as evidenced by its change in color during the assay, thereby inhibiting the response at the QCM associated with reaction 2. Investigations with more inert supports are currently in progress.

Concluding Remarks

The results described above demonstrate that amplification routes via catalytic processes, such as enzymatic reactions, can significantly extend the detection limits of piezoelectric assay. Since antibodies can be elicited for a wide variety of analytes, the methodology can be generally applied to various substances (e.g. proteins, enzymes, hormones, etc.). The method requires, in addition to an antibody, only an appropriate anti-analyte–enzyme conjugate to convert the substrate to a product capable of inducing a mass change at the surface of the quartz crystal. Detection can be accomplished by simple deposition of insoluble assay products or by reactions of the assay products with films on the QCM that produce mass changes due to adsorption–complexation processes or changes in ion population. As demonstrated here, the latter is particularly advantageous if reusable sensors are desired.

One key advantage of enzymatically amplified sandwich methods is that detection limits are independent of the mass of the analyte. Therefore, detection of low molecular weight analytes such as hormones and drugs is possible under conditions where detection of direct binding will be difficult. The versatility regarding the ease of modification of the QCM surface makes piezoelectric detection widely applicable toward a variety of analytes and suggests that chemical design of new receptors on the surface of the QCM will play a significant role in expanding the scope of piezoelectric immunoassay.

Acknowledgment. We thank J. M. Odom for preparation of the APS reductase antibody, S. Y. Tseng for preparation of the APS reductase–alkaline phosphatase conjugate, and E. J. Delawski and F. T. Gelormini for technical assistance.

Registry No. BCIP, 38404-93-2; hCG, 9002-61-3; Pv-Fc, 34801-99-5; APS reductase, 9027-75-2; quartz, 14808-60-7.

Synthesis, Characterization, and Reactivity of Oxomanganese(IV) Porphyrin Complexes

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Abstract: The preparation, isolation, and characterization of two types of oxomanganese(IV) porphyrin complexes are described. The reaction of chloro(5,10,15,20-tetramesitylporphyrinato)manganese(III) [Mn^{III}TMP(Cl), **1**] with 1.2 equiv of tetramethylammonium hydroxide (TMA(OH)) and 1.2 equiv of *m*-chloroperoxybenzoic acid (*m*-CPBA) in CH_2Cl_2 produced a second complex formulated as Mn^{IV}TMP(O) (**2**). The reaction of **1** in CH_2Cl_2 containing excess tetra-*n*-butylammonium hydroxide (TBA(OH)) at +1.20 V generated a stable oxomanganese(IV) porphyrin complex, [Mn^{IV}TMP(O)(OH)] (**3**). When the reaction stoichiometry was altered, mixtures of complexes **2** and **3** could be prepared. The aerobic reaction of **1** in $CHCl_3$ containing 6 N NaOH and a phase-transfer catalyst resulted in the formation of a similar complex, Mn^{IV}TMP(O)(X) (**2a**). The addition of excess TBA(OH) to CH_2Cl_2 solutions of either **2** or **2a** resulted in the quantitative formation of **3**. The EPR spectra of **2**, **2a**, and **3** all displayed a strong broad resonance at $g \sim 4$ and a weak unresolved signal at $g \sim 2$ consistent with a high-spin ($S = {}^3/_2$) assignment of the Mn^{IV} ions. The Mn^{IV}=O stretching frequency in **2** was identified at 754 cm^{-1} by FT-IR spectroscopy. In the case of **3** the Mn^{IV}=O stretching frequency was at 712 cm^{-1}. The reaction of **2a** with *cis*-β-methylstyrene under anaerobic conditions produced a mixture of *cis*- and *trans*-epoxide in a ratio of 0.17. The reaction of **2** with *cis*-β-methylstyrene under aerobic conditions produced a different *cis*-epoxide/*trans*-epoxide ratio and product distribution than those of the identical reaction run under anaerobic conditions. In the presence of $H_2{}^{18}O$, the stereoisomeric epoxides showed a significantly different ^{18}O content. Further, ^{18}O was found to reside in the oxidation products when this reaction was carried out in the presence of $^{18}O_2$. Mechanisms for the epoxidation of olefins by **2** under anaerobic and aerobic conditions are discussed, which involve atom transfer from both oxomanganese(V) and oxomanganese(IV) species.

The oxygen activation and transfer reactions of cytochrome P-450 have attracted attention for over a decade. The remarkable reactivity of P-450 is believed to derive from an oxoiron(IV) porphyrin cation-radical species, which has been suggested as the ultimate oxidant in this enzymatic system.[1] Oxidized synthetic metalloporphyrin complexes have been extensively studied as simple active site models for monooxygenases and peroxidases and have provided a means to isolate and characterize reactive intermediates implicated in these biological systems.[2] Indeed, structurally characterized oxometalloporphyrins of iron[3] and chromium[4] are known to be capable of oxidizing organic substrates. Further, dioxoruthenium(VI) and oxoruthenium(IV) porphyrin complexes have recently been identified as active species in the catalytic aerobic epoxidation of olefins.[5]

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Manganese porphyrin complexes have also received considerable scrutiny due to their unusually high reactivity toward olefin epoxidation and, particularly, the hydroxylation of unactivated C–H bonds.[6] A wide variety of catalytic systems employing manganese porphyrin complexes and oxidants such as iodosylbenzene,[7] NaOCl,[8] H_2O_2,[9] alkyl hydroperoxides,[10] ClO_4^-, and IO_4^-[11] have been developed. In addition, several aerobic processes for olefin epoxidation have been described.[12] While it has been suggested that an $Mn^V(O)$ species may be responsible for the observed reactivity in all of these systems, this complex has never been isolated or fully characterized.

A variety of other monomeric and dimeric, high-valent manganese porphyrin complexes are known. Several of these complexes are capable of oxidizing organic substrates.[13] A manganese(IV) bis(iodosylbenzene) adduct[13c] and a dimeric (μ-oxo)-manganese(IV) bis(iodosylbenzene) species[13e] have been shown to functionalize both alkenes and alkanes. Further, two Mn(IV) complexes generated by NaOCl or NaOBr oxidation have been isolated and shown to be capable of transferring an oxygen atom to styrene and triphenylphosphine.[13j,k]

The stabilities of oxometalloporphyrin complexes of Cr(IV),[4] Fe(IV),[3e-g] and Ru(IV)[5c] suggest that a similar species should be accessible in the manganese system. Preliminary characterization of an oxomanganese(IV) porphyrin complex has been described by Weiss.[14] We have recently reported that the peroxy acid or electrochemical oxidation of chloro(5,10,15,20-tetramesitylporphyrinato)manganese(III) [Mn^{III}TMP(Cl), **1**] produced stable oxomanganese(IV) porphyrin complexes.[15] The Mn^{IV}=O moiety

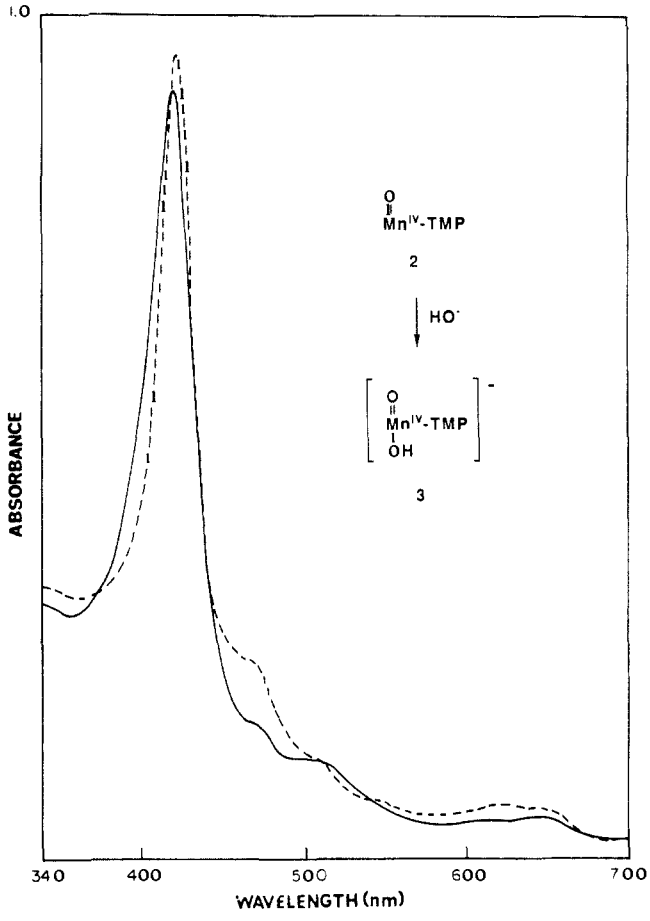

Figure 1. Electronic absorption spectra of Mn^{IV}TMP(O) complexes. Porphyrin concentration was 7.32×10^{-6} M. (A) (—) Mn^{IV}TMP(O) (**2**) generated by the reaction of **1** with 2.0 equiv of TMA(OH) and 1.2 equiv of *m*-CPBA in CH_2Cl_2 (λ_{max} = 423, 472, 520 nm). (B) (---) Mn^{IV}TMP(O)(OH) (**3**) generated by the addition of TBA(OH) to a CH_2Cl_2 solution of **2**.

was unambiguously identified by assignment of the Mn^{IV}=O stretching mode in these species by a combination of FT-IR and resonance Raman (RR) spectroscopy.[16] We report here the preparation of several oxomanganese(IV) porphyrin complexes and their characterization by UV–vis, EPR, NMR and FT-IR spectroscopies. In addition, we describe the reactivity of these species with olefins under anaerobic and aerobic conditions and show that reactivity patterns are distinctly different for oxomanganese(IV) and oxomanganese(V) complexes.

Results

Preparation and Characterization of Oxomanganese(IV) Porphyrin Complexes. The oxidation of tetramesitylmanganese(III) porphyrins with *m*-chloroperoxybenzoic acid under basic conditions has been shown to afford oxomanganese(IV) complexes. The reaction of chloro(5,10,15,20-tetramesitylporphyrinato)manganese(III) [Mn^{III}TMP(Cl), **1**] with $(CH_3)_4NOH$ and 1.2 equiv of *m*-chloroperoxybenzoic acid (*m*-CPBA) in CH_2Cl_2 at 0 °C caused the immediate formation of a red species, **2**, which was assigned the formulation Mn^{IV}TMP(O) (vide infra). It was possible to isolate **2** either by precipitation with hexane at −78 °C or by chromatography of the reaction mixture on basic alumina at −78 °C. The room-temperature bulk electrolysis of **1** with excess (n-Bu)$_4$NOH (TBA(OH)) in CH_2Cl_2 (0.1 M (n-Bu)$_4N^+ClO_4^-$) at +1.20 V resulted in the formation of a similar red species, **3**, which we formulate as [Mn^{IV}TMP(O)(OH)]$^-$. It was possible to convert **2** into **3** by the reaction of **2** with TBA(OH). Samples of **2** purified by chromatography always contained some **3**; how-

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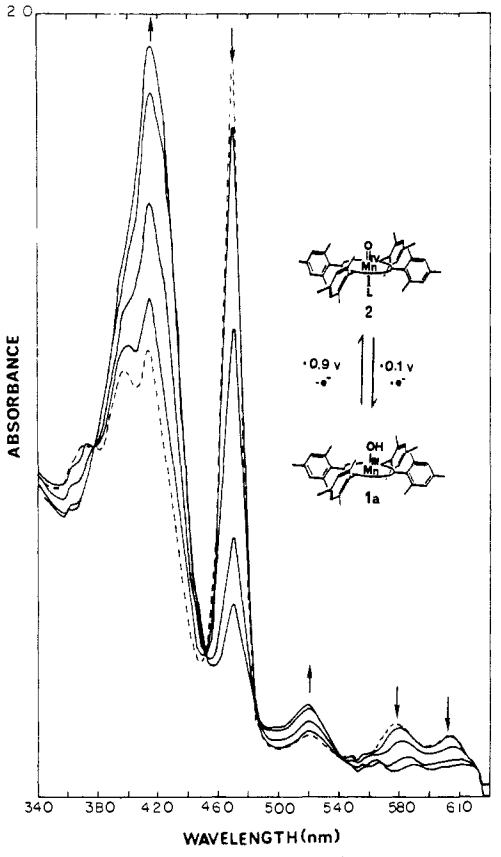

Figure 2. Key: (---) Visible spectrum of $Mn^{III}TMP(OH)$ (**1a**) resulting from the electrochemical reduction of $Mn^{IV}TMP(O)$ (**2**) at −0.1 V. (—) Visible spectrum of the reoxidation of **1a** at +0.9 V generating **2**. Porphyrin concentration was 1.6×10^{-4} M.

ever, the reactions of **2** were not dependent on the nature of the isolation procedure.

That **2** and **3** are at the oxidation state of Mn^{IV} and similar in structure was demonstrated by their visible and EPR spectra. The electronic absorption spectra of **2** and **3** (Figure 1) are characteristic of oxidized manganese porphyrin complexes. The visible spectrum of **2** had a broad Soret band at 422 nm. By contrast, the visible spectrum of **3** has a sharper red-shifted Soret at 425 nm.

Thin-layer spectroelectrochemical analysis of **2** in CH_2Cl_2/0.1 M TBAP at 0 °C revealed that **2** could be isosbestically reduced at +0.1 V generating the visible spectrum of $Mn^{III}TMP(OH)$ (**1a**). Figure 2 shows that the reoxidation of this solution at +0.9 V quantitatively produced the spectrum of **2**. This redox cycling could be repeated several times without significant porphyrin degradation. We conclude from this result that shuttling between **2** and **1a** under these conditions is a chemically reversible process.

The EPR spectra of **2** and **3** (Figure 3) have the characteristic $g \sim 4$, $g \sim 2$ signal of high-spin, d^3, monomeric Mn(IV) complexes. However, the relative intensity and position of these signals varied slightly upon going from the five-coordinate species **2** to the six-coordinate species **3**.

It was also possible to prepare the $Mn^{IV}TMP(O)$ complex by the aerobic reaction of **1** in $CHCl_3$ with TBA(OH). This reaction resulted in the disappearance of the visible absorbances due to **1** and the formation of a red species, $Mn^{IV}TMP(O)(X)$ (**2a**) with absorption bands similar to **2** and **3**. Either CH_2Cl_2 or benzene could be used as solvent in the presence of several hundred equivalents of $CHCl_3$ or $CHBr_3$. Furthermore, when TBA(OH) was replaced by triethylbenzylammonium chloride (TEBA) and 6 N NaOH, an excellent phase-transfer system for carbene formation,[17] the generation of **2a** proceeded with an approximate 5-fold increase in rate. It was possible to do preparative scale

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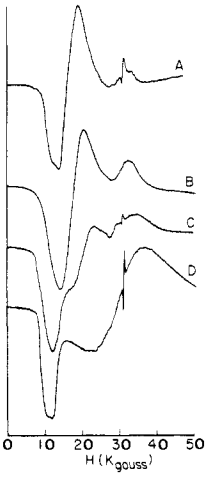


Figure 3. EPR spectra of $Mn^{IV}TMP(O)$ complexes in CH_2Cl_2 at −150 °C. Spectrometer settings: scan range 10000 G, field set 5000 G, modulation amplitude 2.0×10^1, modulation frequency 100 kHz, microwave power 10 mW, microwave frequency 9.052 GHz. (A) $Mn^{IV}TMP(O)$ (**2**). (B) $Mn^{IV}TMP(O)$ (**2**) containing some **3**. (C) $Mn^{IV}TMP(O)(X)$ (**2a**). (D) $Mn^{IV}TMP(O)(OH)$ (**3**).

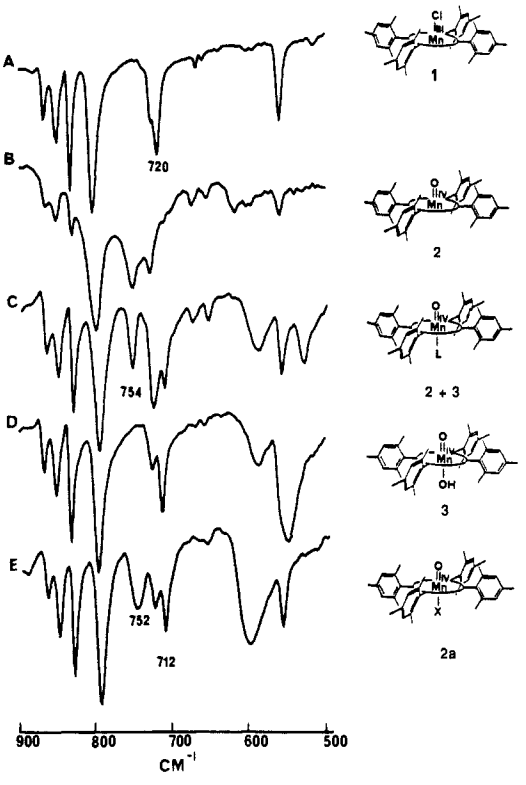


Figure 4. Infrared spectra (KBr pellet) of $Mn^{IV}TMP(O)$ complexes: (A) $Mn^{III}TMP(Cl)$ (**1**); (B) $Mn^{IV}TMP(O)$ (**2**) prepared by the reaction of **1** with 1.2 equiv of TMA(OH) and 1.2 equiv of *m*-CPBA in CH_2Cl_2 and precipitated from hexane; (C) $Mn^{IV}TMP(O)$ (**2**) generated by the reaction of **1** with 2.0 equiv of TMA(OH) and 1.2 equiv of *m*-CPBA in CH_2Cl_2 and isolated by chromatography; (D) $Mn^{IV}TMP(O)(OH)$ (**3**) prepared by electrooxidation of **1** at +1.20 V in CH_2Cl_2 containing excess TBA(OH); (E) $Mn^{IV}TMP(O)(X)$ (**2a**) prepared by the aerobic reaction of **1** in CH_2Cl_2 containing $CHCl_3$ and 6 N NaOH.

reactions under these conditions and to isolate **2a** by low-temperature alumina chromatography. If either $CHCl_3$, NaOH, or O_2 were excluded, **2a** was not formed. The EPR spectrum of **2a** was nearly identical with that of **2** isolated by chromatography (Figure 3). The conversion of **2a** to **3** could also be achieved by the addition of TBA(OH). Accordingly, we conclude that **2a** is a mixture of **2** and **3**.

IR, NMR, and Mass Spectra. The KBr pellet IR spectra of **1**, **2**, **2a**, and **3** are shown in Figure 4. On the basis of the visible

Table I. Anaerobic Reaction of Oxomanganese(IV) and Oxomanganese(V) Porphyrin Complexes with β-Methylstyrene

β-methylstyrene	oxidant (temp, °C)	yields, %		cis/trans	yield, %
cis-	**2**[b] (25)	16	28	0.57	44
cis-	**2**[a,b] (25)	8	16	0.50	24
cis-	**3**[b] (25)	4	62	0.06	66
cis-	**3**[a,b] (25)	4	70	0.05	74
cis-	**2a** (25)	4	32	0.12	36
cis-	**2a** (25)	4	30	0.13	34
trans-	**2a** (25)		34		34
cis-	**4** (−78)	46	12	3.6	58
cis-	**4**[a] (−78)	90	9	9.6	99
cis-	**2** (−78)		8		8
trans-	**4** (−78)		5		5
trans-	**4**[a] (−78)		22		22
trans-	**2** (−78)		<1		<1

[a] Reactions run in the presence of 25 equiv of pyridine. [b] Cf. ref 15. [c] Yields based on equivalents of Mn^{IV} used. Small amounts of benzaldehyde were also detected.

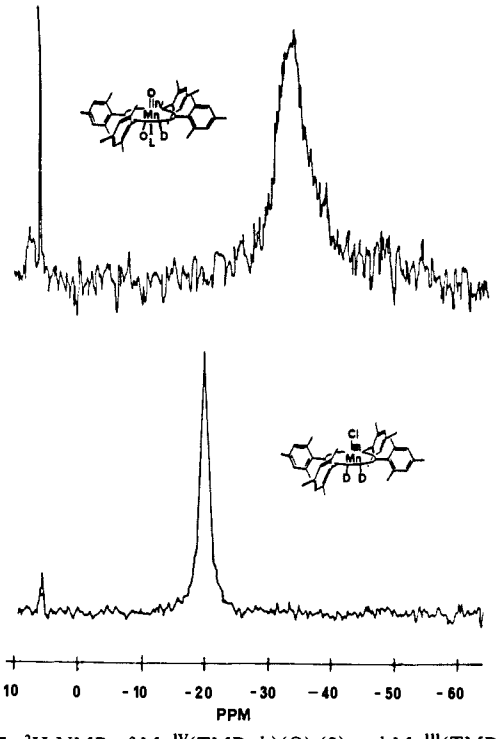


Figure 5. ^2H NMR of Mn^{IV}(TMP-d_8)(O) (**2**) and Mn^{III}(TMP-d_8)(Cl) in CH_2Cl_2 at −40 °C. The resonance at δ 5.2 is $CHDCl_2$.

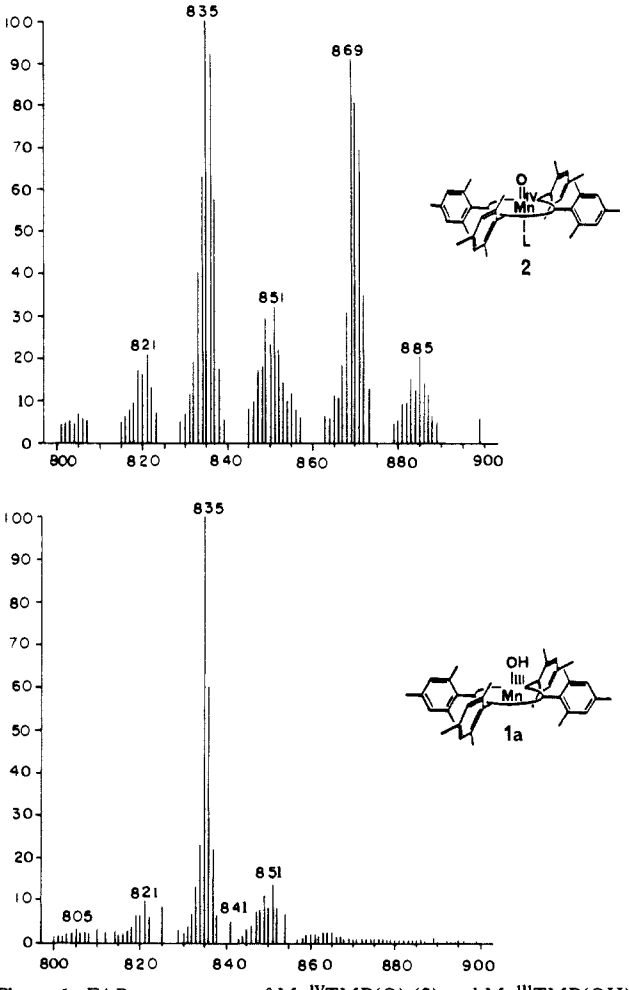


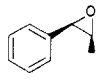
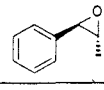
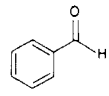
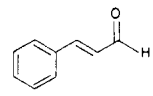
Figure 6. FAB mass spectra of Mn^{IV}TMP(O) (**2**) and Mn^{III}TMP(OH) (**1a**). The sample was prepared on a *m*-nitrobenzyl alcohol matrix.

spectra taken on the oxidized porphyrins recovered from the KBr pellets, decomposition to Mn^{III} did not occur to any appreciable extent during the preparation of the samples. In addition to the absorptions found in **1** the spectrum of **2** displayed a new band at 754 cm^{-1} and the spectrum of **3** contained a new band at 712 cm^{-1}. When samples of either **2** or **3** were reacted with cyclooctene or *cis*-β-methylstyrene, epoxide was produced, and the IR spectra of the resulting porphyrin products were devoid of absorptions at 754 and 712 cm^{-1}.

The 300-MHz ^1H NMR of **2** in benzene-d_6 displayed broad resonances at δ 9.2 and 2.5, which were absent when **2** was prepared from chloro(5,10,15,20-tetradurenylporphyrinato)manganese(III) [Mn^{III}TDP(Cl)]. Accordingly, these signals were assigned to the *m*-aryl and *p*-methyl protons, respectively. The signals expected for the *o*-methyl and the porphyrin β-pyrrole protons were not observable due to extensive line broadening resulting from their close proximity to the paramagnetic manganese ion. The ^2H NMR of **2** in CH_2Cl_2 at −40 °C prepared from Mn^{III}(TMP-d_8)(Cl) is shown in Figure 5. The spectrum of **2** revealed a single resonance at δ −32 assigned to the β-pyrrole deuterons. The spectrum of Mn^{III}(TMP-d_8)(Cl) taken under identical conditions displayed a similar, lower field resonance, at δ −21. The FAB mass spectrum of **2** shown in Figure 6 gave a strong isotopic cluster centered at m/z = 869 consistent with the molecular formula Mn^{IV}TMP(O)(OH) and two weaker clusters at m/z = 885 and 851. Samples of Mn^{III}TMP(OH) gave only a weak cluster at m/z = 851, and Mn^{III}TMP(Cl) showed no parent peak (m/z = 870).

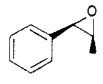
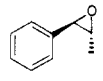
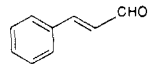
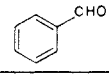
Epoxidation of Olefins by Oxomanganese(IV) Porphyrins. The reaction of **2** in CH_2Cl_2 with *cis*-β-methylstyrene under anaerobic conditions at room temperature produced *trans*-β-methylstyrene oxide as the major product in 28% yield along with *cis*-β-methylstyrene oxide (16%) and benzaldehyde (12%). The results

Table II. Oxidation of *cis*-β-Methylstyrene by **2** under a Variety of Aerobic and Anaerobic Reaction Conditions

conditions	yields, %				cis/trans	total[c] yield, %
						
air[a]	8.3	5.4	20	11	1.55	44.7
O_2[a]	4.3	2.6	9.3	5.7	1.70	21.9
CO[a]	3.7	2.8	7.7	2.3	1.30	16.5
$BrCCl_3$[b]	5.7	3.5	9.6	8.4	1.60	27.2
anaerobic	2.0	5.4	3.2	2.4	0.37	13.0

[a] Run at ambient pressure. [b] Run aerobically with 5 equiv of $BrCCl_3$. [c] Yields based on moles of porphyrin used.

Table III. Incorporation of ^{18}O into the Oxidation Products of the Aerobic Reaction of **2** with *cis*-β-Methylstyrene

	^{18}O enrichment,[a] %	^{18}O enrichment,[b] %
	46	64
	61	53
	80	73
	79	85

[a] Reaction run in the presence of $^{18}O_2$ and $H_2{}^{16}O$. [b] Reaction run in the presence of $^{18}O_2$ and $H_2{}^{18}O$.

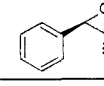
contained in Table I demonstrate that similar reactivity was observed for the reaction of either **2a** or **3** with *cis*-β-methylstyrene under identical conditions. Further, the addition of pyridine to the reaction mixture had little effect on the stereospecificity of the epoxidation. Neither *cis*-β-methylstyrene nor *cis*-β-methylstyrene oxide isomerized under the reaction conditions.

Solutions of the transiently stable Mn(V)TMP(O) (**4**)[6a,b] were prepared by the oxidation of **1** at −78 °C with *m*-CPBA and allowed to react with *cis*-β-methylstyrene. Addition of a large excess of TBA(I) to quench the reaction and analysis of the oxidation products showed a 58% yield of epoxide with a cis/trans ratio of 3.6. The addition of pyridine to the reaction mixture before *m*-CPBA oxidation increased the *cis*-epoxide/*trans*-epoxide ratio to 9.6. The results summarized in Table I indicate that **4** reacted extremely efficiently with olefins and did so with a much higher degree of stereospecificity than that observed for epoxidations mediated by **2**, **2a**, or **3**. Control experiments revealed that the reaction of *cis*-β-methylstyrene with *m*-CPBA at −78 °C for 1 h followed by quenching the reaction with TBA(I) produced no epoxide. By contrast, when **2** was reacted with *cis*-β-methylstyrene at −78 °C, the yield of epoxide was drastically reduced, and, significantly, only *trans*-β-methylstyrene oxide was formed.

Epoxidation of *cis*-β-Methylstyrene by 2 under Aerobic Conditions. The effect of O_2 on the oxidation of *cis*-β-methylstyrene by **2** was studied under a variety of conditions. The results listed in Table II indicate that the distribution and yield of the oxidation products were sensitive to the amount of O_2 present. When **2** was reacted with *cis*-β-methylstyrene under 1 atm of air, cinnamaldehyde and benzaldehyde were the major oxidation products. Further, the resulting epoxides were produced in a cis/trans ratio of 1.55. By contrast, if the identical reaction was run anaerobically, the overall yield was much lower and produced epoxide as the major product in a cis/trans ratio of 0.33.

The oxidation of *cis*-β-methylstyrene by **2** was also examined under 1 atm of O_2. These conditions generated a product distribution identical with that of the aerobic system; however, the overall yield was cut in half. The results contained in Table III show that when this reaction was run in the presence of $^{18}O_2$ (98% enriched), the amount of ^{18}O incorporated varied dramatically among the products. In addition, if this reaction was carried out under $^{18}O_2$ in CH_2Cl_2 saturated with $H_2{}^{18}O$ (98% enriched), the relative amount of ^{18}O incorporated into the *cis*- and *trans*-epoxide was significantly altered.

Table IV. Oxidation of *cis*-β-Methylstyrene by **1** with Various Oxidants

oxidant	yields,[a] %		cis/trans
			
NaOCl	11.3	1.86	6.23
NaOCl[b]	38.0	1.18	32.0
H_2O_2	0.04	trace	~6
H_2O_2[c]	3.29	0.39	9.00
cumyl hydroperoxide	0.07	0.07	1.00
cumyl hydroperoxide[c]	0.87	0.60	1.44
IO_4^-	26.0	1.30	19.7
IO_4^-[b]	6.00	0.42	14.1
iodosylbenzene	7.40	2.37	3.10
iodosylbenzene[b]	9.95	1.01	9.82
ascorbate + O_2[d]	0.05	0.11	0.45
ascorbate + O_2[b]	0.03	0.16	0.22
colloidal Pt + H_2/O_2	NR	NR	
colloidal Pt + H_2/O_2[c]	0.63	0.27	2.34
CO(1 atm) *tert*-butyl hydroperoxide			0.48
$O_2/CHCl_3/HO^-$	0.04	1.0	0.41[e]
$O_2/CHCl_3/HO^-$		1.22[f]	*e*

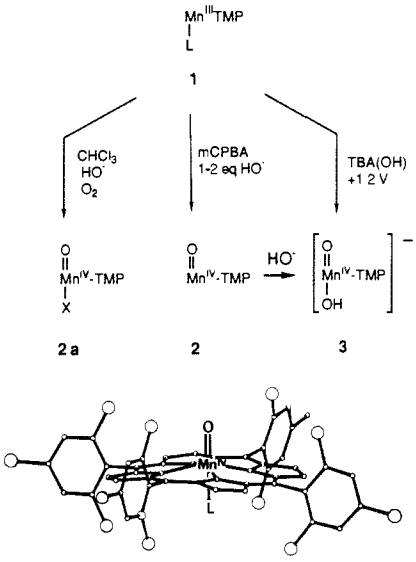
[a] Yields are reported in equivalents based on porphyrin. [b] Reactions run with 25 equiv of pyridine. [c] Reactions run with imidazole. Refer to the Experimental Section for amount. [d] The cis/trans ratio observed was between 0.45 and 0.30 for olefin concentrations between 0.09 and 3.84 M. [e] A 20–36% yield of 1-phenyl-2-methyl-3,3-dichlorocyclopropane was also formed. Pyridine suppressed the formation of cyclopropane (2%) but had little effect on the yield of epoxides. [f] *trans*-β-Methylstyrene was the substrate.

The formation of large quantities of aldehydes and the involvement of O_2 in the oxidation prompted us to investigate what effect radical scavengers would have on the reaction. Thus, *cis*-β-methylstyrene was reacted with **2** under 1 atm of CO and also under air in the presence of 5 equiv of $BrCCl_3$. In each case there was a decrease in the overall yield of oxidation products. Only small changes occurred in the distribution of products as compared to that of the aerobic reaction.

Stereochemistry of the Epoxidation of *cis*-β-Methylstyrene by 1 with Several Different Oxidants. The stereochemistry of the epoxidation of *cis*-β-methylstyrene by **1** and NaOCl, H_2O_2, cumene hydroperoxide, $NaIO_4$, iodosylbenzene, ascorbate/O_2, and colloidal Pt H_2/O_2 in the presence and absence of pyridine or imidazole was investigated. The results contained in Table IV show that the yield and cis/trans ratio of the epoxide product varied with the oxidant used and with the pyridine or imidazole content of the mixture. In the case of the ascorbate/O_2 system, the concentration of olefin in the organic phase was also varied over a range from 0.09 to 3.84 M.

It was possible to generate **2a** catalytically by the reaction of **1** in $CHCl_3$ with 6 N NaOH, TEBA, and O_2. The reaction with *cis*- and *trans*-β-methylstyrene under these conditions resulted in the data presented in Table IV. Although epoxides were formed in each case, the major product formed was 1,1-dichloro-2-phenyl-3-methylcyclopropane, which resulted from the attack of dichlorocarbene on *cis*- or *trans*-β-methylstyrene. Similarly,

Scheme I



1,1-dichlorobicyclo[6.1.0]nonane resulted from the identical reaction with cyclooctene. Epoxide formation required the presence of **1**. When the reaction was carried out with $^{18}O_2$, the resulting epoxide was shown by mass spectrometry to have 71% ^{18}O.

The epoxidation reaction of *cis*-β-methylstyrene proceeded with a low degree of stereospecificity. The addition of 25 equiv of pyridine caused a slight decrease in the cis/trans ratio of the products. Benzaldehyde and cinnamaldehyde were detected in trace amounts in the reactions with *cis*-olefin but were not present in the *trans*-olefin reaction. Control experiments established that no epoxide or aldehyde was produce in the absence of **1**.

Discussion

Several different methods have now been described to prepare oxomanganses(IV) porphyrin complexes, including peroxy acid, electrochemical, and aerobic oxidation (Scheme I). The reaction of $CHCl_3$, NaOH, and O_2 under phase-transfer conditions represents a particularly unusual route. Several lines of evidence suggest that the oxidant responsible in this case is the carbonyl oxide **5**, which is expected to result from the reaction of dichlorocarbene with O_2. The direct observation of carbonyl oxides formed by the reaction of triplet carbenes with ground-state triplet O_2 has been reported.[18] The oxene moiety in **5** is related to that of iodosylbenzene and thus should be able to oxidize manganese porphyrin complexes in a similar manner. The presence of dichlorocarbene was confirmed by the isolation of dichlorocyclopropane derivatives in both the presence and absence of the manganese porphyrin catalyst. That the exclusion of O_2 resulted in the inhibition of the formation of **2a** suggested that molecular oxygen was involved with its production. This notion was confirmed by the observation that when **2a** was generated from $^{18}O_2$ and $Na^{16}OH$ and was allowed to react with olefin, the resulting epoxide was 70% enriched in ^{18}O. Thus, we conclude that the carbonyl oxide **5** was predominantly responsible for the oxidation of **1** to **2a** under these conditions.

The observation that the new IR bands located at 754, 752, and 712 cm^{-1} in **2**, **2a**, and **3** disappeared after reaction with olefin indicates that these bands are associated with the oxidizing functionality of these complexes. We have recently reported the characterization of the Mn^{IV}=O bond in **2** and **3** by resonance Raman and FT-IR spectroscopy.[16] These studies revealed that the position of the Mn^{IV}=O stretching frequency varied with the coordination environment of the porphyrin complex. In the case of the six-coordinate complex $[Mn^{IV}TMP(O)(OH)]^-$ (**3**), the Mn^{IV}=O stretch was located at 712 cm^{-1}. This extremely low frequency was attributed to interactions between the Mn^{IV}=O group and a Mn–O–H bending mode of the *trans*-hydroxo ligand. The Mn^{IV}=O stretching frequency for the five-coordinate complex was 754 cm^{-1}.

On the basis of the results presented here, it is clear that the relative amounts of $Mn^{IV}TMP(O)$ (**2**) and $[Mn^{IV}TMP(O)(OH)]^-$ (**3**) are very sensitive to the reaction conditions and the isolation procedure. Thus, in our preliminary report,[15] the band at 712 cm^{-1} for **3** was noted and assigned to the Mn^{IV}=O stretch, but the corresponding band at 754 cm^{-1} for **2** was not discerned. Mixtures of $Mn^{IV}TMP(O)$ (**2**) and $[Mn^{IV}TMP(O)(OH)]^-$ (**3**) were further supported by the FAB mass spectra, which showed a cluster at m/z = 869 and 851 consistent with the presence and absence of a hydroxide, respectively. Replacement of the hydroxoligand in **3** by methanol or methoxide could be responsible for the small cluster at m/z = 885.

Several other lines of evidence support the conclusion that a mixture of **2** and **3** can result from the *m*-CPBA oxidation of **1**. The addition of TBA(OH) to a CH_2Cl_2 solution of **2** was shown to produce a porphyrin complex whose FT-IR spectra was identical with that of **3** in that it contained only a band at 712 cm^{-1}.[16] This conversion could also be monitored by visible spectroscopy. Thus, the ratio of $Mn^{IV}TMP(O)$ (**2**) to $[Mn^{IV}TMP(O)(OH)]^-$ (**3**) in various preparations depended on the availability of hydroxide ion. When a strict 1:1 stoichiometry of peroxy acid to base was maintained and when chromatography on basic alumina was eliminated, it was possible to generate samples of $Mn^{IV}TMP(O)$ (**2**), which displayed only the 754 cm^{-1} band in the IR spectrum.

The FT-IR spectrum of **2a** revealed bands at 752 and 712 cm^{-1}. Since 6 N NaOH was required in its preparation, the appearance of the 712 cm^{-1} band is not surprising. The 2 cm^{-1} downshift in the Mn^{IV}=O stretching frequency to 752 cm^{-1} can be attributed to the coordination of a weak donor ligand trans to the oxo moiety. Chloride and water are two possibilites since both are present in the carbene system. Resonance Raman spectroscopy has been used by Spiro et al. to investigate the effects of various trans-coordinated ligands on the position of the V^V=O stretching frequency of related porphyrin complexes.[19] It was possible to distinguish between the five-coordinate species and the six-coordinate complex containing a water molecule trans to the oxo group since the latter shifted the V^V=O stretching frequency down 8 cm^{-1}. Thus, the small downshift observed in the Mn^{IV}=O frequency in the case of **2a** would be suggestive of the oxo aquo assignment.

The EPR spectra of **2**, **2a**, and **3** all displayed broad, strong resonances in the $g \sim 4$ region and weak unresolved signals at $g \sim 2$. The simplicity of the spectra and the anisotropy in the resonances are consistent with a high-spin, d^3, assignment of the manganese ion located in an environment of lower than O_h symmetry.[20] Similar spectral properties have been reported for other manganese(IV) porphyrin complexes[13i,15] and for several hexacoordinate Cr^{III} species, which are isoelectronic with Mn^{IV}.[21] Their spectra have been interpreted to result from an axial distortion from pure octahedral symmetry. μ-Oxo dimeric Mn^{IV} porphyrins have been shown to be EPR silent due to antiferromagnetic coupling between the d^3 ions.[13e,f]

It is noteworthy, however, that the EPR spectrum reported for a proposed five-coordinate oxomanganese(IV) porphyrin complex, generated at −70 °C by the oxidation of either $Mn^{III}TPP(Cl)$,

(18) (a) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (b) Dunkin, I. R.; Bell, G. A. *Tetrahedron* **1985**, *41*, 339. (c) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842. (d) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

(19) Su, Y. O.; Czernuszewicz, R. S.; Miller, L. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4150.

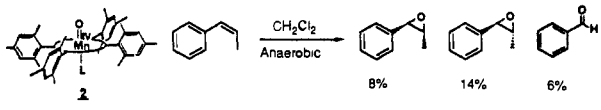
(20) (a) Pal, S.; Gosh, P.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 3704–3706. (b) Richens, D. T.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3681–3683.

(21) (a) Singer, L. S. *J. Chem. Phys.* **1955**, *23*, 379–388. (b) Ferrante, R. F.; Wolkerson, J. L.; Graham, W. R. M. Wellner, W. *J. Chem. Phys.* **1977**, *67*, 5904.

chloro[5,10,15,20-tetra(pentafluorophenyl)porphyrinato]manganese(III) [Mn^{III}TPFPP(Cl)], or chloro[5,10,15,20-tetra(pivaloylphenyl)porphyrinato]manganese(III) [$Mn^{III}T_{piv}PP(Cl)$] with peroxycarbonate, differs significantly from the EPR spectra of the complexes reported here.[14] The spectra reported for the species derived from the peroxycarbonate oxidation contain a weak signal at $g \sim 4$ and a strong resonance at $g \sim 2$. By contrast, when **2** was prepared from Mn^{III}TPP(Cl), its EPR spectrum was similar to that of the corresponding complex prepared from Mn^{III}TMP(Cl), which we have described above. This observation argues that changes in the porphyrin ligand do not have a dramatic effect on the nature of the EPR spectra. Accordingly, the differences in these manganese(IV) complexes must derive from the method of oxidation and are most probably due to differences in axial coordination.

Recently, Goff and co-workers have demonstrated the usefulness of ^2H NMR in detecting the β-pyrrole resonances of several oxidized Mn(TPP-d_8)(Cl) species.[13n] The low gyromagnetic ratio of the deuterium nucleus results in narrower line widths than those found with protons in paramagnetic molecules. The single ^2H resonance observed in **2**-*pyrrole*-d_8 (Figure 5) is supportive of an axially symmetric species and distinctly different from the multiline spectrum reported for MnTPP(Cl) oxidized by ClO_2.[13n]

Epoxidation of Olefins by Oxomanganese(IV) Porphyrins under Aerobic and Anaerobic Conditions. Our initial studies of olefin epoxidation by **2** and **3** under anaerobic conditions indicated that *cis*-β-methylstyrene was oxidized predominantly to *trans*-β-methylstyrene oxide by these complexes. Further, we also reported that the oxidation of cyclooctene by **2** in the presence of $^{18}O_2$ generated cyclooctene oxide, which was 49% enriched in ^{18}O.[15] This suggested that under aerobic conditions dioxygen was intimately involved in the oxidation of olefins promoted by **2** and **3**.

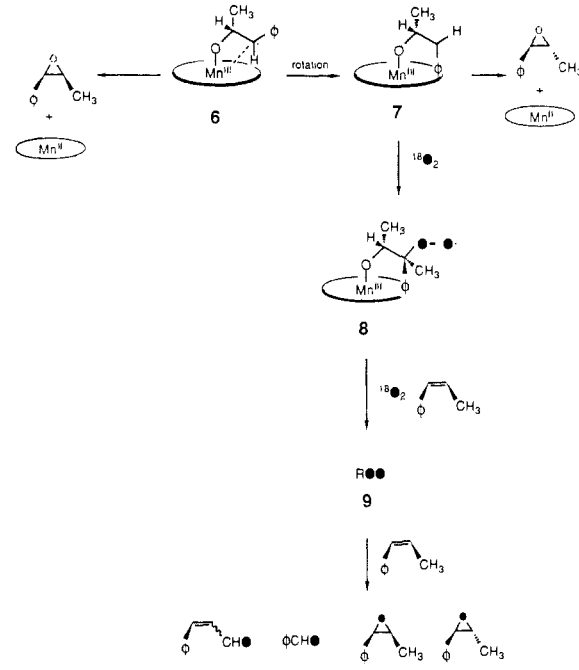


2

The difference in product distribution and yield between aerobic and anaerobic oxidations of *cis*-β-methylstyrene by $Mn^{IV}(O)$ is striking (Table II). Of particular interest is the dramatic change in the ratio of *cis*- to *trans*-epoxide, 1.55 for the aerobic reaction and 0.37 under anaerobic conditions. The inversion of the *cis*-epoxide/*trans*-epoxide ratio in the presence of air and the increased yields of benzaldehyde and cinnamaldehyde suggest that the intermediate that leads to the direct formation of *trans*-epoxide has been diverted to the production of aldehyde. That the aldehydic products are 80% enriched in ^{18}O when the reaction is carried out under $^{18}O_2$ confirms our original suggestion that dioxygen is involved in the aerobic oxidation of olefins by oxomanganese(IV) porphyrinates. Indeed, the large quantities of aldehydes produced are characteristic of an autoxidative process.

Any mechanism proposed to explain the oxidation of olefins by oxomanganese(IV) porphyrin complexes must allow an opportunity for rotation about the olefinic C–C bond prior to epoxide formation since *cis*-olefin produces mostly *trans*-epoxide. In addition, the increase in the *cis*-epoxide/*trans*-epoxide ratio and ^{18}O incorporation into the oxidation products under aerobic conditions must be accounted for. A mechanism consistent with these observations and requirements is shown in Scheme II. The generation of the benzylic radical intermediate, **6** from the one-electron oxidation of olefin by $Mn^{IV}(O)$ is the first step in this process. Under anaerobic conditions radical attack on oxygen, prior to, or after rotation about the C–C bond would produce the corresponding *cis*- or *trans*-epoxide. The formation of epoxides by the reaction of a carbon radical with an oxygen atom is not without precedent. Indeed, the autoxidation of olefins to epoxides and the metal-catalyzed epoxidation of alkenes by alkyl hydroperoxides both proceed via this mechanism.[22]

Scheme II



The increase in the yields of aldehydic products at the expense of *trans*-epoxide observed in the aerobic reaction of olefins with **2** requires that the intermediates that lead to *cis*- and *trans*-epoxide differ in their reactivities with molecular oxygen. We suggest that **6** is less susceptible toward reaction with O_2 than **7** due to an interaction between the carbon radical and either the metal center or the porphyrin macrocycle. To the extent that the stabilizing influence in **8** is a carbon–metal bond, this intermediate is related to the oxa metallacycle invoked by Collman for the manganese porphyrin catalyzed epoxidation of olefins.[8e-g] The cisoid orientation of the benzylic radical in **6** could favor such an interaction. By contrast, the transoid orientation of **7** now places the bulky phenyl group in close proximity to the porphyrin ring. This configuration would produce an unfavorable steric interaction and would cause the carbon radical to be moved farther from the metal, inhibiting any possible interaction between these groups. Thus, **7** would be more characteristic of a free radical than **6** and would be more susceptible toward reaction with O_2. Trapping of the radical in **7** by O_2 would produce the alkylperoxy radical (**8**), which is incapable of closing directly to form *trans*-β-methylstyrene oxide. Instead, **8** could act as an initiator of a radical chain autoxidation process, which would generate more alkyl peroxide radical species such as **9**.

Alkylperoxy radicals have long been known as active intermediates in the autoxidation of olefins, a process which has been extensively studied.[22] In the case of the radical chain oxidation of styrene and α-methylstyrene by molecular oxygen, benzaldehyde was the major monomeric product.[23] In addition, the yields of aldehyde and epoxide have been shown to decrease dramatically as O_2 pressure increased due to formation of polyperoxides. We have observed a similar decrease in product yields when **2** was reacted with *cis*-β-methylstyrene under 1 atm of O_2 (Table II). That the aerobic reaction of **2** with olefin in the presence of $BrCCl_3$ and CO reduced the yields of oxidation products supports this interpretation.

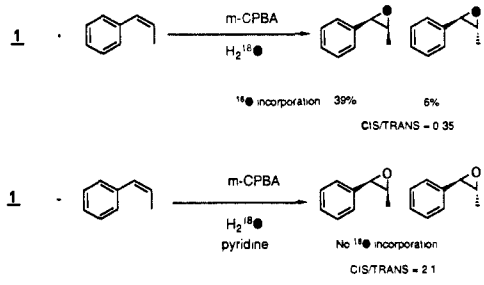
Epoxidation of Olefins by Oxomanganese(IV) Porphyrins in the Presence of $H_2{}^{18}O$ and $^{18}O_2$. The incorporation of ^{18}O from dioxygen into the epoxides indicates that they are produced partially by an autoxidative process. However, the differences in isotopic enrichment between *cis*-β-methylstyrene oxide (46%) and *trans*-β-methylstyrene oxide (61%) cannot be explained by

(22) (a) Brill, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 141. (b) Brill, W. F.; Barone, R. J. *J. Org. Chem.* **1964**, *29*, 140–143. (c) Brill, W. F.; Indictor, N. *J. Org. Chem.* **1964**, *29*, 710–713.

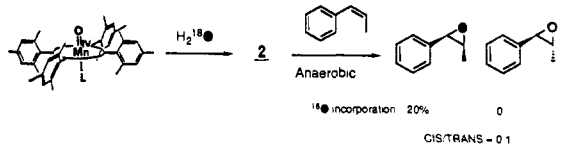
(23) (a) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2465–2480. (b) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2480–2496. (c) Lyons, J. E.; Turner, J. O. *Tetrahedron Lett.* **1972**, *29*, 2903–2906.

the direct reaction of **2** with the olefin since the amount of isotopic enrichment in each epoxide would have to be the same. Thus, an additional route must exist that can produce epoxides with differing degrees of ^{18}O enrichment. We have suggested that such differences can be accommodated if oxomanganese(IV) and oxomanganese(V) porphyrins have different stereoselectivities for olefin epoxidation *and* different exchange rates of the oxo ligand.[15]

The results obtained for the epoxidation of *cis*-β-methylstyrene catalyzed by $Mn^{III}TMP(Cl)$ (**1**) in the presence of $H_2{}^{18}O$ were most revealing in this regard. Under anaerobic conditions and at room temperature, the addition of *m*-CPBA caused an immediate color change from green to red. It is important to note that the reaction of *m*-CPBA with **1** was fast even at −78 °C, and the direct reaction between *m*-CPBA and olefin was shown to be negligible under the conditions of the ^{18}O experiments. The *cis*- and *trans*-epoxides, formed in a ratio of 0.35, were found to have 39% ^{18}O and 6% ^{18}O, respectively. When the identical reaction was carried out in the presence of pyridine, the cis isomer became the major product, and there was no isotopic enrichment in either epoxide.

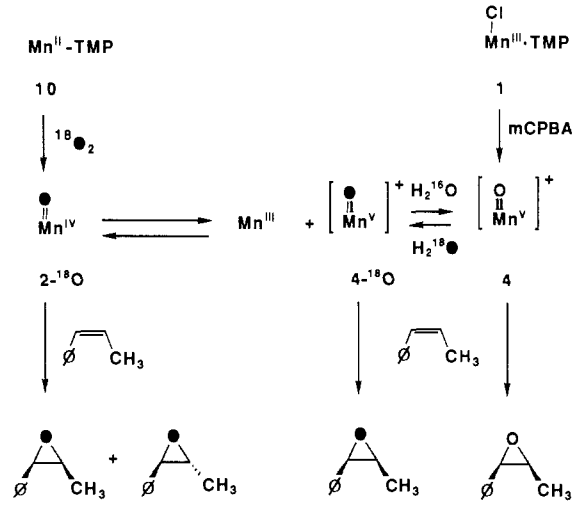


In a separate experiment, **2** was allowed to stir in CH_2Cl_2 saturated with $H_2{}^{18}O$ and reisolated by evaporation of solvent. The epoxidation of *cis*-β-methylstyrene under anaerobic conditions with this sample of **2** afforded mostly *trans*-epoxide (cis/trans = 0.1). Most significantly, however, the *cis*-epoxide was 20% enriched in ^{18}O while the *trans*-epoxide showed no isotopic incorporation. Thus, one is left to explain this most curious result; *the portion of epoxide that was formed with loss of olefin configuration did not undergo oxygen exchange with water, but the portion that was formed by the stereoretentive pathway showed significant incorporation of the label.*



We conclude from these data that two oxidants, oxomanganese(IV) and oxomanganese(V), are present in these systems and that they produce epoxide from olefins by differing mechanisms. This situation is exactly analogous to that observed for the oxidation of alcohols by chromate reagents, in which Cr(IV), Cr(V), and Cr(VI) species all play a role.[24a,b] Consistent with this analogy, we have observed large differences in the relative reactivity of norbornene and styrene with **2** (1:2) and **4** (4.5:1).[24c] The oxomanganese(IV) species (**2**) transfers oxygen to *cis*-β-methylstyrene by a nonstereoretentive pathway. By contrast, the transient and EPR silent species, **11**, which we have suggested to be an oxomanganese(V) complex,[6a,b] must undergo oxygen transfer to olefins with predominant retention of configuration. The ^{18}O results require the manganese(IV) species to exchange the oxo ligand with water slowly while the formally cationic manganese(V) complex, **11**, must readily exchange the oxo ligand with added $H_2{}^{18}O$. While the addition of pyridine to the Mn^{IV} reactions had little effect, it apparently prevented ^{18}O exchange

Scheme III



with the oxomanganese(V) complex, enhanced both the rate and the stereospecificity of oxygen transfer to olefin, and inhibited the conversion of Mn^{V} to Mn^{IV}.

A unified mechanism consistent with all of these observations is shown in Scheme III. Under aerobic conditions with $^{18}O_2$, we propose that the oxomanganese(IV) species, **2**, with its oxo ligand labeled, would be derived from the aerobic oxidation of a Mn(II) complex, **10**. Nonstereoretentive epoxidation of *cis*-β-methylstyrene by **2** would be expected for Mn^{IV}, a one-electron oxidant. That the portion of *cis*-epoxide formed with **2** had a significantly larger degree of ^{18}O incorporation from $H_2{}^{18}O$ than the trans isomer can be accommodated if there is a route to the exchange-labile Mn^{V} complex. Disproportionation of **2** would accomplish this. Thus, Mn^{V} can be accessed in a solution that originally contained only Mn^{IV}. The low-temperature oxidation of Mn^{III} indicates that a $Mn^{V}(O)$ complex is initially formed by the reaction with *m*-CPBA.[6a] Rapid reduction to **2** in the absence of pyridine would accommodate the observed loss of configuration and lack of ^{18}O exchange.

An analogous situation arises in the solution behavior of oxochromium(IV) porphyrin complexes.[4a,c,25] When $Cr^{IV}TTP(O)$ was treated with CH_2Cl_2 saturated with $H_2{}^{18}O$, no oxometal exchange could be observed in the IR spectrum of the isolated porphyrin product. It was also determined that under these conditions $Cr^{IV}TTP(O)$ was incapable of epoxidizing olefins. However, treatment of a CH_2Cl_2 solution of $Cr^{IV}TTP(O)$, $H_2{}^{18}O$, and norbornene with 1 equiv of propionic acid produced Cr^{III} and a 70% yield of norbornene oxide, which was 80% enriched in ^{18}O.

Thus, one concludes that there is an acid-catalyzed disproportionation of $Cr^{IV}TTP(O)$ to $[Cr^{V}TTP(O)]^{+}$, a species which is known to be effective at epoxidizing olefins and capable of exchanging its oxo ligand with water. The high degree of ^{18}O incorporation into the epoxide requires that the exchange phenomenon be rapid relative to oxygen atom transfer to olefin.

Oxomanganese(V) vs Oxomanganese(IV) Olefin Epoxidation with Various Manganese Porphyrin Systems. The interest in oxidations catalyzed by manganese porphyrin complexes has lead to the development of a wide variety of oxidation systems.[7-12] It has been generally assumed that $Mn^{V}(O)$ was responsible for the observed activity. Now that it is clear that both $Mn^{V}(O)$ and $Mn^{IV}(O)$ are capable of epoxidizing olefins, it is of interest to determine which complex is generated under the conditions of various catalytic oxidations. The differences in stereospecificities of the epoxidation of *cis*-β-methylstyrene by $Mn^{V}(O)$ and $Mn^{IV}(O)$, and the effect that added pyridine or imidazole has on these reactions, were used as a probe to investigate which oxidized manganese porphyrin complexes were ultimately responsible for oxygen atom transfer to the olefin.

(24) (a) Wiberg, K. B. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic: New York, 1965; Part A, p 69 ff. (b) Rocek, J.; Radkowsky, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 7123. (c) Stern, M. K. Ph.D. Thesis, Princeton University, 1988.

(25) Kruper, W. J., Jr. Ph.D. Thesis, University of Michigan, 1982.

The stereochemistry of the epoxidation of *cis*-β-methylstyrene by **1** and NaOCl, H_2O_2, cumyl hydroperoxide, $NaIO_4$, iodosylbenzene, $CHCl_3/O_2$, ascorbate/O_2, and colloidal Pt H_2/O_2 in the presence and absence of pyridine was investigated. The results contained in Table IV show that the yield and cis/trans ratio of epoxide varied with the oxidant used and on whether pyridine was present in the reaction mixture.

The reaction of NaOCl with **1** under phase-transfer conditions is an excellent system for the catalytic epoxidation of olefins.[8] The *cis*-epoxide/*trans*-epoxide ratio of 32 in the presence of pyridine suggests that $Mn^V(O)$ is the active oxidant under these conditions. However, the situation in the absence of pyridine is not as clear. While a *cis*-epoxide/*trans*-epoxide ratio of 6.23 is characteristic of $Mn^V(O)$, in our hands, this ratio changed dramatically when different batches of NaOCl were used. Similar findings have also been reported by Collman et al.[8e-g] Further, Meunier has reported a cis/trans ratio of 0.53 for the epoxidation of *cis*-stilbene in the absence of pyridine.[8a]

We interpret these results as evidence for the presence of both $Mn^V(O)$ and $Mn^{IV}(O)$ in the reaction milieu in the absence of pyridine. The amount of each oxidant in solution is apparently sensitive to the concentration of NaOCl in the aqueous phase. Thus, the addition of pyridine may enhance the rate and stereospecificity of oxygen transfer to olefin by inhibiting the conversion of $Mn^V(O)$ to $Mn^{IV}(O)$.

The oxidation of *cis*-β-methylstyrene by **1** and iodosylbenzene also showed a high *cis*-epoxide/*trans*-epoxide ratio of 3.1, which increased to 9.82 upon the addition of pyridine. Again it seems that these results suggest that a $Mn^V(O)$ species was generated first under these conditions. In the absence of pyridine, decomposition to Mn^{IV} is in competition with epoxidation by Mn^V; however, in the presence of added pyridine, this pathway was not preferred.

Recently, it has been reported that the product of the reaction of $Mn^{III}TPP(OAc)$ with IO_4^- under photochemical conditions was capable of oxidizing alkenes and alkanes.[11] Our results demonstrate that **1** and IO_4^- is an effective system for the catalytic epoxidation of olefins in the dark.[11b,26] The high ratio of *cis*- to *trans*-β-methylstyrene oxide in the presence and absence of pyridine indicates that $Mn^V(O)$ is predominantly responsible for the observed activity under these conditions.

The epoxidation of alkenes by either H_2O_2 or alkyl hydroperoxides with manganese porphyrin complexes has been demonstrated by Mansuy to be an effective catalytic system.[9,10] It was proposed that, in the absence of imidazole, manganese(III) porphyrins catalyzed the homolytic cleavage of the O–O bond, resulting in the generation of Mn^{IV} and hydroxyl radicals. When imidazole was present, heterolytic cleavage forming Mn^V and hydroxide was suggested. We have demonstrated elsewhere that acylperoxomanganese(III) porphyrins will decompose by either heterolytic or homolytic mechanisms.[6b] Both homolytic and heterolytic O–O bond cleavage has been proposed by Weiss for the oxidation of $Mn^{III}TPP(Cl)$ with peroxycarbonate.[14] Further, $Fe^{III}TMP$(peroxybenzoates) have been shown to decompose to either $Fe^{IV}TMP(O)$ π-cation radical or iron(III) porphyrin *N*-oxide by heterolytic or homolytic cleavage of the O–O bond, respectively.[27]

The epoxidation of *cis*-β-methylstyrene by H_2O_2 and **1** with or without imidazole resulted in a high *cis*-epoxide/*trans*-epoxide ratio, in both cases suggesting that heterolytic cleavage of the O–O bond predominates, generating $Mn^V(O)$. The higher yields of epoxide in the presence of imidazole indicate that ligand coordination facilitates the cleavage process. Imidazole may also serve as a general base catalyst of O–O bond heterolysis.[27,28] By contrast, the reaction of cumyl hydroperoxide with **1** and *cis*-β-methylstyrene produced low yields and a low cis/trans ratio of epoxide regardless of the presence of axial base. A reasonable explanation for this result is that cumyl hydroperoxide is sterically inhibited from coordinating to the manganese ion by the mesitylene *o*-methyl groups of the TMP ligand. The low conversion to epoxide and low cis/trans ratio may result from a different olefin oxidation process, namely the metal-catalyzed decomposition of alkyl hydroperoxide to alkylperoxy radical.[22,23,29]

Several lines of evidence support this conclusion. The reaction of cumyl hydroperoxide with unhindered $Mn^{III}TPP$ results in much higher epoxide yields and in the case of *cis*-stilbene produces epoxide in a cis/trans ratio of 9.75. Mansuy has also reported that cumyl hydroperoxide shows no selectivity in alkane hydroxylation with several different "basket handle" porphyrins regardless of the metal, but when iodosylbenzene was used as the oxidant, hydroxylation was dramatically dependent on these parameters.[10b] He was led to conclude that in the case of cumyl hydroperoxide a different active species was generated that did not include the metal center. The Co^{III}-catalyzed decomposition of *tert*-butyl hydroperoxide, a process known to produce alkyl peroxide radicals,[22] resulted in low epoxide yields and a cis/trans ratio of 0.48 in the presence of *cis*-β-methylstyrene. These observations suggest that the product distribution generated from the reaction of cumyl hydroperoxide, **1**, and olefin most likely results from a mixture of two oxidative processes: one due to an oxidized manganese porphyrin complex, presumably $Mn^V(O)$, and one resulting from alkyl peroxide radicals.

The ability of cytochrome P-450 to oxidize alkenes and alkanes with molecular oxygen in the presence of reducing equivalents has prompted investigations into mimicking this process with synthetic metalloporphyrins. Mansuy and co-workers have shown that a $Mn^{III}TPP(Cl)$, ascorbate, O_2 system is capable of epoxidizing olefins.[12e] Further, Tabushi and co-workers have demonstrated that manganese porphyrins, colloidal Pt, and an H_2/O_2 mixture is also an effective system for olefin oxidation.[12b] Both of these processes were investigated in an effort to determine whether $Mn^{IV}(O)$ or $Mn^V(O)$ were generated by the reaction of Mn^{II} with dioxygen.

The reaction of **1** with ascorbate, O_2, and *cis*-β-methylstyrene produced similar results regardless of pyridine content. In both cases the yield and *cis*-epoxide/*trans*-epoxide ratio was low. This reaction was also investigated with various concentrations of olefin ranging from 0.09 to 3.84 M. The data contained in Table IV indicate that the *cis*-epoxide/*trans*-epoxide ratio remained relatively constant regardless of olefin concentration. The Tabushi system produced dramatically different results. In the absence of pyridine there was no reaction, but with pyridine present both *cis*- and *trans*-epoxide were generated in a ratio of 2.34. These results were surprising since, a priori, one would have expected that both the Mansuy and the Tabushi system would proceed by a similar mechanism.

The yields and distribution of epoxides generated by the Tabushi system are remarkably similar to those found in the case of H_2O_2 oxidation. One possible explanation for these results is that the Tabushi system generates H_2O_2, which reacts with the manganese porphyrin complex instead of, or at least more often than, molecular oxygen. Indeed, the catalytic efficiency of this process is extremely low, generating mostly water. In addition, H_2O_2 has been detected in this system.[12c]

The Mansuy aerobic process is unique among all catalytic oxidation systems investigated in that it displayed a *cis*-epoxide/*trans*-epoxide ratio of 0.52. This was not increased by the addition of pyridine. These results argue that the active oxidant is $Mn^{IV}(O)$. It is possible that the Mansuy system actually generates $Mn^V(O)$, which is rapidly reduced to $Mn^{IV}(O)$ by the ascorbate present in the reaction. However, the invariance in the *cis*-epoxide/*trans*-epoxide ratio with increase in olefin concentration does not support this hypothesis. It would have been expected that if Mn^V was initially produced, the *cis*-epoxide/*trans*-epoxide ratio would rise with increase in the olefin concentration due to trapping of the Mn^V complex by the alkene

(26) McMurry, T. J. Ph.D. Thesis, University of Michigan, 1983.
(27) (a) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834–7836. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7836–7837.
(28) Traylor, T. G.; Lee, W. A.; Stynes, D. *J. Am. Chem. Soc.* **1984**, *106*, 755.
(29) Sheldon, R. A. *J. Chem. Soc., Chem. Commun.* **1971**, 788.

before its reduction to Mn^{IV}. Accordingly, we suggest that $Mn^{IV}(O)$ is the predominant product of the direct reaction between Mn^{II} and O_2.

The epoxidation of *cis*-β-methylstyrene catalyzed by **1** in the presence of $CHCl_3$ and O_2 also proceeded with a low degree of stereospecificity. This observation is consistent, with a $Mn^{IV}(O)$, probably **2a**, being the predominant species in solution. Furthermore, that the addition of pyridine caused only a slight change in the cis/trans ratio of the products here as well supports this conclusion.

Conclusion

The results of our investigations into oxomanganese porphyrin complexes have shown that (1) oxomanganese(IV) porphyrin complexes are stable species that can be generated by both chemical and electrochemical oxidation of manganese(III) porphyrin species, (2) these complexes are capable of transferring their oxo group to olefins to form epoxides, (3) the reactivity of $Mn^{IV}(O)$ is distinctly different from that of $Mn^{V}(O)$ in that the Mn^{IV} complexes exchange their oxo groups slowly with water and produce predominantly *trans*-epoxide from *cis*-olefin and nitrogenous ligands such as pyridine have little effect on their reactivity. By contrast, $Mn^{V}(O)$ complexes exchange the oxo oxygen atom rapidly with water, epoxidize olefins in a predominantly stereoretentive fashion, and show dramatic increases in the rate and stereospecificity of olefin epoxidation in the presence of pyridine, (4) oxomanganese(IV) porphyrin complexes may be accessed directly by the reaction of Mn^{II} with molecular oxygen. On the basis of the results presented here, both $Mn^{IV}(O)$ and $Mn^{V}(O)$ are competent oxidants of olefins and display dramatically different reactivities. Accordingly, mechanisms advanced for oxygen transfer from manganese porphyrins must take account of this dual reactivity.

Experimental Section

Capillary column gas chromatography was performed on an HP5890 instrument with flame-ionization detector. Peak areas were measured by electronic integration using an HP3392A integrator. Mass spectra were taken on an HP5970 MSD equipped with an HP5890 GC. FAB mass spectra were acquired on a Kratos MS50RFTC mass spectrometer. Visible spectra were measured on either a Cary 2390 or an IBM 9430 spectrophotometer. FT-IR and EPR spectra were obtained on a Nicolet 5DBX spectrometer and a Varian E12 spectrometer, respectively. Electrochemical experiments were performed with either a BAS 100 electrochemical analyzer or a BAS SP-2 potentiostat using a reticulated vitrious carbon working electrode, a platinum-wire auxiliary electrode, and a Hg/HgO reference electrode. The reference potential of this electrode using a 0.1 N NaOH filling solution is 0.234 V vs NHE.

Materials. 5,10,15,20-Tetramesitylporphyrin was prepared by literature methods.[13k,28] Metalation to produce Mn^{III}TMP(Cl) was achieved by the method of Kruper, which is described elsewhere.[29] 5,10,15,20-Tetramesitylporphyrin-*pyrrole*-d_8 was prepared by condensation of pyrrole-d_5 with mesitaldehyde as described above. 5,10,15,20-Tetradurenylporphyrin ($TDPH_2$) was prepared by the condensation of durenecarboxaldehyde with pyrrole according to literature methods.[30] Benzene and dichloromethane were distilled from LAH and CaH_2, respectively. Ethyl acetate, $CHBr_3$, and $CHCl_3$ were chromatographed on basic alumina prior to use. Tetrabutylammonium perchlorate was recrystallized three times from ethanol and dried in vacuo overnight. Although no sudden decomposition was observed, proper precautions were taken.

Epoxidation Reactions. General Procedures. All epoxidation reactions were performed under an N_2 or helium atmosphere with 2-adamantanone as an internal standard unless otherwise stated. The internal standard was added once the reaction was complete except where noted. Authentic samples of *cis*- and *trans*-β-methylstyrene oxide were prepared by *m*-CPBA oxidation of the corresponding olefin in CH_2Cl_2. Oxidation products were characterized by GC/MS and were compared to authentic samples. Product yields were determined in most cases by direct injection of the reaction mixtures onto either a SPB-1 or SPB-35 30 meter fused silica capillary column. Epoxidations carried out in the presence of pyridine contained 25 equiv of pyridine with respect to porphyrin and were run under identical conditions as those of the corresponding reactions in the absence of pyridine. Tricaprylylmethylammonium chloride was used as a phase-transfer agent (PTA) unless otherwise specified. Olefins were passed through a short basic alumina column prior to use to remove any traces of epoxides and other oxygenated materials.

The reactions in Table II were all carried out in 5-mL round-bottomed flasks containing **2** (4.8 mg, 5.52 μmol), *cis*-β-methylstyrene (5 μL, 38.5 μmol), and 200 μL of a stock CH_2Cl_2/2-adamantanone internal standard solution (0.03 M). The reaction vessels were sealed with rubber septa and purged with the respective gas for 10 min to establish the appropriate atmosphere. All reactions were run for 3 h. Direct reaction between **2** and adamantane produced less than a 1% yield of total oxidation products.

Preparation of Mn^{III}TMP(OH) (1a). Mn^{III}TMP(Cl) (**1**) (50 mg, 57.4 μmol) was dissolved in 40 mL of benzene to which was added 25 mL of a 20% NaOH solution. The mixture was refluxed for several hours during which time the ligand exchange was monitored by visible spectroscopy. A shift in the Soret band from 478 to 472 nm and a growth in absorbance at 420 nm indicated the reaction was complete. The reaction mixture was cooled and the organic phase was washed with five 40-mL portions of distilled water. Evaporation of the solvent, followed by drying of the resulting brown solid under vacuum, produced 42 mg of Mn^{III}TMP(OH) (86% yield).

Preparation of Mn^{IV}TMP(O) (2). a. By Precipitation. Mn^{III}TMP(Cl) (**1**) (25 mg, 28.7 μmol) was dissolved in 1 mL of CH_2Cl_2 to which 1.2 equiv of $(CH_3)_4NOH$ in 10 μL of MeOH was added. The reaction mixture was allowed to stir at room temperature for several minutes and then was cooled to 0 °C. In 100 μL of CH_2Cl_2, 1.2 equiv of *m*-CPBA (5.9 mg, 34.4 μmol) was added slowly to the porphyrin solution. An immediate color change from green to red was evident. The red solution was pipeted into 15 mL of hexane, which was maintained at −40 °C. The solution volume was reduced by half by blowing a stream of nitrogen over the reaction flask for 12 h. During this time the temperature did not rise above −25 °C. The resulting solution was placed in a refrigerator at −80 °C for 24 h. This treatment resulted in the formation of a precipitate, which was collected by vacuum filtration. A considerable amount of porphyrin, Mn^{III} and Mn^{IV}, remained in solution. The resulting purple-red powder was vacuum-dried, producing 5.2 mg of Mn^{IV}TMP(O) (**2**) (21% yield).

b. By Chromatography. Mn^{III}TMP(Cl) (**1**) (31.4 mg, 36 μmol) was dissolved in 2 mL of CH_2Cl_2 to which 2 equiv of $(CH_3)_4NOH$ in methanol was added. The reaction mixture was allowed to stir at room temperature for several minutes and then was cooled to 0 °C. In 100 μL of CH_2Cl_2, *m*-CPBA (7.4 mg, 43 μmol) was dissolved and was added slowly to the porphyrin solution. A distinct color change from green to red was evident after the complete addition of oxidant. The solution was allowed to stir at 0 °C for 1 min and then was chromatographed at −78 °C on a jacketed basic alumina (Activity IV) column. Elution with CH_2Cl_2/ethyl acetate (1:1) resolved a single red band, which was collected in a receiver flask maintained at −78 °C. A considerable amount of green, Mn^{III} porphyrin was retained at the top of the column. Evaporation of the solvent at −78 °C and drying the precipitate under vacuum at room temperature for 2 h produced **2**, a purple-red powder, in 56% isolated yield.

Preparation of 3. Mn^{III}TMP(Cl) (**1**) (35 mg, 40.1 μmol) was dissolved in 8 mL of a 0.1 M CH_2Cl_2/TBAP solution containing 100 μL of an aqueous 40% tetrabutylammonium hydroxide (TBA(OH)). Bulk electrolysis of the mixture at +1.20 V caused the formation of a stable red species. The reaction solution was pipeted into 30 μL of pentane cooled to −78 °C, which resulted in the immediate precipitation of the TBAP. The pentane solution was allowed to stand at −78 °C for 5 min after which it was filtered through a cooled fritted disk, with the filtrate being collected in a receiver flask maintained at −78 °C. The filtrate was immediately chromatographed on basic alumina (Activity IV) at −78 °C. A single red band, which traveled slower than **2**, was collected in a cooled receiver flask. Evaporation of the solvent at low temperature and vacuum drying of the resulting solid produced **3**, a purple powder, in 37% yield.

Preparation of 2a. Mn^{III}TMP(Cl) (**1**) (30 mg, 34.4 μmol), triethylbenzylammonium chloride (TEBA; 0.23 mg, 1 μmol), 200 μL of 50% NaOH colution, and 300 μL of $CHCl_3$ were mixed with 1 mL of CH_2Cl_2. The solution was stirred vigorously for 1 h during which time a color change from green to red occurred. The reaction mixture was applied directly to the top of a basic alumina column (Activity IV), which was maintained at −78 °C. Elution with 1:1 CH_2Cl_2/ethyl acetate resolved a single red band, which was isolated in a fashion identical with that of **2** and **3** affording a purple powder, **2a**, in 47% yield.

Spectroelectrochemical Reduction and Oxidation of 2. Spectroelectrochemical measurements were performed in a home made quartz cell with an optically transparent (RVC) working, Pt-wire auxiliary, and Hg/HgO reference electrode. Reduction and reoxidation of Mn^{IV}TMP(O)(L) (**2**) was performed in the following manner.

(30) Badger, G. M.; Jones, R. A.; Laslett, R. L. *Aust. J. Chem.* **1964**, *17*, 1022.

$Mn^{III}TMP(Cl)$ (**1**); 0.7 mg, 0.80 μmol) was dissolved at 0 °C in 5 mL of CH_2Cl_2/0.1 M TBAP. Addition of 2.0 equiv of $(CH_3)_4NOH$ (0.29 mg, 1.6 μmol) followed by 1.2 equiv of *m*-CPBA (0.16 mg, 0.96 μmol) resulted in the generation of **2**. The solution was transferred to the spectroelectrochemical cell. At a potential of +0.1 V **2** was cleanly reduced, generating the visible spectrum of $Mn^{III}TMP(OH)$ (**1a**). Reoxidation at +0.9 V resulted in the isosbestic generation of the visible spectrum of **2**. This reduction/oxidation process was cycled several times without any detectable porphyrin decomposition.

Anaerobic Reaction of $Mn^{III}TMP(Cl)$ (1) with *cis*-β-Methylstyrene and *m*-CPBA in the Presence of $H_2{}^{18}O$. $Mn^{III}TMP(Cl)$ (**1**; 5.2 mg, 5.97 μmol) was dissolved in 300 μL of CH_2Cl_2 containing 2.0 equiv of $(CH_3)_4NOH$ (2.1 mg, 11.9 μmol) in 10 μL of MeOH, *cis*-β-methylstyrene (5 μL, 38.6 μmol), and 20 equiv of $H_2{}^{18}O$. To this solution was slowly added 1.2 equiv of *m*-CPBA (1.2 mg, 7.1 μmol) in 50 μL of CH_2Cl_2. The reaction was stirred for 3 h after which time the oxidation products were isolated by vacuum distillation. GC/MS analysis revealed the *cis*- and *trans*-epoxides, formed in a cis/trans ratio of 0.35. The parent region of the mass spectrum showed prominant M and M − 1 peaks. Accordingly, the $^{18}O/^{16}O$ ratio could be determined simply by comparing the intensities of the M and M + 2 peaks (m/z = 134 and 136). *cis*-β-Methylstyrene oxide was found to be 39% enriched in ^{18}O, and *trans*-β-methylstyrene oxide contained 6% ^{18}O.

Anaerobic Reaction of $Mn^{III}TMP(Cl)$ (1) with *cis*-β-Methylstyrene and *m*-CPBA in the Presence of Pyridine and $H_2{}^{18}O$. $Mn^{III}TMP(Cl)$ (**1**; 5.4 mg, 6.19 μmol) was dissolved in 300 μL of CH_2Cl_2, which contained 2.0 equiv of $(CH_3)_4NOH$ (2.2 mg, 12.3 μmol) in 10 μL of MeOH, 25 equiv of pyridine, and 20 equiv of $H_2{}^{18}O$. A solution of 1.2 equiv of *m*-CPBA (1.2 mg, 7.4 μmol) in 50 μL of CH_2Cl_2 was added dropwise. The reaction was allowed to stir for 3 h under a helium atmosphere after which time the oxidation products were isolated by vacuum distillation. GC/MS analysis revealed that *cis*- and *trans*-epoxides were produced in a cis/trans ratio of 0.35 and there was no ^{18}O incorporation in either epoxide.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$ and NaOCl with and without Pyridine. $Mn^{III}TMP(Cl)$ (**1**; 2.1 mg, 2.4 μmol), *cis*-β-methylstyrene (15 μL, 115 μmol), and PTA (4.7 mg, 10 μmol) were dissolved in 1 mL of CH_2Cl_2. The reaction mixture was covered with a rubber septum and was purged with N_2. Injected into the reaction vessel via syringe was 2 mL of a 0.16 M (determined by iodometric titration) NaOCl solution. The reaction was stirred for 1.5 h. Both the yield and cis/trans ratio of the oxidation products were found to vary with different NaOCl solutions.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$ and H_2O_2 with and without Imidazole. $Mn^{III}TMP(Cl)$ (**1**; 2.1 mg, 2.4 μmol) and *cis*-β-methylstyrene (10 μL, 77 μmol) were dissolved in 1 mL of a 2:1 CH_3CN/CH_2Cl_2 solution. In the case of epoxidation with imidazole, 1.65 mg (24 μmol) of the base was added. The reaction vessel was sealed with a septum and purged with N_2. A 2-μL aliquot of 30% H_2O_2 (24 equiv) was diluted with 200 μL of CH_3CN. This solution was added to the reaction mixture via syringe in 50-μL aliquots over a period of 30 min. The reaction was allowed to proceed for 1.5 h.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$ and Cumene Hydroperoxide with and without Pyridine. $Mn^{III}TMP(Cl)$ (**1**; 2.1 mg, 2.4 μmol) and *cis*-β-methylstyrene (10 μL, 77 μmol) were dissolved in 1 mL of CH_2Cl_2. In the case of epoxidation with imidazole, 1.65 mg (24 μmol) of the amine was added. The reaction vessel was sealed with a rubber septum and was purged with N_2. Cumene hydroperoxide (80%, 3 μL, 15 μmol) was added via syringe. The mixture was allowed to react for 1.5 h.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$ and $NaIO_4$. $Mn^{III}TMP(Cl)$ (**1**; 5.2 mg, 6 μmol), *cis*-β-methylstyrene (20 μL, 154 μmol), and tetrabutylammonium chloride (1 mg, 3.6 μmol) were dissolved in 2 mL of CH_2Cl_2. The reaction vessel was sealed with a rubber septum and was purged with N_2. To this mixture was added by syringe 3 mL of a 0.4 M $NaIO_4$ solution, which had been degassed through three freeze–pump–thaw cycles. The reaction was stirred for 1.5 h.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$ and Iodosylbenzene. $Mn^{III}TMP(Cl)$ (**1**; 2.1 mg, 2.4 μmol) and *cis*-β-methylstyrene (10 μL, 77 μmol) were dissolved in 1 mL of CH_2Cl_2. While the solution was purged with a steady stream of N_2, iodosylbenzene (6 mg, 27 μmol) was added as a solid in one portion. The mixture was allowed to react for 1.5 h.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$, Ascorbate, and O_2. $Mn^{III}TMP(Cl)$ (**1**; 7.1 mg, 8.15 μmol), *cis*-β-methylstyrene (50 μL, 385 μmol), PTA (16 mg, 40 μmol), and ascorbic acid (88 mg, 0.5 mmol) were dissolved in 2 mL of benzene and 15 mL of Tris buffer (pH = 8.5) in a 25-mL round-bottomed flask. The system was purged with O_2 for 15 min and then was stirred vigorously for 4 h. The two phases were allowed to separate, and the organic layer was analyzed by GC.

Epoxidation of *cis*-β-Methylstyrene by 1, Ascorbate, and O_2 with Varying Olefin Concentration. In each reaction 2.4 mg (2.7 μmol) of **1** was used. In a 5-mL round-bottomed flask was placed porphyrin, PTA (5.2 μmol) in 100 mL of benzene, and various amounts of olefin: 25, 50, 100, and 200 μL. Each reaction was diluted with benzene to a total volume of 400 μL. To each reaction was added 500 μL of a 1.0 M Tris buffer solution (pH 8.5) that was 0.4 M in ascorbate. The reaction vessels were sealed with rubber septa and were purged with O_2 for 15 min. The reactions were stirred for 4 h.

Epoxidation of *cis*-β-Methylstyrene by $Mn^{III}TMP(Cl)$, Colloidal Pt, and H_2/O_2. Colloidal platinum was prepared by dissolving K_2PtCl_4 (3.6 mg, 8.6 μmol) in 2 mL of distilled water. The solution was diluted with 1 mL of ethanol. Hydrogen gas was bubbled through the system for 15 min while the vessel was being sonicated in an ultrasonic bath. $Mn^{III}TMP(Cl)$ (**1**; 3.3 mg, 3.7 μmol), imidazole (7.0 mg, 0.10 mmol), *cis*-β-methylstyrene (20 μL, 154 μmol), and 1 mL of the colloidal platinum solution were mixed with 1 mL of benzene in a 10-mL round-bottomed flask. The vessel was sealed with a rubber septum and a 50:50 mixture of H_2/O_2 was bubbled through the system for 10 min. The reaction was stirred for 2 h.

Anaerobic Reaction of 2a with Olefins. The reactions in Table III were run under a helium atmosphere in 5-mL round-bottomed flasks containing **2a** (5.0 mg, 5.75 μmol), olefin (5 μL, 38.5 μmol), and 200 μL of CH_2Cl_2 and 1-bromonaphthalene (5.7 μmol) as an internal standard. After 3 h the reactions were diluted with 2 mL of 1:1 ether/pentane and chromatographed on a short basic alumina column to isolate the oxidation products.

Reaction of 2a with Olefins under Catalytic Conditions. $Mn^{III}TMP(Cl)$ (**1**; 5.5 mg, 6.3 μmol), TEBA (0.5 mg, 2.2 μmol), olefin (20 μL), and 300 μL of 6 N NaOH were mixed with 500 μL of $CHCl_3$. The flask was sealed with a rubber septum, and the system was purged with O_2 for 10 min. The reaction was stopped after 12 h of vigorous stirring. In all cases polymeric material was present in the bottom of the flask. The reaction mixture was diluted with 500 μL of CH_2Cl_2 prior to GC analysis.

Oxidation of *cis*-β-Methylstyrene by 2 in the Presence of $^{18}O_2$. Into a 50-mL Schlenk flask **2** (13 mg, 14.9 μmol) was placed. The vessel was evacuated, and $^{18}O_2$ (98%, Cambridge Isotopes) was introduced. Through a septa-covered injection port, 200 μL of CH_2Cl_2 containing *cis*-β-methylstyrene (10 μL, 77 μmol) was added. The reaction was stirred for 1.5 h during which time a color change from red to green occurred. The oxidation products were isolated by distillation and analyzed by GC/MS.

Epoxidation of *cis*-β-Methylstyrene by 2 in the Presence of $^{18}O_2$ and $H_2{}^{18}O$. Into a 50-mL Schlenk flask **2** (5.0 mg, 5.75 μmol) was placed. The vessel was evacuated, and $^{18}O_2$ was introduced. Via syringe, 250 μL of CH_2Cl_2 containing 10 μL of $H_2{}^{18}O$ and 10 μL of *cis*-β-methylstyrene was injected. The reaction was allowed to stir for 1.5 h. The oxidation products were isolated by distillation and analyzed by GC/MS.

Catalytic Oxidation of Cyclooctene by 2a in the Presence of $^{18}O_2$ and $Na^{16}OH/H_2{}^{16}O$. $Mn^{III}TMP(Cl)$ (**1**; 5.3 mg, 6.0 μmol), cyclooctene (50 μL, 0.38 mmol), 100 μL of 6 N NaOH/H_2O, TEBA (0.15 mg, 0.70 μmol), and 500 μL of $CHCl_3$ were placed in a 10-mL Schlenk tube equipped with a magnetic stir bar. The solution was degassed by three freeze–pump–thaw cycles after which $^{18}O_2$ was introduced into the reaction vessel. The mixture was stirred vigorously overnight. The oxidation products were isolated by distillation and analyzed by GC/MS.

Epoxidation of *cis*-β-Methylstyrene by *tert*-Butyl Hydroperoxide. To a solution of 50 μL of *cis*-β-methylstyrene and 10 mL of benzene was added 300 μL of 70% *tert*-butyl hydroperoxide. The reaction mixture was stirred for 8 h, while being heated to 45 °C in an oil bath.

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Registry No. **1**, 85939-49-7; **1a**, 105694-20-0; **2**, 115775-87-6; **3**, 108535-08-6; **4**, 117308-16-4; *cis*-2-methyl-3-phenyloxirane, 4541-87-1; *trans*-2-methyl-3-phenyloxirane, 23355-97-7; 1-phenyl-2-methyl-3,3-dichlorocyclopropane, 56895-69-3; *cis*-β-methylstyrene, 766-90-5; *trans*-β-methylstyrene, 873-66-5.