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Atom transfer reactions of high-valent chromium and manganese porphyrins

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Iowa State University, 1991

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Atom transfer reactions of high-valent chromium and manganese porphyrins

by

James G. Goll

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1991

Dedication

To my father

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LIST OF ABBREVIATIONS

acac	acetylacetonate
anal.	analyzed
calcd.	calculated
Cl_8TPP	dianion of tetra(2,6-dichloro)phenyl porphyrin
Cp	cyclopentadienide
DMF	N,N-dimethylformamide
e	solvent dielectric constant
$E_{½}$	half-wave potential
en	ethylenediamine
ENDOR	electron-nuclear double resonance
EPR	electron paramagnetic resonance
Et	ethyl
EXAFS	extended X-ray absorption of fine structure
exp.	experimentally
INDO	intermediate neglect of differential overlap
IR	infra-red
m-CPBA	*meta*-chloroperoxybenzoic acid
MFA	N-methylformamide
Me-Im	methylimidazole
MS	mass spectrum
nm	nanometers
NMNO	N-methylmorpholine-N-oxide
NMR	nuclear magnetic resonance

OAc	acetate
OEP	dianion of octaethylporphyrin
ORTEP	Oak Ridge thermal ellipsoid program
Ph	phenyl
POR	dianion of a general porphyrin
py	pyridine
SCE	standard calomel electrode
S_N1	substitution nucleophilic first order
S_N2	substitution nucleophilic second order
TBAOH	tetrabutylammonium hydroxide
THF	tetrahydrofuran
TMP	dianion of tetramesitylporphyrin
TPP	dianion of tetraphenylporphyrin
trpy	2,2′,2"-terpyridyl
TTP	dianion of tetratolylporphyrin
UV-vis	ultraviolet-visible
V	volts
X	monoanionic ligand
XANES	X-ray absorption near edge structure
XO	general oxygen source
ε	molar absorptivity

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PREFACE

Chapters 1 and 2 are based in part on a series of three papers on nitrogen atom transfer. The first two have already been published. One is published in J. Am. Chem. Soc. **1989**, *111*, 3755, the other in Inorg. Chem. **1990**, *29*, 3915. The final paper in the series has been submitted to J. Am. Chem. Soc. for publication. Work presented on nitrogen atom transfer between porphyrinatomanganese nitride and porphyrinatomanganese chloride was done primarily by Don Czapla.

Chapter 3 is based in part on a communication published in Inorg. Chem. **1990**, *29*, 3916 on oxygen atom transfer. A second paper based on this chapter will be submitted for publication.

Chapter 4 contains the experimental details for the entire dissertation.

CHAPTER 1

INTRODUCTION

Although electron transfer reactions have been intensively studied for over forty years, our understanding of these processes is far from complete. Redox reactions can occur by either an inner-sphere or outer-sphere mechanism.[1] In an inner-sphere mechanism, the redox partners share a common ligand that bridges the coordination spheres during the electron transfer. A classic example of inner-sphere electron transfer is shown in eq. 1.[2] A wide variety of ligands can

$$\mathrm{Cr^{2+} + Co\text{-}Cl^{2+} \rightarrow Cr\text{-}Cl^{2+} + Co^{2+}} \qquad (1)$$

serve as bridging groups for inner-sphere processes.[1] Mono-atomic bridges, such as halides and oxides, are particularly versatile in terms of being able to mediate one- and two-electron processes. An outer-sphere mechanism, however, operates by transferring an electron during a collision between the reactants. No bridging ligand is required. The electron transfer between $\mathrm{Cr^{2+}}$ and $\mathrm{Cr^{3+}}$ (eq. 2) is representative of an outer-sphere process.[3] Electron transfer

$$\mathrm{Cr^{*3+} + Cr^{2+} \rightleftharpoons Cr^{*2+} + Cr^{3+}} \qquad (2)$$

reactions can be further classified into cross reactions and self-exchange reactions. Cross reactions are those having a thermodynamic driving force, such as eq. 1, while self-exchange reactions have no thermodynamic driving force, eq. 2. Self-exchange reactions are unique and of interest since the intrinsic reactivities of the reagents are reflected in the rate constants and in the variation of the rate constants.

Most redox reactions typically involve one-electron or a series of one-electron steps. Multi-electron transfer processes which occur in a single step are exceedingly uncommon in comparison. Few of these occur by an outer-sphere mechanism.[4-6] A difficulty in outer-sphere cases is distinguishing the single-step, multi-electron transfer from a series of sequential one-electron steps. An example of a single step multi-electron process is given in eq. 3.[5] Pulse

$$\mathrm{Tl}^{*3+} + \mathrm{Tl}^{+} \rightleftharpoons \mathrm{Tl}^{3+} + \mathrm{Tl}^{*+} \tag{3}$$

radiolysis experiments were used to measure rates of processes involving Tl^{2+}, and these were found to be too slow to explain the chemistry. Most redox processes that involve a single multi-electron step are atom transfer processes, an inner-sphere process where the bridging group is transferred from the oxidant to the reductant. One rational for this observation is that multi-electron changes often are attended by drastic structural reorganizations of the first coordination spheres of the reactants. Atom transfer between the two partners serves to correlate nuclear motions, providing a facile pathway for multi-electron transfers. In the work presented here, inter-metal electron transfer mediated by atom transfer in metalloporphyrin systems has been studied.

Porphyrins

Porphyrins are naturally occurring macrocycles found in the tissues of animals and plants. Metalloporphyrins, commonly with iron as the central metal, are encountered in enzymes and proteins that carry oxygen and catalyze oxygen chemistry in biological systems. Numerous synthetic porphyrins have been synthesized, two common ones widely used in research are 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) and 5,10,15,20-tetratolylporphyrin (TTP), shown in Figure 1.1. Both structures share the porphine skeleton, which consists of four pyrrole groups linked by four bridging methine units. The porphyrin nomenclature arises from the substitution pattern about the porphyrin periphery. Octaethylporphyrin has eight ethyl groups substituted at the β-positions of pyrrole of the porphine macrocycle and tetratolylporphyrin has four

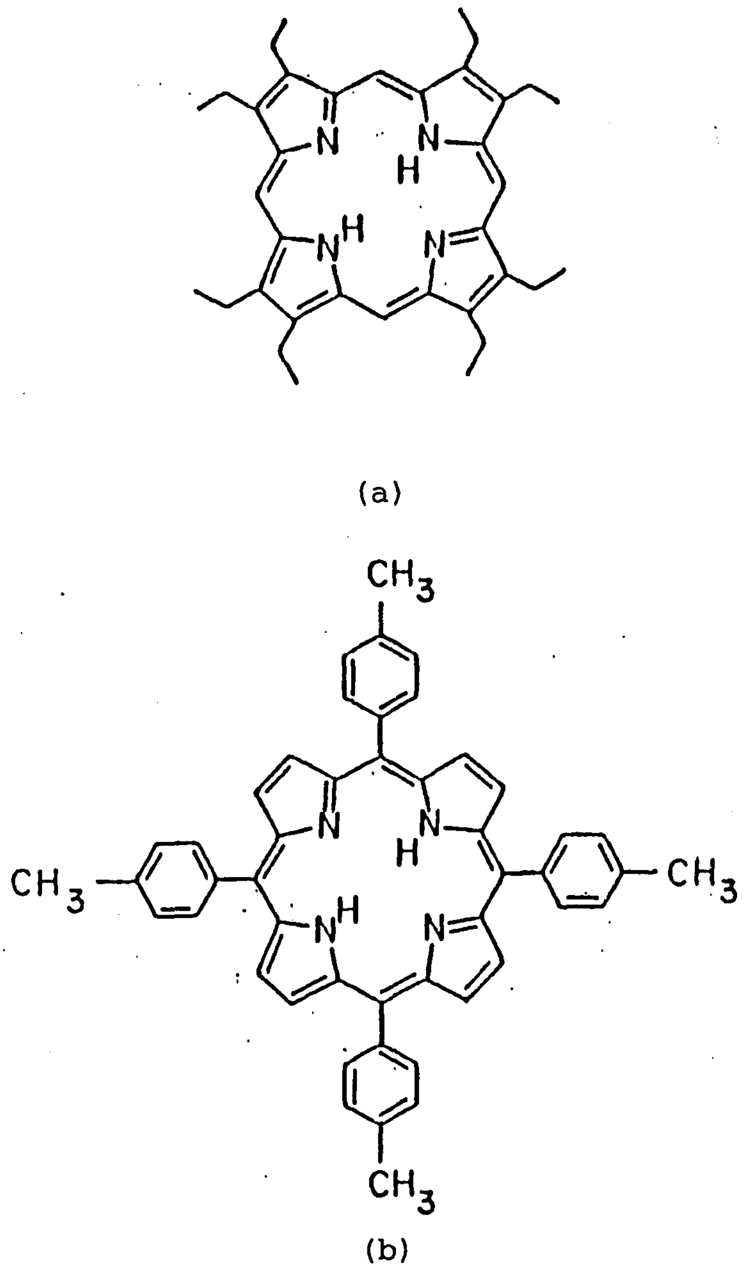


Figure 1.1. Structure of octaethylporphyrin (a) and tetratolylporphyrin (b)

tolyl rings substituted at the *meso*-positions of the macrocycle.

Metalloporphyrins are well suited for atom transfer studies for a number of reasons. Porphyrins are fairly rigid chelates known to complex a wide range of metals in a variety of oxidation states.[7] For example, porphyrin complexes of ruthenium and osmium are known to vary in oxidation state from 0 to +6.[8-10] Chromium and manganese porphyrin complexes are known to exist with metal oxidation states of 2, 3, 4, and 5.[11-15] Furthermore, structural integrity is maintained by the porphyrin ligand over a range of metal oxidation states and may allow more facile multi-electron transfer by minimizing the reorganization of the coordination sphere.

The porphyrin serves as a powerful UV-visible[16] and ^{1}H NMR[17] spectroscopic probe. The molar absorptivities in the UV-vis spectra can range from 10^5 for the Soret band, found between 350 to 500 nm to 10^3-10^4 for the so-called Q-bands, found between 500 and 700 nm. Therefore, one can monitor porphyrins and metalloporphyrins at very low concentrations. This is very advantageous when one acquires rate data for fast reactions. Second order rate constants can be determined that vary from 10^{-1} to 10^3 M^{-1} s^{-1} using conventional UV-visible spectroscopy. The porphyrin ligands also have very simple ^{1}H spectra due to the high symmetry of the molecule. Tetratolylporphyrin shows four signals due to the β-pyrrole, *ortho*-phenyl, *meta*-phenyl, and tolyl-methyl protons. Similarly, octaethylporphyrin shows three signals which arise from the *meso*-H, methylene, and methyl resonances. When diamagnetic metalloporphyrin complexes are present, ^{1}H NMR spectroscopy can be used to determine rate constants that are too slow to measure easily by UV-vis spectroscopy and to determine equilibrium constants.

Metalloporphyrins bind many types of axial ligands, such as halide, oxide, nitride, water, pyridine, or can remain coordinatively unsaturated, allowing for the study of a wide variety of systems and effects. In addition porphyrin complexes are soluble in innocent, non-donor organic solvents which permits the study of processes which are uncomplicated by solvent coordination. Finally, a large number of structurally characterized porphyrin complexes exist.[18] Thus, use of metalloporphyrin complexes should allow a systematic study which addresses fundamental issues concerning the kinetic and thermodynamic factors involved in multi-electron transfer.

Before this work began, inner-sphere, inter-metal atom transfer processes had been reported in only a few cases using metalloporphyrins. Single-electron transfer mediated by atom transfer has already been demonstrated for (TTP)Co-X where X is Cl, Br, I and a variety of pseudohalides (eq. 4).[19] Also

$$\text{(TTP)Co-X} + \text{(TTP)Co(II)} \rightleftharpoons \text{(TTP)Co(II)} + \text{(TTP)Co-X} \qquad (4)$$

(TPP)Fe-Cl,[20] (TPP)Mn-Cl, and (TPP)Cr-Cl[21] have been reduced to (TPP)Fe(II), (TPP)Mn(II), and (TPP)Cr(II) respectively by bis-(acetylacetonato) chromium(II) by an inner-sphere process (eq. 5, M = Cr, Mn, Fe). Prior to this work, the only multi

$$\text{(TPP)M-Cl} + \text{Cr(acac)}_2 \rightarrow \text{(TPP)M(II)} + \text{Cl-Cr(acac)}_2 \qquad (5)$$

electron, inter-metal process of metalloporphyrins had been reported by Groves and Takahashi in which a nitrogen atom was transferred from a manganese to a chromium porphyrin (eq. 6).[22]

$$\text{(TPP)Mn}{\equiv}\text{N} + \text{(TPP)Cr(II)} \rightarrow \text{(TPP)Mn(II)} + \text{(TPP)Cr}{\equiv}\text{N} \qquad (6)$$

Reported herein are the thermodynamic and kinetic aspects of the first example of nitrogen atom transfer in the open literature and the first *reversible* nitrogen atom transfer reaction. Two- and three-electron transfers mediated by nitrogen atom transfer have been demonstrated, eq. 7 where X = a monoanionic ligand or no ligand, and they are discussed in Chapter 2.

$$\text{(TTP)Mn}{\equiv}\text{N} + \text{(OEP)Mn-X} \rightleftharpoons \text{(TTP)Mn-X} + \text{(OEP)Mn}{\equiv}\text{N} \qquad (7)$$

Secondly, *reversible* oxygen atom transfer has been demonstrated between chromium porphyrins (eq. 8).

$$(\mathrm{TTP})\mathrm{Cr{=}O} + (\mathrm{OEP})\mathrm{Cr{-}Cl} \rightleftharpoons (\mathrm{TTP})\mathrm{Cr{-}Cl} + (\mathrm{OEP})\mathrm{Cr{=}O} \qquad (8)$$

Thermodynamic, kinetic, and mechanistic factors of these processes will be discussed in Chapter 3.

Concomitant to our studies, Bottomley and Neely reported additional examples of nitrogen atom transfer between (POR)Mn≡N and (POR)Cr-Cl and between (POR)Cr≡N and (POR)Cr-Cl (eq. 9, M = Mn, Cr).[23,24] The reaction was reversible when a

$$(\mathrm{TTP})\mathrm{M{\equiv}N} + (\mathrm{OEP})\mathrm{Cr{-}Cl} \rightarrow (\mathrm{TTP})\mathrm{M{-}Cl} + (\mathrm{OEP})\mathrm{Cr{\equiv}N} \qquad (9)$$

chromium nitride was used and irreversible when a manganese nitride was used. Reversible oxygen atom transfer between titanium porphyrins has also been discovered by Woo and Hays (eqs. 10, 11).[25]

$$(\mathrm{TTP})\mathrm{Ti{=}O} + (\mathrm{OEP})\mathrm{Ti{-}Cl} \rightleftharpoons (\mathrm{TTP})\mathrm{Ti{-}Cl} + (\mathrm{OEP})\mathrm{Ti{=}O} \qquad (10)$$

$$(\mathrm{TTP})\mathrm{Ti{=}O} + (\mathrm{OEP})\mathrm{Ti(Cl)_2} \rightleftharpoons (\mathrm{TTP})\mathrm{Ti(Cl)_2} + (\mathrm{OEP})\mathrm{Ti{=}O} \qquad (11)$$

CHAPTER 2

NITROGEN ATOM TRANSFER REACTIONS OF MANGENESE PORPHYRINS

Multi-electron transfer processes which occur in a single step are uncommon. A rare heterogeneous example involves the redox chemistry of $[Os(O)_2(OH)trpy]^+$ (trpy= 2,2′,2″-terpyridyl) in which the oxidation states VI and III are interrelated by a reversible three electron process where all three electrons are transferred at the same potential on a glassy carbon electrode (eq. 1).[26] Only a few examples of multi-electron outer-sphere electron transfer exist.[4-6] In a recent example, Schwartz[5] showed using pulse radiolysis and rate studies that Tl^{2+} was not involved in the reduction of Tl^{3+} by Fe^{2+} (eq 2).

$$[Os(O)_2(OH)(trpy)]^+ + 3\ e^- + 2\ H^+ \rightarrow (trpy)Os(OH)_3 \qquad (1)$$

$$Tl^{3+} + 2\ Fe^{2+} \rightarrow Tl^+ + 2\ Fe^{3+} \qquad (2)$$

Lappin[6] has observed the oxidation of a nickel(II)bis(oxime-imine) to a nickel(IV)bis(oxime-imine) by bromine (eq. 3).

$$Ni(II)L + Br_2 \rightarrow Ni(IV)L^{2+} + 2\ Br^- \qquad (3)$$

Only a few systems involving multi-electron atom-transfer redox couples between metals have been observed. One of the first recognized two-electron processes was the Pt(II)/Pt(IV) exchange discovered by Basolo, et al. (eq 4). In this example, ^{14}C-labeled ethylenediamine (*en) was used as a probe to monitor the exchange.[27-30]

$$\begin{aligned} &\textit{trans}\text{-Pt}(^{*}\text{en})_2\text{Cl}_2^{2+} + \text{Pt}(\text{en})_2^{2+} \rightleftharpoons \\ &\text{Pt}(^{*}\text{en})_2^{2+} + \textit{trans}\text{-Pt}(\text{en})_2\text{Cl}_2^{2+} \end{aligned} \tag{4}$$

Subsequently, Taube[31] and Hunt[32-34] have demonstrated that halogen atom transfer can mediate a two-electron exchange between metallocenes of ruthenium and osmium (eq. 5) where M = Ru or Os, X = I or Br and Cp = C_5H_5. More recently, Creutz

$$\text{Cp}_2\text{M-X}^{+} + \text{Cp}_2\text{M} \rightleftharpoons \text{Cp}_2\text{M} + \text{Cp}_2\text{M-X}^{+} \tag{5}$$

and coworkers[35] have examined a multi-electron atom-transfer self exchange reaction using $CpM(CO)_3^-$ and $CpM(CO)_3X$ in CD_3CN where M = Mo or W and X = Cl, Br, I, or CH_3 (eq. 6) using NMR line-broadening and magnetization transfer methods as well as conventional kinetic techniques.

$$\text{CpMo(CO)}_3^{-} + \text{CpMo(CO)}_3\text{X} \rightleftharpoons \text{CpMo(CO)}_3^{-} + \text{CpMo(CO)}_3\text{X} \tag{6}$$

An oxo ligand has been used to mediate two-electron transfer in several systems. Holm[36] has extensively reviewed oxo-transfer reactions. The majority of inter-metal oxo reactions involve molybdenum and tungsten complexes. Recently, oxo-transfer has been demonstrated between two vanadium compounds.[37] More specific details will be provided in Chapter 3.

Although much is known about how the nature of the bridging group affects the rate of inner-sphere electron transfer, it is not well understood how the bridging group influences the number of electrons involved in the redox process.[2,38-40] For example, monatomic bridges, such as the halides and oxides, are capable of mediating one- and two-electron processes. Furthermore, the consideration of the other monatomic bridges such as the nitrido ligand (N^{3-}) has received little attention. To some extent, this can be attributed to the weak donor property of the nitrido lone pair of electrons.[41] Nonetheless, the nitride is well known as a bridging ligand in a number of stable compounds. Both symmetric and asymmetric M-N-M linkages are possible and have been the subject of a recent theoretical study.[42]

An analysis of electron transfer involving a bridging nitride indicates that several types of reaction are possible. Some limiting cases are illustrated in eqs. (7-10).

$$L_nM^x{\equiv}N: + M^yL_m \rightarrow L_nM^x{\equiv}N{:}\!\rightarrow\! M^yL_m + L \qquad (7)$$

$$L_nM^x{\equiv}N: + M^yL_m \rightarrow L_nM^{x-1} + :N{\equiv}M^{y+1}L_m + L \qquad (8)$$

$$L_nM^x{\equiv}N: + M^yL_m \rightarrow L_nM^{x-2} + :N{\equiv}M^{y+2}L_m + L \qquad (9)$$

$$L_nM^x{\equiv}N: + M^yL_m \rightarrow L_nM^{x-3} + :N{\equiv}M^{y+3}L_m \qquad (10)$$

Equation 7 involves simple bond formation with no formal change in oxidation state. The complex $(Et_2PhP)_3Cl_2Re{\equiv}N{:}\!\rightarrow PtCl_2(PEt_3)$, prepared by mixing the rhenium nitrido complex with $PtCl_2(PEt_3)_2$ in benzene, is an example of this type of situation.[43] In this case, the Pt(II) complex is a poor reductant and no redox reaction occurs. If an appropriate reducing agent is used, eqs. 8-10 are possible and represent one-, two-, and three-electron transfer processes, respectively.

In our work, we have investigated the inner-sphere electron transfer properties of metalloporphyrin nitrides. Consequently, the remainder of this section will present a brief review of nitrido metalloporphyrin complexes.

Six metalloporphyrins, iron,[44] rhenium,[45] manganese,[46] chromium,[47,48] molybdenum,[49] and osmium[50] have been characterized with the terminal nitrido ligand. The iron porphyrin nitride has been observed only at low temperature, 150 K, by resonance Raman spectroscopy.[51,52] The terminal nitride decomposes to yield a μ-nitride dimer. The related phthalocyanine ligand, where a nitrogen atom replaces the *meso*-CH group in the porphyrin skeleton, forms μ-nitride complexes with ruthenium[53] and iron.[54] The family of nitrido metalloporphyrins and metallophthalocyanines is summarized in Figure 2.1.

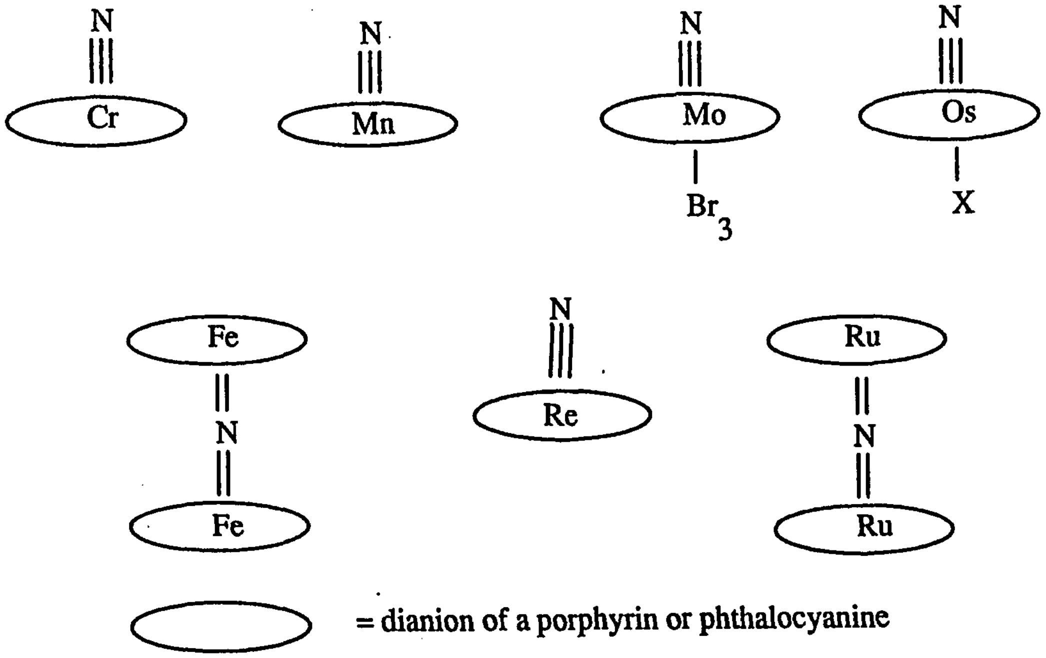


Figure 2.1. Metalloporphyrin and metallophthalocyanine nitride complexes

{(TPP)Fe}$_2$N, where TPP is the dianion of tetraphenylporphyrin, was the first nitrido metalloporphyrin to be synthesized. This dimer was prepared by Summerville and

Cohen[44] via thermal decomposition of (TPP)FeN$_3$ in boiling xylene under a nitrogen atmosphere (eq 11). The product was

$$4\ (TPP)Fe\text{-}N_3 \rightarrow 2\ \{(TPP)Fe\}_2N + 5\ N_2 \qquad (11)$$

air stable in solid or solution. More recently, Büchler[55] has prepared the dimer by photolysis of (TTP)FeN$_3$, where TTP is the dianion of tetratolylporphyrin. Ellis and Lyons[56,57] have observed {(TPP)Fe}$_2$N and tetrakis-(pentafluorophenyl) porphyrinatoiron nitride as a byproduct of molecular oxygen oxidation of alkanes in refluxing benzene catalyzed by the corresponding azido complex. The related iron and ruthenium phthalocyanine nitrides have been prepared by Ercolani by heating the metal(II)phthalocyanine in the presence of sodium azide in refluxing α-chloronaphthalene (eq 12, L = phthalocyanine).

$$2\ LM(II) + NaN_3 \rightarrow (LM)_2N + N_2 \qquad (12)$$

Several physical studies on the iron bridged nitride revealed that the two metal atoms are chemically identical and therefore strongly magnetically coupled. They are best described as low-spin iron centers in an oxidation state of 3.5. The techniques used to support this conclusion include an X-ray crystal structure determination,[58] photoelectron spectroscopy,[59] and magnetic susceptibility measurements.[44,60] Further characterization has been done on these iron nitride dimers using UV-vis,[44,54,55] IR,[44,54] resonance Raman,[61,62] EPR,[44,54,63,64] NMR,[44,60] and Mössbauer spectroscopies,[44,65,66] elemental analysis,[44] and X-ray powder diffraction.[54] $\{(TPP)Fe\}_2N$ has D_{4h} symmetry with an iron-nitrogen distance of 1.661 Å and an 0.32 Å displacement of the iron from the mean porphyrin plane. In the analogous μ-oxo dimer, iron-oxygen distance is 1.763 Å and the iron is displaced from the mean porphyrin plane by 0.50 Å.[58] These differences are consistent with a low-spin configuration of the μ-nitride dimer and a high-spin configuration of the μ-oxo dimer. These properties are presumably due to the greater ability of nitrogen to form π bonds. Hoffmann has done a theoretical study that explains the electron configuration of the nitride dimer.[67,68]

A kinetic study of the decomposition of $(TPP)FeN_3$ (eq. 11) to the μ-nitrido dimer determined that the rate limiting step was first order in the azido complex. This can be explained by rate limiting formation of the intermediate terminal nitrido iron complex.[44] This was followed by rapid formation of the μ-nitrido dimer from the intermediate terminal nitride complex.

Electrochemical measurements on $[(TPP)Fe]_2N$ reveal that the first oxidation occurs on the metal to give a dimer with two iron(IV) centers.[54,69,70] The second oxidation occurs at the porphyrin ring as determined by IR spectroscopy. The cations have been studied by Mössbauer spectroscopy.[71] Reducing the dimer by one electron results in formation of a dimer containing two iron(III) centers. Addition of two more electrons gave a dimer with two iron(II) centers. The redox pathway for the dimer is given below.

$$[(TPP)(TPP)^{+\cdot}Fe^{IV,IV}]_2N^{2+} \quad + \quad e^- \quad \rightarrow \quad [(TPP)Fe^{IV,IV}]_2N^{+}$$

$$[(TPP)Fe^{IV,IV}]_2N^{+} \quad + \quad e^- \quad \rightarrow \quad [(TPP)Fe^{III\frac{1}{2},III\frac{1}{2}}]_2N$$

$$[(TPP)Fe^{III\frac{1}{2},III\frac{1}{2}}]_2N \quad + \quad e^- \quad \rightarrow \quad [(TPP)Fe^{III,III}]_2N^{-}$$

$$[(TPP)Fe^{III,III}]_2N^{-} \quad + \quad e^- \quad \rightarrow \quad [(TPP)Fe^{II\frac{1}{2},II\frac{1}{2}}]_2N^{2-}$$

$$[(TPP)Fe^{II\frac{1}{2},II\frac{1}{2}}]_2N^{2-} \quad + \quad e^- \quad \rightarrow \quad [(TPP)Fe^{II,II}]_2N^{3-}$$

The phthalocyanine iron nitride has similar electrochemical behavior. Chemical oxidation of $\{(TPP)Fe\}_2N$ with one equivalent phenoxathiin hexachloroantimonate or with a half equivalent of iodine in the presence of a silver salt produces the monocation. When two equivalents of phenoxathiin hexachloroantimonate were used, a dication was formed.[71] The cation of the phthalocyanine iron nitride dimer was obtained through oxidation of the neutral dimer with either the ferricinium cation or tetracyanoquinodimethane.[54] A study on the oxygen binding capabilities of this cation has been completed.[72] This experiment determined that one oxygen molecule was bound to one iron of the dimer which resulted in the two irons becoming inequivalent.

The ruthenium nitride dimer has been characterized in a similar manner. X-ray powder patterns show that the ruthenium dimer was isostructual with its iron analog.[54] Spectroscopic measurements, UV-vis, EPR, and IR as well as magnetic susceptibility and elemental analysis are within expected values for the ruthenium dimer.[53]

Although nitrido osmium amine complexes have been known for over 25 years, the synthesis of nitrido osmium porphyrin did not appear until about eleven years ago.[50] In 1980, Büchler successfully prepared $N{\equiv}Os(VI)(OEP)ClO_4$ by the oxidation of $(NH_3)_2Os(II)(OEP)$ with peroxyacetic acid (eq 13).

$$(OEP)Os(NH_3)_2 + CH_3CO_3H + HClO_4 \rightarrow ClO_4(OEP)Os{\equiv}N \qquad (13)$$

The compound was characterized by NMR, IR, and UV-vis spectroscopy. To date, no crystal structure has been published nor have any investigations of the reactivity of $N{\equiv}Os(VI)(OEP)ClO_4$ been conducted other than substitution of perchlorate with fluoride or methoxide.

Dehnicke[49] prepared the first nitrido molybdenum porphyrin in 1981 by the insertion of $N{\equiv}MoBr_3$ into H_2TPP as shown below (eq. 14). Like the nitrido osmium porphyrin, the nitrido

$$(TPP)H_2 + Br_3Mo\equiv N \rightarrow (Br_3)Mo\equiv N \qquad (14)$$

molybdenum porphyrin has the central metal in the +6 oxidation state. The molybdenum complex was characterized by IR and UV-vis spectroscopy, mass spectrometry and elemental analysis. Again no crystal structure has been determined, nor have reactivity studies been reported.

The nitrido manganese porphyrin was prepared by oxidative ammonolysis.[46] This involves treating (POR)Mn-OCH_3 with an aqueous ammonium solution, where POR is a dianion of a general porphyrin, followed by addition of with sodium hypochlorite (eq. 15). Alternatively photochemical[55,73] or thermal[74]

$$(POR)Mn\text{-}OCH_3 + NH_3 + NaOCl \rightarrow (POR)Mn\equiv N \qquad (15)$$

decomposition of the azido complex (eq 16) yields the corresponding nitride. Dinitrogen formed during this reaction

$$(POR)Mn\text{-}N_3 \rightarrow (POR)Mn\equiv N + N_2 \qquad (16)$$

has been detected by mass spectrometry.[74] The complexes are pentacoordinate and the central metal atom is in the +5 oxidation state. Manganese porphyrin nitride complexes have been characterized by NMR,[46,55] IR,[46,55,74,75] UV-vis,[46,55,74,75] and resonance Raman[76] spectroscopies, mass spectrometry,[46,55] and elemental analysis.[46,55,74] The crystal structure of tetrakis(4-methoxyphenyl)porphyrinatomanganese nitride has been determined by Hill.[75] The metal-nitrogen bond length was found to be 1.515(3) Å, the second shortest metal-nitrogen distance reported to date.

Spectroelectrochemical studies have been done on several of the manganese nitride complexes. Bottomley[77] found that two reversible oxidations and reductions occur, all of which porphyrin based. Other redox studies have been done on these compounds. Gamma radiation has been shown to reduce the manganese(V) nitride to a manganese(II) species in work done by Imamura.[73] The reduction of (OEP)Mn≡N with sodium anthracenide causes reduction of the porphyrin ligand. The reduced species was treated with methyl iodide to produce a porphodimethene nitrido manganese complex as the only isolated product. This product has been structurally characterized by X-ray diffraction and has the shortest metal-nitrogen distance, 1.512(2) Å.[78]

Büchler[79] has found that (POR)Mn≡N reacts with triphenylphosphine to produce a phosphineimidatomanganese porphyrin shown below (eq 17). The use of trimethylphosphite

$$\text{(TTP)Mn}\equiv\text{N} + \text{PPh}_3 \rightarrow \text{(TTP)Mn-N=PPh}_3 \qquad (17)$$

yields a similar product, a porphyrinatomanganese (methylamido)dimethoxophosphate, formed by migration of a methyl group from oxygen to nitrogen, (POR)Mn-$N(CH_3)P(O)(OCH_3)_2$. Groves and Takahashi[80] demonstrated that treatment of (POR)Mn≡N with trifluoroacetic anhydride gave an imido manganese porphyrin product (eq 18). The manganese

$$(POR)Mn{\equiv}N + (CF_3CO)_2O \rightarrow CF_3CO_2(POR)Mn{=}NC(O)CF_3 \qquad (18)$$

imido complex reacts with alkenes to produce aziridenes[80,81] (eq 19). Bottomley and Neely[81] have studied the kinetics of this

$$\begin{aligned} &CF_3CO_2(POR)Mn{=}NC(O)CF_3 + \text{alkene} \rightarrow \\ &\qquad (POR)Mn(OC(O)CF_3) + \text{aziridine} \qquad (19) \end{aligned}$$

reaction using a wide variety of porphyrins and acetic anhydrides. Porphyrinatomanganese nitride complexes have been used in spectroscopic investigations of metalloenzymes. The reactive metal center was replaced with the more inert nitride, eliminating problems due to undesired reactions during measurements.[82,83]

The nitrido chromium porphyrin was prepared by oxidative ammonolysis of (POR)Cr-OH[47] (eq. 20) or by photolytic decomposition of the azide[48,55,74] (eq. 21) in a manner similar to that for the manganese analog. This complex was

$$(POR)Cr\text{-}OH + NH_3 + NaOCl \rightarrow (POR)Cr{\equiv}N \quad (20)$$

$$(POR)Cr\text{-}N_3 \rightarrow (POR)Cr{\equiv}N + N_2 \quad (21)$$

also found to be five coordinate with the chromium in the +5 oxidation state. These complexes have been characterized by NMR,[48] IR,[47,48,55] UV-vis,[47,48,55] EPR,[47,48] and resonance Raman[76] spectroscopies, mass spectrometry,[47,48,55] and elemental analysis.[47,48,55] Büchler has also studied these nitrides by ^{14}N electron nuclear double resonance spectroscopy.[47] Spectroelectrochemical studies revealed that the oxidations and reductions of the nitridochromium porphyrins are ligand-based, not metal-based.[84] Groves[48] has done an X-ray diffraction study on (TTP)Cr≡N. The metal-nitrogen distance was found to be 1.565(6) Å. When treated with triphenyl phosphine, trimethyl phosphite, or acidic anhydrides, chromium porphyrin nitrides gave products similar to those described for the manganese nitride complexes (eqs. 17, 18).[79,84] However, the imido chromium complex was not reactive toward alkenes.

In contrast to manganese chemistry, chromium nitride compounds have been synthesized without using porphyrins. Nitride compounds have been prepared by azide decomposition of chromium complexes chelated with N,N'-ethylene-bis(salicylideniminato)[85] and 1,2-bis(2-pyridinecarboxamido) benzene ligands[86] in place of a porphyrin. A crystal structure of the 1,2-bis(2-pyridinecarboxamido)benzene chromium nitride has been determined. This complex has the shortest chromium-nitrogen distance, 1.560(2) Å, known to date.[86] As with the porphyrinatomanganese nitride, the chromium analog has also been used as a spectroscopic probe in studies of metalloenzymes.[87,88]

The remainder of this chapter describes our work with the atom transfer chemistry of manganese porphyrin nitrides.

Results

Reduction of nitridomanganese(V) porphyrin with manganese(II) porphyrin. Treatment of $\mathrm{(TTP)Mn{\equiv}N}$ with (OEP)Mn, where OEP is the dianion of octaethylporphyrin, in toluene under anaerobic conditions results in spectral changes which are consistent with the transfer of a terminally bound nitrogen ligand between two metal complexes shown in eq. 22.

$$\mathrm{(TTP)Mn{\equiv}N + (OEP)Mn \rightleftharpoons (TTP)Mn + (OEP)Mn{\equiv}N} \qquad (22)$$

The UV-vis spectrum of the resulting mixture contained two new Soret bands for (TTP)Mn(II) at 435 nm and $\mathrm{(OEP)Mn{\equiv}N}$ at 404 nm. The Soret bands for $\mathrm{(TTP)Mn{\equiv}N}$ (422 nm) and (OEP)Mn (418 nm) overlapped to form a single peak centered at 420 nm and did not completely disappear, indicating that eq. 22 is an equilibrium process with $K = 1.2 \pm 0.5$ at 20.0 ± 0.1 °C. The reversibility of eq. 22 was confirmed by the complementary experiment in which (OEP)Mn≡N was treated with (TTP)Mn. This generates a final UV-vis spectrum that has peak positions identical to those observed for the forward process. Since the Mn(V) nitrido complexes are low-spin d^2 and diamagnetic, it was also possible to independently establish the extent of reaction by ^1H NMR. This was most conveniently accomplished by monitoring the β-pyrrole proton signal of (TTP)Mn≡N (8.94 ppm) and the *meso*-proton signal of (OEP)Mn≡N (10.29 ppm) against an internal standard, the methine proton of triphenylmethane (5.51 ppm) in toluene-d_8. Flame sealed NMR tubes containing mixtures of (TTP)Mn≡N, (OEP)Mn, (OEP)Mn≡N, (TTP)Mn, and Ph_3CH in toluene-d_8 maintain mass balance indefinitely in terms of total nitrido complex concentration. The equilibrium constants for eq. 21 over an 80° range were measured by ^1H NMR and are listed in Table 2.1.

Table 2.1. Equilibrium constants for eq. 22 in toluene-d_8

(°C)	K
-40	0.59 ± 0.19
-20	0.66 ± 0.28
0	1.02 ± 0.30
20	1.23 ± 0.46
40	1.36 ± 0.61

The thermodynamic parameters ΔH° = 2.0 ± 0.2 kcal/mol and ΔS° = 7.1 ± 0.6 cal/mol·K were derived from this temperature dependence.

The forward rates of eq. 22 in toluene were examined spectrophotometrically by following the absorbance changes at 402 nm as shown in Fig. 2.2. Kinetic runs were performed with starting concentrations ranging from 1.13×10^{-6} to 1.04×10^{-5} M and Mn≡N/Mn(II) ratios ranging from approximately 1:1 to 1:5. In all cases, the data were found to obey an integrated rate law for reversible second-order reactions derived by King.[89] Plots of $\ln[\Delta/\{\alpha + \Delta(1-1/K)\}]$ vs. αt are linear for more than three half-lives. A typical plot is shown in Figure 2.3. Table 2.2 lists concentration data and forward and reverse rate constants for eq. 22 at 20 °C and Table 2.3 summarizes forward rate constants as a function of temperature. Initial concentrations and rate data for eq. 22 at 2O °C.

A less comprehensive examination of the behavior of eq. 22 in tetrahydrofuran was also undertaken. Proton NMR studies show that, within experimental error, use of THF as solvent does not shift the equilibrium (K_{THF} = 1.8 ± 0.2) at 20 °C. However, the rate of nitrogen atom transfer decreases by three orders of magnitude, $k_{1(THF)} = 2.3 \pm 0.3\ M^{-1}\ s^{-1}$. Kinetic data for eq. 22 in THF were also found to obey the integrated rate law derived by King for more than three half-lives.

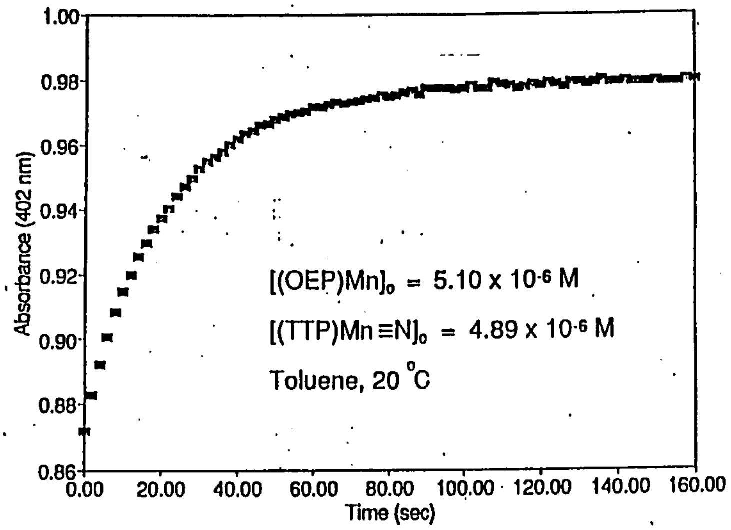


Figure 2.2. Representative absorption vs. time plot for eq. 22 at 20 °C

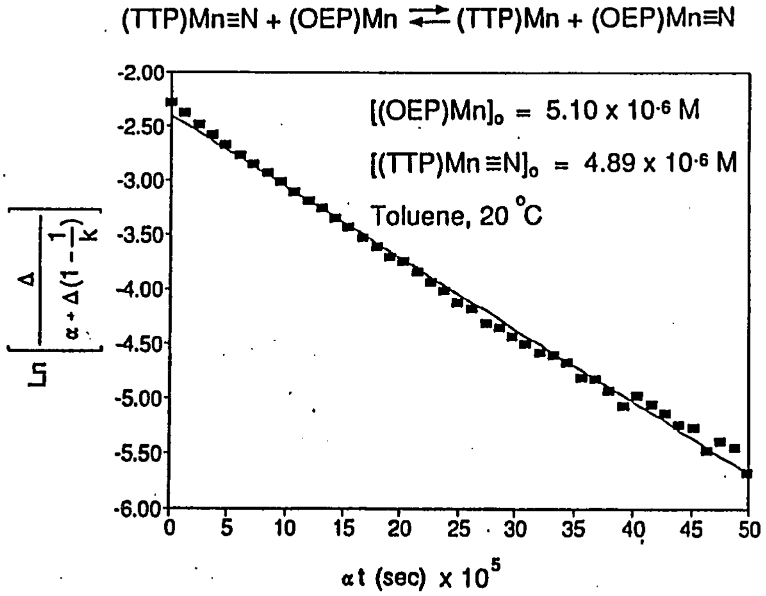


Figure 2.3. Plot of $\ln[\Delta/\{\alpha + \Delta(1-1/K)\}]$ vs. αt for eq. 22 at 20 °C

Table 2.2. Initial concentration and rate data for eq.22 at 20 °C

$[N{\equiv}Mn(TTP)]_0$ µM	$[Mn(OEP)]_0$ µM	10^{-3} k_1 M^{-1} s^{-1}	$[N{\equiv}Mn(OEP)]_0$ µM	$[Mn(TTP)]_0$ µM	10^{-3} k_{-1} M^{-1} s^{-1}
3.39	3.40	7.7	3.29	3.36	2.2
3.56	3.54	6.2	6.67	3.36	2.6
4.03	4.45	6.6	6.58	3.36	3.0
1.13	4.54	5.4	3.89	1.95	3.4
5.49	4.83	5.6	9.71	1.95	3.3
5.00	4.86	5.5	10.4	2.10	4.1
3.00	5.74	4.4		avg. = 3.2 ± 0.5	
1.42	5.67	3.7			
3.39	6.81	5.5			
	avg. = 5.6 ± 1.2				

Table 2.3. Forward rate constants for eq. 22 in toluene

T (°C)	10^{-3} k_1 (M^{-1} s^{-1})
-10	0.8 ± 0.3
0	1.5 ± 0.6
10	2.9 ± 0.3
20	5.6 ± 1.2

Reduction of nitridomanganese porphyrins with manganese(III) porphyrins. (OEP)Mn≡N is also capable of transferring its terminally bound nitrogen to manganese(III) porphyrins (eq. 23). This was readily demonstrated by UV-vis

$$\text{(OEP)Mn}{\equiv}\text{N} + \text{(TTP)Mn-Cl} \rightleftharpoons \text{(OEP)Mn-Cl} + \text{(TTP)Mn}{\equiv}\text{N} \qquad (23)$$

or ^{1}H NMR spectroscopy using the methods discussed above. For example, the UV-vis spectra of a toluene solution of (OEP)Mn≡N and (TTP)Mn-Cl showed a gradual decrease over several hours in the Soret bands of the starting nitrido (404 nm) and chloro (478 nm) complexes. New Soret bands corresponding to the formation of (TTP)Mn≡N (422 nm) and (OEP)Mn-Cl (360 nm) simultaneously appeared. In a similar fashion to eq. 22, the Mn≡N/Mn-Cl exchange process is reversible.

Effect of solvent. A set of kinetics runs were performed in N-methylformamide. In this solvent, the second order rate constant for nitrogen atom transfer between (OEP)Mn≡N and (TTP)Mn-Cl was found to be $k_1 = 20 \pm 2\ M^{-1}\ s^{-1}$.

Effect of axial ligands. Axial ligand effects were studied in these systems by varying the monoanionic ligand on the starting manganese(III) porphyrin complexes as shown in eq. 24.

$$\text{(OEP)Mn}{\equiv}\text{N} + \text{(TTP)Mn-X} \rightleftharpoons \text{(OEP)Mn-X} + \text{(TTP)Mn}{\equiv}\text{N} \qquad (24)$$

Discussion

We have found that nitrogen atom transfer between two metals can be extremely facile. It is possible to observe this remarkable process by using different porphyrin ligands as spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction. This eliminates complications due to ligand loss or stereochemical rearrangements. Because the equilibrium constant of eq. 22 is near unity, nitrogen atom transfer between (TTP)Mn≡N and (OEP)Mn can be considered as a pseudo-self-exchange reaction. Consequently, the rate constant for eq. 22 is a good measure of the intrinsic tendency for nitrogen atom transfer. As indicated in Table 2.2, these rate constants are on the order of $10^3\ M^{-1}\ s^{-1}$. Interestingly this is on the same order of magnitude found for the $Mn^{III/II}$ porphyrin self exchange rate constant for outer-sphere electron transfer measured by Hambright. The temperature dependence of these rates yields activation parameters of $\Delta H^{\ddagger} = 9.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -10 \pm 2$ cal/mol·K.

Since the manganese nitrido complex, which formally contains Mn(V), was reduced to a manganese(II) complex, eq. 22 presents a formal 3-electron redox process. Thus, the reaction pathway for eq. 22 is of great interest since it is an unprecedented process. Of fundamental concern is the issue of outer-sphere versus inner-sphere mechanisms. Insight into this question is provided by chemical studies. For example, Büchler has shown that sodium anthracenide, an outer-sphere reducing agent, was capable of adding two electrons to the porphyrin ligand of (OEP)Mn≡N, but does not reduce the metal.[78] Moreover, Bottomley[81] has demonstrated that the first and second electrochemical reductions of (TTP)Mn≡N and (OEP)Mn≡N are ligand-based. Formation of the singly reduced complexes occurs at $E_{1/2} = -1.10$ V (N≡Mn(TTP)) and $E_{1/2} = -1.30$ V (N≡Mn(OEP)) vs. SCE. Since the Mn^{III}(POR)/Mn^{II}(POR) reduction potentials are -0.45 V (OEP)[91] and -0.33 V (TTP)[92] vs. SCE, neither Mn(OEP) nor Mn(TTP) are capable of reducing the manganese nitrido complexes in an outer-sphere process. Thus, eq. 22 most likely proceeds by an inner-sphere mechanism. Furthermore, it is unlikely that eq. 22 proceeds through the intermediacy of free N^{3-} ions or N atoms since these are presumably too high in energy to be involved. An irreversible transfer has been demonstrated by Takahashi and Groves when a chromium(II) metalloporphyrin was used as the nitrogen atom acceptor.[22] Attempts to detect the putative binuclear μ-nitrido intermediate by resonance Raman or UV-vis difference spectroscopy were unsuccessful, indicating that this intermediate is present in unobservable concentrations. However, further evidence in support of a bridged intermediate was provided by the use of a coordinating solvent. For example, in THF, the rate constant for eq. 22 decreases by three orders of magnitude. In this case, THF presumably coordinates to the Mn(II) reductant and inhibits formation of the μ-nitrido species. The activation parameters $\Delta H^{\ddagger} = 9.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -10 \pm 2$ cal/mol·K for eq. 22 in toluene are also consistent with an inner-sphere process. The small value of $\Delta H^{\ddagger}$ suggests that significant bond formation (Mn≡N---Mn) occurs to offset the energy needed to cleave a Mn≡N triple bond. In addition, the negative entropy of activation indicates that the mechanism of eq. 22 is associative in nature.

A salient result emerging from this study involves the remarkable aspect of controlling the number of redox equivalents exchanged in an electron transfer process. By a judicious choice of substrates, nitrido manganese porphyrins can serve as either a three-electron or a two-electron oxidant. Thus, when Mn(III) porphyrins are used as the reductant, a net two-electron redox process occurs (eq. 23). Few redox reagents are capable of this flexibility.[93-95] A consideration of the redox chemistry of chloromanganese(III) porphyrins indicates that eq. 23 does not involve an outer-sphere mechanism. Chemical and electrochemical oxidation of (TPP)Mn-Cl produces a porphyrin-based π-cation radical.[96-98] The Cl-Mn(TPP$^{+\cdot}$)/Cl-Mn(TPP) couple occurs at $E_{1/2}$ = 1.18 V vs. SCE.[99] However, the N≡Mn(OEP)/N≡Mn(OEP$^{-\cdot}$) reduction occurs at $E_{1/2}$ = -1.30 V vs. SCE.[81] Thus, an outer-sphere process between N≡Mn(OEP) and Cl-Mn(TTP) is not thermodynamically possible. Although eq. 23 clearly proceeds by an inner-sphere process, it presents a more complex mechanistic situation since a double exchange of ligands (N/Cl) is involved. Both nitrido and chloro ligands are good bridging species and it is of fundamental interest to determine if a preference exists for a particular bridging ligand in this process and if the process is associative or dissociative in nature.

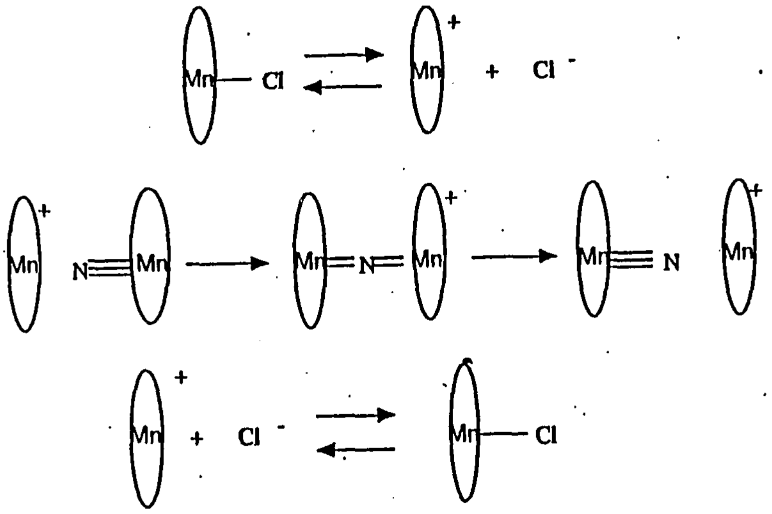
The most consistent mechanism for the Mn≡N/Mn-X exchange process involves an initial dissociation of the monoanionic ligand from the manganese(III) complex. Nitrogen atom transfer subsequently occurs between the cationic Mn(III) porphyrin and the nitrido complex through a μ-nitrido intermediate (Scheme I). This was determined by Woo and

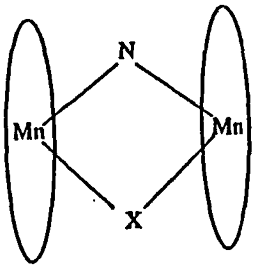
Czapla[100] by demonstrating that eq. 23 was inhibited by added chloride ion. When a sterically encumbered porphyrin, Baldwin's capped-porphyrin Figure 2.4, was used with the manganese chloride, the reaction proceeds. This porphyrin eliminates the possibility of an S_N2 type of mechanism. A pathway involving a double bridged intermediate, **A**, can also be eliminated since steric factors provide further evidence against a double bridged species. For example, if **A** was an important intermediate, a bulky axial ligand should inhibit the formation of **A** and result in a rate inhibition. However, when the larger ligand, pivalate, was used in place of the smaller chloride, no significant change in rate was observed.

Table 2.4. Monoanionic axial ligand comparison for eq. 23

X	T °(C)	K	k_1 (M^{-1} s^{-1})
$(CH_3)_3CCO_2$	20	0.33 ± 0.05	$(1.3 \pm 0.1) \times 10^{-2}$
Cl	22	23.5 ± 3.6	$(1.0 \pm 0.1) \times 10^{-2}$

Scheme I





A

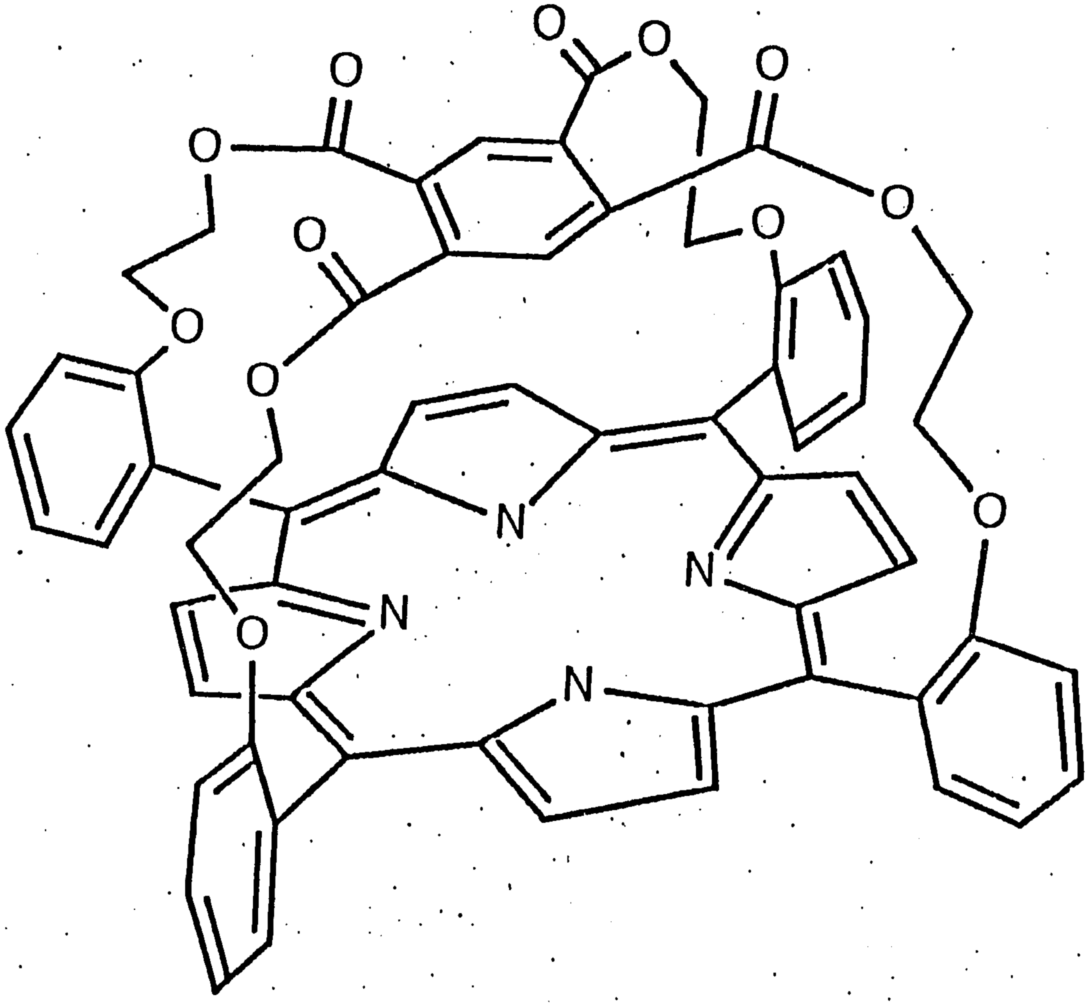


Figure 2.4. Structure of Baldwin's capped-porphyrin

Solvent effects on the rate of eq. 23 are also consistent with a pre-equilibrium dissociation of the halide from the chloromanganese(III) complex. In solvents with low dielectric constants, the rates of exchange are slow. For example, at 50 °C in $CDCl_3$ (e = 4.7) the rate constant is $k_1 = 0.15\ M^{-1}\ s^{-1}$. However, in the much more polar solvent N-methylformamide (e = 182) rate enhancement of 100-fold was observed ($k_1 = 20\ M^{-1}\ s^{-1}$ at 50 °C). This large increase in rate is in accord with formation of a cationic $[Mn(POR)]^+$ intermediate. In fact, the ionization of (TTP)MnCl in N-methylformamide was clearly evident from spectrophotometric studies, particularly from the positions of bands VI and Va. In $CHCl_3$, CH_2Cl_2, and toluene these bands appear at $\lambda_{VI} = 375$ nm and $\lambda_{Va} = 399$ nm[100]. However in N-methylformamide, these bands shift to 400 and 420 nm. The red-shift in these bands are characteristic of cationic Mn(III) porphyrin complexes.[101-103]

The mechanism proposed for the Mn≡N/Mn-Cl exchange process (eq. 23) is in stark contrast to that proposed for the irreversible heterometallic analog Mn≡N/Cr-Cl (eq. 25).[23]

$$\text{(OEP)Mn}\equiv\text{N} + \text{(TPP)Cr-Cl} \rightarrow \text{(OEP)Mn-Cl} + \text{(TTP)Cr}\equiv\text{N} \qquad (25)$$

In the latter process, Bottomley reports evidence in support of an S_N2-type mechanism. In this case, backside attack of the manganese nitrido complex is postulated to induce dissociation of the chloride ligand from Cr(III). This indicates that Mn(III) porphyrins are more labile than Cr(III) porphyrins. The same mechanism is thought to be at work when a chromium nitride was used.[24] A rationale for this can be found in the electronic structure of the two reductants. The manganese(III) complex, which has a high spin d^4 configuration, has one more electron than the high spin d^3 Cr(III) complex. Theoretical calculations[105,106] indicate that this extra electron on manganese resides in a z^2 orbital which is primarily Mn-Cl antibonding in character. Thus, the manganese chloro complex should be more labile than the chromium analog.

From chemical and mechanistic studies, it is clear that the multi-electron redox processes of nitrido manganese porphyrins illustrated here involve a transient binuclear μ-nitrido intermediate. This is in stark contrast to the iron system in which the μ-nitrido diiron porphyrin complex (e.g. $[Fe(TPP)]_2N$) is thermally stable with respect to disproportionation to nitrido iron(V) porphyrin and iron(II) porphyrin complexes. An examination of the electronic structure of μ-nitrido metalloporphyrin dimers provides a basis for understanding this difference. The d-orbital energy level diagram for $[Fe(TPP)]_2N$ shown in Figure 2.5 was derived by Tatsumi and Hoffmann using Extended Hückel calculations on $[(NH_2^-)_4Fe\text{-}N\text{-}Fe(NH_2^-)_4]^{4-}$ as a computational model for the binuclear complex.[67,68] The a_1, e_1, and b_2 levels are primarily Fe-N_{bridge} antibonding in character whereas the lowest energy e_2 and e_3 molecular orbitals are essentially Fe-N_{bridge} nonbonding interactions. This energy level diagram correctly accounts for the ground state electronic properties of the d^9 binuclear complex, $[Fe(TPP)]_2N$. Dissociation of the μ-nitrido iron dimer is strongly disfavored because it would produce a high energy species, (TPP)Fe≡N. Iron(V) nitrido porphyrin complexes have only been observed at low temperatures in an argon matrix and decompose above 150 K.[51,52] The instability of (TPP)Fe≡N has been ascribed to an electronic configuration (d^3) which necessarily contains electrons in Fe-N π^* orbitals. The iron-nitrogen stretching frequency shows the effect. The Fe≡N stretch is at 876 cm^{-1} compared to 1017 cm^{-1} for Cr≡N and 1049 cm^{-1} for Mn≡N.

To a first approximation, the energy level diagram in Figure 2.5 should apply to the (TTP)Mn≡N/(OEP)Mn system. Although it is not clear whether the d^7 μ-nitrido manganese dimer will adopt a high spin or a low spin electronic state, either case leads to the same prediction. A high spin case would involve singly-occupying the Mn-N_{bridge} a_1 and e_1 antibonding levels, resulting in a strong destabilization of the μ-nitrido species. Alternatively, a low spin state produces an electronically degenerate e_3^3 configuration. In this situation the μ-nitrido complex is destabilized by a Jahn-Teller effect. An asymmetrically bridged dimer would involve a Mn(IV) species which contains electrons in π antibonding orbitals which would weaken the bridging bonds. This effect manifests itself in the IR spectra of (POR)Mn=O where the Mn=O stretching frequency was lower than that found for Ti, V, Cr=O.[107] Thus the difference between the iron and manganese systems appears to arise largely from electronic factors.

The facility in which nitrogen atom transfer occurs between two metalloporphyrin complexes is readily understood in terms of the physical properties of the compounds involved. For example, in the three-electron Mn≡N/Mn(II) process, the oxidant (Mn≡N) is kinetically inert but contains a ligand capable of serving as a bridge. The Mn(II) porphyrin reductant has a high spin d^5 electronic configuration which confers lability to the two axial coordination sites. Furthermore, the reductant becomes inert upon oxidation. These are important criteria for establishing an atom transfer reaction.

Charges in coordination sphere can also play a key role in redox reactions. When large changes ($\geq 2\ e^-$) in oxidation state occur, drastic reorganization of the first coordination sphere is often involved (e.g., Pt(IV)-Pt(II), V(IV)-V(II), Sn(IV)-Sn(II)). However, in metalloporphyrin complexes, the

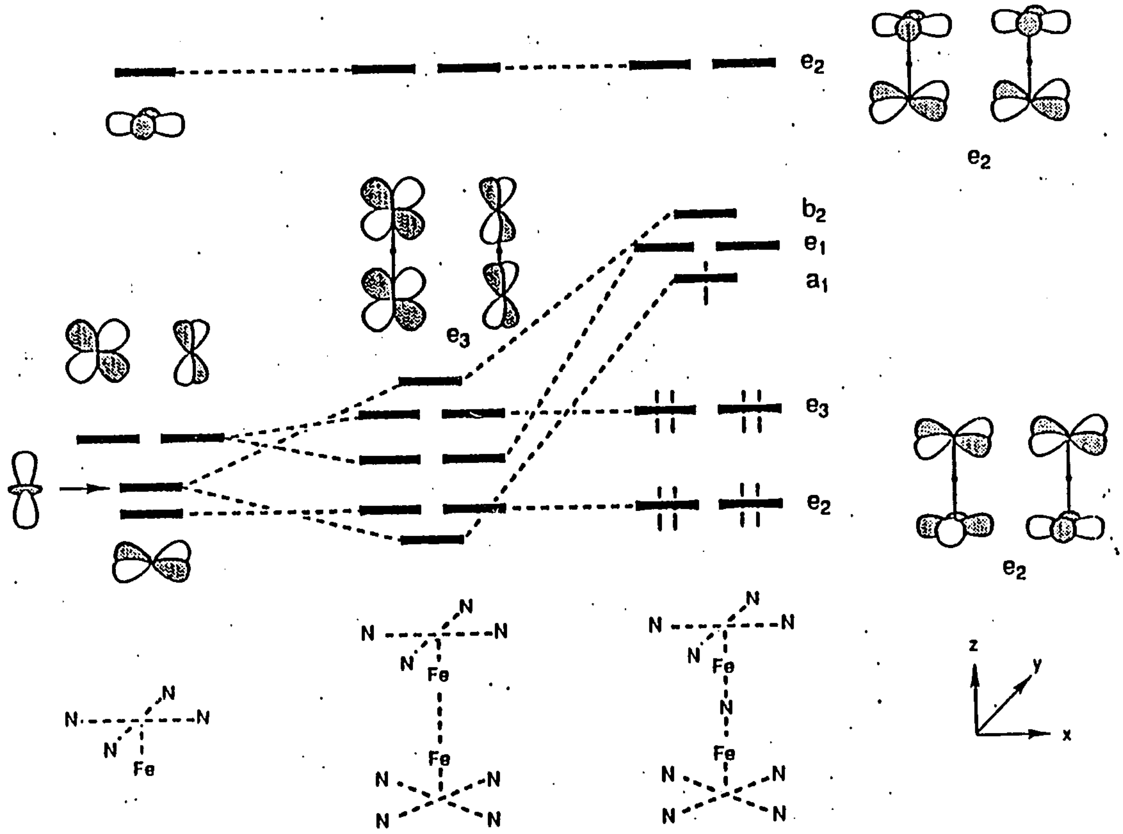


Figure 2.5. Molecular orbital diagram for $[(NH_2^-)_4Fe\text{-}N\text{-}Fe(NH_2^-)_4]^{4-}$

planar aromatic nature of the porphyrin ligand can greatly attenuate structural changes. In general, only modest changes in M-$N_{pyrrole}$ distances are observed. The greatest structural change typically involves displacement of the metal out of the N_4-porphyrin plane. When the complex is five-coordinate, this displacement is always towards the axial ligand. Metrical parameters for some of the manganese porphyrin complexes are listed in Table 2.5.

It is clear from Table 2.5 that the inner sphere reorganization energies for nitrogen atom transfer between metalloporphyrins are likely to be small. For the three-electron process, eq. 22, the ensuing change in the Mn-$N_{pyrrole}$ distance is on the order of 0.07 Å. The greatest structural change involves a Mn out-of-plane displacement of 0.11 Å. The nitrogen atom transfer reaction of (POR)Mn≡N with (POR)Mn(II) thus involves an economy of motion in which the bridging nitrogen moves from Mn(V) to Mn(II) without requiring any other significant nuclear motion.

Concluding remarks

A number of significant results have evolved from this study. Of primary importance was the demonstration that a terminally bound nitrido ligand can serve as a good bridging species in electron transfer processes. Furthermore, it was possible to vary the number of redox equivalents exchanged in

Table 2.5. Structural comparison (Å) of manganese porphyrins

	Mn-$N^{a}_{pyrrole}$	Mn-Ct[b]	Mn-X
Mn(TPP)[c]	2.090(9)	0.28	--
Cl-Mn(TPP)[d]	2.008(7)	0.27	2.363(3)
N≡Mn(T*p*-MPP)[e]	2.021(2)	0.388	1.512(2)
[(H$_2$O)Mn(TPP)]SbF$_6$[f]	1.995(4)	0.19	2.105(4)
[(H$_2$O)$_2$Mn(TPP)]ClO$_4$[f]	2.004(2)	0	2.271(2)

[a] Average Mn-N distance

[b] Displacement out of the N_4 porphyrin plane.

[c] Gonzalez, B.; Kouba, J.; Yee, S.; Reed, C. A.; Kirner, J. F.; Scheidt, W. R. *J. Am. Chem. Soc.* **1975**, *97*, 3247.

[d] Tulinsky, A.; Chen, B. M. L. *J. Am. Chem. Soc.* **1977**, *99*, 3647.

[e] TpMPP is 5,10,15,20-tetrakis(*p*-methoxylphenyl) porphyrin. Hill, C. L.; Hollander, F. J. *J. Am.Chem. Soc.* **1982**, *104*, 7318.

[f] Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 4155.

an atom transfer process by choosing an appropriate substrate. In the reactions examined here, nitrogen atom transfer can mediate both three- and two-electron processes. When given a choice of potential bridging ligands (e.g. N vs Cl or pivalate) the multi-electron processes studied here preferentially selects the multiply-bonded ligand. It is thus clear that, in utilizing what have long been considered to be thermodynamically robust metal-nitrido complexes, consideration must be given to the lability of these systems.

CHAPTER 3

OXYGEN ATOM TRANSFER OF CHROMIUM PORPHYRINS

Introduction

Many oxygen-transfer reactions are important in synthetic and biological oxidations. Enzymes such as cytochrome P-450, peroxidases, catalases, xanthine oxidase, sulfite oxidase, and nitrate reductase operate via atom-transfer processes in the course of oxidizing an organic substrate.[107-111] Holm[36] and Jorgensen[112] have reviewed the subject of oxygen transfer in two separate reviews. Most of the examples of oxygen transfer occur between a metal oxo donor and non-metal oxo acceptors such as alkenes and phosphines. Examples of inter-metal oxygen atom-transfer are much less common. Typically, reactions of a metal oxo complex with transition metal reducing agents yield μ-oxo bridged products. This process has been termed by Holm as incomplete atom transfer (eq. 1).[36] When the oxo ligand was completely cleaved from the donor species the process was termed complete atom transfer (eq. 2) where M is an oxo donor and X is an oxo acceptor. Complete inter-metal oxo transfer thus far is quite rare and examples

$$M{=}O + X \rightarrow M{-}O{-}X \qquad (1)$$

$$M{=}O + X \rightarrow M + O{=}X \qquad (2)$$

have been limited to molybdenum,[36] tungsten,[36,113] and vanadium[37] complexes. Oxo transfer between two ruthenium centers has been implicated in the aerobic epoxidation of alkenes by ruthenium porphyrins.[114]

There are several possibilities that can occur upon reaction of an oxo complex with another metal. The possibilities are given in equations 3-7 below.

$$L_nM^x{=}O\!: + M^yL_m \rightarrow L_nM^x{=}O\!:\!\rightarrow M^yL_m + L \qquad (3)$$

$$L_nM^x{=}O\!: + M^yL_m \rightarrow L_nM^{x-1} + \,:\!O{=}M^{y+1}L_m \qquad (4)$$

$$L_nM^x{=}O\!: + M^yL_m \rightarrow L_nM^{x-1}\text{-}O\text{-}M^{y+1}L_m \qquad (5)$$

$$L_nM^x{=}O\!: + M^yL_m \rightarrow L_nM^{x-2} + \,:\!O{=}M^{y+2}L_m \qquad (6)$$

$$L_nM^x{=}O\!: + M^yL_m \rightarrow L_nM^{x} + \,:\!O{=}M^{y}L_m \qquad (7)$$

Equation 3 involves the formation of an adduct in which no redox reaction occurs. Several examples of this type have been demonstrated using organometallic compounds with a terminal oxide (eq.8).[115] Equations 4 and 5 are one electron-

$$(C_5H_5)_2M{=}O + [M'(PPh_3)_2(CO)(CH_3CN)]^+ \rightarrow$$
$$[(C_5H_5)_2M{=}O\rightarrow M'(PPh_3)_2(CO)]^+ \qquad M = \text{Mo, W and } M' = \text{Rh, Ir} \qquad (8)$$

transfer processes. Vanadium complexes have been used to demonstrate complete inter-metal one-electron atom transfer (eq. 4). When $V(O)_2Cl_2^-$ was treated with $VCl_4(CH_3CN)_2^-$ an oxygen atom was transferred from the dioxo complex resulting in the formation of two $V(O)Cl_4^{2-}$(eq 9).[37] Molybdenum

$$V(O)_2Cl_2^- + VCl_4(CH_3CN)_2^- + 2\ Cl^- \rightarrow 2\ V(O)Cl_4^{2-} + 2\ CH_3CN \qquad (9)$$

diethyldithiocarbamate oxo complexes have been used to demonstrate incomplete atom transfer (eq. 5). where a net one-electron occurs (eq. 10). Holm has shown that oxygen atom

$$L_2Mo(O)_2 + L_2Mo(O) \rightarrow L_2Mo(O)\text{-}O\text{-}(O)MoL_2 \qquad (10)$$

transfer between molybdenum(IV) and molybdenum(VI) mediates two-electron transfer for a variety of complexes.[36] An example is given in eq. 11 (L-NS = 2,6-bis(2,2-diphenyl-2-thioethyl)-pyridinate(2^-) and ssp = 2-(salicylideneamino) benzenethiolate(2^-). Templeton has also used inter-metal

$$MoO_2(L\text{-}NS_2) + MoO(ssp)(DMF) \rightleftharpoons$$
$$MoO(L\text{-}NS_2)(DMF) + MoO_2(ssp)(DMF) \qquad (11)$$

oxygen atom transfer reactions in the preparation of a series oxo-tungsten(IV)-acetylene complexes (eq 12).[113]

$$W(CO)(HC{\equiv}CH)(S_2CN(C_2H_5)_2)_2 + Mo_2O_3(S_2P(OC_2H_5)_2)_4$$
$$\rightarrow O{=}W(HC{\equiv}CH)(S_2CN(C_2H_5)_2)_2 + 2\ Mo(O)(S_2P(OC_2H_5)_2)_2 + CO \qquad (12)$$

Equation 7 results in an oxygen-transfer with no net electron transfer. This has been demonstrated in this group using titanium porphyrins (eq 13).[25]

$$(TTP)TiCl_2 + (OEP)Ti{=}O \rightarrow (OEP)TiCl_2 + (TTP)Ti{=}0 \qquad (13)$$

Monatomic bridges such as oxide are particularly versatile in terms of being able to mediate one- and two-electron processes. Although much is known about how the nature of the bridging group affects the rate of inner-sphere electron transfer, it is not well understood how the bridging group influences the number of electrons involved in the redox process. In the work presented here, we focus on oxygen atom transfer reactions of metalloporphyrin complexes.

Metalloporphyrins are important in oxygen chemistry of biological systems. In nature, iron oxo porphyrins are suggested by current evidence as the active species in the enzymes cytochrome P-450, catalases, and peroxidases.[106-110] Cytochrome P-450 is known to oxidize alkenes and alkanes. Synthetic porphyrins of several metals have been used as spectroscopic and reactivity models for these enzymes.[116,117]

Many have also been used to catalyze oxidation reactions. A tremendous amount of effort has been put into the development of the models and the preparation of more efficient and selective catalysts. In the following pages, a review of monomeric metalloporphyrins with at least one terminal oxo ligand will be presented. Preparative methods will be presented first, followed by the techniques of characterization. Some representative reactions are also included.

Titanium oxo porphyrins were prepared by treating the free-base porphyrin, $(POR)H_2$, with titanium tetrachloride in refluxing N,N-dimethylformamide in air (eq. 14).[118] Alternatively, free-base porphyrin can be treated with diphenyltitanium in refluxing mesitylene or triethylbenzene in air (eq 15).[119,120] These compound have been characterized by

$$TiCl_4 + (POR)H_2 \rightarrow (POR)Ti{=}O \tag{14}$$

$$Ti(C_6H_5)_2 + (POR)H_2 \rightarrow (POR)Ti{=}O \tag{15}$$

UV-vis,[118-120] NMR,[118] and IR[118,120] spectroscopies, mass spectrometry,[118] elemental analysis.[118,120] Electrochemical studies reveal a redox chemistry that was based on the porphyrin ligand and not the metal center.[118,121] A porphodimethene titanium oxo can be prepared by chemical reduction (eq. 16) of (OEP)Ti=O followed by treatment of the dianion with methyl iodide (eq. 17).[122,123]

$$(OEP)Ti{=}O + 2\ NaC_{10}H_{14} \rightarrow [(OEP)Ti{=}O]^{2-} \qquad (16)$$

$$[(OEP)Ti{=}O]^{2-} + CH_3I \rightarrow (OEP(CH_3)_2)Ti{=}O + 2\ I^- \qquad (17)$$

Crystal structures have been determined for this complex and (OEP)Ti=O.[124] A list of structurally characterized metalloporphyrin oxo complexes can be found in Table 3.7 at the end of the chapter.

Treatment of (POR)Ti=O with hydrogen peroxide or benzoyl peroxide resulted in the formation of the titanium peroxo complex (eq. 18).[124,125] The dichloro and difluoro titanium porphyrins were synthesized from the oxo by treatment with oxalyl chloride (eq. 19) and hydrogen fluoride (eq. 20) respectively.[126]

$$(POR)Ti{=}O + H_2O_2 \rightarrow (POR)Ti(O_2) \qquad (18)$$

$$(POR)Ti{=}O + C_2O_2Cl_2 \rightarrow (POR)TiCl_2 \qquad (19)$$

$$(POR)Ti{=}O + 2\ HF \rightarrow (POR)TiF_2 \qquad (20)$$

Synthesis of vanadyl (V=O) porphyrins involved treating vanadyl sulfate[127] or vanadium(III) chloride[128] with the porphyrin in refluxing DMF (eq. 21) or heating $V(CO)_6$ with porphyrin in n-decane[120] in air (eq 22). UV-vis,[120,127,128] IR,[128] EPR, ENDOR,[129] and resonance Raman[130] spectroscopies as well as

$$V(O)SO_4 + (POR)H_2 \rightarrow (POR)V{=}O \tag{21}$$

$$V(CO)_6 + (POR)H_2 \rightarrow (POR)V{=}O \tag{22}$$

mass spectrometry[128] and elemental analysis[127] have been used to characterize the vanadyl porphyrins. Electrochemical studies indicate that in the redox chemistry of vanadyl porphyrins was confined to the porphyrin ligand.[131,132] Three vanadyl porphyrins have been crystallographically characterized.[133-135] The dichloro and dibromo vanadium porphyrin can be prepared by treatment of the oxo with oxalyl or sulfonyl halide (eqs. 23, 24, X = Cl, Br).[136]

$$(POR)V{=}O + C_2O_2X_2 \rightarrow (POR)VX_2 \tag{23}$$

$$(POR)V{=}O + SOX_2 \rightarrow (POR)VX_2 \tag{24}$$

A study of base binding to the vanadyl group has also been done by Walker.[137]

Niobium oxo porphyrins were prepared from the trioxoniobium porphyrin dimer by treatment with H-X where X =

acetate or fluoride (eq. 25).[138-141] UV-vis,[140,141] NMR,[138,139,141] and

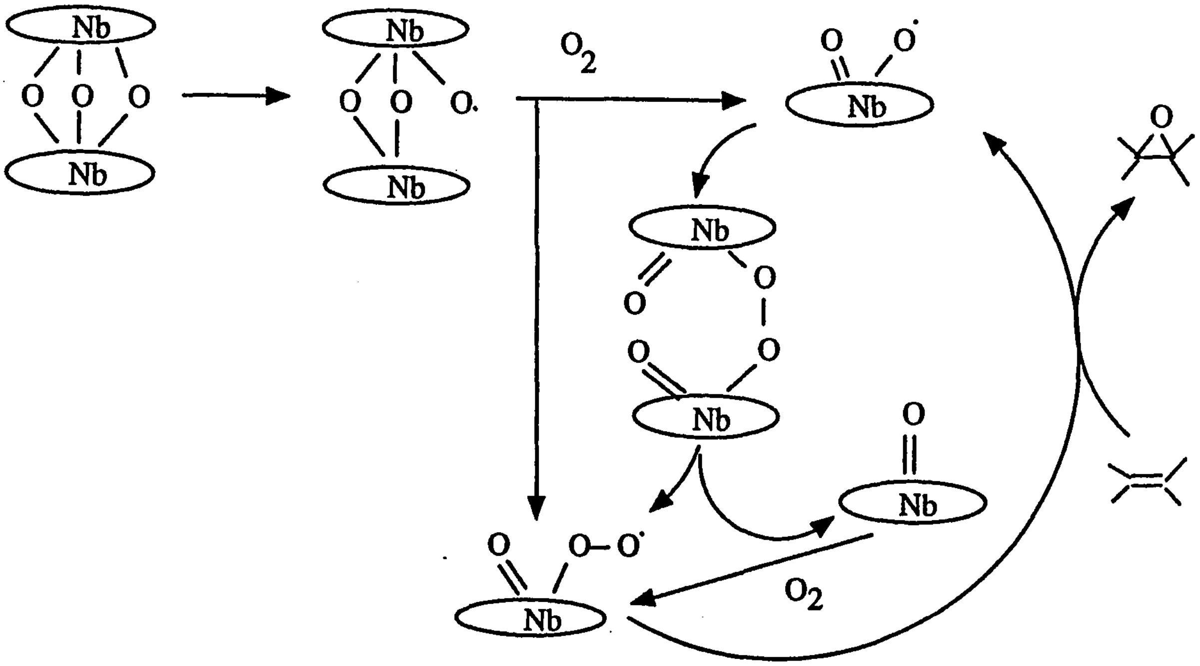
$$[(POR)NbO]_2O + 2\ HX \rightarrow 2\ (POR)Nb(O)X + H_2O \qquad (25)$$

IR[139-141] spectroscopies, mass spectrometry,[139,141] and elemental analysis[138,139,141] have been used to characterize these compounds. Three crystal structure determinations have been done.[138,139,142] Electrochemical studies for these Nb(V) complexes reveal that the first reduction takes place on the metal followed by two reductions on the porphyrin. Oxidation of (POR)Nb(O)X has been shown to take place on the porphyrin ligand.[140,141,143] Chemical reduction of a niobium(V) oxo with zinc amalgam resulted in formation of an isolable Nb(IV)porphyrin oxo complex (eq 26).[140] This complex has been

$$(POR)Nb(O)X + Zn/Hg \rightarrow (POR)Nb{=}O \qquad (26)$$

characterized by UV-vis, IR, and EPR spectroscopy. Electrochemical studies show two porphyrin based oxidations and reductions.[140] A very interesting photochemical cleavage of $\{(POR)Nb\}_2O_3$ takes place in the presence oxygen to yield terminal oxo complexes with oxygen radical ligands.[144,145] The radicals have been characterized by EPR and have been shown to epoxidize alkenes (Scheme I). Pyridine binding studies have been done on the Nb(V) terminal oxo complexes.[141]

Scheme I



Several oxo porphyrins of molybdenum in different oxidation states have been prepared. A dioxo molybdenum(VI) complex was prepared by photolysis of a diperoxo molybdenum porphyrin (eq. 27).[146] This compound has been characterized by

$$(POR)Mo(O_2)_2 \rightarrow (POR)Mo(O)_2 + O_2 \qquad (27)$$

UV-vis, NMR, and IR spectroscopies, mass spectrometry, and elemental analysis.[146] The IR spectra revealed that the two oxo ligands are in a cis orientation. This was later confirmed by an X-ray diffraction study.[147] The dioxo readily loses one oxygen when treated with triphenylphosphine resulting in the formation of the molybdenum(IV) oxo complex and the phosphine oxide (eq. 28).[146]

$$(POR)Mo(O)_2 + Ph_3P \rightarrow (POR)Mo(O) + Ph_3P{=}O \qquad (28)$$

Several preparations of oxo molybdenum(V) porphyrins have been demonstrated. Molybdenum hexacarbonyl was used to insert molybdenum into a porphyrin in refluxing decaline followed by treatment with HCl to yield (POR)Mo(O)Cl (eq. 29).[148,149] When free-base porphyrin was treated with molybdenum dichloride[150] in refluxing benzonitrile (eq. 30) or with molybdenum oxide trichloride[151] in refluxing mesitylene, (eq. 31) the same

$$Mo(CO)_6 + (POR)H_2 \rightarrow (POR)Mo(O)Cl \qquad (29)$$

$$MoCl_2 + (POR)H_2 \rightarrow (POR)Mo(O)Cl \qquad (30)$$

$$Mo(O)Cl_3 + (POR)H_2 \rightarrow (POR)Mo(O)Cl \qquad (31)$$

product can be prepared. Cleavage of the u-oxo dimer of molybdenum(V) with H-X, where X = fluoride, methoxide, or phenoxide, results in the formation of a monomeric oxo species (eq 32).[152] The various molybdenum(V) complexes have been

$$[(POR)Mo(O)]_2O + 2\ HX \rightarrow 2\ (POR)Mo(O)X + H_2O \qquad (32)$$

studied by UV-vis,[148-150,152,153] IR,[148,150,152] resonance Raman,[154] and EPR[148] spectroscopies, mass spectrometry,[150] and magnetic susceptibility.[148,149] A crystal structure has been reported for (TPP)Mo(O)Cl.[149]

Molybdenum(V) oxo complexes were chemically reduced with zinc amalgam or photochemically reduced to provide the molybdenum(IV)porphyrin oxo complex(eq. 33).[151] The

$$(POR)Mo(O)X + Zn/Hg \rightarrow (POR)Mo{=}O \qquad (33)$$

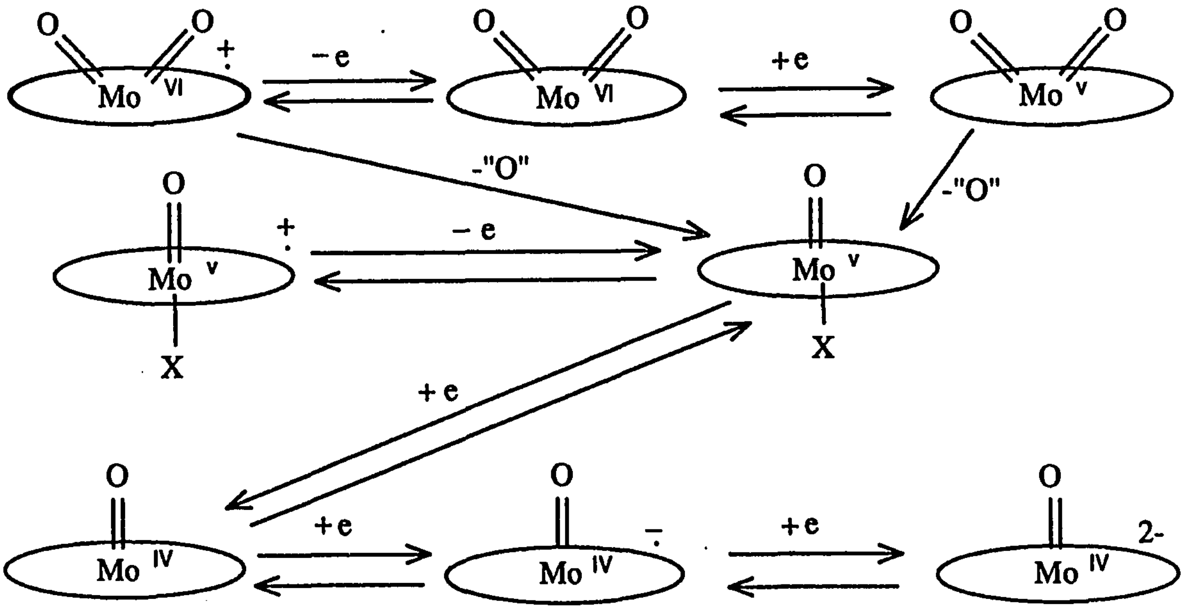
epoxidation of alkenes with tertiary-butyl hydroperoxide was catalyzed with (TPP)Mo(O)X.[156]

Molybdenum(IV)oxo[147,151,155] complexes have been characterized by UV-vis, IR, and NMR spectroscopies, mass spectrometry, and elemental analysis.[151] An X-ray structure of (TTP)Mo=O has been determined.[151] Treating the mono-oxo complex with hydrogen chloride gas under nitrogen in benzene resulted in the formation of the dichloride complex (eq 34).

$$(POR)Mo{=}O + 2\ HCl \rightarrow (POR)MoCl_2 + H_2O \qquad (34)$$

Electrochemical characterization of the molybdenum oxo complexes has been achieved. The dioxo complex can be oxidized to form a porphyrin radical cation. Reduction, however, occurs at the metal center to yield a Mo(V), then a Mo(IV) complex. Starting with a Mo(V) compound, an oxidation occurs on the porphyrin ligand while reduction occurs on the metal. The resulting Mo(IV) can be oxidized back to the Mo(V). Two reductions on the Mo(IV) complex involve the porphyrin ligand and not the metal. The electrochemical pathways are shown in Scheme II.[157]

Scheme II



Tungsten oxo porphyrins have been synthesized by treating H_2WO_4 (eq. 35) or $K_3W_2Cl_9$ and $SnCl_2$ (eq. 36)[150] with porphyrin in

$$H_2WO_4 + (POR)H_2 \rightarrow (POR)W(O)OPh \qquad (35)$$

$$K_3W_2Cl_9 + SnCl_2 + (POR)H_2 \rightarrow (POR)W(O)OPh \qquad (36)$$

refluxing phenol or benzonitrile. Alternatively $W(CO)_6$ can be used to insert tungsten into free porphyrin by heating in refluxing DMF/octane followed by treatment with hydrochloric acid (eq.37).[159] The resulting products were characterized by

$$W(CO)_6 + (POR)H_2 \rightarrow HCl \rightarrow (POR)W(O)Cl \qquad (37)$$

UV-vis,[150,152,158,159] IR,[150,152,158,159] and NMR[159] spectroscopies, mass spectrometry,[152,158] elemental analysis,[152,158,159] and magnetic susceptibility.[152,158] An electrochemical study reveals that a one electron reduction of the metal was possible.[160] The ligand trans to the oxo ligand were exchanged using H-X[150,152,158] X = F, CH_3CO_2, OC_6H_5, or OCH_3. Treatment of (POR)W(O)Cl with hexachlorodisilane followed by treatment with anhydrous hydrogen chloride yields the reduced $(POR)WCl_2$ (eq. 38).[159] An

$$(POR)W(O)Cl + Si_2Cl_6 + HCl \rightarrow (POR)WCl_2 \qquad (38)$$

unstable cis-dioxo tungsten complex which slowly demetallated, was prepared from the oxo peroxo complex by treatment with triphenylphosphine (eq. 39).[161]

$$(TPP)W(O)(O_2) + PPh_3 \rightarrow (TPP)W(O)_2 + Ph_3P{=}O \qquad (39)$$

A similar synthesis of rhenium oxo porphyrins was achieved by treating Re_2O_7 with porphyrin in refluxing phenol (eq. 40).[150,152,158] This compound has been characterized

$$Re_2O_7 + (POR)H_2 \rightarrow (POR)Re(O)OPh \qquad (40)$$

by UV-vis,[150,152,158] IR,[150,152,158] and NMR[152,158] spectroscopies, mass spectrometry,[152,158] and elemental analysis.[150,152] No reactivity studies have been undertaken.

Ruthenium porphyrin dioxo complexes were prepared by oxidizing a corresponding carbonyl complex with *meta*-chloroperoxobenzoic acid, *m*-CPBA, iodosobenzene, PhIO, or molecular oxygen (eq. 41).[9,114,162-165] However, one must use

$$(POR)Ru(CO) + m\text{-CPBA} \rightarrow (POR)Ru(O)_2 \qquad (41)$$

either a sterically encumbered porphyrin or use an alcohol solvent to prevent the formation of a u-oxo complex. UV-vis,[9,114,162,163,165] IR,[9,162-164] NMR,[9,163,164] and resonance Ramam[165] spectroscopies, elemental analysis,[9,164] and magnetic susceptibility[164] have been used to characterize these compounds. The IR and Raman studies show that the stereochemistry of the oxo ligands was trans. An electrochemical study showed a metal-based reduction and a ligand based oxidation.[9] The ruthenium dioxo has been reduced using three equivalents of triphenylphosphine[163] or trimethylphosphite[9] to yield the Ru(II) phosphine or bis-phosphite complex (eq. 42, 43).[163] Using (TMP)Ru(O)$_2$ and one

$$\text{(TMP)Ru(O)}_2 + 3\ \text{Ph}_3\text{P} \rightarrow \text{(TMP)Ru(II)PPh}_3 + 2\ \text{Ph}_3\text{P=O} \qquad (42)$$

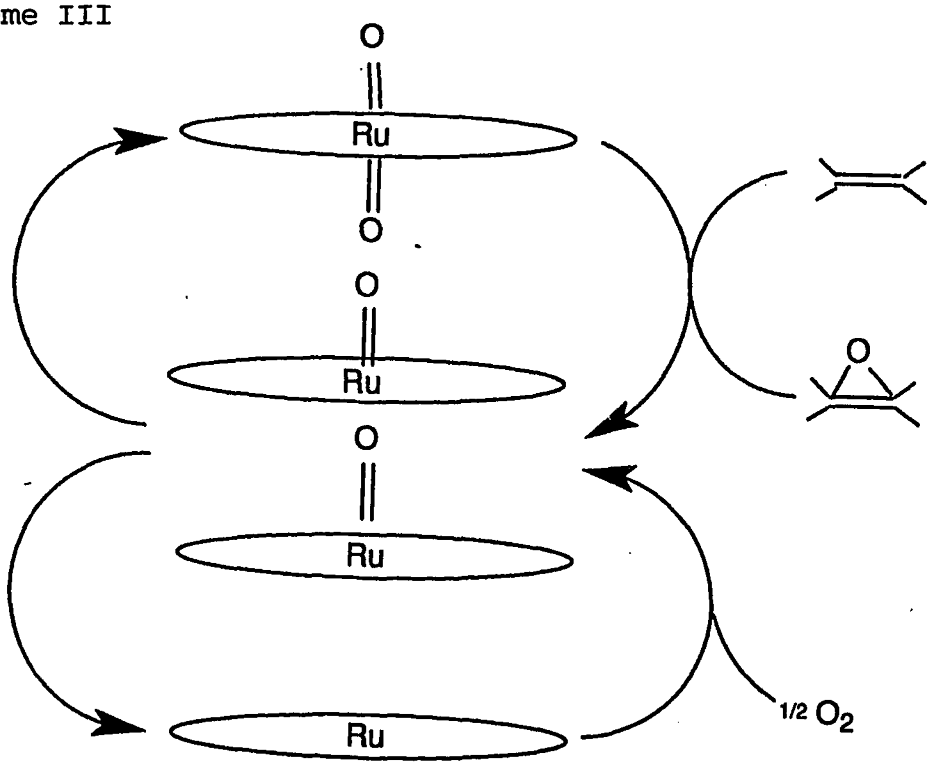
$$\text{(TMP)Ru(O)}_2 + 4\ (\text{CH}_3\text{O})_3\text{P}$$
$$\rightarrow \text{(TMP)Ru(II)(P(OCH}_3)_3)_2 + 2\ (\text{CH}_3\text{O})_3\text{P=O} \qquad (43)$$

equivalent of triphenylphosphine, a mono oxo ruthenium porphyrin was formed (eq. 44).[163] The dioxo compounds have

$$\text{(TMP)Ru(O)}_2 + \text{Ph}_3\text{P} \rightarrow \text{(TMP)Ru=O} + \text{Ph}_3\text{P=O} \qquad (44)$$

been used to epoxidize alkenes with subsequent formation of a μ-oxo ruthenium dimer.[164] (TMP)Ru(O)$_2$ can be used for epoxidation of alkenes.[166] An example of catalytic aerobic epoxidation has been demonstrated by Groves[114] (Scheme III). Ruthenium(IV)(OEP) radical cation oxo complexes have been prepared by treating (OEP)Ru(PPh$_3$)Br with iodosobenzene (eq. 45).[167,168] This oxo species has been characterized with UV-vis

Scheme III



$(OEP)Ru(III)(PPh_3)Br + PhIO \rightarrow (OEP^{+\cdot})Ru(IV)(O)Br$ (45)

and EPR spectroscopies.[167,168] Treating the radical cation porphyrinatoruthenium oxide with triphenylphosphine yielded triphenylphosphine oxide and a ruthenium(IV)porphyrin μ-oxo dimer (eq. 46).[168] Alkenes were catalytically oxidized with

$2\ (OEP^{+\cdot})Ru(IV)(O)Br + Ph_3P \rightarrow [BrRu(OEP)]_2O + Ph_3P{=}O$ (46)

iodosobenzene using $(OEP^{+\cdot})Ru(IV){=}O$ as the catalyst.[167,168] The high valent radical cation species was reduced by one electron to form $(OEP)Ru{=}O$ (eq. 47).

$$(OEP^{+\cdot})Ru(IV)(O)Br \rightarrow (OEP)Ru(IV)(O) + Br^{\cdot} \qquad (47)$$

In addition to using the aforementioned reactions (eqs. 44, 47), a ruthenium(IV)porphyrin oxo complex was prepared by using limiting amounts of molecular oxygen.[163] The mono-oxo complex has been characterized by UV-vis,[163,164] IR,[163,164] NMR,[163,164] and resonance Raman[165] spectroscopies, magnetic susceptibility,[163,164] and elemental analysis.[164] A metal based reduction was achieved electrochemically (eq. 48). The

$$(OEP)Ru(IV)(O)(ROH) + e^{-} \rightarrow [(OEP)Ru(III)(O)(ROH)]^{-} \qquad (48)$$

alcohol adduct of (OEP)Ru=O in dichloromethane:pyridine solution epoxidized alkenes. It also exchanged oxygen with water readily but then formed the μ-oxo dimer.[164]

Osmium also formed dioxo complexes. (POR)Os(CO)py was oxidized with hydrogen peroxide, tertiary-butyl hydroperoxide, or *m*-CPBA which gave (POR)Os$(O)_2$ (eq. 49).[68-70] These dioxo

$$(POR)Os(CO)py + 2\ mCPBA \rightarrow (POR)Os(O)_2 \qquad (49)$$

complexes have been studied by UV-vis,[10,169,170] NMR,[10,169-171] and IR[10,169-171] spectroscopies, and elemental analysis.[169-171] A crystal structure has been determined for (TTP)Os$(O)_2$ which showed the trans stereochemistry of the oxo ligands.[170]

Luminescence spectra of the dioxo complexes have also been studied.[171,172] They have also been used to examine the cis and trans substituent effects of oxo ligands.[173] Iterative Extended Hückel calculations have been done on these dioxo compounds as part of a study of π bonding axial ligands and the effect on the UV-vis spectrum.[171] Several reduction reactions have been demonstrated on $(POR)Os(O)_2$. Treating the dioxo complex with tin dichloride,[10] triphenylphosphine,[169] or ascorbic acid[170,174] in alcohol formed the dialkoxide (eq. 50).

$$(POR)Os(O)_2 + 2\ Ph_3P + 2\ ROH \rightarrow (POR)Os(OR)_2 + 2\ Ph_3PO \qquad (50)$$

Reduction of $(OEP)Os(O)_2$ with hydrazine or ascorbic acid in dichloromethane in the presence of phenylthiol or bromine yielded the (POR)Os(IV) dithiolate and dibromide respectively (eq. 51, 52).[174] Reduction of $(OEP)Os(O)_2$ with hydrazine in

$$\begin{aligned} &2\ (POR)Os(O)_2 + N_2H_4 + 4\ PhSH \rightarrow \\ &\quad 2\ (POR)Os(SPh)_2 + N_2 + 4\ H_2O \qquad (51) \end{aligned}$$

$$(POR)Os(O)_2 + N_2H_4 + Br_2 \rightarrow (POR)OsBr_2 + N_2 + 2\ H_2O \qquad (52)$$

tetrahydrofuran resulted in the preparation of the osmium(II) dinitrogen complex $(OEP)Os(N_2)(THF)$ (eq. 53).[175] Treating

$$(OEP)Os(O)_2 + N_2H_4 + THF \rightarrow (OEP)Os(II)N_2(THF) + 2\ H_2O \qquad (53)$$

$(OEP)Os(O)_2$ with triphenylphosphine in dichloromethane produced a bis-triphenylphosphine oxide adduct which has been crystallographically characterized. If excess triphenylphosphine was present the phosphine substituted for the phosphine oxide (eqs. 54, 55). If benzene was used in

$$(OEP)Os(O)_2 + 2\ Ph_3P \rightarrow (OEP)Os(II)(OPPh_3)_2 \qquad (54)$$

$$(OEP)Os(II)(OPPh_3)_2 + 2\ Ph_3P \rightarrow (OEP)Os(II)(PPh_3)_2 \qquad (55)$$

place of dichloromethane only the bis-phosphine adduct was observed. $(TTP)Os(O)_2$ only formed the bis-phosphine adduct under similar conditions. No reaction with cyclohexene, norbornene, or benzyl alcohol has been observed.[176]

A porphyrinatoosmium(V) oxo complex was presumed to be formed from treatment of $(POR)Os(PBu_3)Br$ with iodosobenzene. This complex is thought to be the reactive species in the catalytic epoxidation of alkenes.[177]

High-valent manganese oxo porphyrins have been prepared by oxidation of manganese(III)porphyrins. Treatment of (TPP)MnCl with iodosobenzene at -78 °C resulted in the formation of a manganese(V) oxo complex which has been characterized by UV-vis spectroscopy and magnetic susceptibility measurements (eq. 56).[14] This complex exchanged

$$(TPP)MnCl + PhIO \rightarrow (TPP)Mn(V)(O)Cl \qquad (56)$$

oxygen with water indicating that an oxo complex rather than an iodosobenzene adduct was formed. When (TMP)MnCl was treated with sodium hypochlorite at -80 °C a different complex was formed (eq. 57).[178] Two key differences between these two

$$\text{(TMP)MnCl} + \text{NaOCl} \rightarrow \text{(TMP)Mn(IV)(OCl)}^{+} \qquad (57)$$

oxidized products were the magnetic susceptibility, 2.9 μ_B (eq. 56) and 4.0 μ_B (eq. 57) and the lack of oxygen exchange with water. It appeared that the hypochlorite-derived complex was better described as a manganese(IV) species of some kind. This complex has also been studied by UV-vis and IR[178] spectroscopies as well as EXAFS and XANES.[82] Reduction of this compound by two electrons reformed the starting manganese(III) complex.

A wide variety of reagents have been used to form high-valent manganese complexes that oxidize a variety of substrates. Among the oxidants used were sodium hypochlorite,[178,179] oxygen and sodium borohydride[180] or ascorbic acid,[181] iodosobenzene,[14,182] *m*-CPBA and related salts,[183] *p*-cyanodimethylaniline,[184] hydrogen peroxide,[185] periodate, or perchlorate.[186] Alkenes,[82,178,180-183,185,186] alcohols,[179] nitrosoalkanes,[186] and phosphines[178] have all been oxidized using these manganese systems. Mechanistic studies have been undertaken by Groves,[14] Collman,[188,189] Bruice,[184,190,191] and Miyamoto.[192]

Manganese(IV) porphyrins have also been prepared recently by the oxidation of (TMP)MnCl with *m*-CPBA in methanol in the presence of tetramethylammonium hydroxide, TBAOH,[12] by decomposition of a manganese(III) peroxycarbonate,[193] or by the photochemical reaction of nitrate and nitrite with (TTP)Mn(III) (eq. 58-60).[194] The resulting oxo complexes have

$$\text{(POR)Mn-X} + m\text{-CPBA} + \text{TBAOH} \rightarrow \text{O=Mn(IV)(POR)} \qquad (58)$$

$$\text{(POR)Mn-}O_2CO_2 \rightarrow \text{O=Mn(IV)Mn(POR)} + CO_3^{-\cdot} \qquad (59)$$

$$\text{(POR)Mn-}NO_3 \rightarrow \text{(POR)Mn=O} \qquad (60)$$

been studied by UV-vis,[106,193] EPR,[106,193] ^2H[12,99,195] and ^1H[12,195] NMR, IR,[106,195] and resonance Raman[106] spectroscopies, and mass spectrometry.[195] The manganese(IV) oxo complex reacted with additional hydroxide to form a six coordinate anion (eq. 61).[195] The Mn=O stretch drops from 754 cm^{-1} to 712 cm^{-1} upon

$$\text{(POR)Mn=O} + OH^- \rightarrow [\text{(POR)Mn(O)OH}]^- \qquad (61)$$

coordination of the hydroxide. When (POR)Mn=O was treated with triphenylphosphine, the phosphine oxide was produced along with a Mn(II)porphyrin (eq. 62). Alkenes were

$$(POR)Mn{=}O + Ph_3P \rightarrow (POR)Mn(II) + Ph_3PO \qquad (62)$$

epoxidized under anaerobic and aerobic conditions using the manganese(IV)porphyrin oxide.[12,195]

High-valent iron porphyrins are of extreme interest as models for iron porphyrin containing enzymes. The first characterized iron(IV) oxo was prepared by treating an iron peroxide dimer with bases such as N-methylimidazole, pyridine, or piperidine at -80 °C (eq. 63).[196] The product was stable

$$[(POR)Fe]_2O_2 + 2\ py \rightarrow 2\ py(POR)Fe(IV)(O) \qquad (63)$$

indefinitely below -30 °C, but forms the ubiquitous μ-oxo dimer at higher temperatures. Laser irradiation of $(TPP)Fe\text{-}O_2$ at 15 K during a resonance Raman study unexpectedly also yields the iron(IV) oxo complex (eq. 64).[197,198] The iron(IV)

$$(TPP)Fe\text{-}O_2 \rightarrow (TPP)Fe{=}O + \tfrac{1}{2}\ O_2 \qquad (64)$$

oxo complex was generated electrochemically from the iron(III) hydroxide using the sterically demanding tetramesitylporphyrin (eq. 65).[199,200] Several chemically generated iron(IV) systems

$$(TMP)Fe\text{-}OH \rightarrow (TMP)Fe{=}O + e^- + H^+ \qquad (65)$$

have also been developed. (TPP)Fe(II) was treated with N-methylmorpholine-N-oxide, NMNO, to prepare the iron(IV) oxide (eq. 66).[201] An iron(II) metallated derivative of

$$\text{(POR)Fe(II)} + \text{NMNO} \rightarrow \text{(POR)Fe=O} \qquad (66)$$

hematoporphyrin was treated with hydrogen peroxide in aqueous solution to provide an iron(IV) oxo complex that exists in water (eq. 67).[202] Weiss[203] has prepared the ferryl porphyrin

$$\text{(POR)Fe(II)} + H_2O_2 \rightarrow \text{(POR)Fe=O} + H_2O \qquad (67)$$

from the iron(III) chloride complex of *tetra*(2,6-diclorophenylporphyrin), Cl_8TPP, by oxidation with *m*-CPBA (eq. 68). These complexes have been studied by a variety of

$$(Cl_8TPP)\text{Fe-Cl} + m\text{-CPBA} \rightarrow (Cl_8TPP)\text{Fe=O} \qquad (68)$$

techniques. These include UV-vis,[196,198,200,202,203] NMR,[196,198,201-203] and EPR[202] spectroscopies as well as magnetic susceptibility measurements,[196,201-203] Mössbauer[203] and resonance Raman[197,198] spectroscopies. EXAFS studies indicate that the Fe=O bond lengths range between 1.64 and 1.66 Å in these model compounds.[87,88,204] Weiss has determined that axially coordinated bases diminish the strength of the iron-oxygen bond.[203]

The isolated iron(IV) oxo complex transferred an oxygen to triphenylphosphine (eq. 69).[201,205] This reaction was also

$$\text{py(POR)Fe=O} + \text{Ph}_3\text{P} \rightarrow \text{py(POR)Fe(II)} + \text{Ph}_3\text{PO} \qquad (69)$$

done catalytically with an iron(II) porphyrin complex in the presence of a nitrogen base using molecular oxygen to form the ferryl species as the active oxidant. An oxo bridged complex has been prepared treating a copper(I) macrocycle with the iron(IV) oxo complex (eq. 70).[206] The resulting dimer consisted of iron(III) and copper(II) metal centers.

$$\text{(TPP)Fe(IV)(O)} + \text{LCu(I)} \rightarrow \text{(TPP)Fe(III)-O-Cu(II)L} \qquad (70)$$

An iron(IV) porphyrin radical cation oxo complex has also been prepared and characterized. Tetramesitylporphyrin iron chloride was oxidized with *m*-CPBA at -80 °C to give the iron(IV) radical cation oxo complex (eq. 71).[207] Additionally

$$\text{(TMP)Fe-Cl} + m\text{-CPBA} \rightarrow (\text{TMP}^{+\cdot})\text{Fe(IV)(O)Cl} \qquad (71)$$

this complex was prepared by oxidation of either (TMP)Fe=O or $(\text{TMP}^{+\cdot})\text{Fe(III)ClO}_4$ with chlorine or bromine[208] or electrochemical oxidation of (TMP)Fe=O.[199,200,208] A robust *tetrakis*-(2,6-dichlorophenyl)porphyrin radical cation iron(IV) oxide was prepared by oxidation of the corresponding iron(III) perchlorate with pentafluoroiodosobenzene, *m*-CPBA, or ozone at -35 °C in acetonitrile.[209] The TTP derivative has recently been prepared by photodecomposition of the iron(III) nitrate.[194] These complexes have been studied by NMR,[114] UV-vis,[200,207] Mössbauer,[207] and resonance Raman spectroscopies,[210] magnetic susceptibility[207,209] and EXAFS.[87,88,204] The porphyrin dianion is produced upon the reduction of $[(POR^{+\cdot})Fe(IV)(O)]^+$.[209] The oxo ligand is labile and oxygen was exchanged with water (eq. 72).

$$[(POR^{+\cdot})Fe(IV)(^{16}O)]^+ + H_2{}^{18}O \rightarrow [(POR^{+\cdot})Fe(IV)(^{18}O)]^+ + H_2{}^{16}O \qquad (72)$$

The iron oxo complexes have been implicated in several oxidation processes. Alkenes have been oxidized using iron porphyrins and with a wide range of oxidant such as, iodosobenzene,[211] *m*-CPBA,[207,209] hydrogen peroxide,[185] hydroperoxides,[205] p-cyano-N,N-dimethylanaline-N-oxide,[212] and oxygen with hydrogen on colloidal platinum.[213] Under similar conditions amines were dealkyated.[214] Several mechanistic studies have been undertaken to elucidate the reaction pathway.[188,192,215-222] Several theoretical investigations on these processes have also done using extended Hückel, INDO, and valence bond calculations to investigate the energetics of possible reaction pathways.[223-225]

Several chromium(IV) oxo porphyrins have been prepared by Groves, Büchler, Bruice, and West[11,226-232] two of which have been characterized by X-ray crystal structures.[11,227] (TTP)Cr(II) has treated with oxygen yield a chromium(IV) oxo complex (eq. 73). Treatment of (POR)Cr-OH with a variety of oxidizing

$$(TPP)Cr(II) + \tfrac{1}{2}\,O_2 \rightarrow (TPP)Cr{=}O \qquad (73)$$

agents such as iodosobenzene, sodium hypochlorite, tertiary-butyl-hydroperoxide, or *m*-CPBA provides a method for synthesis of (POR)Cr=O (eq. 74).

$$(POR)Cr\text{-}OH + XO \rightarrow (POR)Cr{=}O \qquad (74)$$

Tetrakis-(2,6-dimethyl-3-sulfonato)phenylporphorinato chromium oxo was electrochemically generated from the corresponding diaquo complex in the presence of sodium perchlorate. The porphorinatochromium oxides were readily characterized by UV-vis,[11,226,227,230-232] IR,[11,226,227] and NMR[11,226,227] spectroscopies, elemental analysis,[226,227] mass spectrometry[226,227] and magnetic susceptibility.[11] Two one-electron reductions and oxidations were observed for the oxo complexes, however the nature of the redox active site has not been determined.[233] Base binding studies have also been done using a variety of nitrogen donors.[234] (TTP)Cr=O can be used as an oxidizing agent. Büchler[226] has demonstrated that benzyl alcohol can be oxidized to benzaldehyde by (TTP)Cr=O resulting in the formation of Cr(III) porphyrin complexes. We have found similar reactivity. If (POR)Cr=O was kept in solutions of chloroform, tetrahydrofuran, dichloromethane, or methanol loss of the oxo complex and formation of Cr(III) porphyrin species were observed. Presumably, the solvent was oxidized.

Groves has studied the reaction of triphenylphosphine with (POR)Cr=O.[227] If a limited amount of phosphine was used, a chromium(III) μ-oxo species was formed along with the phosphine oxide (eq. 75).[235] When a large excess of phosphine was used only the (POR)Cr(II) complex was observed (eq. 76).

$$2\ (\mathrm{POR})\mathrm{Cr{=}O} + \mathrm{Ph_3P} \rightarrow [(\mathrm{POR})\mathrm{Cr}]_2\mathrm{O} + \mathrm{Ph_3PO} \qquad (75)$$

$$(\mathrm{POR})\mathrm{Cr{=}O} + \mathrm{xs}\ \mathrm{Ph_3P} \rightarrow (\mathrm{POR})\mathrm{Cr(II)} + \mathrm{Ph_3PO} \qquad (76)$$

Kinetic studies have been done on this two-electron transfer process to determine the rate constants and activation parameters which are found in Table 3.1.

West[236-240] has done several studies on the inner-sphere redox processes of (POR)Cr=O with transition metal reductants. When (POR)Cr=O was treated with (POR)Fe(II)(pip)$_2$ or

Table 3.1. Rate constants for oxidation of triphenylphosphine by oxochromium(IV) porphyrins

Porphyrin Complex	Rate (M^{-1} s^{-1})
(TPP)Cr=O	0.47
(TTP)Cr=O	0.37
(TMP)Cr=O	0.054

(POR)Cr(II), formation of a μ-oxo dimer occurs. The general reaction shown in eq. 77 represents a one-electron redox involving incomplete oxygen atom transfer. (TTP)Mn(II)(py)

$$\text{(POR)Cr(IV)(O)} + L_nM^m \rightarrow \text{(POR)Cr(III)-O-}M^{m+1}L_n \qquad (77)$$

and (TTP)Co(II)(Me-Im) did not react with the chromium(IV) oxo complex.[236] Several other macrocylic compound of iron(II) and manganese(II) also formed oxygen bridged systems with (POR)Cr=O. When iron was used, L represents macrocyclic ligands such as N,N'-ethane-1,2-diylbis(salicylidene-iminato) (salen), N,N'-ethane-1,2-diylbis(thiosalicylidene-iminato), (tsalen), N,N'-phenylenebis(salicylidene-iminato) (salphen), N-N'-4-azaheptane-1,7-diylbis(salicylidene-iminato) (salah), or N,N'-4-methyl-4-azaheptane-1,7-diylbis(salicylidene-iminato) (salmah). When manganese was used, L was salah or salmah. Bis(diethyldithiocarbamato) complexes of iron(II) and molybdenum(IV) oxo also resulted in similar dimers.

Chromium(V)porphyrin oxo compounds have also been prepared by treating the chromium(III)porphyrinato chloride with iodosobenzene[14] (eq 78), *m*-CPBA, or p-cyano-N,N-dimethylaniline-N-oxide under photolytic conditions.[228-232]

$$\text{(TPP)Cr-Cl} + \text{PhIO} \rightarrow \text{(TPP)Cr(O)Cl} \qquad (78)$$

Electrochemical oxidation of the chromium(IV) oxo also yielded the chromium(V) oxo complex.[233] These chromium oxo compound have been characterized by UV-vis,[14] IR,[14] and EPR[241] spectroscopies as well as magnetic susceptibility measurements.[14] The chromium(V) oxo complex reacted with chromium(III) in a comproportionation reaction to give two chromium(IV) oxo complexes (eq 79).[228,229,233] This process is

$$\begin{gathered}\text{(POR)Cr(V)(O)Cl} + \text{(POR)Cr(III)-Cl} + H_2O \rightarrow \\ \text{Cl(POR)Cr-O-Cr(POR)Cl} \rightarrow 2\ \text{(POR)Cr(O)} \qquad (79)\end{gathered}$$

thought to proceed through a bridging oxo intermediate in which one electron was transferred. Tertiary-butylamine can replace the chloride ligand of (TPP)Cr(O)Cl as determined by EPR.[241] It has been discovered that the oxo ligand on chromium was easily exchanged for the oxygen of water.[14] Several catalytic oxidation studies using alkenes[14,229-233,242] and alcohols[235] have been done using a chromium(V) species as the active catalyst. Several kinetic studies on these processes have been undertaken to determine the mechanism of these reactions.[230-232] However, when styrene ozonide was used as the oxygen atom source, the porphyrin ligand was oxidized to provide an isoporphyrine complex in which one of the meso positions was hydroxylated.[243]

Figure 3.1 contains the known metalloporphyrin terminal oxo complexes. To this point, however no complete inter-metal atom transfer has been reported with metalloporphyrin oxo complexes before this work was undertaken. We report here the first *reversible* oxygen atom transfer between metalloporphyrins.

Results

Reduction of oxochromium(IV) porphyrin with chromium(III) porphyrin. Treatment of (TTP)Cr=O with (OEP)Cr-Cl in benzene results in spectral changes which are consistent with the transfer of a terminally bound oxygen ligand between two metal complexes shown in eq. 80. The UV-vis spectrum of the resulting mixture contained two new Soret bands for (TTP)Cr-Cl

$$\text{(TTP)Cr=O} + \text{(OEP)Cr-Cl} \rightleftharpoons \text{(TTP)Cr-Cl} + \text{(OEP)Cr=O} \qquad (80)$$

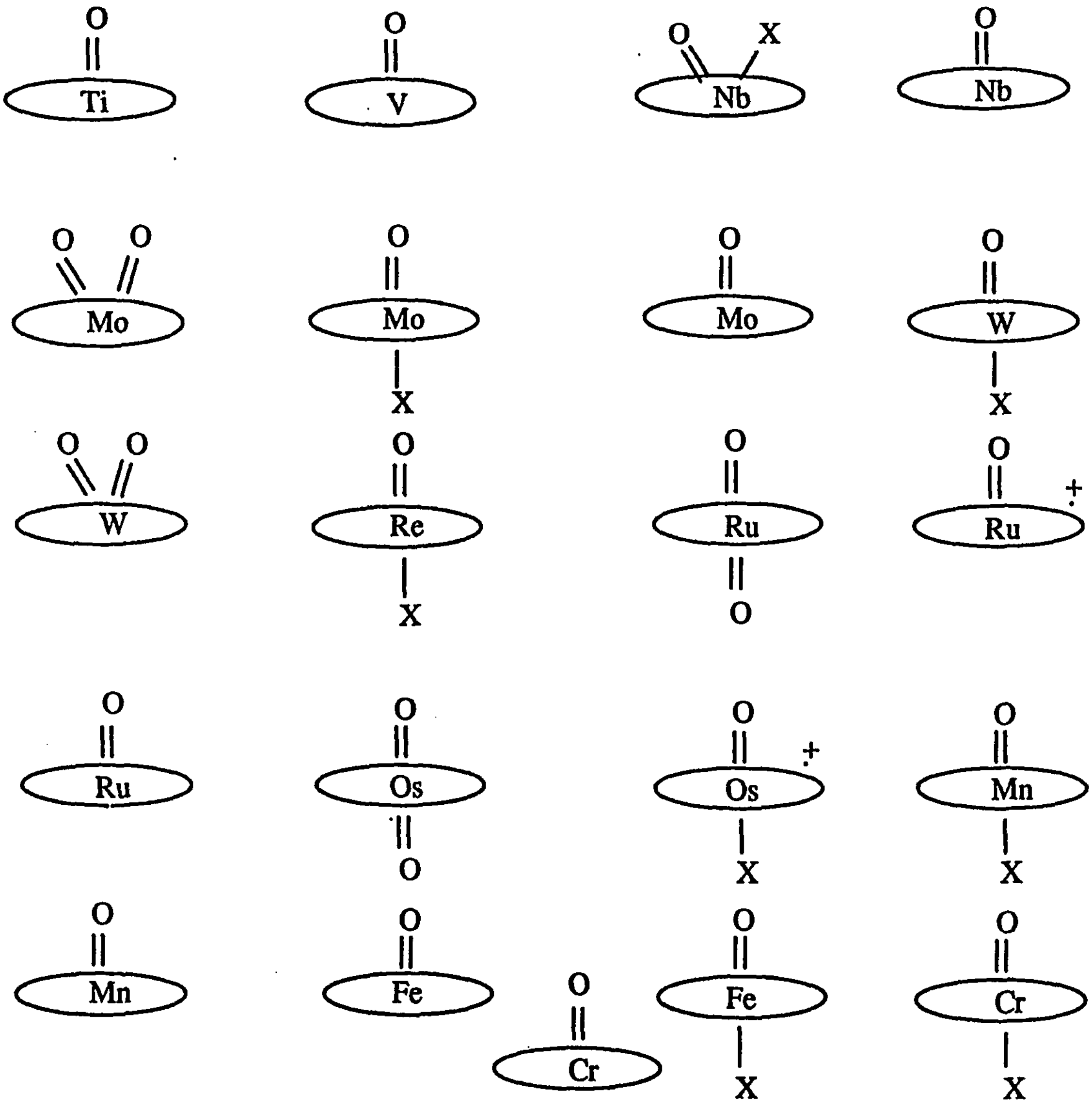


Figure 3.1. Metalloporphyrin oxide complexes

at 450 nm and (OEP)Cr=O at 416 nm. The band centered at 434 nm was a combination of the Soret bands of(TTP)Cr=O (430 nm) and (OEP)Cr-Cl (436 nm) and did not completely disappear, indicating that eq. 80 was an equilibrium process. The reversibility of eq. 80 can be confirmed by the complementary experiment in which (OEP)Cr=O was treated with (TTP)Cr-Cl. This generates a final UV-vis spectrum that has peak positions identical to those observed for the forward process. Since the Cr(IV) oxo complexes are low-spin d^2 and diamagnetic, it was also possible to independently establish the extent of reaction by ^1H NMR. This was most conveniently accomplished by monitoring the tolyl methyl proton signal of (TTP)Cr=O (2.38 ppm) and the methyl resonance of (OEP)Cr=O (1.84 ppm) against an internal standard, the 9,10 protons of anthracene (8.15 ppm) in benzene-d_6. Flame sealed NMR tubes containing mixtures of (TTP)Cr=O, (OEP)Cr-Cl, (OEP)Cr=O, (TTP)Cr-Cl and anthracene in benzene-d_6 maintained mass balance during the course of the experiment in terms of total oxo complex concentration. The equilibrium constants for eq. 80 over a 40° range were measured by ^1H NMR and are listed in Table 3.2. The thermodynamic parameters $\Delta H^\circ = -2.1 \pm 0.4$ kcal/mol and $\Delta S^\circ = -4.6 \pm 1.2$ cal/mol·K were derived from this temperature dependence. The forward rates of eq. 80 in toluene were examined spectrophotometrically by following the absorbance

Table 3.2. Equilibrium constants for eq. 80 in benzene-d_6

T (°C)	K
10	3.7 ± 0.1
20	3.1 ± 0.1
30	2.7 ± 0.1
40	2.6 ± 0.1

changes at 572 nm as shown in Fig. 3.2. In all cases, the data were found to obey an integrated rate law for reversible second-order reactions (eq. 81).[88] Plots of ln $[\Delta/\{\alpha + \Delta(1-1/K)\}]$ vs. αt are linear for more than three half-lives.

$$\ln\left[\frac{\Delta}{\alpha + \Delta(1-1/K)}\right] = -\alpha kt + \text{constant} \tag{81}$$

A typical plot is shown in Fig. 3.3. Table 3.3 summarizes forward rate constants as a function of temperature and Table 3.4 summarizes reverse rate constants for eq. 80.

Effect of axial ligands. Axial ligand effects were studied in these systems by varying the monoanionic ligand on the starting chromium(III) porphyrin complexes as shown in eq. 82. A comparison of two different axial ligands, pivalate and chloride is presented in Table 3.5.

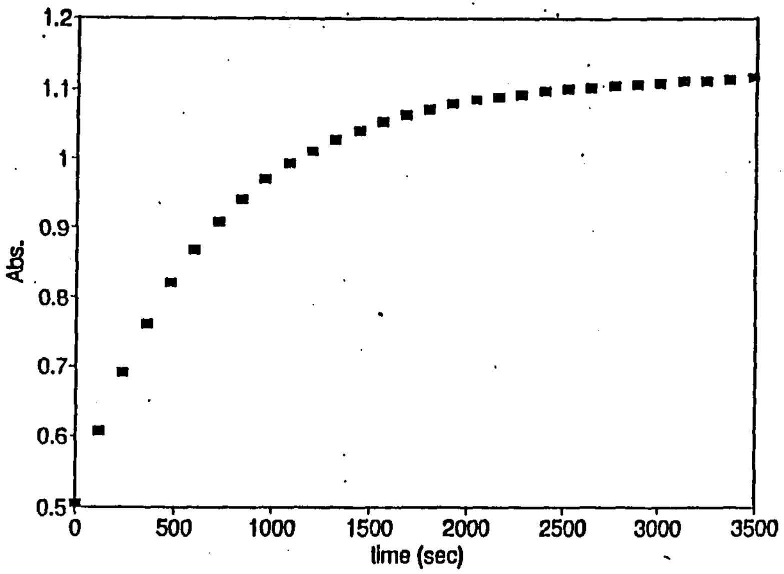


Figure 3.2. Representative absorption vs. time plot for eq. 80 at 50 °C

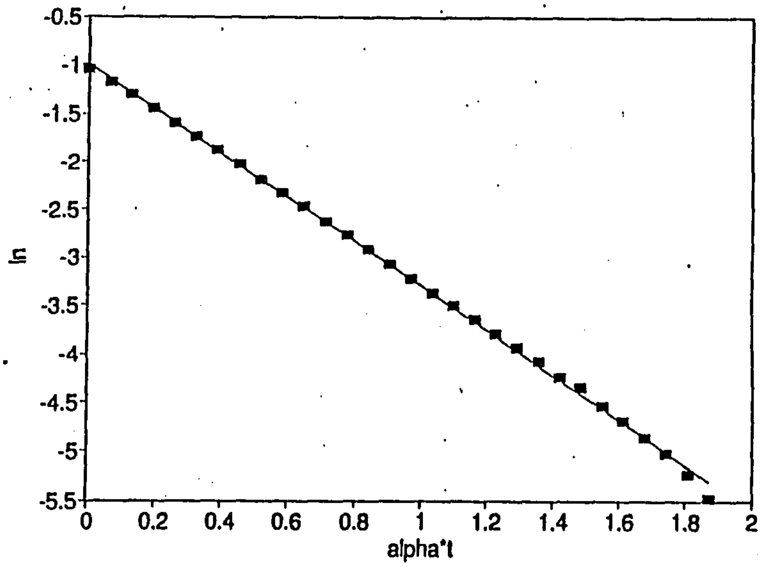


Figure 3.3. Plot of $\ln[\Delta/\{\alpha + \Delta(1-1/K)\}]$ vs. αt for eq. 80 at 50 °C

$$\text{(OEP)Cr=O} + \text{(TTP)Cr-X} \rightleftharpoons \text{(OEP)Cr-X} + \text{(TTP)Cr=O} \qquad (82)$$

Table 3.3. Forward rate constants for eq. 80 in benzene

T (°C)	k_1 (M^{-1} s^{-1})
40	2.9 ± 0.8
50	3.0 ± 1.1
60	3.9 ± 1.3

Table 3.4. Reverse rate constants for eq. 80 in benzene

T (°C)	k_1 (M^{-1} s^{-1})
30	0.39 ± 0.03
40	0.87 ± 0.08
50	1.4 ± 0.1

Table 3.5. Monoanionic axial ligand comparison for eq. 82

X	T °(C)	k_1 (M^{-1} s^{-1})
$(CH_3)_3CCO_2$	50	1.5 ± 0.5
Cl	50	3.0 ± 1.1

Kinetics of oxygen atom transfer as a function of added axial ligand. The influence of added monoanionic axial ligands on the transfer of oxygen between Cr^{IV}=O and Cr^{III}-Cl was studied using bis(triphenylphosphoranylidene)ammonium chloride as the external source of chloride in CH_2Cl_2 solutions. The rate data from these experiments were still found to follow second-order reversible kinetics (eq. 81). The rate constants for atom transfer with a ten fold excess of chloride ion and without added chloride ion in dichloromethane is summarized in Table 3.6.

Table 3.6. Rate constant comparison for eq. 80 in CH_2Cl_2 in the presence of added chloride

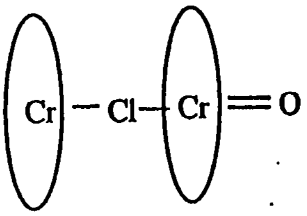
[(OEP)Cr-Cl)] 10^4 M	[PPNCl] $10\ ^4$ M	k_1 (M^{-1} s^{-1})
4.98	0	13 ± 2
4.98	0.498	12 ± 1

Discussion

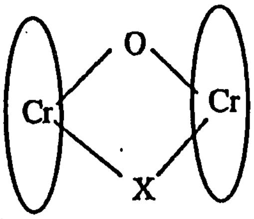
We have found that complete oxygen atom transfer between two metalloporphyrins can be achieved. It was possible to observe this process by using different porphyrin ligands as UV-vis and ^1H NMR spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction, eliminating complications due to ligand loss. Furthermore, stereochemical rearrangements found in other systems that undergo complete atom transfer are not possible here.[36,37] Rate constants of reaction 80 have been measured for the reaction in both the forward and reverse directions. As indicated in Table 3.2, these rate constants range between 0.39 and 3.9 M^{-1} s^{-1}. The temperature dependence of the forward rate yields activation parameters of $\Delta H^{\ddagger} = 2.6 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -46 \pm 5$ cal/mol·K. For the reverse direction, these values are $\Delta H^{\ddagger} = 12 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -21 \pm 6$ cal/mol·K. These rate and activation parameters, are similar to those obtained by Groves[235] $\Delta H^{\ddagger} = 6.96$ kcal/mol and $\Delta S^{\ddagger} = -39$ kcal/mol·K, for the two-electron oxygen transfer (eq. 76) from (POR)Cr=O to triphenylphosphine.

Electrochemical studies on chromium porphyrins provide evidence which indicates that eq. 80 does not involve an outer-sphere mechanism. For example, the half-wave reduction potential for the $[(TTP)Cr\text{-}Cl]^+/(TTP)Cr\text{-}Cl$ couple occurs at $E_{1/2} = 0.80$ V vs. SCE in CH_2Cl_2.[233,244] The corresponding potential for reducing (TTP)Cr=O to $[(TTP)Cr{=}O]^-$ occurs at $E_{1/2} = -1.12$ V vs. SCE.[233] Thus, (TTP)Cr-Cl is not thermodynamically capable of reducing the chromium oxo porphyrin complex in an outer-sphere pathway.

Although eq. 80 proceeds by an inner-sphere process, mechanistic aspects of this reaction are complicated by the bridging abilities of both the chloro and the oxo ligands. In order to address this issue we have compared the reduction of (TTP)Cr=O with both (OEP)Cr-Cl and $(OEP)Cr\text{-}O_2CC(CH_3)_3$. The rate constants for these two reactions are very similar, regardless of whether chloride (k_{Cl} = 3.0 M^{-1} s^{-1}) or pivalate (k_{piv} = 1.5 M^{-1} s^{-1}) was the axial ligand on chromium(III). This serves to rule out a binuclear intermediate in which the mono-anionic ligand is involved in bridging the two metals. Thus the μ-chloro bridged adduct, **A**, and the doubly bridged species, **B**, must not be important intermediates along the reaction pathway.



A

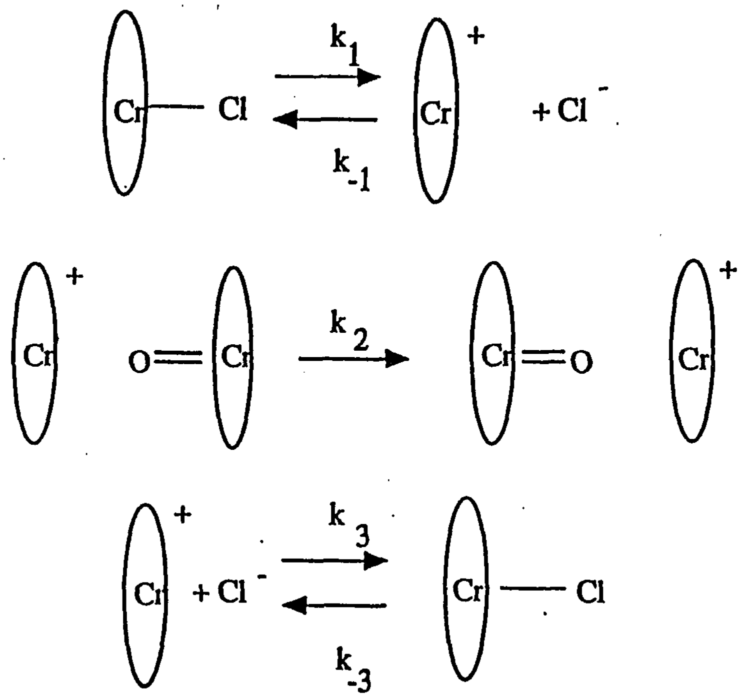


B

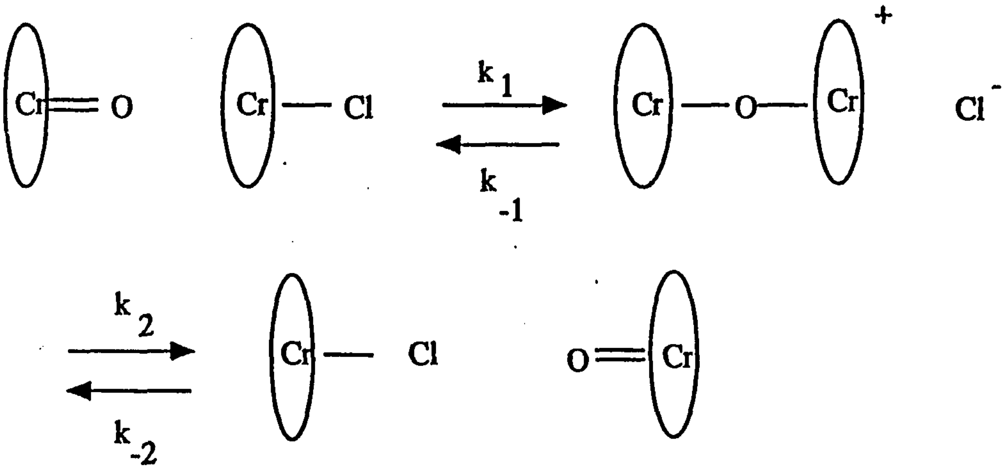
It is clear that the redox reaction between (TTP)Cr=O and (OEP)Cr-Cl involves a μ-oxo intermediate. Formation of this intermediate can occur by either an S_N1-type mechanism (Scheme I) or by an S_N2-type mechanism (Scheme II).

These two processes can be distinguished by their chloride ion dependencies. The S_N1 mechanism has a forward rate constant

Scheme I



Scheme II



which is inversely dependent on the chloride ion concentration (eq. 83).

$$k_f = \frac{k_1 k_2}{k_{-1}[Cl^-]} \tag{83}$$

However, the forward rate constant for the S_N2 is independent of the chloride concentration (eq. 84).

$$k_f = \frac{k_1 k_2 [Cl^-]}{k_{-1}[Cl^-] + k_2[Cl^-]} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{84}$$

Since the oxygen/chloride exchange rates between (TTP)Cr=O and (OEP)Cr-Cl are independent of $[Cl^-]$, eq. 80 must involve attack of the chromium oxo complex at the trans-position of the chloro complex. This mechanism is analogous to the S_N2 process proposed by Bottomley[23] for the N/Cl exchange between (TTP)Mn≡N and (OEP)Cr-Cl (eq. 85).

$$\text{(TTP)Mn}{\equiv}\text{N} + \text{(OEP)Cr-Cl} \rightarrow \text{(OEP)Cr}{\equiv}\text{N} + \text{(TTP)Mn-Cl} \tag{85}$$

The reduction products of oxo chromium porphyrins are strongly dependent on the nature of the reducing agent. When a chromium(II) porphyrin was the reductant, the reaction stops at μ-oxo formation (eq. 78). However, use of chromium(III) porphyrins results in reversible oxygen atom transfer. An examination of the electronic structure of μ-oxo metalloporphyrins dimers provide a rationale for the stark contrast in these processes. The d-orbital energy level for

$[Fe(TTP)]_2O$ shown in Figure 3.4 was derived by Tatsumi and Hoffmann[67,68] using Extended Hückel calculations on $[(NH_2^-)_4Fe\text{-}O\text{-}Fe(NH_2^-)_4]^{4-}$ as a computational model. To a first approximation, this energy level diagram should apply to the $[(POR)Cr\text{-}O\text{-}Cr(POR)]^{0,+1}$ system. When Cr(III) was the reductant, the cationic μ-oxo dimer has five d-electrons. Although it is not clear whether this species will adopt a high spin or a low spin electronic state, either case results in a single electron occupying a degenerate e_1 or e_2 level. Thus the d^5 μ-oxo species is Jahn-Teller destablized. No such destablization exists for the neutral d^6 μ-oxo dimer, in accord with its relative stability towards complete oxygen transfer.

Concluding remarks

A number of interesting results have evolved from this study. It is possible to vary the number of redox equivalents exchanged in an atom transfer process by choosing an appropriate substrate. In the reactions examined here (eqs. 80, 82) and the reaction with phosphine by Groves (eq. 76) oxygen atom transfer can mediate both one- and two-electron processes. Furthermore complete atom transfer can be achieved rather that partial atom transfer using the appropriate reductant.

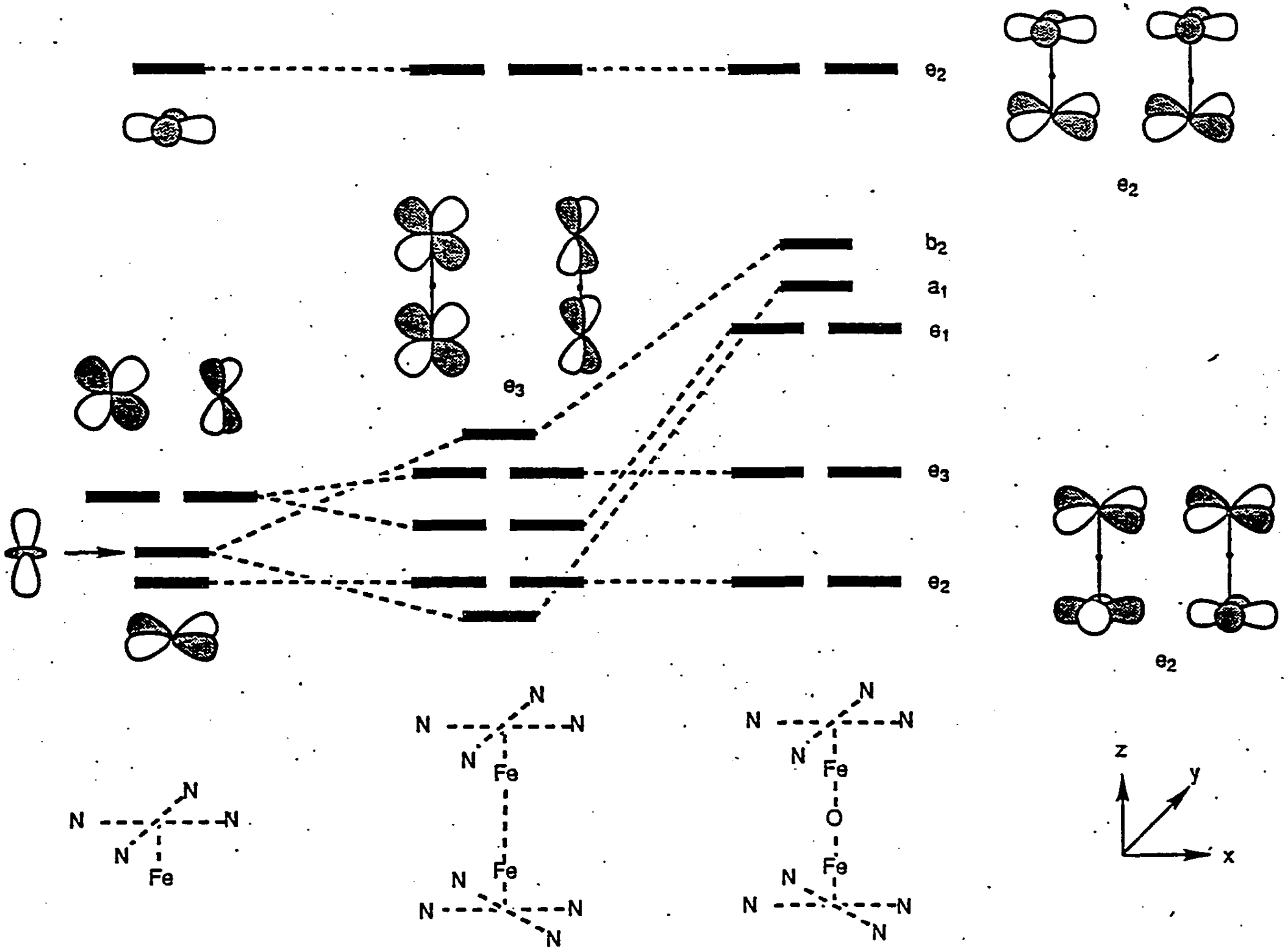


Figure 3.4. Molecular orbital diagram for $[(NH_2^-)_4Fe\text{-}O\text{-}Fe(NH_2^-)_4]^{4-}$

Table 3.7. Structurally characterized metalloporphyrin oxide complexes

Compound	d (M-O) (Å)	Reference
(OEP)Ti=O	1.613(5)	124
(Deoxophylloerythro-etioporphyrin)V=O	1.62(1)	130
(Etioporphyrin)V=O	1.599(6)	131
(TPP)V=O	1.625(16)	132
(TPP)Nb(O)O_2CCH_3	1.716	138
(TPP)Nb(O)O_2CCH_3	1.720(6)	139
(TPP)Nb(O)F	1.749(3)	142
(TTP)Mo$(O)_2$	1.709(9), 1.744(9)	147
(TPP)Mo(O)Cl	1.714(3)	149
(TTP)Mo=O	1.656(6)	151
(TTP)Os$(O)_2$	1.743(3)	170
(TPP)Cr=O	1.62(2)	11
(TTP)Cr=O	1.572(6)	227

CHAPTER 4

EXPERIMENTAL

Instrumentation

UV-visible spectroscopic measurements were obtained using either a Cary 17 or a Hewlett-Packard HP 8452A diode array spectrophotometer. IR spectra were recorded on either an IBM IR98 Fourier Transform spectrometer or a Perkin-Elmer 680 IR spectrometer. Samples were prepared as mineral oil mulls. NMR spectra were recorded on either a Nicolet NT300, Bruker WM300, or Varian VXR 300 MHz spectrometer. Mass spectra were obtained on either a Kratos 50 or Finnigan 4000 mass spectrometer.

Chemicals

Toluene, benzene, and tetrahydrofuran were distilled from purple solutions of sodium/benzophenone, chloroform from phosphorus pentoxide, and dichloromethane from calcium hydride. Ethanol-free chloroform was prepared by first washing the chloroform with water then distilling the chloroform from sodium carbonate. Pentane, absolute ethanol, N,N-dimethylformamide, and N-methylformamide were stored over molecular sieves overnight. Methanol, diethyl ether, and hexanes were used as received. Other material was used as received without further purification.

Preparation of Tetratolylporphyrin, (TTP)H_2. Tetratolyl porphyrin (TTP)H_2 was prepared and characterized by the method of Adler[245] and purified by the method of Dolphin.[246] Propionic acid (2.5 liters) was brought to a boil, then a solution containing 50 ml (0.424 mmol) of *p*-tolualdehyde in propionic acid (75 ml) was added dropwise over a period of 5 minutes. A solution containing 50 ml of pyrrole (0.721 mmol) in propionic acid (75 ml) was added dropwise. The reaction was heated to reflux in propionic acid for 25 minutes and cooled. The resulting precipitate was filtered on a glass frit. Purple crystals, 22.9 g, 23% were obtained. The crude porphyrin was purified by the following procedure. In a typical purification, 10.85 g (16.2 mmol) (TTP)H_2 was dissolved in 1 L of ethanol-free chloroform. A solution containing 2.5 g (11 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 75 ml of toluene was added to the porphyrin solution which was heated at reflux for 3 hours. The reaction solution was then transferred to a 5 cm diameter column prepared from 140 g of neutral alumina, (ICN Biomedical) and the product was eluted with dichloromethane. After removing the solvent, 10.73 g (98.9%) of purified (TTP)H_2 was recovered. UV-Vis (CH_2Cl_2): λ_{max} 645, 592, 552, 518, 418 nm. ^{1}H NMR ($CDCl_3$): 8.83 (s, 8H, β-H), 8.08 (d, 8H o-H), 7.53 (d, 8H, *m*-H), 2.69 (s, 12H, CH_3), -2.74 (s, 2H, NH).

Preparation of tetratolylporphyrinatomanganese chloride, (TTP)Mn-Cl. (TTP)Mn-Cl was prepared using the method of Adler[247] and characterized by the method of Boucher.[248] (TTP)H_2 (5.2668 g, 7.7852 mmol) and manganese(II) chloride tetrahydrate (2.4838 g, 12.550 mmol) were heated to reflux in 500 ml of N,N-dimethylformamide until the peak at 418 nm due to (TTP)H_2 disappeared from the UV-vis spectrum. The solution was cooled and added to a equal volume of water to precipitate the product. The precipitate was filtered on Celite and washed with water. The product was removed from the Celite with dichloromethane, and the solvent was removed under reduced pressure. A yield of 5.65 g, 88%, was obtained. UV-Vis (Toluene): λ_{max} (log ε) 622 (4.11), 586 (3.96), 532 (3.76), 478 (5.10), 393 (4.68), 373 (4.75) nm.

Preparation of Octaethylporphyrinatomanganese chloride, (OEP)Mn-Cl. (OEP)Mn-Cl was prepared by Adler's[247] method and characterized by Dolphin's method.[249] (OEP)H_2 (0.1584 g, 0.2962 mmol) and manganese(II) chloride tetrahydrate (0.5393 g, 2.725 mmol) were heated to refluxed in 50 ml of N,N-dimethylformamide until the peak at 398 nm due to free (OEP)H_2 disappeared. The solution was cooled, then added to an equal volume of water to precipitate the product. The precipitate was filtered on Celite, and washed with water. The product g, 97%, was obtained. UV-Vis (CH_2Cl_2): λ_{max} (log ε) 562 (4.18), 472 (4.72), 360 (4.87) nm.

Preparation of tetratolylporphyrinatomanganese acetate, (TTP)Mn-O_2CCH_3. (TTP)H_2 (1.7834 g, 2.6588 mmol) and manganese(II) acetate tetrahydrate (3.0382 g, 12.397 mmol) were heat to reflux overnight in 150 ml of N,N-dimethylformamide according to the method of Adler.[247] The reaction was cooled, then added to 250 ml of cold water. The product was filtered on Celite and washed with water then removed with dichloromethane. The solvent was removed under reduced pressure. The product was characterized by Büchler's method.[79] A yield of 1.92 g, 95%, of green (TTP)Mn-OAc was obtained. UV-vis (CH_2Cl_2): λ_{max} (log ε) 614 (4.01), 578 (3.96), 470 (5.03), 398 (4.64), 374 (4.65) nm.

Preparation of Tetratolylporphyrinatomanganese pivalate, (TTP)Mn-$O_2CC(CH_3)_3$. (TTP)Mn-Cl (0.141 g, 0.190 mmol) and $AgClO_4$ (0.260 g, 1.25 mmol) were heated in 50 ml of THF for 45 minutes. Sodium pivalate (0.456 g, 3.67 mmol) was added and the reaction was stirred for one hour. The THF was removed under reduced pressure then the reaction mixture was redissolved in 50 ml of toluene. The product was filtered on a medium glass frit, then the toluene was removed under reduced pressure. The yield was 0.144 g, 94%, based on (TTP)Mn-Cl. UV-vis (CH_2Cl_2): λ_{max} 614, 578, 470, 398, 374 nm. ^1H NMR ($CDCl_3$): 8.06 (br, 8H, m-H), 2.97 (br, 12H, CH_3), -19.8

(br, β-H). IR (mull): νco = 1622 cm^{-1}. Anal. calc. for $C_{53}H_{45}MnN_4O_2$: C, 77.16; H, 5.50; N, 6.80. Found: C, 77.38; H, 5.70; N, 6.20. MS [M^-]: calcd. 824.3. Found: 824.5.

Preparation of Octaethylporphyrinatomanganese acetate, (OEP)Mn-O_2CCH_3. (OEP)H_2 (0.4925 g, 0.9209 mmol) and manganese(II) acetate tetrahydrate (1.0032 g, 4.0932 mmol) were heated to reflux for 6 hours in 50 ml of N,N-dimethylformamide according to the method of Adler.[247] The reaction was cooled, then added to 100 ml cold water. The product was filtered on Celite and washed with water. Dichloromethane was used to remove the product from the Celite, and the solvent was removed under reduced pressure. The product was characterized by Dolphin's method.[249] A yield of 90%, 0.545 g was obtained based on (OEP)H_2. UV-vis (Toluene): λ_{max} 618, 582, 534, 474, 398, 372 nm.

Preparation of Zinc Amalgam. Zinc amalgam was prepared according to the method of Caesar.[250] Mercury(II) chloride, 9.90 g (27.4 mmol), was dissolved in an acid solution of 5 ml concentrated HCl and 125 ml water. Zinc dust (56.8 g , 8.69 mmol) was added and the reactants were stirred 15 minutes. The mixture was filtered on a glass frit and washed with water then acetone. The product was dried overnight, under vacuum and the yield of zinc amalgam obtained was 59.3 g.

Preparation of Tetratolylporphyrinatochromium Chloride, (TTP)Cr-Cl. (TTP)H_2 (1.20 g, 4.32 mmol) was heated to reflux in 300 ml of N,N-dimethylformamide using Adler's method.[247] One gram quantities of anhydrous chromium(II) chloride were added until the UV-vis spectrum revealed the absence of the free porphyrin at 418 nm. The product was cooled, precipitated with an equal volume of cold water, filtered on celite, and washed with water. The chromium porphyrin chloride was removed from the celite using methanol. The methanol was removed under reduced pressure. The product was then dissolved in acid-free, anhydrous dichloromethane as described by Basolo and Hoffman[251] then loaded onto a 4 cm (diameter) by 12 cm column of basic alumina (Fisher). The free base porphyrin was eluted with dichloromethane, then the metallated porphyrin was eluted with methanol, which resulted in the exchange of the axial ligand from chloride to methoxide on the chromium porphyrin. The methanol was removed from the chromium porphyrin with a rotary evaporator under reduced pressure. The product was dissolved in dichloromethane and treated with 5 ml of trimethylsilyl chloride for about five minutes to yield (TTP)Cr-Cl. The product was charcterized by Adler's method.[247] The solvent was removed under reduced pressure. The yield was 1.473 g, 68%, based on $(TTP)H_2$. UV-vis (Toluene): λ_{max} (log ε) 604 (3.83), 566 (3.84), 526 (3.20), 448 (5.17), 396 (4.41) nm.

Preparation of Octaethylporphyrinatochromium Chloride, (OEP)Cr-Cl. (OEP)Cr-Cl was prepared by the procedure of

Adler[247] amended by Hoffman and Basolo.[249] (OEP)H_2 (0.5850 g, 1.09 mmol) was heated in 70 ml of refluxing N,N-dimethylformamide, then 1 g portions of $CrCl_2$ were added, and the solvent heated to reflux for 10 minutes until the UV-vis spectrum indicated that no free (OEP)H_2 remained. The reaction was placed in 100 ml cold water to precipitate the metalloporphyrin. The product was filtered on Celite and washed with water, then the product was extracted from the celite with methanol. The methanol was evaporated and the product was redissolved in dichloromethane. The solution was placed on a 4 cm (diameter) by 12 cm column of basic alumina (Fisher). The octaethylporphyrin was eluted with dry acid-free dichloromethane. The product was then eluted with methanol/dichloromethane, 3:1. The solvent was removed and the product was redissolved in dichloromethane and treated with 1 ml trimethylsilyl chloride for five minutes. The CH_2Cl_2 was removed under reduced pressure. The product was characterized by Gouterman's method.[105] The yield based on (OEP)H_2 was 0.372 g, 55%. UV-vis (Toluene): λ_{max} (log ε) 574 (4.04), 544 (4.13), 436 (5.13), 384 (4.48), 374 (4.54) nm.

Preparation of Octaethylporphyrinatochromium Hydroxide, (OEP)Cr-OH·½H_2O. (OEP)CrCl (74.6 mg, 0.103 mmol) was dissolved in 75 ml of CH_2Cl_2. Twenty five milliliters of 2 M NaOH was added and the reaction was stirred on a rotary evaporator for

1 hour. The CH_2Cl_2 was removed under reduced pressure then the product was filtered on a glass frit, washed with water, and dried. Spectra were compared to those obtained by Büchler.[230] The yield of (OEP)Cr-OH·½H_2O based on (OEP)Cr-Cl was 62.6 mg, 85%. UV-vis (CH_2Cl_2): λ_{max} 646, 572, 540, 420, 382 nm.

Preparation of Tetratolylporphyrinatomanganese(II), (TTP)Mn(II). (TTP)Mn(II) was prepared by Reed's procedure.[21] (TTP)Mn-Cl (0.4654 g, 0.6131 mmol) and 1.83 g zinc amalgam were stirred overnight in 50 ml of tetrahydrofuran in a glovebox. The zinc amalgam was removed by filtration on a glass frit. The filtrate was filtered and eluted through a 2 cm plug of neutral alumina. The reaction was dried under vacuum. A blue product (TTP)Mn(II) was obtained in 53% yield, 0.26 g. (TTP)Mn-OAc may be used in place of (TTPMn-Cl). A hydride, such as lithium aluminum hydride may be used in place of zinc amalgam as the reducing agent as shown by Wayland.[252] Tetrahydrofuran can be used in place of toluene as the solvent. Spectra were compared to those obtained by Reed.[21] UV-vis (Toluene): λ_{max} (log ε) 604 (4.05). 563 (4.18), 435 (5.63) nm.

Preparation of Octaethylporphyrinatomanganese(II), (OEP)Mn(II). (OEP)Mn(II) was prepared by Reed's procedure.[21] (OEP)Mn-Cl (32.5 mg, 0.0522 mmol) and 1.7 g of zinc amalgam were stirred 9 hours in 65 ml of toluene in a glovebox. Additional zinc amalgam (1.79 g) was then added, and the reaction was stirred an additional 21 hours. The zinc amalgam was filtered on a glass frit. The solution was concentrated to 5 ml and filtered. The product was washed with 30 ml hexanes and dried. A fluffy purple-blue material was obtained, 13 mg, yield 42%. (OEP)Mn-OAc can be used in place of (OEP)Mn-Cl. A hydride, such as lithium aluminum hydride can be used in place of zinc amalgam, as the reducing agent as shown by Wayland.[252] Tetrahydrofuran can be used in place of toluene as the solvent. UV-vis (Toluene): λ_{max} (log ε) 578 (4.00), 545 (4.08), 418 (5.30) nm.

Preparation of Tetratolylporphyrinatomanganese Nitride, (TTP)Mn≡N. The preparation developed by Büchler was used to prepare (TTP)Mn≡N.[46] (TTP)Mn-OAc (2.08 g, 2.65 mmol) was dissolved in methanol and eluted down an alumina column with methanol. The methanol was removed and the product redissolved in 400 ml dichloromethane. This solution was treated with 12 ml of an ammonia solution made by diluting 2 ml of concentrated ammonia with 10 ml of water and allowed to stir for fifteen minutes. A 10% sodium hypochlorite solution (6 ml) was added and the reaction was stirred an additional 15 minutes, resulting in a red solution. The solution was then washed with two 100 ml portions of water to remove the excess ammonia and hypochlorite and the sodium chloride formed during the reaction. The organic layer was dried with magnesium sulfate. The magnesium sulfate was removed by filtration on a glass frit. The filtrate was placed on a neutral alumina column and the product was eluted with dichloromethane. Unreacted manganese(III) porphyrin can be recovered by eluting with methanol. The product was dried under reduced pressure. Spectra were compared to those obtained by Bũchler.[46] A yield of, 1.82 g, 93% based on (TTP)Mn-OAc was obtained. UV-vis (Toluene): λ_{max} (log ε) 535 (4.34), 421 (5.70) nm. ^{1}H NMR ($CDCl_3$): 8.94 (s, 8H β-H), 8.03 (br, 8H *o*-H), 7.53 (d, 8H *m*-H), 2.68 (s, 12H CH_3).

Preparation of Octaethylporphyrinatomanganese Nitride, (OEP)Mn≡N. Bũchler's procedure was used to prepare and characterize (OEP)Mn≡N.[46] (OEP)Mn-OAc (0.3745 g, 0.5781 mmol) was dissolved in 75 ml of methanol then eluted with methanol through a 4 cm by 6 cm column of neutral alumina. The methanol was removed and the product was redissolved in 125 ml of dichloromethane. Five milliliters of an ammonia solution, made up by diluting 2 ml of concentrated ammonia with 3 ml of water, was added and the reaction was stirred 15 minutes. Five milliliters of a 10% sodium hypochlorite solution was added and the reaction stirred an additional 15 minutes. The reaction mixture was then washed with two 100 ml portions of water to remove the excess ammonia and hypochlorite and the sodium chloride formed in the reaction. The organic layer was transferred to a neutral alumina column and the product was eluted with dichloromethane. Unreacted (OEP)Mn(III) can be recovered by elution with methanol. A yield of 0.310 g, 89%, based on (OEP)Mn-OAc was obtained. UV-vis (Toluene): λ_{max} (log ε) 562 (4.60), 526 (4.10), 404 (5.50) nm. ^{1}H NMR ($CDCl_3$): 10.21 (s, 4H *m*-H), 4.08 (m, 16H, CH_2), 1.91 (t, 24H CH_3).

Preparation of Tetratolylporphyrinatochromium Oxide, (TTP)Cr=O. (TTP)Cr=O was prepared and characterized by a method developed by Groves.[231] (TTP)Cr-Cl (0.585 g, 0.774 mmol) was dissolved in 20 ml dichloromethane. Iodosobenzene (0.604 g, 2.32 mmol) was added and the reaction was stirred for five minutes. Finely ground sodium hydroxide, 2.04 g, was added and the reactants stirred 10 minutes. The reaction was complete when the Soret peak at 450 nm due to the Cr(III) was no longer observed. The reaction mixture was then placed on a grade 4 basic alumina column. The (TTP)Cr=O was eluted with dichloromethane as a cherry red band. The product was dried then washed with diethyl ether to remove iodosobenzene. A yield 0.331 g, 58%, based on (TTP)H_2 was obtained. UV-vis (Toluene): λ_{max} (log ε) 544 (4.25), 434 (5.25), 376 (4.35) nm. ^{1}H NMR ($CDCl_3$): 9.08 (s, 8H β-H), 8.11 (d,8H, *o*-H), 7.55 (d, 8H *m*-H), 2.69 (s, 12H, CH_3).

Preparation of Octaethylporphyrinatochromium Oxide, (OEP)Cr=O. (OEP)Cr=O was prepared and characterized by the method described by Büchler.[230] (OEP)Cr-OH (0.1332 g, 0.2180 mmol) was treated with 7 ml of a 10 % sodium hypochlorite solution in 100 ml of 49:1 dichloromethane:ethanol and stirred for 10 minutes. The UV-vis spectrum was taken to observe the growth of a peak at 416 nm due to the oxo complex. The excess aqueous NaOCl solution was removed using a separatory funnel. The dichloromethane was removed and the product redissolved in benzene. The solution was place on a grade 4 basic alumina column and eluted with benzene. A yield of 77.3 mg, 59%, was obtained based on $(OEP)H_2$. UV-vis (Toluene): λ_{max} (log ε) 572 (4.43), 534 (4.20), 416 (4.94) nm. 1H NMR ($CDCl_3$): 10.89 (s, 4H, *m*-H), 4.13 (m, 16H, CH_2), 1.95 (t, 24H CH_3).

Methods

Sample Preparation for Equilibrium and Kinetic Studies. (TTP)Mn(II) and (OEP)Mn(II) were prepared by reduction of a corresponding (POR)Mn(III) with zinc amalgam or lithium aluminum hydride under a nitrogen atmosphere. Excess reductant was removed by filtration in the glovebox and the concentration of the filtrate containing the (POR)Mn(II) was determined by UV-vis spectroscopy just prior to use. (TTP)Mn≡N, (OEP)Mn≡N, $(TTP)Mn\text{-}(O_2CC(CH_3)_3)$, and (TTP)Mn-Cl were recrystallized from toluene/pentane, (TTP)Cr=O, (OEP)Cr=O, and (TTP)Cr-Cl from benzene/pentane, and (OEP)Mn-Cl and (OEP)Cr-Cl from dichloromethane/pentane. The concentrations of stock solutions were determined by UV-vis spectroscopy prior to use.

Equilibrium Measurements. Samples for equilibrium studies were prepared by adding stock solutions of known volume and concentration of either (TTP)Mn≡N and (OEP)Mn(II) or (OEP)Mn≡N and (TTP)Mn(II) along with triphenylmethane as an internal standard to an NMR tube. The solvents of the stock solutions were evaporated on a high vacuum line. The NMR solvent, d_8-toluene or d_8-tetrahydrofuran, was then added by vacuum transfer and the tube was flame sealed under a pressure of approximately 600 torr of nitrogen. The equilibrium constant was determined by integrating the β-H signal of (TTP)Mn≡N against the meso signal of (OEP)Mn≡N. The two nitride signals were integrated against the methine signal of the internal standard to verify that the amount of total nitride was maintained. The NMR spectra were monitored in a temperature-controlled probe until no further change was observed.

Samples for equilibrium determinations for the chromium oxo-chloro exchange were prepared by adding known volumes of stock solutions of known concentrations of all components of the equilibrium: (OEP)Cr-Cl, (OEP)Cr=O, (TTP)Cr-Cl, (TTP)Cr=O and an internal standard, anthracene. The solvent was evaporated on a high vacuum line. The NMR solvent, d_6-benzene, was transferred under vacuum and the tube was flame sealed under a pressure of approximately 600 torr of nitrogen. The equilibrium constant was determined by integrating the tolyl-methyl signal of (TTP)Cr=O against the ethyl-methyl signal of (OEP)Cr=O. The oxo signals were integrated against the 9,10 hydrogens of anthracene to verify that mass balance was maintained. Again the spectrum was monitored in a temperature-controlled until no further change was observed.

Kinetic Measurements. Rate data for the (POR)Mn≡N/(POR)Mn(II), (POR)Mn≡N/(POR)Mn-Cl and (POR)Cr=O/(POR)Cr-Cl systems were obtained on a UV-visible spectrometer equipped with a thermally regulated cell holder. Kinetic runs of the (POR)Mn≡N/(POR)Mn(II) system were done under either a blanket of argon or nitrogen. Solutions of the manganese porphyrins and additional solvent were loaded into a 10 mm cuvette in a glovebox, sealed with a septum then removed from the glovebox and placed in the spectrophotometer. The reaction was monitored at a single wavelength. Molar absorptivities of the various metalloporphyrins at the wavelengths used are given in Table 5.2. When the solvent was toluene, the wavelength monitored on the Cary 17 was 403 nm and on the Hewlett-Packard HP 8452A was 402 nm. When tetrahydrofuran was used as the solvent, the wavelength monitored was 560 nm. A spectrum from 350 to 700 nm was taken at the end of each run to check for the absence of (POR)Mn(III) which may have been formed by adventitious air oxidation. Runs at lower temperatures were prepared by loading one of the components and the solvent in the cuvette. This was cooled in the freezer in the glovebox. The final component was then added and the cuvette was taken from the glovebox and placed under a stream of argon or nitrogen directed from above the cell holder. Any water condensed on the outer surfaces were wiped away and the run started.

The (OEP)Mn≡N/(TTP)Mn-Cl system was prepared by taking a known volume of a stock solution of one of the metalloporphyrins in N-methylformamide, placing it in a 10 mm cuvette, followed by addition of the solvent and then the complementary metalloporphyrin. The cuvette was placed in the cell holder and the data were taken as previously described.

The (POR)Cr=O/(POR)Cr-Cl system was prepared similarly to the manganese systems. Solutions of the oxo and the appropriate chloride were loaded in a 1 mm cuvette in the air. The cuvette was placed in the cell holder and the run was monitored at 572 nm. A spectrum from 500 to 700 nm was taken to verify that the oxo complex was not reduced during the course of the run. Kinetic runs were also done in the presence of a ten-fold excess of chloride in the form of bis(triphenylphosphoranylidene)ammonium chloride.

Rate data for the (POR)Mn≡N/(POR)Mn-$O_2C(CH_3)_3$ system were obtain by ^1H NMR spectroscopy. Samples were prepared as described for equilibrium studies. The NMR spectrum was monitored with time.

Rate constants were obtained using an integrated rate law for second order equilibrium reaction as derived by King[88].

T_1 values of the porphyrinatochromium oxo complexes and anthracene were obtained by standard NMR techniques. The values are given in Table 5.1.

Table 5.1. T_1 values of porphyrinatochromium oxo complexes and anthracene in benzene-d_6

Compound	proton	T_1 sec.
(OEP)Cr=0	*meso*-H	0.399(57)
(OEP)Cr=0	methyl-H	0.522(52)
(TTP)Cr=0	β-H	0.902(30)
(TTP)Cr=0	methyl-H	1.12(3)
anthracene	9,10-H	1.16(2)

Table 5.2. Molar absorptivities of metalloporphyrins at wavelengths used for kinetics

Compound	Solvent	Wavelength nm	Molar Absorptivity x 10^{-4} ($M^{-1}cm^{-1}$)
(TTP)Mn≡N	Toluene	403	3.90
(OEP)Mn≡N	Toluene	403	29.7
(TTP)Mn(II)	Toluene	403	2.22
(OEP)Mn(II)	Toluene	403	7.09
(TTP)Mn≡N	Toluene	402	3.23
(OEP)Mn≡N	Toluene	402	24.1
(TTP)Mn(II)	Toluene	402	1.67
(OEP)Mn(II)	Toluene	402	5.83
(TTP)Mn≡N	THF	560	0.222
(OEP)Mn≡N	THF	560	3.11
(TTP)Mn(II)	THF	560	1.17
(OEP)Mn(II)	THF	560	0.448
(TTP)Mn≡N	MFA	560	0.495
(OEP)Mn≡N	MFA	560	2.70
(TTP)Mn-Cl	MFA	560	0.912
(OEP)Mn-Cl	MFA	560	0.617
(TTP)Cr=O	Benzene	572	0.307
(OEP)Cr=O	Benzene	572	2.69
(TTP)Cr-Cl	Benzene	572	0.641
(OEP)Cr-Cl	Benzene	572	0.764

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