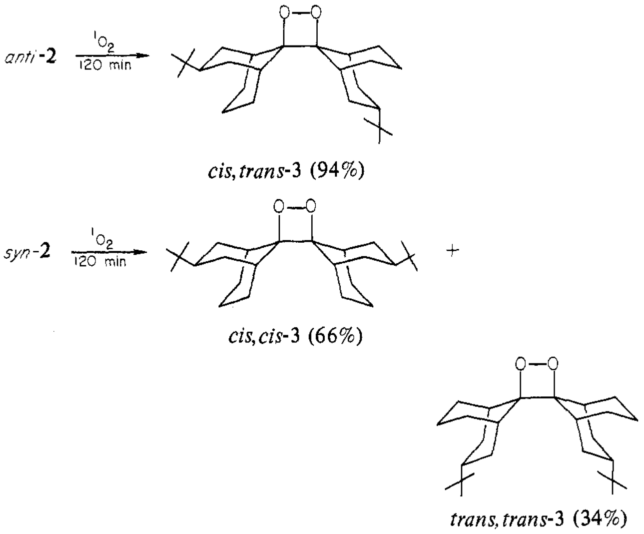
Scheme I



$$anti\text{-}\mathbf{2} \xrightarrow[420\ \text{min}]{\text{DCA},\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (49\%) + \text{recovered } \mathbf{2}\ (25\%)$$

$$syn\text{-}\mathbf{2} \xrightarrow[300\ \text{min}]{\text{DCA},\ ^3O_2} cis,cis\text{-}\mathbf{3}\ (27\%) + trans,trans\text{-}\mathbf{3}\ (22\%) + \text{recovered } \mathbf{2}\ (15\%)$$

$$anti\text{-}\mathbf{2} \xrightarrow[300\ \text{min}]{-e^-,\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (34\%) + cis,cis\text{-}\mathbf{3}\ (24\%) + trans,trans\text{-}\mathbf{3}\ (21\%) + \text{recovered } \mathbf{2}\ (11\%)$$

$$syn\text{-}\mathbf{2} \xrightarrow[80\ \text{min}]{-e^-,\ ^3O_2} cis,trans\text{-}\mathbf{3}\ (23\%) + cis,cis\text{-}\mathbf{3}\ (51\%) + trans,trans\text{-}\mathbf{3}\ (11\%) + \text{recovered } \mathbf{2}\ (9\%)$$

Clearly, the dye-sensitized photooxygenations of *anti*- and *syn*-**2** are stereospecific in the fashion anticipated for the concerted cycloaddition of singlet oxygen. In contrast, the electrode-catalyzed oxygenation is not stereospecific, and this behavior is consistent with the Barton-type mechanism[17] involving the reaction of cation radical and $^3O_2$, already suggested by Nelsen[8] and Clennan.[9] Furthermore, in this case ^{13}C NMR spectra of recovered olefin demonstrated that extensive isomerization occurred under the same conditions. The same isomerization of the olefins was observed in the exhaustive electrolysis of *anti*- and *syn*-**2** under an argon atmosphere. So, as anticipated isomerization takes place in the cation-radical species. To our surprise, the DCA-sensitized photooxygenation, proceeding presumably by way of cation radical–$O_2^{-}\cdot$ reaction (Foote mechanism), occurred stereospecifically. In this case recovered olefin retained its configuration. In contrast to this result, Foote has reported that isomerization of starting olefin occurs in the DCA-sensitized photooxygenation of stilbene.[6c] Therefore, our results seem to indicate a borderline behavior; i.e., singlet oxygen and electron transfer oxygenations are competitive, as suggested very recently by Foote.[18] To elucidate further the similarities and differences among the three mechanism (singlet oxygen and Foote- and Barton-type), we have examined the oxygenations of several other olefins (Table I). Olefins **4**–**6**[19] have fairly low oxidation potentials and showed similar reactivity except for **6**, which was inert to both DCA-sensitized and electrode-catalyzed oxygenations. Work is in progress to define further the characteristics of the electron-transfer oxygenations.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 57030049).

Registry No. 1, 30541-56-1; *anti*-**2**, 83665-47-8; *syn*-**2**, 83709-00-6; *cis,cis*-**3**, 83665-48-9; *cis,trans*-**3**, 83709-01-7; *trans,trans*-**3**, 83709-02-3; **4**, 83665-49-0; **5**, 55993-21-0; **6**, 51689-29-3.

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[17] (a) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magunas, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055. (b) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248. (c) Landis, M. E.; Madoux, D. C. *Ibid.* **1979**, *101*, 5106.

[18] On this point, Foote indicated that singlet oxygen can be produced from DCA in the interaction with olefins on the basis of the product distribution and the solvent isotope effects, identical with those from rose bengal sensitized reactions; see ref 6c. Abstracts of 15th Symposium of Oxidation Reactions, Nagoya, Japan, 1981, p 101, and private communication with C. S. Foote.

[19] Olefins **4**–**6** were prepared from the pyrolyses of corresponding thiadiazolines at 150 °C in n-Bu_3P[20] and purified by preparative GLC.

[20] (a) Schaap, A. P.; Faler, G. R. *J. Org. Chem.* **1973**, *38*, 3061. (b) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079.

[21] Physical data of **1** and **6** are consistent with the literature.[5c,10a,10b] **4**: mp 132–135 °C; ^1H NMR ($CDCl_3$) δ 2.10 (m, 24 H), 2.60 (brs, 4 H); ^{13}C NMR ($CDCl_3$) δ 96.0 (s), 95.1 (s). **5**: mp 130–132 °C; ^1H NMR ($CDCl_3$) δ 1.90 (m, 24 H), 2.60 (brs, 4 H); ^{13}C NMR ($CDCl_3$) δ 95.4 (s).

On the Mechanism of Oxidation of Hydroxycyclohexadienyl Radicals with Molecular Oxygen

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It is well recognized that molecular oxygen efficiently oxidizes cyclohexadienyl radicals to arenes.[1] On the basis of the kinetic evidence, Dorfman et al.[2] proposed a mechanism for the oxidation of hydroxycyclohexadienyl radical (**1**), formed by the reaction of hydroxyl radical with benzene, with molecular oxygen. In this mechanism a peroxy radical (**2**) formed by the addition of oxygen with **1** plays a role in giving rise to phenol with the liberation of hydroperoxy radical as shown in Scheme I.

In the course of our studies on the free radical aromatic hydroxylation with hydroxyl radical generated from α-azohydroperoxide (**3**)[3-5] in anhydrous organic media (Scheme II), we have found that the isomer distribution ratio of phenols formed by this reaction varies with the concentration of oxygen introduced. Such phenomena of the variation of the isomer ratio under oxygen have also been reported in the aromatic hydroxylation with Fenton's reagent[6] and by radiolysis of water.[7-9] In order to explain the variation of the isomer ratio of phenols, we have proposed a mechanism involving peroxy radicals **5** and **6** and dihydrodiols **7** and **8** (see Scheme III). In the hope of elucidating the mechanism, we have undertaken in the present study the aromatic hydroxylation with **3** (see Scheme II) under $^{18}O_2$. This report describes our observations on the ^{18}O incorporation into aromatics and offers a mechanistic interpretation for this reaction.

To a toluene solution (4 mL) of α-azohydroperoxide (**3**; 0.04 mmol) in a Pyrex tube (10 × 100 mm) was introduced $^{18}O_2$ (99% contents; 10.9 mg) through a vacuum line, and then the tube was sealed. The mixture was irradiated with a high-pressure mercury

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[2] Dorfman, L. M.; Taub, I. A.; Bühler, R. E. *J. Chem. Phys.* **1962**, *36*, 3051–3061.

[3] Tezuka, T.; Narita, N. *J. Am. Chem. Soc.* **1979**, *101*, 7413–7415.

[4] Tezuka, T.; Narita, N.; Ando, W.; Oae, S. *J. Am. Chem. Soc.* **1981**, *103*, 3045–3049.

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[6] Walling, C.; Johnson, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 363–367.

[7] Fendler, J. H.; Gasowski, G. L. *J. Org. Chem.* **1968**, *33*, 2755–2757.

[8] Eberhardt, M. K.; Yoshida, M. *J. Phys. Chem.* **1973**, *77*, 589–597.

[9] Bhatia, K. *J. Phys. Chem.* **1975**, *79*, 1032–1038.

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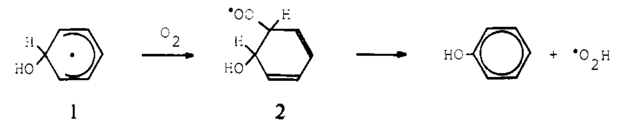
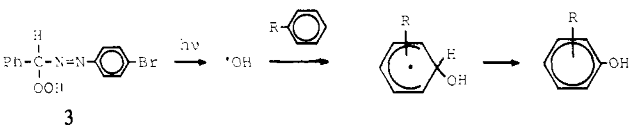
Scheme I



Scheme II



Scheme III

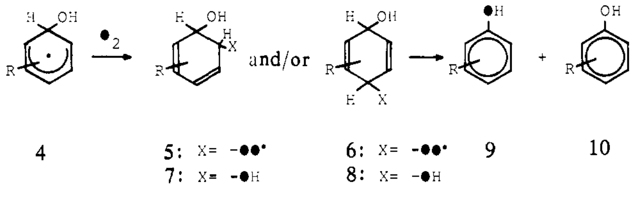


Table I. ^{18}O Contents[a] in Cresol and Phenol (Percent)

cresol				phenol	
m/e	ortho	meta	para	*m/e*	rel int
M$^+$(180)[b]	100.0	100.0	100.0	M$^+$(166)[b]	100.0
M + 1	15.4	15.8	16.3	M + 1	17.0
M + 2	26.6	33.1	34.2	M + 2	76.7
^{18}O net contents	14	19	19	^{18}O net contents	40

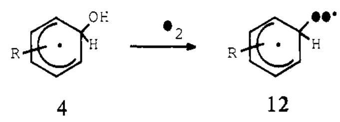
[a] The reaction was carried out twice, and the ^{18}O contents were analyzed by GC/mass spectra after silyation. [b] *m/e* for trimethylsilyl ether.

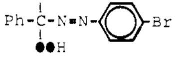
lamp through a Pyrex filter for 3 h at 20 °C. The ^{18}O contents in *o*-, *m*-, and *p*-cresols formed by this reaction were measured by means of the GC/mass spectrum, revealing that an appreciable amount of ^{18}O was incorporated into toluene (Table I). The control in which a toluene solution of a mixture of *o*-, *m*-, and *p*-cresols (10^{-2} M) was photolyzed under $^{18}O_2$ indicated that more than 90% of the oxygen of cresol was not affected by $^{18}O_2$. The correction by subtracting the control values and natural abundance gave the net contents of ^{18}O in *o*-, *m*-, and *p*-cresols as 14%, 19%, and 19%, respecitvely (Table I). The ortho:meta:para isomer ratio of cresol in this reaction was found to be 51:25:24, differing from the ratio observed under bubbling through oxygen (44:40:16) or under argon (71:9:20) in the reaction with **3**.[10] It is evident, therefore, that the incorporation of ^{18}O in toluene accompanies the variation of the isomer ratio of cresol.

A considerable amount of ^{18}O was also incorporated in benzene to give [^{18}O]phenol, when **3** was decomposed photochemically in benzene under $^{18}O_2$ (Table I). The yields of phenols, except for cresol (7–10%), more than doubled under oxygen compared with that under argon (from ca. 20% to 50% for phenol) in the reaction with **3**.[4]

Several mechanistic implications arise from these observations. The incorporation of the ^{18}O into aromatics indicates that a reaction path(s) other than that proposed by Dorfman et al.[2] is involved in the oxidation of hydroxycyclohexadienyl radical (**4**) with molecular oxygen. We consider that the formation of [^{18}O]phenol (**9a**) can be accounted for by the dihydrodiol mechanism (Scheme III), in which **4a** formed from benzene and hydroxyl radical reacts with $^{18}O_2$ to give the peroxy radical **5a** and/or **6a** that collapses to the dihydrodiol **7a** and/or **8a** by the disproportionation.[11-13] The dehydration of **7a** and/or **8a**[14,15] in two different ways gives phenol incorporated with and without ^{18}O (**9a** and **10a**). However, the relatively low ^{18}O contents and the nearly equal distribution of ^{18}O at the ortho, meta, and para positions of cresol[16] indicate that in addition to the dihydrodiol mechanism Dorfman's mechanism is also involved in the reaction; hence the dihydrodiol (Scheme III) together with Dorfman's mechanism (Scheme I) accounts for all our present observations.

Scheme IV





11

As for the mechanism of the ^{18}O incorporation, the following alternatives are to be added. If the oxygen of **3** is replaced by $^{18}O_2$ by the radical-chain reaction[17] in the dark or during photolysis prior to the reaction by which **11** is formed, the ^{18}O incorporation is explicable. However, this possibility is ruled out by the following experiment. To a benzene solution of **3** in a Pyrex tube was introduced $^{18}O_2$, and the mixture was allowed to stand in the dark at 10 °C for 4 h or photolyzed at 20 °C for 3 h. The GC/mass spectroscopic analysis indicated that ^{18}O was not found in α-azohydroperoxide recovered.[18] Meanwhile, it is considered that the ^{18}O incorporation is explainable by the mechanism shown in Scheme IV, in which the hydroxy group of **4** is replaced by $^{18}O_2$ to give **12**, from which [^{18}O]phenols are derived. However, this possibility is probably eliminated, though not strictly, since this mechanism is not consistent with the fact that the isomer ratio of phenols varies under oxygen.[4,10,16]

The mechanism in which molecular oxygen abstracts a methylene hydrogen of cyclohexadienyl radical as suggested by Hendry and Schuetzle[19] does not explain the ^{18}O incorporation. Howard and Ingold have suggested that cyclohexadienyl peroxy radicals decay unimolecularly or bimolecularly, depending on the radical concentration.[20] Our present observations demonstrate the existance of the second reaction path such as shown by Scheme III in the oxidation of hydroxycyclohexadienyl radicals with molecular oxygen.

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(10) The isomer ratio of cresol varied with the oxygen concentration, reaching the ratio ortho:meta:para = 44:40:16 when a sufficient amount of oxygen was supplied.

(11) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871–3877.

(12) Hiatt, R. "Organic Peroxide"; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. II, Chapter 1.

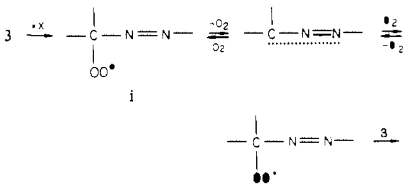
(13) One of the byproducts of this reaction may be catechol, though we have not identified it in the reaction mixture (see the Russell mechanism[11]). However, as to the other possible byproducts, see: Balkrishan, N. J. I.; Reddy, M. P. *J. Phys. Chem.* **1977**, *81*, 17–22. Hoshino, M.; Akimoto, H.; Okuda, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 718–724.

(14) Nakajima, M.; Tomida, I.; Takei, S. *Chem. Ber.* **1959**, *92*, 163–172. Gibson, D. T.; Koch, J. R.; Schuld, C. L.; Kallio, R. E. *Biochemistry* **1968**, *7*, 3795–3802.

(15) We thank Professor Norio Kurihara for his helpful suggestion.

(16) Several discussions can be made on the ^{18}O contents, isomer ratios, and mechanisms depending on the initial isomer ratio of **4b**. All these details will be reported in our full paper.

(17)



(18) A small amount (<16%) of ^{18}O was found in the ion peak *m/e* 105, which arises from both benzaldehyde and benzoic acid, a secondary product, in the reaction mixture obtained after the complete photodecomposition of **3**. This value, however, does not correspond directly to the amount (%) of **11**.

(19) Hendry, D. G.; Schuetzle, D. *J. Am. Chem. Soc.* **1975**, *97*, 7123–7127.

(20) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 785–792.

Acknowledgment. We thank Dr. Sueo Nishi for his advice on the GC/mass spectra, Professor Shigeru Oae for his encouragement, and Professor Manfred K. Eberhardt for his helpful suggestions concerning our manuscript.

Registry No. 1, 11084-15-4; **3**, 72437-42-4; benzene, 71-43-2; toluene, 108-88-3.

Structural Characterization of a Complex of Manganese(V): Nitrido[tetrakis(*p*-methoxyphenyl)porphinato]manganese(V)

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Received August 30, 1982

The current intense interest in high-valent manganese porphyrins derives from the ability of these complexes to oxidize water both thermally[1] and photochemically[2] and to oxidize hydrocarbons under very mild conditions.[3,4] Although two Mn(IV) porphyrin complexes, the dimeric complex $[N_3Mn^{IV}TPP]_2O$[5,6] and the monomeric complex $(CH_3O)_2Mn^{IV}TPP$,[7] were recently structurally characterized by X-ray crystallography, no Mn(V) porphyrin complexes have been structurally characterized.[8] Indeed the only complexes with Mn in the 5+ oxidation state for which there exists compelling evidence are those with oxide and halide ligands.[9,10] We report here the principal structural properties of the complex nitrido[tetrakis(*p*-methoxyphenyl)porphinato]manganese(V) (NMn^VTpMPP,[5] **1**) and selected physical and chemical properties of **1** and the analogous TPP and T*p*TP complexes.[5]

In the course of our research on catalytic hydrocarbon functionalization by Mn porphyrin complexes,[3,4a,6] we examined the effect of introducing ammonia to the $XMn^{III}TPP$–iodosylbenzene system in order in assess the possibility of activating both ammonia and hydrocarbon to form carbon–nitrogen bonds. When $XMn^{III}TPP$, X = Cl, Br, and OAc, and iodosylbenzene react with a large excess of ammonia in dichloromethane solution, the crude nitride complex NMn^VTPP precipitates from solution in yields as high as 96% based on $XMn^{III}TPP$. In a typical preparation 0.25 g (3.4×10^{-4} mol) of $AcOMn^{III}TPP$ is added to 25 mL of degassed CH_2Cl_2 containing 2 mL of NH_3 in a Schlenk flask under a stream of argon. To this green solution are added 1.0 g (4.5×10^{-3} mol) of iodosylbenzene in 0.05-g portions and 3 mL of NH_3 dropwise over a period of 15 min. After an additional 30 min of stirring, the minimally soluble crude NMn^VTPP is collected and recrystallized from toluene–hexane.[11] The reaction of ammonia with the isolated high-valent MnTPP–iodosylbenzene complexes[4] also produces the nitride complex in ca. 70% yield, but the reactions of ammonia with the other high-valent Mn porphyrins, $[YMn^{IV}TPP]_2O$ (Y = N_3 or OCN, or $(CH_3O)_2Mn^{IV}TPP$), lead only to the usual thermally stable $[Mn^{III}TPP]^+$ decomposition products. Recently Buchler and co-workers prepared nitrido manganese(V) porphyrin complexes by another synthetic method.[10]

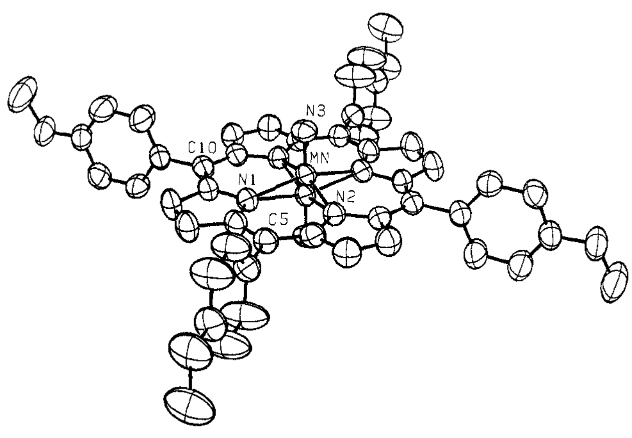

Figure 1. ORTEP diagram of **1** displaying 50% probability ellipsoids. The Mn≡N moiety is disordered 50–50 above and below the N_4 plane.

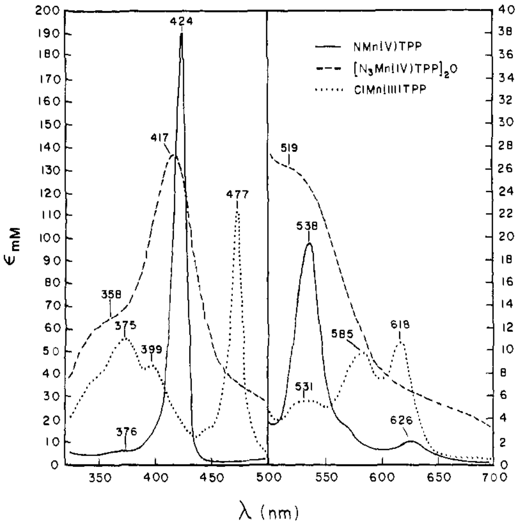

Figure 2. Electronic spectra of NMn^VTPP, $[N_3Mn^{IV}TPP]_2O$, and $ClMn^{III}TPP$. The spectrum of NMn^VTPP from λ 320–500 nm is half scale. All spectra are recorded as ca. 1 mM solutions in chlorobenzene at 25 °C.

The tetrakis(*p*-methoxyphenyl)porphyrin ligand, T*p*MPP, unlike the TPP, T*m*TP, and T*p*TP[5] ligands, facilitated the growth of diffraction-quality single crystals of the manganese(V) porphyrin nitride complex. The lustrous red prisms of a chlorobenzene solvate of **1** submitted to structural analysis by X-ray crystallography were grown by allowing hexane to diffuse into a chlorobenzene solution of **1** at 25 °C over a period of 3 days. The unit cell and refinement results are as follows: $NMn^V(TpMPP)\cdot nC_6H_5Cl$, $n \leq 1$, monoclinic with space group $C2/c$, $Z = 4$, $a = 30.5128$ (22) Å, $b = 9.5508$ (10) Å, $c = 15.2593$ (14) Å, $V = 4442.1$ (12) Å^3, M_r for $n = 1$ is 914.35 amu, unique reflections used in least squares = 2117 with $F_0^2 > 3\sigma(F_0^2)$, $R = 4.19\%$.[12] Disordered chlorobenzene molecules occupy holes

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(1) (a) Porter, G. *Proc. R. Soc. London, Ser. A* **1978**, *362*, 281–303. (b) Tabushi, I.; Kojo, S. *Tetrahedron Lett.* **1975**, 305–308.

(2) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans 2* **1979**, *75*, 1543–1552.

(3) Hill, C. L.; Smegal, J. A. *Nouv. J. Chim.* **1982**, *6*, 287–289.

(4) (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374–6375. (b) Groves, J. T.; Kruper W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375–6377.

(5) Abbreviations: TPP, T*m*TP, T*p*TP, T*p*MPP designate the tetraphenyl, tetra-*m*-tolyl, tetra-*p*-tolyl, and the tetrakis(*p*-methoxyphenyl) porphyrin dianion ligands, respectively.

(6) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964–3972.

(7) The complex $(CH_3O)_2Mn^{IV}TPP$ has been prepared by three synthetic methods and characterized by X-ray crystallography and other physical methods. Cf.: Camenzind, M. J.; Hollander, F. J.; Hill C. L. *Inorg. Chem.*, in press.

(8) Buchler, Scheidt, and their co-workers recently completed the X-ray structure of a porphodimethenenitridomanganese(V) complex: Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.*, in press.

(9) Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1972**, *7*, 353–384.

(10) Buchler and co-workers recently prepared nitrido manganese(V) porphyrin complexes by oxidizing Mn(III) porphyrin complexes with hypochlorite in the presence of ammonia: Buchler, J. W.; et al. *Z. Naturforsch.*, *B*, in press. Their nitrido complexes have properties similar to the properties of ours.

(11) The complexes NMn^VTPP and NMn^VTpTP crystallize from toluene–hexane or benzene–hexane as solvate-free crystals, and **1** crystallizes from *N*-methylpyrrolidinone (NMP)–water or chlorobenzene–hexane as NMP or chlorobenzene solvates, respectively.

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