The dimers were isolated by crystallization from pentane (affording a dimer with mp 104–106 °C) and by chromatography on SiO_2 (oily second dimer). Their structures were established by NMR (δ_{CDCl_3} 3.56 and 3.71, OMe s) and appropriate C,H or exact mass analysis. Orthoformate 3 is most likely formed by phenolic capture of MeOCOPh, with the phenol produced by reaction of MeOCOPh with adventitious water.[10] The oily orthoformate was isolated by HPLC and characterized by NMR (δ_{CDCl_3} 3.57, OMe; 6.20, CH) and by GC/MS exact masses for its $(PhO)CH^+$ (10%) and $PhOCH^+OMe$ (100%) fragment ions.

Thermal decompositions (15 h, 25 °C) of diazirine 1 in acrylonitrile, methyl acrylate, α-chloroacrylonitrile, and tetramethylethylene led to products 4–7. In the latter case, olefin 7[11]



4, X = CN
5, X = COOMe

6

7
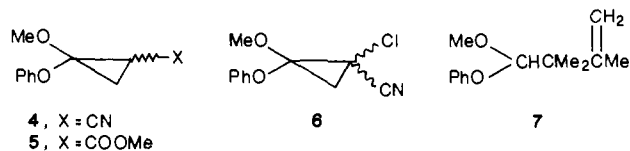
could result either from rearrangement of the anticipated cyclopropane or from an "ene" reaction between MeOCOPh and $Me_2C=CMe_2$. A similar product is formed in the analogous reaction of MeOCPh.[12]

Adducts 4–6 were formed in >90% yield (GC), purified by Kugelrohr distillation or chromatography (5), and characterized by appropriate NMR and exact mass spectra.[13] Isomer ratios were ca. 1.3:1 (4), 4:1 (5), and 2:1 (6), but syn/anti assignments have not been made.

The calculated[2] "carbene selectivity index" (m_{CXY}) of MeOCOPh is 2.11, only slightly lower than that calculated for $(MeO)_2C$ (2.22) and clearly in the region of the selectivity spectrum associated with nucleophilic carbenes.[2,14] Initial competition experiments for additions of thermally generated (25 °C) MeOCOPh to equimolar binary mixtures of $Me_2C=CMe_2$, $CH_2=CHCN$, or $CH_2=CClCN$ give a substrate reactivity order of 1:28:870, respectively, in accord with nucleophilic selectivity by MeOCOPh.

Ab initio restricted Hartree–Fock calculations were carried out on MeOCOPh by using standard basis sets and methods available in the GAUSSIAN 82 series of programs.[15,16] The carbene's geometry, including all C–O bond lengths and angles,[17] was optimized with the minimal STO-3G basis set; energies were subsequently obtained from 4-31G calculations at the optimized geometries.[16,17] "Low-energy" conformers 8a–c were revealed by the calculations; a fourth conformer, where the CH_3 group of 8c adopts the position it holds in 8a, lies >16 kcal/mol above 8a.

With oxacarbenes, strong interaction between oxygen lone pair electrons and the (singlet) carbene vacant 2p orbital generates

	8a	8b	8c
ϵ_{LU}, eV	+3.35	+3.33	+4.29
ϵ_{HO}, eV	–10.49	–10.78	–10.64
E_{rel}, kcal/mol	0.00	+1.27	+2.18
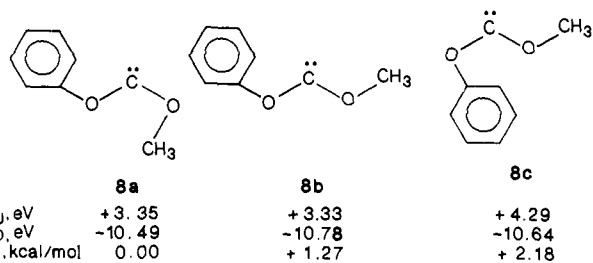
significant $-^-C=O^+-$ double-bond character in the carbenic C–O bonds, with consequent restricted rotation and the existence of "isomeric" carbenes at low temperatures; this holds true for MeOCOPh too.[18,19]

We also obtain the orbital energies associated with the filled carbenic σ orbitals (HOMO) and vacant p orbitals (LUMO) of 8a–c (see above). These are quite similar to the calculated orbital energies of $(MeO)_2C$ (analogue of 8b), ϵ_{LU} = +4.09, ϵ_{HO} = –10.81 eV,[20] so that the nucleophilicity of MeOCOPh is again understandable. More specifically, we estimated the differential orbital energies ($\epsilon_{CXY}^{LU} - \epsilon_{alkene}^{HO} = \Delta\epsilon_E$) and ($e_{alkene}^{LU} - \epsilon_{CXY}^{HO} = \Delta\epsilon_N$) associated with the electrophilic or nucleophilic modes of addition[2] of 8a–c to tetramethylethylene and acrylonitrile. With MeOCOPh, nucleophilic addition to acrylonitrile is favored for conformers 8a–c ($\Delta\epsilon_N$ < 11 eV, $\Delta\epsilon_E$ > 14 eV), and electrophilic addition of 8a and 8b to tetramethylethylene is not precluded ($\Delta\epsilon_E$ < 11.6 eV, $\Delta\epsilon_N$ > 12.7 eV), although steric hindrance to addition and the possibility of an ene reaction might account for the actual product, 7.

The ease and simplicity of generation of MeOCOPh invite its further study as a representative nucleophilic carbene in reactions with a variety of sensitive substrates under extremely mild conditions. This work is in progress.

(10) The yield of 3 increased with added water to the ultimate exclusion of 2: MeOCOPh + H_2O → [MeOCH(OPh)OH] → PhOH + MeOOCH (not isolated). Decomposition of 1 in PhOH/MeCN gave mainly 3.

(11) Kugelrohr distillation gave a 4.6:1:3.8 mixture of 2, 3, and 7; $\delta_{CDCl_3}^7$ 1.40 (s, 6 H, 2Me), 1.83 (s, 3 H, allylic Me), 3.53 (s, 3 H, OMe), 4.97 (d, J ~ 4 Hz, 2 H, =CH_2), 5.93 (s, 1 H, CH), 7.2 (m, aryl, with contributions from 2 and 3). Purification of 7 is difficult, and we still regard the assignment of this structure as tentative. The mass spectrum even under chemical ionization, failed to show a molecular ion; m/e 177 was observed and attributed to the fragment ion $MeO(PhO)C=CMeC^+H_2$.

(12) Włostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. J. Chem. Soc., Chem. Commun. 1982, 432.

(13) For example: $\delta_{CDCl_3}^4$ 1.50–2.23 (m, 3 H, cyclopropyl CH), 3.50 (s, ratio 1:1.5, total 3 H, OMe of each isomer), 7.27 (m, 5 H, aryl). The isomers could be separated by HPLC or chromatography; definitive spectra were obtained on separated isomers at 400 MHz. MS, m/e calcd for $C_{11}H_{12}NO_2$ (M + 1, 100%) 190.0868; found 190.0879.

(14) (a) For example, the calculated m_{CXY} values associated with experimentally ambiphilic carbenes are considerably lower, including 1.74 (PhOCF), 1.59 (MeOCCl), and 1.49 (PhOCCl). (b) Cf.: Moss, R. A.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. J. Org. Chem. 1986, 51, 2168 and references therein.

(15) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release H, Carnegie-Mellon University, Pittsburgh, PA, 1984.

(16) The procedures were strictly analogous to those employed in ref 14b.

(17) Complete numerical results will appear in our full paper.

(18) We calculated "transition-state" carbenes[17] for the conversions 8a ⇌ 8b and 8b ⇌ 8c at E_{rel} = 18.6 and 15.0 kcal/mol, respectively, above 8a.

(19) For experimental examples, see: Kesselmayer, M. A.; Sheridan, R. S. J. Am. Chem. Soc. 1986, 108, 99. Kesselmayer, M. A.; Sheridan, R. S. Ibid. 1986, 108, 844.

(20) Rondan, N. G.; Houk, K. N.; Moss, R. A. J. Am. Chem. Soc. 1980, 102, 1770.

Olefin Epoxidation by Manganese(IV) Porphyrins: Evidence for Two Reaction Pathways

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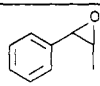
Synthetic metalloporphyrin complexes of iron,[1] manganese,[2] chromium,[3] and ruthenium[4] have been the focus of intense studies as models for the monooxygenase enzyme cytochrome P-450.

(1) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. J. Am. Chem. Soc. 1979, 101, 1032–1033. (b) Groves, J. T.; Haushaulter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. J. Am. Chem. Soc. 1981, 103, 2884–2886. (c) Groves, J. T.; Nemo, T. E. J. Am. Chem. Soc. 1983, 105, 5786. (d) Nee, M. W.; Bruice, T. C. J. Am. Chem. Soc. 1982, 104, 6123. (e) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. J. Am. Chem. Soc. 1985, 107, 4343–4345. (f) Groves, J. T.; Watanabe, Y. J. Am. Chem. Soc. 1986, 108, 507–508.

Manganese porphyrin complexes have received much of this attention due to their high catalytic activity toward hydroxylation of unactivated C–H bonds.[2a,5] An oxoMn(V) complex [2b] has been suggested as the oxidant in this system, however, no such species has been definitively characterized. Several manganese(IV) porphyrin complexes have been reported.[6] Two of these compounds, a monomeric manganese(IV) bis(iodosylbenzene) adduct[6b] and a (μ-oxo)manganese(IV) bis(iodosylbenzene) species,[5b] are capable of oxidizing alkenes and alkanes. Recently a high-valent manganese porphyrin species generated by hypochlorite oxidation has been isolated and shown to be capable of transfering an oxygen atom to styrene and triphenylphosphine.[6c,d] Further, aerobic manganese porphyrin systems have been described by Tabushi[2d] and by Mansuy.[2l] We report here the isolation, characterization, and reactivity of a monomeric manganese(IV) porphyrin complex capable of epoxiding olefins in the absence of an auxillary oxidant.

The reaction of chloro(5,10,15,20-tetramesitylporphinato)-manganese(III) [Mn^{III}(TMP)Cl, (1)] in CH$_2$Cl$_2$ containing 2.0 equiv of methanolic (CH$_3$)$_4$NOH with 1.2 equiv of *m*-chloroperoxybenzoic acid (*m*-CPBA) at 0 °C caused the immediate formation of a red species 2. Chromatography of the reaction mixture on basic alumina (activity IV) at −78 °C afforded a purple-red powder in 56% yield upon evaporation which was stable at room temperature for hours and for days at −30 °C (423, 472, 520 nm in benzene). That 2 had the formal oxidation state of Mn(IV) was confirmed by an anisotropic EPR spectrum with a strong broad resonance at g 4.5 and a weak unresolved signal at g 2.3 similar to other monomeric, $s = {}^3/_2$ Mn(IV) complexes.[5c,6d,7] This assignment for 2 was further supported by the magnetic susceptibility determined in solution (Evan's method) which gave μ_{eff} = 3.74 μ_B. Thin-layer spectroelectrochemical analysis of 2 in CH$_2$Cl$_2$/0.1 M tetrabutylammonium perchlorate (TBAP) at −30 °C revealed that 2 could be isosbestically reduced at +0.1 V generating the visible spectrum of a Mn(III) porphyrin complex.[8] Reoxidation of this solution at +0.9 V cleanly produced 2 with no evidence of porphyrin decomposition. The 300-MHz ^{1}H 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 Mn^{III}(TDP)Cl (TDP = 5,10,15,20-tetradurenylporphyrin). Accord-

Table I. Epoxidation of *cis*- and *trans*-β-Methylstyrene by Mn(IV) and Mn(V) Porphyrin Complexes

		epoxide (cis)	epoxide (trans)	cis/trans	yield, %
styrene	+ 2[a]	8	14	0.57	44
	+ 2[b]	5	21	0.23	52
	+ 2[c]		8		16
	+ 2[a,d]	4	8	0.50	24
	+ 2[b,d]	4	2	2	12
	+ 3[a]	2	31	0.06	66
	+ 3[d]	2	35	0.05	74
	+ 4[c]	46	12	3.6	58
	+ 4[c,d]	90	9	9.6	99
trans-β-methylstyrene	+ 2[a]		8		16
	+ 2[a,b]		30		60
	+ 2[c,d]		<1		<1
	+ 3[a]		5		10
	+ 4[c]		5		5
	+ 4[c,d]		22		22

[a] Reactions run at room temperature for 3 h. [b] Aerobic reactions; yields and ratios varied with O$_2$ concentration. [c] Reactions run at −78 °C for 1 h. [d] Reactions run in the presence of pyridine. Neither olefin nor epoxide isomerized under the reaction conditions. Small amounts of benzaldehyde were detected among the products.

ingly, these signals were assigned to the meta aryl and para methyl protons, respectively. The ^{2}H NMR of 2 (−40°) prepared from Mn(TMP)(pyrrole-d_8)Cl revealed a single resonance at δ −32 supportive of an axially symmetric species.[9] The FAB mass spectrum of 2 gave an isotopic cluster centered at m/z 869 consistant with the molecular formula of Mn(TMP)(O)(H$_2$O), whereas Mn^{III}(TMP)(OH) gave no peaks in this region.

The major product formed from the reaction of 2 with *cis*-β-methylstyrene was *trans*-β-methylstyrene oxide. Identical reactions run in the air gave slightly higher yields of epoxide. Furthermore, if cyclooctene was reacted with 2 in the presence of ^{18}O$_2$, the resulting epoxide was formed in 40% yield and had 49% ^{18}O incorporation.[10]

Bulk electrolysis of 1 in CH$_2$Cl$_2$/0.1 M (TBAP) cooled to −20 °C at +1.2 V produced the corresponding π-cation radical[6d,11] 3a, which upon addition of TBA(OH) −20 °C caused an immediate formation of 3, a stable manganese(IV) complex with visible and EPR spectra and reactivity similar to those of 2 (Table I). Strong π-donor ligands have been shown to shift the site of oxidation from porphyrin to metal in other metalloporphyrin π-cation radical systems.[11a,12] The addition of TBA(OH) to a CH$_2$Cl$_2$ solution of 2 generated visible and EPR spectra similar to those of 3, suggesting that 2 and 3 differ only in the nature of an axial ligand, aquo and hydroxo, respectively.[13]

Oxidation of Mn^{III}(TMP)Cl (1) in CH$_2$Cl$_2$ containing 2.0 equiv of methanolic (CH$_3$)$_4$NOH with 1.2 equiv of *m*-CPBA *at −78 °C* formed a red EPR-silent species, 4.[14] The results summarized in Table I indicate that 4 was extremely efficient at epoxidizing

(2) (a) Groves, J. T.; Kruper, W. J., Jr.; Haushaulter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375–6377. (b) Groves, J. T.; Watanabe, Y.; McMurry, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4489–4490. (c) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456–6458. (d) Tabushi, I.; Kodera, M. *J. Am. Chem. Soc.* **1986**, *108*, 1101 and references therein. (e) Collman, J. P.; Brauman, J. T.; Meuneir, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005. (f) Collman, J. P.; Kodadek, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2588–2594. (g) Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 6871–6873. (h) Meunier, B.; Guilmet, E.; De-Carvalho, M. E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668–6676. (i) Meunier, B.; De Poorter, B. *J. Chem. Soc., Perkin Trans-2* **1985**, 1735–1740. (j) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515. (k) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *J. Chem. Soc., Chem. Commun.* **1986**, *4*, 277–279. (l) Mansuy, D.; Fontecave, M.; Bartoli, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, *6*, 253–254.

(3) (a) Groves, J. T.; Haushaulter, R. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1163–1166. (b) Groves, J. T.; Kruper, W. J., Jr.; Haushaulter, R. C.; Butler, W. *Inorg. Chem.* **1982**, *21*, 1363–1368.

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(5) (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374–6375. (b) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515. (c) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515–3521. (d) Hill, C. L.; Smegal, J. A.: Henly, T. J. *J. Org. Chem.* **1983**, *18*, 3277–3281. (e) Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781–2784. (f) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1986**, 341–343.

(6) (a) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301–4308. (b) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 2920–2922. (c) Bortolini, O.; Meunier, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1364. (d) Bortolni, O.; Ricci, M.; Meunier, B.; Friant, P.; Ascone, I.; Goulon, J. *Nouv. J. Chim.* **1986**, *10*, 39–49.

(7) Richens, D. T.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3681–3683.

(8) Thin-layer spectroelectrochemistry was performed in a homemade quartz cell using an optically transparent riticulated vitrious carbon working electrode and a platinum wire auxillary electrode. All potentials were measured vs. a Hg/HgO reference electrode using a 0.1 M NaOH filling solution. The reference potential of this electrode is 0.234 V vs. NHE.

(9) Rodgers, K. R.; Goff, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 611–612.

(10) The conversion of 2 to 1 under anaerobic conditions was first order in [2] and [cyclooctene] for at least two half-lives.

(11) (a) Speer, L. O.; Maliyackel, A. C.; Holbrook, S.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1986**, *108*, 1949–1953. (b) Carnieri, N.; Harriman, A.; Portor, G.; Kalyanasundaram, K. *J. Chem. Soc., Dalton Trans.* **1982**, 1231. (c) Phillippi, M. A.; Shinomura, E. T.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1322.

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(13) We suggest [Mn^{IV}(TMP)(O)(OH)] as the formulation of 3. Preliminary X-ray absorption spectroscopy data obtained on solid 2 and 3 in collaboration with Prof. James Penner-Hahn shows very similar absorbance edges for these compounds. Furthermore, edge data collected on Mn^{IV}(TPP)(OCH$_3$)$_2$ is distinctly different than on 2 and 3 suggesting a less symmetrical structure for the Mn(IV) species discussed here. Samples of 2 were observed to have an IR band at 712 cm^{-1} which we tentatively assign to the Mn=O stretch. A description of the resonance Raman spectra of oxomanganese(IV) complexes obtained in collaboration with Prof. T. G. Spiro are to be described elsewhere.

Scheme I

olefins and did so with a much higher degree of stereospecificity than that observed for epoxidations mediated by **2** or **3**. A 300-μL solution of **4** formed by the reaction of $Mn^{III}(TMP)Cl$ (1.92 $\times$ 10^{-2} M) with 1.2 equiv of *m*-CPBA in CH_2Cl_2 was allowed to react with 10 μL of *cis*-β-methylstyrene for 1 h at -78 °C. 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 significantly increased the stereospecificity of the epoxidation as well as the rate.[2h] When **2** was subjected to identical reaction conditions, the yield of epoxide was drastically reduced and, significantly, only *trans*-epoxide resulted from cis olefin. Accordingly, two different oxidizing species, **2** and **4**, with different EPR spectra and different stereospecificities can be produced by the *m*-CPBA oxidation of **1**.

That two distinct oxidants were produced by the *m*-CPBA oxidation of **1** was confirmed by a series of $H_2{}^{18}O$ exchange experiments. $Mn^{III}(TMP)Cl$ (**1**) was dissolved in 300 μL of CH_2Cl_2 containing 2 equiv of $(CH_3)_4NOH$, 20 equiv of $H_2{}^{18}O$, and 5 μL of *cis*-β-methylstyrene. Under anaerobic conditions, the addition of 1.2 equiv of *m*-CPBA caused an immediate color change from green to red.[15] After 3 h the oxidation products were isolated and analyzed by GC/MS. *The resulting epoxides, formed in a cis/trans ratio of 0.35, were found to have greatly differing degrees of ^{18}O enrichment, 39% for the cis epoxide and*

6% *for the trans epoxides.* When the identical reaction was carried out in the presence of 25 equiv of pyridine the cis/trans ratio increased to 2.1 and there was *no isotopic enrichment in either epoxide.* By contrast, when **2** was allowed to stir in CH_2Cl_2 saturated in $H_2{}^{18}O$, reisolated by evaporation of solvent, and reacted with *cis*-β-methylstyrene under anaerobic conditions, the resulting epoxides were generated in a cis/trans ratio of 0.1. Most significantly, however, the *cis*-epoxide was 20% enriched in ^{18}O while the *trans*-epoxide showed no isotopic incorporation.

We conclude from this data that the oxomanganese(IV) species (**2** and **3**) transfer oxygen to *cis*-β-methylstyrene by a nonstereoretentive pathway. By contrast the unstable and EPR-silent species, **4**, which we suggest to be an oxomanganese(V) complex, undergoes 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 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 prevented ^{18}O-exchange with the oxomanganese(V) complex, inhanced the rate and the stereospecificity of oxygen transfer to olefin, and inhibited the conversion of Mn(V) to Mn(IV).

A unified mechanism consistant with these observations is shown in Scheme I. Non-stereoretentive epoxidation of *cis*-β-methylstyrene by **2** and **3** 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 than the trans isomer requires a route to the exchange-labile Mn(V) complex. Disproportionation of **2** would accomplish this.[16] The low-temperature oxidation of Mn(III) indicates that the oxomanganese(V) complex is initially formed. Rapid reduction to manganese(IV) in the absence of pyridine would accommodate the observed loss of configuration and lack of ^{18}O exchange.

Recently there has been much attention in the literature given to the mechanism of oxygen transfer from high-valent manganese porphyrins to olefins under catalytic conditions. Although a high degree of stereospecificity has been observed in these systems, the reaction of a cis olefin always produced some *trans*-epoxide. On the basis of the results presented here, two different oxidants, oxomanganese(V) and oxomanganese(IV), are produced in these catalytic systems and it is the Mn(IV) complex that is responsible for the nonstereoretentive portion of the epoxidation reaction. The incorporation of ^{18}O from dioxygen indicates that similar manganese(IV) species are accessible under aerobic conditions.

(14) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785–786.
(15) The reaction of *m*-CPBA with **1** is fast even at -78 °C, and, therefore, direct reaction between peracid and olefin is negligable.

(16) When **2** is allowed to react with NH_4OH, a nitridomanganese(V) porphyrin complex can be isolated in small amounts. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074. Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc* **1982**, *104*, 7318–7319.