perturbations could account for the discrepancy. The higher methanol concentrations (above 2.47 M, ~10% by volume) apparently have little further adverse effect on the equilibrium. This behavior unfortunately does add a degree of uncertainty to the meaning of this result. The result is, however, consistent with an adamantane-like structure of formula $H_4V_4O_{14}^{4-}$ for the tetravanadate ion. In this structure each of the vanadiums is pentacoordinate and the product tetramer carries a net charge of −4. Such a structure would also be in accord with the results from the study of this ion in liquid crystalline solution.[18]

Registry No. MeOH, 67-56-1; PO_4^{3-}, 14265-44-2; $VO_4H_2^-$, 34786-97-5; $HO_3VOVO_3H^{2-}$, 37353-31-4; $MeOVO_3H^-$, 111291-05-5; $(MeO)_2VO_2^-$, 111291-06-6; $(MeO)O_2VOVO_3H^{2-}$, 111291-07-7; $(MeO)O_2VOVO_2(OMe)^{2-}$, 111291-08-8.

Contribution from the Laboratoire de Chimie de Coordination du CNRS, 31077 Toulouse Cedex, France, and Section Biologie, Institut Curie, 91405 Orsay, France

Proximal Effect of the Nitrogen Ligands in the Catalytic Epoxidation of Olefins by the NaOCl/Manganese(III) Porphyrin System†

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Using synthetic manganese porphyrin complexes with an imidazole or a pyridine ligand covalently attached to the macrocycle, we report the control of the reaction rate, product selectivity, and stereoselectivity by the axial ligand trans to the active site of the catalyst. The results clearly illustrate the proximal effect on nitrogen ligands in this cytochrome P-450 model.

Since the earlier work on metalloporphyrin-catalyzed oxygenation of the hydrocarbons,[1-3] many studies have documented this catalytic transfer of an oxygen atom from an oxidant (PhIO, NaOCl, $KHSO_5$, ROOH, or H_2O_2 or O_2 and an electron source) to an olefin or a saturated hydrocarbon (for recent reviews, see ref 4 and 5). Among the factors that control the oxygen-transfer step, much attention has been paid to the macrocyclic ligand itself: the presence of the bulky substituents at the 2,6-positions of the phenyl groups in the meso positions of the tetrapyrrolic planar structure are able to create a cage around the active metal/oxo species generated during the catalytic cycle. Such a cage effect makes it possible to avoid the dimerization of the catalyst, via the formation of a μ-oxo linkage and the self-destruction of the porphyrin complex ("bleaching effect"), and to control the possible radical species that might be involved in some stages of the catalytic cycle (cage radicals versus free radicals).

Besides this role of the macrocyclic ligand itself, the important effect of an additional nitrogen base acting as the fifth ligand on the rate and the chemo- and stereoselectivity has also been evidenced. The influence of pyridine or N-substituted imidazole has been successively evidenced with NaOCl,[6,7] O_2 and electrons,[8] ROOH,[9] H_2O_2,[10] and peracids[11] as oxygen sources.

These results have to be regarded as the preliminary approach in mimicking the proximal and distal effects that are involved in the chemical and biochemical properties of hemoproteins such as cytochrome P-450, peroxidase, catalase, and hemoglobin, all containing iron protoporphyrin IX as a prosthetic group.[12] The nature of the proximal group in the fifth position is well-established by X-ray structures: an imidazole of an histidine residue in hemoglobin and myoglobin[13] and cytochrome C peroxidase,[14] a phenoxy group from tyrosine in catalase,[15] and a cysteinato ligand in cytochrome P-450.[16]

For most of these proteins, the nature of (the) distal ligand(s) is also known: a histidine is involved in catalase[15] and in myoglobin for the stabilization of the iron–dioxygen complex by hydrogen bonding,[13] while histidine and arginine residues are in distal positions in cytochrome C peroxidase.[14] However, little is known about the electronic effects that are induced by these proximal and distal protein ligands during the different steps of the catalytic cycle and, in particular, about the formation and the reactivity control of the high-valent iron–oxo entities that are the key intermediates in the oxygenase, peroxidase, and catalase systems.

Table I. *cis*-Epoxide:*trans*-Epoxide Ratios in the Manganese Porphyrin Catalyzed Epoxidation of *cis*-Stilbene by NaOCl

run no.	catalyst[e]	extra ligand[e]	% *cis*-epoxide	% *trans*-epoxide
1	Mn(TPP)OAc		35	65
2	Mn(TPP)OAc	py[a]	70	30
3	Mn(TPP)OAc	*N*-Ap-Im[b,c]	85	15
4	**1** (py)[d]		89	11
5	**1**	py	92	8
6	**2** (py)[d]		89	11
7	**2**	py	86	14
8	**3** (Im)[d]		85	15
9	**3**	py	87	13
10	**3**	*N*-Ap-Im	80	20
11	**4** (py)[d]		93	7
12	**4**	py	84	16
13	**4**	*N*-Ap-Im	84	16

[a] A total of 25 equiv of pyridine versus 1 equiv of catalyst is used. [b] A total of 14.5 equiv of *N*-Ap-Im is used. [c] This ligand has a drastic effect on the rate of these catalytic epoxidations.[7] [d] The nature of the attached fifth ligand is indicated in parentheses. [e] Abbreviations: TPP, tetraphenylporphyrin; py, pyridine; Im, imidazole; *N*-Ap-Im, 4-(imidazol-1-yl)acetophenone.

It is expected from these metalloporphyrin-catalyzed oxygenation reactions in the presence of pyridine or imidazoles that a

† This article is dedicated to the memory of Professor Iwao Tabushi of Kyoto University.

‡ Laboratoire de Chimie de Coordination du CNRS.

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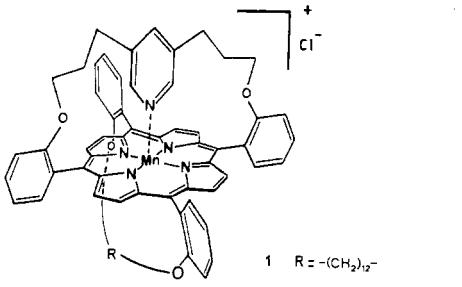

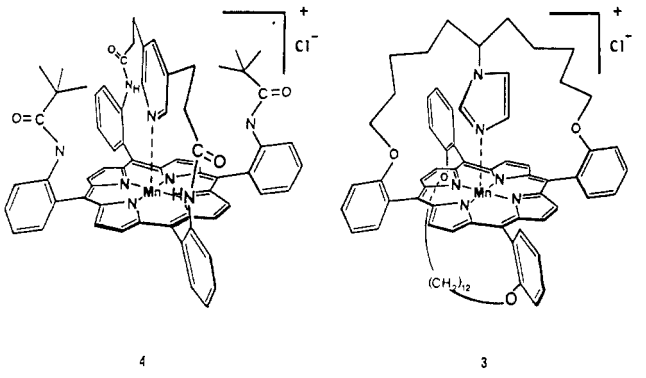

Figure 1. Structures of complex **1**, showing the proximal pyridine and distal aliphatic chain, complex **2**, showing the proximal pyridine and distal aromatic chain, complex **3**, showing the proximal imidazole and the same distal chain as in **1**, and complex **4**, showing the proximal pyridine without any distal chain.

deeper insight on the various factors (ligand field variations, nature of the metal–oxo bond

$$M{=}O: \quad \text{or} \quad M\cdot{-}\ddot{O}\cdot$$

oxygen-transfer kinetics, etc.) implicated in the "proximal effect" can be provided. However, in most of the P-450 models described in ref 4–11, the nitrogen ligand is used in large excess with respect to the metal itself and consequently the proximal effect of pyridine or imidazole might be masked by side effects (distal effects, modification of the organic-phase content, etc.). In order to clarify the proximal effect, we describe here the use of manganese porphyrins in which a pyridine or an imidazole is held in a proximal position by covalent linkages to the macrocycle.[17,18]

Results and Discussion

The four complexes used as catalysts for olefin epoxidation by NaOCl are shown in Figure 1. The first two complexes, **1** and **2**, have a pyridine as proximal ligand and differ only by the nature of the distal chain: aliphatic- or aromatic-containing chain. Complex **3** has the same distal chain as **1** but presents an imidazole in the proximal position, and finally complex **4** has no distal chain and a pyridine in the proximal position. Since the two complexes **1** and **3** have the same distal chain, it is then possible to have a direct comparison between the proximal effect of a pyridine or an imidazole in the fifth coordination position.

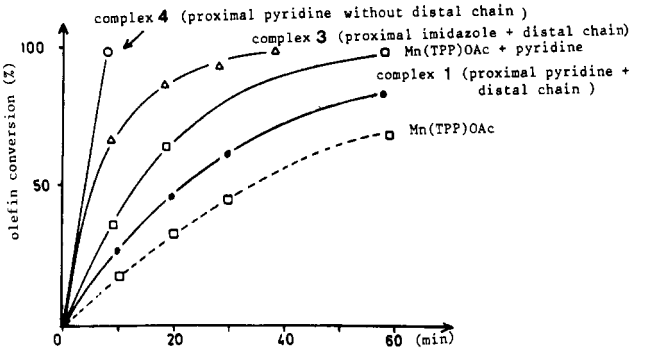

Figure 2. Compared conversions of *cis*-stilbene during its NaOCl epoxidation catalyzed by complexes **1**–**4** and Mn(TPP)OAc.

Epoxidation of *cis*-Stilbene by NaOCl Catalyzed by Manganese Porphyrin Complexes. (i) Influence of the Proximal Effect on the Epoxidation Stereochemistry. Because *cis*-stilbene gives the two possible isomeric epoxides, we have conducted this study on the proximal effect with this particular olefin, for which the epoxidation mechanism may imply a radical pathway as previously suggested.[6b,20,21] In contrast to the case for *cis*-stilbene, aliphatic olefins are stereospecifically epoxidized by this catalystic system.[20,22]

Table I summarizes the ratios of *cis*- and *trans*-stilbene oxides obtained during the NaOCl epoxidation in the presence of catalytic amounts of complexes **1**–**4** and Mn(TPP)OAc. Run 1 indicates that, in the absence of any strong basic fifth ligand, *trans*-stilbene oxide is the major isomer produced during the catalytic reaction. No olefin or product equilibration is observed under these experimental conditions.[6b,20]

Addition of a large excess of pyridine with respect to the manganese porphyrin catalyst reverses the epoxide ratio in favor of the cis isomer (run 2).[6b] The same effect is observed when a N-substituted imidazole, *N*-Ap-Im (*N*-Ap-Im stands for 4-(imidazol-1-yl)acetophenone), is used as a substitute for pyridine. For a smaller base:manganese ratio (14.5:1), the *cis*-epoxide percentage is 85% (run 3).

However, with all of the complexes **1**–**4**, where there is only one axial base per manganese atom, the epoxidation of *cis*-stilbene is highly stereoselective: the percentage of the *cis*-epoxide is always in the range 85–93% (runs 4, 6, 8, and 11). Furthermore, this enhanced stereoselectivity can be entirely attributed to the proximal effect of the nitrogen-attached ligand since the addition of an extra ligand, pyridine or *N*-Ap-Im, does not modify the *cis*-epoxide:*trans*-epoxide ratio (runs 5, 7, 9, and 12 with extra pyridine and runs 10 and 13 with added *N*-Ap-Im).

(ii) Influence of the Proximal Effect on the Epoxidation Rate. Figure 2 describes the different conversion curves during the NaOCl/manganese epoxidation of *cis*-stilbene.

The accelerating effect of added pyridine on Mn(TPP)OAc is clearly evidenced, and a similar effect is reproduced with **1**. However, in **1**, the presence of a distal chain on the face of the metalloporphyrin where the active manganese–oxo group[19] is generated apparently slows down the transfer of the coordinated oxygen species to the substrate. A second factor must also be taken into account. Careful examination of NMR spectra of zinc or iron(II) complexes of the macrocycle corresponding to **1**[29] indicates

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that the pyridine group is not strongly coordinated to the central metal atom. At room temperature, the proportion of noncoordinated pyridine has been estimated to be 5% with zinc and 15–20% with iron complexes. If such a situation is applied for manganese complexes, addition of pyridine must increase the proportion of liganded metal and consequently accelerate the olefin conversion (this effect has been described in a preliminary report[17]) and enhance the stereoselectivity of the epoxidation (this tendency is observed in run 5 compared to run 4). The small amount of available material did not allow a complete kinetic study in order to determine if with such catalysts the rate-determining step is still the breakdown of the manganese–oxo–olefin intermediate[22] or the oxidation of the manganese(III) complex.[23]

The data obtained with **4**, the complex with a proximal pyridine and no distal chain, indicate that the rate of oxygen transfer is considerably higher without the distal chain: the reaction is achieved within 10 min. The origin of the high olefin conversion is probably due to the addition of two different effects: (i) the obvious one, which is the lack of steric hindrance during the oxygen-transfer step because of the absence of a distal chain, and (ii) probably a stronger coordination of the pyridine. Actually, the values of intramolecular association constants for similar iron complexes with a linked pyridine are higher in the amide linkage series compared to that of ether series.[24] These two factors contribute to enhance the oxygen-transfer rate to the olefin with the single-face-hindered complex **4**. With this catalyst, the turnover rate of the reaction is at least 0.5 cycle s^{-1} (the catalytic activity is measured at complete olefin conversion and is not based on the initial rate of the reaction).

The proximal effect of pyridine and imidazole can be compared when **1** and **3** are used. Both exhibit the same aliphatic distal chain, and consequently their distinct catalytic behavior can be entirely attributed to the proximal effect of the nitrogen ligand. Figure 2 shows the greater catalytic activity of **3** compared to that of **1** in the *cis*-stilbene epoxidation: after 10 min, the olefin conversion is only 26% with **1** (proximal pyridine) whereas 70% is reached with **3** (proximal imidazole).

These results establish that imidazole is a better axial ligand than pyridine to enhance the catalytic activity of manganese porphyrins. Still, this is not always the case, especially when these nitrogen bases are not covalently attached to the macrocyclic ligand. Other side effects might largely modify this classification. For example, when these nitrogen donors are only added as free ligands in the reaction mixture, other factors interfere to modulate their influence on the catalyst: (i) the partition coefficient between the organic and aqueous phases when NaOCl is used as the oxygen source (imidazole is more soluble in water than pyridine itself) and (ii) the oxidability of the free nitrogen base in these strong oxidizing mixtures (imidazole itself cannot be used in catalytic NaOCl epoxidation[20] because this ligand is rapidly oxidized; only N-substituted imidazoles can be used[7]). These factors are more important on the ligand effect of free nitrogen bases than the equilibrium constant K_1 corresponding to the axial ligation (K_1 = 1.20 × 10^4 for pyridine and 2.2 × 10^4 for imidazole[25a]). However, these equilibrium constants have been measured for metal(III) complexes while no data are available on the same values for the corresponding metal(IV) or -(V) complexes. Further discussions on the nitrogen ligand effects require such a knowledge of high-valent manganese–oxo complexes, but the great reactivity of these species[19] does not facilitate such studies.

(iii) Effect of the Additional Nitrogen Base on the Conversion Rate of *cis*-Stilbene in the NaOCl Epoxidation Catalyzed by 3, 4, and Mn(TPP)OAc. In order to examine the possible effect of an added nitrogen base on the distal side of the catalyst during olefin epoxidation, we have performed the catalytic epoxidation of *cis*-stilbene by **3** and **4** in the presence and absence of the additional nitrogen base pyridine or *N*-Ap-Im. Mn(TPP)OAc is used as the reference catalyst. The relative rate of olefin conversion is based on the determination of the concentration variation between t_0 and t = 10 min. These values are indicated in Table II.

Table II. Effect of an Additional Nitrogen Base on the Rate of the *cis*-Stilbene Conversion during the NaOCl Epoxidation Catalyzed by **3**, **4**, or Mn(TPP)OAc

run no.	catalyst	extra ligand	rel rate, 10^{-5} M s^{-1}
1	**4** (py)	*b*	>100[a]
2	**3** (Im)		52
3	**3**	py[c]	21
4	**3**	*N*-Ap-Im[d]	28
5	Mn(TPP)OAc		9
6	Mn(TPP)OAc	py[c]	25

[a] Under the same conditions as for runs 2–6, the rate is at least 100 × 10^{-5} M s^{-1}, i.e. 0.5 cycle s^{-1}. The reaction finished within 10 min. [b] No apparent slowdown effect is observed by the addition of extra pyridine or *N*-Ap-Im. [c] A total of 14.5 equiv of added pyridine with respect to **3** or Mn(TPP)OAc. [d] A total of 14.5 equiv of added *N*-Ap-Im with respect to **3**.

Complex **4** is the most efficient catalyst, and under our experimental conditions, the reaction is complete within 10 min; therefore, the influence of additional bases on the reaction rate cannot be determined very accurately. However, this determination is possible with **3**. The relative conversion rate with that complex having a proximal imidazole is 52 × 10^{-5} M s^{-1} (run 2), much greater than the relative rate observed for Mn(TPP)OAc, 9 × 10^{-5} M s^{-1} (run 5), or for Mn(TPP)OAc and 14.5 equiv of extra pyridine/equiv of metal, 25 × 10^{-5} M s^{-1} (run 6).

Complex **3**, with a proximal imidazole and a distal chain, is an efficient catalyst: the relative rate is 52 × 10^{-5} M s^{-1} (run 2). However, the presence of 14.5 equiv of extra pyridine/equiv of metal slows down the epoxidation catalyzed by **3**: the relative rate is then 21 × 10^{-5} M s^{-1} (run 3). The same effect is observed with extra 4-(imidazol-1-yl)acetophenone, the rate being 28 × 10^{-5} M s^{-1} (run 4). There are two possible explanations for this effect of extra nitrogen bases on the epoxidation rate of *cis*-stilbene. One is the possible displacement of the covalently linked imidazole by this extra pyridine or *N*-Ap-Im. It may also be due to the possible coordination of the extra nitrogen ligand in the axial position trans to the linked base. Actually, it is known that, in manganese porphyrin complexes, the equilibrium constant for the coordination of the second pyridine is only 15 times weaker than that for the coordination of the first pyridine:[25a]

$$Mn^{III}(P) + L \underset{}{\overset{K_1}{\rightleftharpoons}} Mn^{III}(P)L \overset{K_2}{\rightleftharpoons} Mn^{III}(P)(L)_2$$

$$K_1 = 15K_2 \text{ for L = pyridine and P = TPP}$$

$$K_1 = 18K_2 \text{ for L = imidazole}$$

This lower value for K_2 compared to that for K_1 is the main reason the rate enhancement by extra pyridine or N-substituted imidazole is induced for manganese(III) tetraphenylporphyrin. In the case of iron(III) porphyrin complexes[26] and with the regular TPP ligand, K_2 is considerably higher than K_1 and, consequently, addition of pyridine inhibits the catalytic activity of Fe(TPP)Cl (unpublished data). However, the disadvantage of the iron porphyrins can be overcome when *o*-phenyl-substituted ligands are used.[27]

Conclusion

This study describes the influence of nitrogen bases such as pyridine and imidazole on the NaOCl epoxidation of olefins

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catalyzed by manganese porphyrins. The catalysts used for this purpose have a pyridine or an imidazole that is fixed in the axial coordination position by two chains attached on the macrocycle itself. With these manganese complexes, it is then possible to distinguish clearly between the true proximal effect of these nitrogen bases and the possible addition of general base effects. These results obtained in the epoxidation of *cis*-stilbene indicate that the stereoselectivity of the reaction is highly controlled by the proximal effect. With catalysts **1–4**, the *cis*-stilbene oxide percentage is always in the range 85–93%, whereas without nitrogen donors, the configuration of the starting olefin is nearly lost during the catalytic epoxidation. In addition, *the comparison of the catalytic activity of* ***1*** *and* ***3*** *shows that imidazole has a stronger proximal effect than pyridine on the acceleration of the oxygen transfer to the olefin.* However, this effect can be partially masked when imidazoles are used as non covalently attached ligands by side-oxidation reactions especially when strong oxidants such as NaOCl or $KHSO_5$ are used as the oxygen source in these biomimetic oxygenation reactions.

Recently, Groves et al.[28] reported that, in the epoxidation of olefins by oxomanganese species generated by peracids, two complexes are able to perform the oxygen transfer: one oxomanganese(IV) complex with a low stereoselectivity, even in the presence of pyridine, and an oxomanganese(V) complex with a high stereoselectivity. The conversion of the latter to the Mn(IV) compound is prevented by the presence of pyridine. So, for complexes **1–4**, where the nitrogen ligand is already coordinated to the metal before oxidation, the situation is even more favorable for the formation of the highly reactive oxomanganese(V) species, which is the primary high-valent metal–oxo complex formed during the catalytic cycle.

Finally, these complexes modeling the prosthetic site of heme-containing monooxygenases illustrate that a good catalytic activity is obtained in the system manganese + nitrogen axial ligand. In that case, the enhanced catalytic activity and epoxidation stereoselectivity are due to a proximal effect of the nitrogen axial ligand, higher in the case of imidazole compared to that of pyridine.

Experimental Section

Materials. All chemicals used were of reagent grade (Aldrich or Fluka). Solvents were purified prior to use. Tetrahydrofuran was distilled from sodium/benzophenone, dimethylformamide was distilled and kept over 4-Å molecular sieves, and dichloromethane was distilled from calcium hydride. Sodium hypochlorite was obtained from Prolabo (Rectapur quality, 0.35 M) and titrated by the iodometric method. Olefins and reference epoxides were respectively purified and prepared as described in ref 20. Merck silica gel 60 (40–60 μm) was used for column chromatography. Merck precoated preparative plates (silica gel 60, 2 mm) were used for TLC purifications. Elemental analyses were carried out by the "Service Central de Microanalyse du CNRS". Optical spectral were recorded by using Varian DMS 100 and Cary 14 spectrometers. ^1H NMR spectra of nonmetalated porphyrins in deuteriochloroform were measured by using a Varian XL 100 spectrometer in the FT mode using 4K data points in the frequency domain (internal reference tetramethylsilane).

Synthesis of Porphyrin Ligands. The ligands corresponding to **1–4** were prepared by literature procedures.[29-31]

Porphyrins Corresponding to 1 and 2. 5α,15α-[2,2′-(Dodecamethylenedioxy)diphenylene]-10β,20β-{2,2′-[3,3′-(pyridine-3,5-diyl)dipropoxy]diphenylene}porphyrin and 5α,15α-{2,2′-[4,4′-(*p*-phenylene)dibutoxy]diphenylene}-10β,20β-{2,2′-[3,3′-(pyridine-3,5-diyl)dipropoxy]diphenylene}porphyrin were prepared by following the published procedure.[29]

Porphyrin Corresponding to 3. 5α,15α-[2,2′-(Dodecamethylenedioxy)diphenylene]-10β,20β-{2,2′-[6-(imidazol-1-yl)undecamethylene-1,9-dioxy]diphenylene}porphyrin. This compound was obtained according to the procedure described for the preparation of ether-"basket handle" porphyrins[29] (14%). Anal. Calcd for $C_{70}H_{73}N_6O_4$: C, 79.14; H, 6.93; N, 7.91. Found: C, 78.94; H, 7.20; N, 8.0. ^1H NMR (ppm): 8.4 (m, 8, Pyr H), 8.08 (m, 4 × H_6-Phe), 7.8–7.3 (m, 12, Phe H), 6.32, 5.91, and 4.95 (Imid H), 3.9 (m, 4, O–CH_2), 2.81 (b, 1, –CH–), +1.32 to –1.72 (18, –CH_2–), –2.54 (s, 2, Pyr *N*-H).

Porphyrin Corresponding to 4. 5α,15α-{2,2′-[3,3′-(Pyridine-3,5-diyl)-dipropionamido]diphenylene}-10α,20α-bis(*o*-pivalamidophenyl)porphyrin. This compound was prepared by following the procedure described for the synthesis of "hybrid" porphyrins.[31] 5α,15α-{2,2′-[3,3′-(pyridine-3,5-diyl)dipropionamido]diphenylene}-10α,20α-bis(*o*-aminophenyl)-porphyrin[30] was treated with pivaloyl chloride in the presence of pyridine in dry tetrahydrofuran. After the usual workup, the porphyrin was recrystallized from dichloromethane/hexane as a purple solid (85%). Anal. Calcd for $C_{65}H_{59}N_9O_4 \cdot 2H_2O$: C, 73.2; H, 5.96; N, 11.82. Found: C, 73.81; H, 6.14; N, 11.96. ^1H NMR (ppm): 8.85 (m, 8, Pyr H), 8.76–7.35 (20, Phe H; +2, NH–CO picket), 7.6 (2, py 2,6-H), 6.05 (s, 2, NH–CO handle), 3.12 (t, 1, py 4-H), 1.25–0.5 (m, 4, CH_2), 0 (s, 6, CH_3), –2.4 (s, 2, Pyr *N*-H).

Preparation of Chloromanganese(III) Complexes. Insertion of manganese into the free base porphyrins was carried out by using $MnCl_2$ in dimethylformamide under the same conditions as used for iron insertion.[29-31] The crude Mn(III) complexes were purified by thin-layer chromatography (Merck, silica gel 60 plates, 2 mm) with dichloromethane/methanol (100:15). Chloromanganese(III) derivatives were generated by shaking a toluene solution of metalloporphyrin with aqueous sodium chloride.

UV–visible data for complexes **1–4** (absorbance maxima and molecular coefficients measured in toluene; λ, nm (ε, L $mmol^{-1}$ cm^{-1})): complex **1** 622 (8.6), 586 (8.2), 480 (81.9), 376 (42.9); complex **2**, 624 (8.9), 586 (7.9), 482 (80.6), 381 (42.9); complex **3**, 621 (9.2), 586 (9.1), 480 (81.2), 374 (36.1); complex **4**, 615 (5.5), 582 (8.1), 480 (82.2), 370 (35.5).

Conductivity measurements have been performed on these metalloporphyrin complexes in methanol solution at 10^{-3} M and the data fitted with an 1:1 electrolyte system in agreement with the cationic structures as described in Figure 1.

Catalytic Epoxidation of Olefins and Product Analysis. All reactions were carried out at 20 °C under nitrogen in a 30-mL Schlenk tube equipped with a stirring bar. One millimole of octadecane (standard for GLC analysis), 1 mmol of olefin, and 2.5 mL of N_2-purged dichloromethane were successively added to 0.0062 mmol of catalyst and 0.0125 mmol of benzyldimethyltetradecylammonium chloride. A 5-mL quantity of 0.35 M NaOCl was then added by syringe to the organic phase. Magnetic stirring was stopped before each aliquot (20 μL) was withdrawn from the organic phase and diluted with diethyl ether (20 μL) before GLC analysis. For conversion and product analysis, the aliquots were injected onto a WCOT 25 m × 0.23 mm CPWax 51 (Chrompack) silica capillary column as part of the equipment of an Intersmat IG 120 chromatograph (oven temperature 200 °C and nitrogen pressure 1.0 bar). Under these analytical conditions, the retention times of *cis*- and *trans*-stilbene oxides were 5.5 and 8.5 min, respectively (the ratios indicated in Table I have been determinated by GLC analysis). The epoxide isomer ratio could also be calculated from ^1H NMR spectra. Before nuclear magnetic resonance studies, the epoxide mixture can be purified from catalyst residues by a chromatographic column of Florisil (60–100 mesh, eluant dichloromethane). The resonances of epoxidic protons are at δ = 3.87 and 4.36 for the trans and cis isomers, respectively[32] (solvent $CDCl_3$). The epoxide selectivity in these catalyzed reactions is in the range 70–85% except in the case of Mn(TPP)OAc as catalyst without extra nitrogen donors. Relative epoxidation rates were calculated from the concentation variation in olefin within the first 10 min of the reaction and are expressed in $M\ s^{-1}$.

Registry No. **1**, 111349-87-2; **2**, 111349-89-4; **3**, 111349-88-3; **4**, 111349-90-7; *cis*-stilbene, 645-49-8.

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