–nitroso bonding. Nitrosobenzene could coordinate iron in several fashions; the most obvious are (1) through the nitrogen lone pair, (2) through an oxygen lone pair, or (3) through the nitrogen–oxygen π bond. Additionally nitrosobenzene could coordinate as its dimer[7] or it could act as a bridging ligand. The best characterized, simple nitroso complex $(C_6H_5NO)_2PdCl_2$[8] has been shown by an X-ray structure determination[9] to have the palladium coordinated to the nitrogen lone pair. The only other nitroso complex which has been characterized by an X-ray structure determination[10] is the dimer $[C_6H_5NOFe(CO)_3]_2$ in which the nitroso group bridges two irons by forming both iron–nitrogen and iron–oxygen bonds.

The interaction of aromatic nitroso compounds with ferrous phthalocyanine (FePc), **1**, has been examined in order to study the coordination of a nitroso group with iron in a porphyrin-like environment. The ring currents produced by the phthalocyanine macrocycle induce significant shifts in the proton magnetic resonance spectra of ligands above and below the phthalocyanine plane.[11] An analysis of these shifts may be used to estimate molecular geometry. In the course of this work some other new adducts of FePc have been prepared and the range of bases which have been shown to add to FePc has been enlarged.



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Experimental Section

Preparation of Compounds. Ferrous phthalocyanine was sublimed under vacuum before use. Bis(*n*-butylamine)ferrous phthalocyanine was prepared as described previously[11] and recrystallized from acetonitrile. Aromatic nitroso compounds were prepared via standard procedures.[12,13]

$(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$. Nitrosobenzene (200 mg, 1.87 mmol) was added to a stirred, filtered solution of 500 mg (0.70 mmol) of $(n\text{-}C_4H_9NH_2)_2FePc$ in 50 ml of dichloromethane. The volume of the deep blue solution was reduced by distillation to 20 ml, and 20 ml of diethyl ether was added. Upon further reduction of the solvent volume, the product formed purple crystals. The product was collected and recrystallized from 1:1 v/v of dichloromethane–diethyl ether containing additional nitrosobenzene; yield, 67%. Anal. Calcd for

Table I. Electronic Spectra of FePc Adducts in Chloroform Solution

Compd	λ_{max}, nm ($\epsilon \times 10^{-4}$)
(C_6H_5NO)FePc(*n*-$C_4H_9NH_2$)	663 (11.53), 599 (3.09), 320 (6.90)
(*p*-$CH_3C_6H_4NO$)FePc(*n*-$C_4H_9NH_2$)	663 (11.47), 602 (3.29), 322 (7.37)
[*p*-$(CH_3)_2CHC_6H_4NO$]FePc(*n*-$C_4H_9NH_2$)	663 (11.45), 600 (3.49), 322 (8.07)
(*p*-$CH_3C_6H_4NO$)FePc($CH_3C_3H_3N_2$)	660 (10.25), 598 (2.90), 320 (6.36)
($C_6H_{11}NC$)FePc($CH_3C_3H_3N_2$)	655 (10.86), 593 (1.12), 330 (6.92)
[$(C_6H_5O)_3P$]FePc(*n*-$C_4H_9NH_2$)	658 (8.19), 600 (2.81), 420 (0.90), 322 (5.79)
$(CH_3C_3H_3N_2)_2$FePc	661 (12.89), 598 (3.10), 424 (1.72), 342 (6.17)
$(C_6H_5CH_2NH_2)_2$FePc	664 (9.81), 604 (2.78), 424 (1.63), 332 (5.76)
$[(C_2H_5O)_3P]_2$FePc	654 (10.07), 595 (2.63), 413 (2.10), 332 (5.83)
$(C_6H_{11}NC)_2$FePc	662 (12.05), 599 (3.62), 395 (1.69), 322 (7.52)
(*n*-$C_4H_9NC)_2$FePc	662 (12.10), 599 (3.55), 393 (1.66), 321 (7.57)
$(C_6H_{11}O_3P)_2$FePc	657 (10.64), 604 (3.23), 412 (1.98), 320 (7.05)

$C_{42}H_{32}FeN_{10}O$: C, 67.38; H, 4.31; N, 18.71. Found: C, 67.43; H, 4.44; N, 18.69.

The following compounds were prepared similarly.

(*p*-$CH_3C_6H_4NO$)FePc(*n*-$C_4H_9NH_2$). Anal. Calcd for $C_{43}H_{34}FeN_{10}O$: C, 67.72; H, 4.49; N, 18.36. Found: C, 67.76; H, 4.59; N, 18.37.

[*p*-$(CH_3)_2CHC_6N_4NO$]FePc(*n*-$C_4H_9NH_2$). Anal. Calcd for $C_{45}H_{38}FeN_{10}O$: C, 68.35; H, 4.84; N, 17.71. Found: C, 68.89; H, 4.70; N, 17.91.

(*p*-$CH_3C_6H_4NO$)FePc($CH_3C_3H_3N_2$). Nitrosotoluene (610 mg, 5.0 mmol) and 0.25 ml (2.95 mmol) of *N*-methylimidazole were added to a refluxing solution of 2140 mg (3 mmol) of (*n*-$C_4H_9NH_2)_2$FePc in 40 ml of dichloromethane. After 5 min of refluxing, the solvent was distilled off until the volume was reduced to 20 ml. The mixture was placed on a dry alumina column (5 × 4.3 cm) and eluted with dichloromethane. The first blue band was collected and the solvent volume was reduced to 10 ml by distillation. After the addition of 10 ml of diethyl ether, the product separated as purple crystals. The product was recrystallized from 2:1 dichloromethane–diethyl ether containing a small amount of *p*-nitrosotoluene; yield 50%. Anal. Calcd for $C_{43}H_{29}FeN_{11}O$: C, 66.93; H, 3.78; N, 19.96. Found: C, 67.06; H, 3.86; N, 20.08.

($C_6H_{11}NC$)FePc($CH_3C_3H_3N_2$). *N*-Methylimidazole (0.25 ml, 2.95 mmol) was added to a solution of 300 mg (0.395 mmol) of bis(cyclohexyl isocyanide)ferrous phthalocyanine in 20 ml of dichloromethane. The solvent was removed under reduced pressure on a rotary evaporator. The resulting solid was recrystallized twice from dichloromethane–acetonitrile; yield 90%. Anal. Calcd for $C_{43}H_{33}FeN_{11}$: C, 67.99; H, 4.38; N, 20.28. Found: C, 68.16; H, 4.36; N, 20.38.

[$(C_6H_5O)_3P$]FePc(*n*-$C_4H_9NH_2$). Triphenyl phosphite (0.5 ml, 1.36 mmol) was added to a refluxing solution of (*n*-$C_4H_9NH_2)_2$FePc (714 mg, 1.0 mmol) in 50 ml of chloroform. The volume of the blue solution was reduced to 10 ml. Diethyl ether (10 ml) and methanol (10 ml) were added to the filtered solution. The solvent volume was reduced to 15 ml by distillation; after cooling of the solution, the crystalline product was collected and recrystallized from chloroform–methanol; yield 70%. The complex was characterized by its ^{1}H NMR spectrum which has the A_2B_2 multiplet of the Pc ligand centered at τ 0.74 and 2.04 and the other resonances listed in Table II.

The following complexes were prepared by refluxing a suspension of FePc in either chloroform or dichloromethane with an excess of the appropriate ligand. After filtration to remove unreacted FePc, the volume of the filtrate was reduced and diethyl ether was added to precipitate the product. Purification was achieved by recrystallization from dichloromethane–diethyl ether.

$(CH_3C_3H_3N_2)_2$FePc. Anal. Calcd for $C_{40}H_{28}FeN_{12}$: C, 65.58; H, 3.85. Found: C, 65.61; H, 3.91.

$(C_6H_5CH_2NH_2)_2$FePc. Anal. Calcd for $C_{46}H_{34}FeN_{10}$: C, 70.60; H, 4.38; N, 17.90. Found: C, 70.26; H, 4.72; N, 18.57.

$[(C_2H_5O)_3P]_2$FePc. This was characterized by its ^{1}H NMR spectrum: τ 0.74, 2.14, A_2B_2 multiplets of Pc; 8.92, methylene quartet (J = 6.7 Hz); 10.38, methyl triplet (J = 6.7 Hz).

$(C_6H_{11}NC)_2$FePc. Anal. Calcd for $C_{46}H_{38}FeN_{10}$: C, 70.23; H, 4.87. Found: C, 69.94; H, 5.01.

(*n*-$C_4H_9NC)_2$FePc. Anal. Calcd for $C_{42}H_{34}FeN_{10}$: C, 68.67; H, 4.66; N, 19.07. Found: C, 68.83; H, 4.41; N, 19.63.

$(C_6H_{11}O_3P)_2$FePc. The axial ligand is the cage phosphite 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane (*caution*! toxic). Anal. Calcd for $C_{44}H_{38}FeN_8O_6P_2$: C, 59.21; H, 4.29. Found: C, 58.84; H, 4.19. ^{1}H NMR resonances: τ 0.67, 2.06, A_2B_2 multiplets of Pc; 7.91, cage methylenes; 10.09, unresolved, overlapping ethyl methylene and methyl.

Physical Measurements. ^{1}H NMR spectra were run on a JEOL JNM-MH-100 spectrometer at 100 MHz. Samples were prepared in chloroform-*d* solution containing internal tetramethylsilane as the reference. Infrared spectra were obtained from hydrocarbon mulls utilizing a Beckman IR-12 spectrophotometer, and a Cary 14 spectrophotometer was used for measuring electronic spectra.

Results and Discussion

Synthesis and Characterization of New Adducts. One of the greatest difficulties in studying FePc adducts is the extremely low solubility of many of the adducts and of FePc itself. The reaction of FePc with the nitroso aromatics which we have examined appears to produce adducts, but these were insufficiently soluble to purify or characterize. However, addition of aromatic nitroso compounds to (*n*-$C_4H_9NH_2)_2$FePc yields mixed-ligand complexes of the type (ArNO)FePc(*n*-$C_4H_9NH_2$). A similar mixed-ligand complex, (C_6H_5NO)FePc($CH_3C_3H_3N_2$), has been prepared with *N*-methylimidazole as the base trans to the nitroso ligand. These adducts as well as the other new FePc adducts do not have melting points below 300° and their infrared spectra are generally not sufficiently informative for characterization purposes. Consequently the electronic spectra for the adducts are reported in Table I to provide convenient means for identifying them. Analytical data for the new adducts are given in the Experimental Section.

It has been found that two other classes of bases—isocyanides and phosphites—can form adducts with FePc. Both bis adducts and mixed adducts with one nitrogen base and one isocyanide or one phosphite have been isolated. Recently some analogous benzyl isocyanide complexes have been reported;[14] however phosphites appear to be a new class of bases which will coordinate FePc. The infrared spectra of the isocyanide adducts clearly show vibrations due to $\nu(C{\equiv}N-)$. In $(C_6H_{11}NC)_2$FePc and (*n*-$C_4H_9NC)_2$FePc these occur at 2159 and 2181 cm^{-1}, respectively, while in ($C_6H_{11}NC$)FePc($CH_3C_3H_3N_2$) this vibration occurs at 2145 cm^{-1}. The isocyanide carbons in these adducts do not appear to be susceptible to nucleophilic attack by amines.

The ^{1}H NMR spectra of the adducts are unambiguous in determining their composition. The spectra of the new adducts indicate that all of the adducts are diamagnetic. ^{1}H NMR data concerning the axial ligands are reported in Table II. In addition, the spectra of all of the adducts display low field multiplets at ca. τ 0.6 and 1.9 which are assigned to the 3,6 and 4,5 protons of the phthalocyanine ligand. In all cases it has been possible to verify the adduct stoichiometry by comparing the integrated intensities of the various adduct protons with the intensities of the proton resonances due to the phthalocyanine ligand. In general the ring-current-induced shifts of the ^{1}H NMR resonance of the axial ligands are quite large and simplify the spectra of these ligands. In the next section these shifts are utilized to estimate the geometry of

Table II. ^{1}H NMR Chemical Shifts for Ferrous Phthalocyanine Compounds[a]

Compd	Phenyl group resonance		
	o-H	m-H	p-H
$(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$	7.13	4.20	3.72
$(p\text{-}CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$	7.16	4.40	8.42[b]
$[p\text{-}(i\text{-}Pr)C_6H_4NO]FePc(n\text{-}C_4H_9NH_2)$	7.14	4.38	7.84,[c] 9.26[b]
$(C_6H_5NO)FePc(CH_3C_3H_3N_2)$	7.07	4.20	3.74
$(p\text{-}CH_3C_6H_4NO)FePc(CH_3C_3H_3N_2)$	7.05	4.40	8.47[b]
C_6H_5NO	2.08	2.38	2.29
$p\text{-}CH_3C_6H_4NO$	2.21	2.65	7.60[b]
$p\text{-}(i\text{-}Pr)C_6H_4NO$	2.15	2.50	7.01,[c] 8.13[b]
$[(C_6H_5O)_3P]FePc(n\text{-}C_4H_9NH_2)$	5.13	3.44-3.72[d]	
$(C_6H_5CH_2NH_2)_2FePc$	5.16	3.46-3.84[d]	

Compd	n-Butylamine resonances				
	NH_2	α-CH_2	β-CH_2	γ-CH_2	δ-CH_2
$(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$	14.52	12.54	11.10	10.55	10.30
$(p\text{-}CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$	14.60	12.54	11.09	10.55	10.30
$[p\text{-}(i\text{-}Pr)C_6H_4NO]FePc(n\text{-}C_4H_9NH_2)$	14.56	12.52	11.04	10.54	10.32
$(n\text{-}C_4H_9NH_2)_2FePc$	17.37	13.00	11.43	10.71	10.40
$[(C_6H_5O)_3P]FePc(n\text{-}C_4H_9NH_2)$	15.96	12.80	11.24	10.61	10.35
$(C_6H_{11}O_3P)FePc(n\text{-}C_4H_9NH_2)$	15.72	12.65	11.23	10.60	10.37

Compd	N-Methylimidazole resonances			
	CH_3	2-H	4-H	5-H
$(C_6H_5NO)FePc(CH_3C_3H_3N_2)$	7.92	8.11	8.37	5.28
$(p\text{-}CH_3C_6H_4NO)FePc(CH_3C_3H_3N_2)$	8.03	8.11	8.33	5.34
$(CH_3C_3H_3N_2)_2FePc$	7.96	8.14	8.41	5.54
$(C_6H_{11}NC)FePc(CH_3C_3H_3N_2)$	8.04	8.00	8.41	5.46

[a] Measured in chloroform-d solution. [b] Methyl group resonance. [c] C–H Resonance. [d] Multiplet.

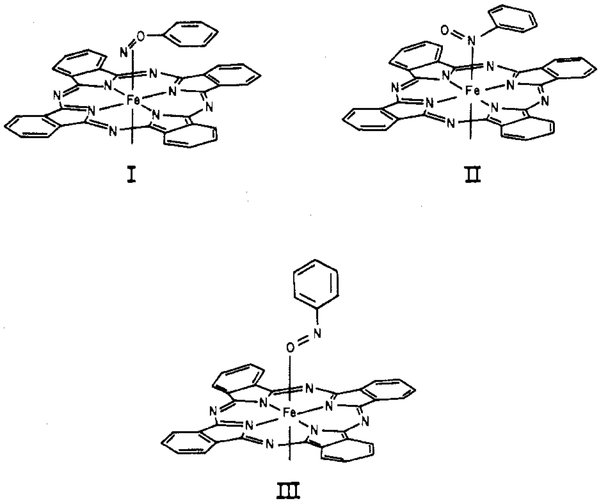
I II III

Figure 1. Models for the nitroso–iron bonding.

Table III. Ring-Current-Induced Shifts

Obsd Upfield Shifts of Nitroso Resonances

Compd	o-H	m-H	p-H
$(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$	4.92	1.82	1.43
$(p\text{-}CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$	4.95	1.75	
$(C_6H_5NO)FePc(CH_3C_3H_3N_2)$	4.99	1.82	1.45
$(p\text{-}CH_3C_6H_4NO)FePc(CH_3C_3H_3N_2)$	4.84	1.75	

Calcd Upfield Shifts of Nitroso Resonances

Model	Ring-ligand atom dist, Å	Angle α, deg	o-H	m-H	p-H
II	2.1	100	4.98	1.69	1.10
II	1.9	110	4.95	1.74	1.17
II	1.7	120	5.00	1.79	1.27
II	1.5	130	4.94	1.85	1.38
III	1.5		3.41	1.51	1.14
III	0.7		4.39	1.92	1.46

the iron–nitroso bond. However the ^{1}H NMR spectra of the isocyanide adducts do not show shifts of sufficient magnitude to offer a convenient simplification of the spectra of these ligands.

Structure of the Nitroso Adducts. The ^{1}H NMR data from Table II may be used to estimate the geometry of the nitroso–iron bond. From the stoichiometry of the adducts, as determined both by chemical analysis and by integration of the ^{1}H NMR spectra, it is certain that only one nitroso monomer is associated with each iron. Three models for the iron–nitroso bonding have been considered. These are shown in Figure 1. The ^{1}H NMR spectra show only one resonance for the 2 and 6 positions of the nitroso ligands and one resonance for the 3 and 5 positions. Consequently, barring accidental degeneracies, either rotation about the nitroso C–N bond is rapid on an NMR time scale or the N–O bond lies in a plane perpendicular to the aromatic ring of the nitroso ligand. Thus the ^{1}H NMR spectra are not consistent with the nitroso group binding iron in a side-on fashion through the N–O π bond, model I. In model I the nitrosophenyl group would be forced to lie closely above and parallel to the phthalocyanine ligand. Large differences in the chemical shift of the 2 and 6 protons and of the 3 and 5 protons would be anticipated to result from the ring current of the macrocyclic ligand. These are not found. Although rapid dissociation of the nitroso ligand, rotation about the N–C bond in the free ligand, and reassociation of the ligand with the metal could equilibrate the 2 with the 6 proton and the 3 with the 5 proton, the kinetics of ligand dissociation (vide infra) are not compatible with this dynamic model.

Two other modes of nitroso coordination have been considered. Model II involves bonding of the nitroso group through the lone pair on the nitroso nitrogen, while model III involves coordination via a lone pair on the nitroso oxygen. The ring-current shifts predicted by these models have been compared with the observed shifts. These observed shifts, which are the differences between the resonance positions of the nitroso protons in the adducts and those resonance positions for the free ligand, are shown in Table III. Classical current loop calculations of the magnitude of this ring-current shift have been made.[15] The tabular results of this calculation,[16] which give the ring-current shift as a function of cylindrical coordinates centered on the middle of the phthalocyanine ring, have been used to calculate the magnitude of the shifts. In these calculations the bond lengths within the nitroso ligand have been taken from the X-ray structural data[9] for $(C_6H_5NO)_2PdCl_2$. In dealing with model II both the ring to nitroso nitrogen distance and the Fe–N–C angle have been treated as variables. The nitroso nitrogen has been placed directly above the center of the phthalocyanine ring. The plane of the phenyl group has been placed perpendicular to the plane defined by the Fe—N═O unit. For reasonable ring to nitroso nitrogen distances little rotation about the N—C bond of the nitroso group is expected since the van der Waals radii of the phthalocyanine ligand and of the ortho protons of the nitroso ligand are in close proximity. The results of this analysis are compared with the observed data in Table III. It can be seen that a reasonable fit of the shifts for the ortho and meta protons may be achieved in a variety of reasonable nitroso group orientations. Obtaining a good fit for the para proton requires a short ring–nitrogen distance. Similar calculations have been performed using model III. In this case the only variable considered was the ring to nitroso oxygen distance. The Fe–O–N and O–N–C bond angles were assumed to be 120°. Free rotation about the nitroso N–C bond was allowed. Results for two such calculations are shown in Table III. It has not been possible to achieve a reasonable fit of the experimental data. Model III places the ortho protons too far from the ring when reasonable ring–oxygen distances are considered. Consequently it is concluded that the nitrogen-bound model II appropriately describes the bonding in this complex.

For low-spin Fe(II) complexes the iron should lie in the plane of the phthalocyanine macrocycle. The distance from the axial donor to the ring should be equivalent to the donor–iron bond length. Structural data[17,18] on low-spin Fe(II) compounds indicate that an Fe–N distance of 1.9–2.0 Å should be expected for the iron–nitroso bond. A complete fit of the ring-current shifts observed in $C_6H_5NOFePc(n\text{-}C_4H_9NH_2)$ requires a considerably shorter Fe–N bond. Alternately a small displacement of the iron from the phthalocyanine ring away from the nitroso ligand could accommodate a more normal Fe–N bond length along with the observed shifts. However since there have been relatively few tests of the ring-current calculations and since it is only the fit of the para proton which is difficult to obtain, we prefer not to overestimate the significance of the ring–nitrogen distance that is derived from these calculations.

From the data of Tables II and III it may be seen that the resonance positions of the nitroso protons are not significantly different in the two compounds $(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$ and $(C_6H_5NO)FePc(CH_3C_3H_3N_2)$. The nature of the trans amine does not appear to alter the iron–nitroso bonding significantly. However a comparison between $(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$ and $(n\text{-}C_4H_9NH_2)_2FePc$ indicates that placing a nitroso ligand trans to the *n*-butylamine ligand may lengthen the ring–amine nitrogen distance beyond the value found for the bis-amine adduct. There does not appear to be any significant difference in the *N*-methylimidazole resonance positions in $(C_6H_5NO)FePc(CH_3C_3H_3N_2)$ and $(CH_3C_3H_3N_2)_2FePc$.

Kinetics of Nitroso Ligand Exchange. The dynamics of exchange of the nitroso ligand between free and coordinated form (eq 1) have been examined through ^1H NMR studies of a mixture of the nitroso ligand and the metal complex.

$$\mathrm{CH_3C_6H_4NO^* + (CH_3C_6H_4NO)FePc(\mathit{n}\text{-}C_4H_9NH_2) \underset{\mathit{k}_{-1}}{\overset{\mathit{k}}{\rightleftharpoons}} CH_3C_6H_4NO + (CH_3C_6H_4NO^*)FePc(\mathit{n}\text{-}C_4H_9NH_2)} \qquad (1)$$

Because of ring-current-induced shifts the methyl resonance of coordinated nitrosotoluene in the complex in chloroform-*d* solution at 22° occurs at higher field by 0.849 ppm than the corresponding resonance of the free ligand. As the temperature of a chloroform-*d* solution containing 0.14 *M* nitrosotoluene and 0.14 *M* $(CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$ is raised, the two methyl resonances broaden, move together, and at 48.5° coalesce into a single resonance at a chemical shift which is the average of the original chemical shifts of the two methyl groups. Cooling of the solution reverses the sequence of observations. The rate of exchange in the intermediate-exchange region was calculated from the difference in chemical shifts of the observed resonances by standard procedures.[19] At 298°, $k = 13.0$ sec^{-1}. Dilution of this solution did not affect the kinetic parameters. Consequently the ligand-exchange process is dissociative in nature. Examination of the temperature dependence of the exchange rate produced a linear Eyring plot with activation parameters of $\Delta H^\ddagger = 20.1 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = 14.2 \pm 0.2$ eu. Although the rate of ligand exchange observed here is unusually fast for low-spin d^6 complexes, this rate is consistent with the acceleration of axial ligand substitution which is found in, and which is apparently characteristic of, porphyrin and phthalocyanine complexes.[20-22]

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Registry No. $(C_6H_5NO)FePc(n\text{-}C_4H_9NH_2)$, 55925-70-7; $(p\text{-}CH_3C_6H_4NO)FePc(n\text{-}C_4H_9NH_2)$, 55925-71-8; $[p\text{-}(CH_3)_2CHC_6H_4NO]FePc(n\text{-}C_4H_9NH_2)$, 55925-72-9; $(p\text{-}CH_3C_6H_4NO)FePc(CH_3C_3H_3N_2)$, 55925-73-0; $(C_6H_{11}NC)FePc(CH_3C_3H_3N_2)$, 55925-74-1; $[(C_6H_5O)_3P]FePc(n\text{-}C_4H_9NH_2)$, 55925-75-2; $(CH_3C_3H_3N_2)_2FePc$, 55925-76-3; $(C_6H_5CH_2NH_2)_2FePc$, 55925-77-4; $[(C_2H_5O)_3P]_2FePc$, 55925-78-5; $(C_6H_{11}NC)_2FePc$, 55925-79-6; $(n\text{-}C_4H_9NC)_2FePc$, 55925-80-9; $(C_6H_{11}O_3P)_2FePc$, 55925-81-0; $(n\text{-}C_4H_9NH_2)_2FePc$, 20219-86-7; triphenyl phosphite, 101-02-0.

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