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                                                        Work type : RES
Contract#: 5 R01 HL33734-03   Mod #: INITIATION Document : GRANT
Prime #:   Contract entity: GTRC

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Main project #:

Project unit: CHEM   Unit code: 02.010.136
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   BOTTOMLEY L A   CHEM

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Sponsor/division codes: 108   / 001

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      Contract value   72,034.00   72,034.00
      Funded   72,034.00   72,034.00
Cost sharing amount   0.00

Does subcontracting plan apply ?: N

Title: ELECTROCHEMICAL STUDIES OF CAPPED METALLOPORPHYRINS

PROJECT ADMINISTRATION DATA

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  Security class (U,C,S,TS) :   ONR resident rep. is ACO (Y/N): N
  Defense priority rating   : N/A   NIH supplemental sheet
  Equipment title vests with: Sponsor   GIT X
    MUST BE INCLUDED IN AWARD BUDGET, OR HAVE PRIOR IPAS APPROVAL.

Administrative comments -
  INITIATION

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 03/06/91

Project No. G-33-679_____   Center No. R6041-3A0_____

Project Director BOTTOMLEY L A_____   School/Lab CHEMISTRY_____

Sponsor DHHS/PHS/NIH/NATL INSTITUTES OF HEALTH_____

Contract/Grant No. 5 R01 HL33734-03_____   Contract Entity GTRC

Prime Contract No. _____

Title ELECTROCHEMICAL STUDIES OF CAPPED METALLOPORPHYRINS_____

Effective Completion Date 890630 (Performance) 890930 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	_____
Final Report of Inventions and/or Subcontracts	Y	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments No invoice, payment on line-of-credit; patent reporting on HHS 568

Subproject Under Main Project No. _____

Continues Project No. G-33-695/R6041-2A0

Distribution Required:

Project Director	Y
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Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
	N

Final Patent Questionnaire sent to PDPI.

PROGRESS REPORT

This section of the proposal details progress achieved during the period 09/15/85 through 10/15/88. The following table lists the personnel supported by this grant, their periods of service and the percentage of their appointments.

Personnel (title)	Dates of Service	Percentage Appointment
Lawrence A. Bottomley (P.I.)	07/01/86-09/30/86	25
	07/01/87-09/30/87	25
	07/01/88-09/30/88	20
Jean-Noel Gorce (R. A.)	10/01/85-03/31/86	25
Frank L. Neely (R. A.)	04/01/86-09/30/88	25
Grant N. Holder (R. A.)	04/01/86-12/31/87	25
John C. Helfrick, Jr. (R.A.)	04/01/86-06/30/88	12.5
James S. Quick (R. A.)	04/01/86-12/31/86	12.5
Ann E. Popp (R. A.)	07/01/86-09/30/86	12.5

The immediate goal of the current research program was the complete characterization of the redox chemistry of synthetic oxygen carrying hemoprotein model compounds which possess metal coordination geometries found *in vivo*. The specific aims for the previous three years were:

1) to synthesize a series of functionalized derivatives of Baldwin's "capped" porphyrin containing Co(II), Fe(III), Ru(II) and Os(II) central metal ions and to investigate, in detail, the electrode reactions of these species in nonaqueous media.

2) to react each of the above capped metalloporphyrins with a series of Lewis bases to form pentacoordinate derivatives.

3) to demonstrate that the pentacoordinate metallo derivatives of Baldwin's "capped" porphyrin remain pentacoordinate during all electron transfer steps.

4) to synthesize Fe(II), Ru(II) and Os(II) "capped" porphyrin complexes with CO, CS, CSe, or dioxygen axially coordinated under the cap, and to investigate, in detail, the electrode reactions of these species in nonaqueous media.

Research Accomplishments During Tenure of Grant: Several hundred milligrams each of Cr, Mn, Fe, Co, Zn and Ru derivatives of C_2Cap have been synthesized. Initial voltammetric and spectroelectrochemical studies on the $Co(C_2Cap)$ complex revealed several interesting aspects. First, the potentials for electrooxidation of the $Co^{II}(C_2Cap)$ complex were not those predicted from consideration of the phenyl ring substituent effect alone. This suggested that the cap causes a significant change in solvation of the porphyrin as compared to other sterically unencumbered porphyrins. Secondly, the kinetics of the heterogeneous rate of electron transfer were comparable to that of the uncapped homologs. Thirdly, the oxidation of $Co^{II}(C_2Cap)$ in

the presence of a one-thousand-fold excess of nitrogenous base proceeded reversibly whereas the corresponding oxidation of the unhindered homologs did not. In the unencumbered Co porphyrins, the Co^{III} to Co^{II} electron-transfer occurred concomitantly with changes in the number of ligands coordinated to the Co center. Under these conditions, the $Co^{II}(C_2Cap)$ complex exhibited only outer sphere redox reactivity and gave oxidation products whose spectra were markedly different from that of the unhindered homologs. (For details, refer to Appendix A.) While the evidence obtained in this study did not satisfy specific aim #3 (vide supra), it did rule out the formation of hexacoordinate $Co^{III}C_2Cap$-nitrogenous base diadducts. The presence and identity of a second axial ligand has yet to be determined. It seems plausible that the supporting electrolyte anion may be pushing the cap away from the porphyrin plane and occupying this site. A second, although unlikely possibility is that the capping function itself may be serving as a ligand. *One of the aims of this renewal is to define the role of the capping group in determining central metal coordination number.*

Electrochemical and spectroelectrochemical studies on the Zn, Cr, Mn and Fe derivatives have been carried out during the second and third year of the grant. In noncoordinating, aprotic media, up to three, single-electron oxidation processes and up to three, single-electron reduction processes are observable within the potential window of the nonaqueous solvent/supporting electrolyte system. Experiments have also been carried out in the presence of nitrogenous bases. Reductions of the five coordinate (nitrogeneous base)$Zn(C_2Cap)$ were comparable, in all respects, to that of other unencumbered porphyrins. This inferred that the supporting electrolyte cation, tetra-n-butylammonium, is probably too large to fit under the cap. Our findings on the redox reactivity of the $Mn(C_2Cap)$ complex have indicated that the cap is effective in the prevention of the formation of nitrogenous base diadducts. This work has been published (see reprint in Appendix).

Basolo and coworkers[9-16] have electronic spectral data which they have interpreted as indicative of nitrogenous base diadduct formation with various Fe capped porphyrins. They proposed that the extent of diadduct formation is dependent upon 1) the size of the ligand; 2) the distance between the metal center and the steric blocking moiety; and 3) the flexibility of the cap linkages. Our spectroelectrochemical studies of $Fe(C_2Cap)$ in the presence of excess nitrogenous base demonstrated that its redox reactivity differs markedly from that of the Fe porphyrins without steric encumbering groups. The latter complexes readily form nitrogenous base diadducts under the conditions investigated. Formal potentials for the reduction of the $\{Fe^{III}C_2Cap\}^+$ complexes were shifted to higher potentials by up to 300 mV compared to the unencumbered $(L_2)Fe(POR)$ complexes. Significant differences in the electrode reaction pathways were observed. We have postponed publication of our results on the $Fe(C_2Cap)$ complexes until conclusive proof of the structure of redox pathway intermediates has been provided. Thus, knowledge of the "capped" metalloporphyrin axial ligand dynamics is essential for the successful attainment of the original aims of this research program (especially item 3 above). *One of the major aims of this renewal is to definitively prove the number and identity of axial ligands for each species involved in the redox pathway of capped metalloporphyrins, especially the Fe derivatives.*

A second major thrust was devoted to completing our characterization of chalcocarbonyl Fe porphyrins without steric encumbering groups. Our objective was two-fold: a) to determine the cis-trans effects operative for chalcocarbonyl Fe porphyrin complexes, and b) to test the possibility of forming novel binuclear Fe porphyrins by reaction of the chalcocarbonyl Fe porphyrins with exo-bidentate ligands. An understanding of the cis-trans effects was deemed essential in the design of synthetic routes for attainment of original aim #4 (vide supra). The porphyrin studied were the thiocarbonyl and selenocarbonyl adducts of 2,3,7,8,12,13,17,18-octaethylporphinatoiron(II) and 5,10,15,20-tetraphenyporphinatoiron(II), hereafter abbreviated

S=C-Fe(OEP), Se=C-Fe(OEP), S=C-Fe(TPP) and Se=C-Fe(TPP), respectively. All four compounds underwent as many as three electrooxidation and two electroreduction process at a Pt electrode, without loss of the diatomic axial ligand. This reactivity contrasted with the structurally analogous OC-Fe(POR) complexes which readily lose the diatomic upon electrooxidation. Reaction of S=C- or Se=C- Fe porphyrins with a series of monodentate nitrogenous bases produced exceptionally stable six-coordinate complexes which could also be sequentially oxidized or reduced with complete retention of the chalcocarbonyl ligand. A paper describing the results obtained for the OEP complexes is included in the Appendix.

In general, when Fe^{II} porphyrins are treated with exobidentate nitrogenous bases, L-L, polymeric materials are produced. This has been recently exploited by Collman et.al.[48] in their preparation of novel metalloporphyrin-based conducting polymers. During the first year of the grant, we hypothesized that the polymerisation reaction could be inhibited either by:

a) prior installation of a nonlabile axial ligand such as CS or CSe, or

b) placement of groups with a high degree of steric hindrance onto one side of the porphyrin.

Reaction of chalcocarbonyl Fe(TPP) complexes with L-L afforded hexacoordinate mononuclear and binuclear complexes in dynamic equilibrium (as shown by nuclear magnetic resonance studies of these reactions). The predominant species in solution could be controlled by varying both the temperature and the relative concentration of L-L to Fe. The redox reactivity of these complexes mirrored that observed with monodentate nitrogenous bases. No evidence inferring metal-metal interaction in the binuclear species was obtained. For further details, see reprint in Appendix.

A convenient and qualitative means for evaluating the capping group's ability to prevent the formation of a hexacoordinate Fe center would be to react $Fe(C_2Cap)$ with L-L. Collman[48] has shown that there exists a strong thermodynamic driving force for the formation of polymers when sterically unhindered porphyrins are treated with L-L. Thus, this experiment should be a reliable indicator of the capping groups ability to impede formation of a hexacoordinate Fe center, at least with nitrogenous bases.

When the ferrous "capped" porphyrin was reacted with a series of exo-bidentate nitrogenous bases, *no evidence of polymer formation was observed*. Similar to our findings for the chalcocarbonyl Fe porphyrins, both mononuclear and binuclear complexes were obtained in the reaction of $Fe(C_2Cap)$ with L-L. However, a small but measurable degree of ligand-mediated metal-metal interaction was observed with the $[Fe(C_2Cap)]_2$L-L complexes. Structurally, the binuclear "capped" porphyrin dimers should possess Fe centers which are displaced from the nitrogen core of the porphyrin (toward the bridging ligand) whereas the binuclear complexes with the nonlabile axial ligand blocking group should possess in-plane Fe centers. We have hypothesized that significant ligand-mediated metal-metal interaction will only be observed for binuclear metalloporphyrins possessing metal centers significantly displaced from the nitrogen core of the porphyrin. This displacement should maximize the metal-ligand pi-orbital overlap and minimize the coulostatic repulsion between the porphyrin and the L-L bridging moiety. Although NMR studies indicate that the Fe centers are out of the plane of the "capped" porphyrin, we wish to confirm our hypothesis with a crystal structure of at least one of the binuclear complexes. Attempts at growing a suitable crystal have, to date, been unsuccessful. We intend to continue our efforts in this direction.

Modifications to Proposed Specific Aims: During the last quarter of the second year of the

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grant, we initiated a study of the chemistry of nitrido Mn^V porphyrins. Groves, Buchler, Hill, Goff and others[39] have shown that high valent oxo-Cr, oxo-Mn and oxo-Fe porphyrins were capable of oxygen atom transfer to olefins and paraffins. This reactivity mimicked that of the monooxygenases, especially cytochrome P-450. Since the nitrido-Mn^V core is isoelectronic with the ferryl moiety, we hypothesized that similar atom transfer reactivity might be possible. Indeed, Groves and Takahashi[49] have previously shown that nitrido Mn tetramesitylporphyrin, $NMn^V(TMP)$, could be activated and the nitrogen subsequently transferred to cyclooctene, producing the corresponding aziridine and $\{Mn^{III}(TMP)\}^+$. We set out to determine if:

a) this reactivity could be generalized to a variety of non-sterically encumbered Mn porphyrins,

b) nitrido derivatives of capped metalloporphyrins could be prepared with complete maintenance of the capping functionality, and

c) if, parts a and b were successful, to place the nitrido-metal "capped" porphyrins within the general framework of high valent metalloporphyrin chemistry.

We found that the nitrido Mn(V) "capped" porphyrin can be prepared quantitatively from the Mn(III) "capped" porphyrin by treatment with aqueous ammonia and sodium hypochlorite. The ester linkages holding the cap above the metalloporphyrin core are not cleaved. The nitrido group can be activated by reaction with trifluoroacetic anhydride forming a nitrene Mn(V) "capped" porphyrin. This species reacts with olefins at rates at least one order of magnitude faster than their planar porphyrin counterparts. To ascertain whether this increase in rate was due to the presence of the capping group or due to the increased porphyrin basicity produced by the ether substituents on the phenyl rings, we explored the effect of porphyrin substituents on the rates of formation of the nitrene complexes. We found that the rate of nitrene formation and, consequently, the rate of nitrogen atom transfer from NMn(POR) to olefins is markedly dependent upon the basicity of the porphyrin ring and upon the steric environment of the NMn(POR) reactant. We demonstrated that the rate of Mn-nitrene formation can be varied over three orders of magnitude through appropriate selection of the porphyrin ring structure. Porphyrins with strongly electron-donating substituents enhance the rate of coordinated nitrene formation. This trend is opposite to that observed for oxygen atom transfer reactivity of oxo-Fe and oxo-Mn porphyrins. The highest rates observed for the formation of coordinated nitrene Mn porphyrins were with $NMn(C_2Cap)$. Although the rate observed for the reaction of this porphyrin was close to that required for utilization as an aziridine synthon, the synthetic complexity in preparing the capped porphyrin will preclude its widespread use. Reprints are included in the appendix.

Various nitrido Cr^V porphyrins were also prepared, including the capped derivative. The redox reactivity of these complexes was investigated by the voltammetric and spectroelectrochemical (electronic and EPR) techniques utilized in the study of the nitrido-Mn analogs. Each NCr(POR) complex investigated underwent two, single electron reversible oxidation and two, single electron reversible reduction reactions at a Pt electrode. The site of each charge transfer reaction was centered on the porphyrin ring. This compares with our findings on nitrido Mn porphyrins but contrasts with the general redox behavior of Cr porphyrins. The reactivity of nitrido Cr porphyrins with olefins in the presence of substituted acetic anhydrides was also explored in an attempt to promote nitrogen atom transfer chemistry analogous to that observed for nitrido Mn porphyrins. The reaction of nitrido Cr porphyrins with substituted acetic anhydrides was observed at rates at least an order of magnitude faster than the corresponding Mn complexes. However, the subsequent transfer of the coordinated

nitrene from the Cr center to olefins was not observed. A spectroelectrochemical investigation revealed that the nitrenoid Cr porphyrins are best described as Cr(IV) cation radicals. This is in contrast to the Mn complexes which formally possess Mn(V) centers and may account for the unreactivity of the nitrenoid Cr porphyrins with olefins. This work has been submitted for publication in *Inorg. Chem.*

During the last two months, we attempted to prepare novel binuclear mu-nitrido complexes. The extensive literature on $[Fe(TPP)]_2N$ indicated that mu-nitrido linkages can be quite stable. Also, West and coworkers[50] had shown that homo- and hetero-binuclear oxo-bridged complexes were easily prepared by reaction of oxo-Cr^{IV} porphyrins with M^{II} macrocyclic complexes. When the partial transfer of the nitrido group from NMn(OEP) to ClCr(TPP) was attempted, we found that the following reaction proceeded rapidly, irreversibly and quantitatively.
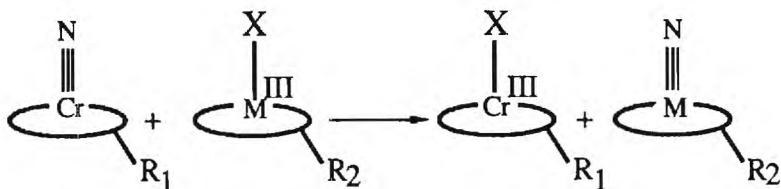
This reaction is the first example of a net, two-electron process involving nitrido metalloporphyrins. More importantly, this reaction pathway is the first example of complete, intermetal, nitrogen atom transfer. The reaction rate was shown to be first order in each of the reactants. The rate can be significantly diminished either by the placement of steric groups on the porphyrin periphery or by addition of nitrogenous bases capable of axial ligation with the Cr^{III} reactant. In very recent experiments, we've shown that this unusual reactivity is not limited to the transfer of the nitride from Mn^V to Cr^{III}. This reaction pathway is operative for Mn to Mn and Cr to Cr transfer as well. Our preliminary findings have just been submitted for publication in *J. Am. Chem. Soc.* Because of the unusual reactivity described therein, a preprint is included in the Appendix.

Publications:

a) Published during the grant period:

"Spectroelectrochemistry of Cobalt 'Capped' Porphyrins" by L. A. Bottomley, J.-N. Gorce and W. M. Davis, *J. Electroanal. Chem.* **1986**, 202, 111-124.

"Spectroelectrochemistry of a Urea-Linked Oxo-Bridged Iron Porphyrin Dimer" by L. A. Bottomley, J.-N. Gorce and J. T. Landrum, *Inorg. Chim. Acta* **1986**, 125, 135-142.

"Spectroelectrochemistry of (u-Oxo)bis[(phthalocyaninato)iron-(III)]" by L. A. Bottomley, C. Ercolani, J.-N. Gorce, G. Pennesi and G. Rossi, *Inorg. Chem.* **1986**, 25, 2338-2342. This work was partially supported by this grant.

"The Electrochemistry of Thiocarbonyl and Selenocarbonyl Iron Octaethylporphyrins" by L. A. Bottomley and J.-N. Gorce, *Polyhedron* **1988**, 7, 589-596.

"Redox Reactivity of Manganese Capped Metalloporphyrins" by L. A. Bottomley, F. L. Neely, J. F. Luck and J. S. Quick, in "Redox Chemistry and Interfacial Behavior of Biological Molecules" G. Dryhurst and K. Niki, eds. Plenum Press, **1988**.

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*Number pages consecutively at the bottom throughout the application. Do not use suffixes such as 5a, 5b

"Spectroelectrochemical Studies of High Valent Nitrido Metalloporphyrins" by L. A. Bottomley, F. L. Neely and J.-N. Gorce *Inorg. Chem.* **1988**, 27, 1300-1303.

"The Reactivity of Pentacoordinate Ferrous Porphyrins with Exo-bidentate Nitrogenous Bases. Mononuclear and Binuclear Complexes in Dynamic Equilibrium" by L. A. Bottomley and J.-N. Gorce, *Inorg. Chem.* **1988**, 27, 3733-3739.

"Nitrogen Atom Activation: The Influence of Porphyrin Ring Structure on the Kinetics of the Reaction of Trifluoroacetic Anhydride with Nitrido Manganese(V) Porphyrins" by L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc.* **1988**, 110, 6748-6752.

b) Manuscripts Currently in Review:

"Spectroelectrochemical Characterization of High Valent Nitrido Chromium(V) Porphyrins and Coordinated Nitrene Chromium(IV) Porphyrins: L. A. Bottomley and F. L. Neely, submitted for publication in *Inorg. Chem.*

"The Nitrogen Atom Transfer Reactivity of Nitrido Manganese(V) Porphyrins with Chromium(III) Porphyrins: L. A. Bottomley and F. L. Neely, submitted for publication in *J. Am. Chem. Soc.*

EXPERIMENTAL DESIGN AND METHODS

Axial Ligation of Capped Porphyrins: Several avenues are available to assist us in determining the number and identity of the ligands bound to the metalloporphyrin. Traditionally, the definitive technique has been x-ray crystallography. However, as detailed in the SIGNIFICANCE section of this proposal, structural features in the solid state do not carry over into solution. In addition, discovery of the appropriate conditions for growing diffraction quality crystals of capped porphyrins in a reasonable period of time have proven elusive. Ibers reported[29] that the crystals used in his crystallographic study of Co(C_3Cap) were obtained by diffusion of methanol vapor into a dilute $CHCl_3$ solution of the porphyrin *over the period of three years* at 5 °C.

A second avenue that we have used extensively is UV-visible spectrometry. We have utilized this technique for following the time course of metal insertion and axial ligation studies of the capped porphyrins. We have probed the reactivity of and made kinetic determinations on various nitrido metalloporphyrins (as described in the progress report section of this proposal). We have performed simultaneous electrochemical and UV-Vis spectrophotometric experiments in an attempt to identify the type and number of axial ligands on each of the electrogenerated intermediates. For example, results from spectroelectrochemical experiments on Co(C_2Cap), Cr(C_2Cap) and Mn(C_2Cap) disproved the notion that more than one substituted pyridine molecule is bound to the central metal ion, regardless of metal atom valence. However, the information inherent in the available data did not permit the determination of the extent of interaction between the oxidized metal center and either the pyrromellitoyl cap or the counterion of the supporting electrolyte.

A third avenue involves the use of magnetic resonance spectroscopy. Extensive use of NMR has been made in probing axial ligand dynamics of a wide variety of hemoproteins and hemoprotein model compounds.[26] Although we have and will continue to use this technique for the characterization of isolated species, present technology prevents us from

(5)   to determine the reactivity trends of the novel metal-imide and metal-acylimido porphyrin complexes prepared under specific aim (4).

In achieving these aims, we anticipate the discovery of novel homo- and hetero-binuclear complexes. These will result from partial N atom transfer between mononuclear nitrido-donor complexes and mononuclear acceptors. We also anticipate the discovery of catalytic metalloporphyrin-based imido group transfer reactions, analogous to the oxygen atom transfer reactions of the oxidative heme enzymes.[2]

BACKGROUND AND PRELIMINARY RESULTS

Our previous efforts have been devoted to the preparation and characterization of stable, high valent metalloporphyrins, especially nitridomanganese porphyrins. For example, we have proven that the nitridomanganese(V) derivative of Baldwin's capped porphyrin, $NMn(C_2Cap)$, can be prepared quantitatively from $\{Mn(C_2Cap)\}^+$ by treatment with aqueous ammonia and sodium hypochlorite. The ester linkages holding the cap above the metalloporphyrin core were not cleaved. A spectroelectrochemical study of $NMn(C_2Cap)$ as well as other nitridomanganese tetraphenylporphyrins containing phenyl ring substituents found that each complex underwent two chemically reversible, single-electron oxidations and reductions with full retention of the nitrido function. All electron transfer reactions occurred solely at the porphyrin ring. No discernible solvent effect was observed.[11,12]

We have probed the reactivity of nitrido metalloporphyrins.[12,13] Treatment of NMn(POR) complexes with substituted acetic anhydrides produces the corresponding acylimido complex. This species can undergo group transfer reaction from the metal center to an olefin forming an aziridine.
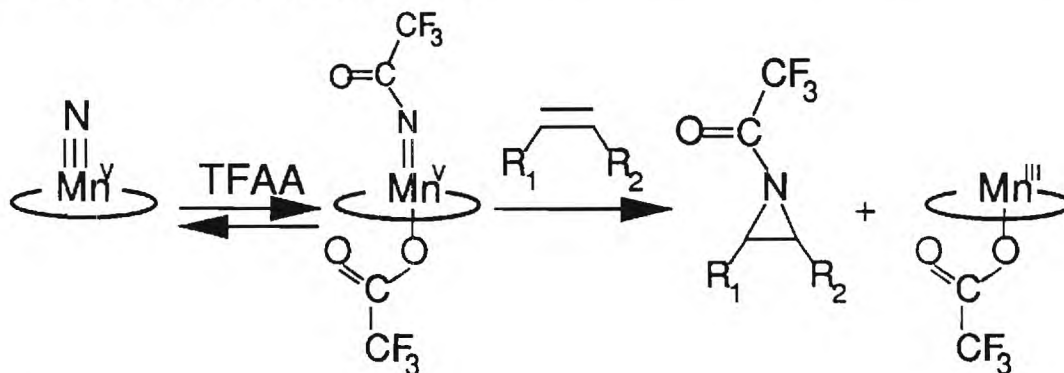
Note that the porphyrin ring is depicted as an oval about the central metal atom in all illustrations contained herein. We found that formation of the acylimido complex was the rate-limiting step in the transformation of the nitride into an aziridine. We showed that the rate of acylimido formation and, consequently, the rate of functionalized nitrogen atom transfer from NMn(POR) to olefins via acylimido group transfer is markedly dependent upon the basicity of the porphyrin ring and upon the steric environment of the NMn(POR) reactant. The rate of acylimidomanganese(V) porphyrin formation can be varied over three orders of magnitude through appropriate selection of the porphyrin ring structure. Porphyrins with strongly electron-donating substituents enhance the reaction rate. This trend is opposite to that observed for oxygen atom transfer reactivity of oxoiron and oxomanganese porphyrins. The $NMn(C_2Cap)$ complex gave the highest reaction rates. Although the rate observed for the reaction of this porphyrin was close to that required for utilization as an aziridine synthon, the synthetic complexity in preparing the capped porphyrin will preclude its widespread use.

Various NCr(POR) complexes were also prepared and their reactions investigated.[14] The redox reactivity of these complexes was examined by the voltammetric and spectroelectrochemical (electronic and EPR) techniques utilized in the study of the nitridomanganese analogs. Each NCr(POR) complex investigated underwent two single electron reversible oxidation and two single electron reversible reduction reactions at a Pt electrode. As with their nitridomanganese counterparts, the site of each charge transfer reaction was centered on the porphyrin ring. The reactivity of NCr(POR) with olefins in the presence of substituted acetic anhydrides was also explored in an attempt to promote the formation of the acylimido complex and subsequent group transfer to the olefin. The reaction of NCr(POR) with substituted acetic anhydrides was observed at rates at least an order of magnitude faster than the corresponding manganese complexes. However, the subsequent transfer of the coordinated acylimido group from the Cr center to olefins was not observed. A spectroelectrochemical investigation revealed that the acylimidochromium porphyrins are best described as chromium(IV) porphyrin cation radicals. This is in contrast to the Mn complexes which formally possess manganese(V) centers and may account for the nonreactivity of the acylimidochromium porphyrins with olefins.

Nitrogen Atom Transfer. In the course of subsequent studies of the reactivity of NMn(POR) with other electrophiles, we attempted the reaction of NMn(POR) with ClCr(POR) in hopes of obtaining novel heterobinuclear μ-nitrido complexes. The extensive literature on [Fe(TPP)]$_2$N indicated that μ-nitrido linkages can be quite stable.[15] Also, West and coworkers[16] had shown that homo- and hetero-binuclear oxo- bridged complexes were easily prepared by reaction of oxochromium(IV) porphyrins with metal(II) macrocyclic complexes. Holm has described the formation of μ-oxo or μ-nitrido dimers as evidence for partial intermetal atom transfer.[1] When the partial transfer of the nitrido group from NMn(OEP) to ClCr(TPP) was attempted, we found that the following reaction proceeded rapidly, irreversibly and quantitatively.[17]
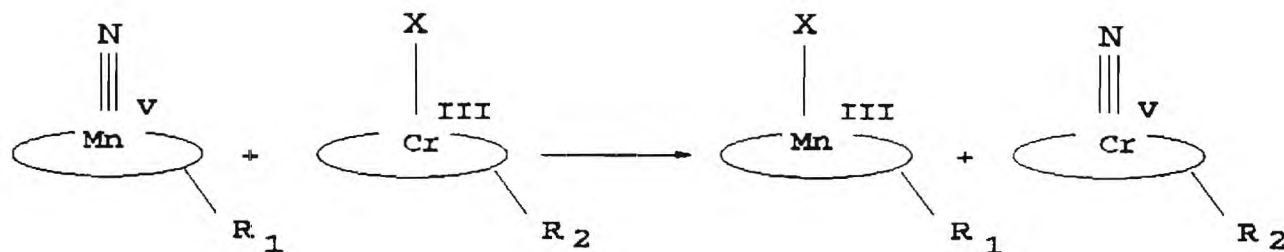
This reaction was the first example of a net two-electron process involving nitrido metalloporphyrins. The rate law was shown to be first order in each of the reactants. The rate was significantly diminished, either by the placement of steric groups on the porphyrin periphery or by addition of nitrogenous bases capable of axial ligation with the Cr(III) reactant. Our preliminary findings were published as a communication.[17] A systematic study[18] of the stereoelectronic aspects of this reaction has shown that the reaction rate is dependent upon the electronic and steric effects of the porphyrin ring substituents, the identity of the anion coordinate-covalently bound to the chromium(III) reactant and also, upon the solvent dielectric constant and donor strength. We have proposed that the mechanism of this reaction involves backside nucleophilic attack of the nitrido metalloporphyrin donor on the metal(III) porphyrin acceptor facilitating a net two-electron transfer process mediated by a binuclear μ-nitrido intermediate. The mechanism proposed for the N atom transfer between NMn(POR) and XCr(POR) is depicted in Fig. 1.
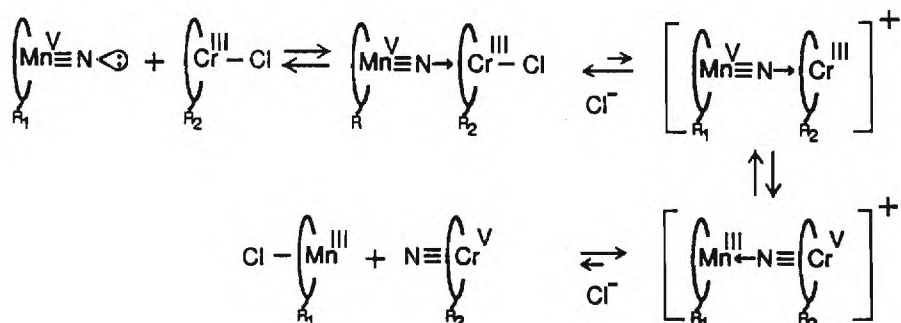
Figure 1. Proposed mechanism for the nitrogen atom transfer between NMn(POR) donors and ClCr(POR) acceptors.

We have recently discovered that this unusual reactivity is not limited to the transfer of the nitride from manganese(V) to chromium(III) porphyrins. Intermetal nitrogen atom transfer is observed between chromium(V) porphyrin donors and chromium(III) porphyrin acceptors and between manganese(V) porphyrin donors and manganese(III) porphyrin acceptors as well.[19,20] In contrast to the transfer of the nitrido group from NMn(OEP) to ClCr(TPP), the reaction of NCr(OEP) with ClCr(TPP) proceeds rapidly to an equilibrium mixture of reactants and products. An identical mixture is obtained when NCr(TPP) reacts with ClCr(OEP). We have determined the equilibrium constant for this reaction to be 1.4 ± 0.15 at 298 K from spectrophotometric data. The rate law was first order in each reactant; the rate constant for the forward reaction was calculated to be 94 ± 9 $M^{-1}s^{-1}$. This result was deduced from the electronic spectral changes acquired as a function of time using King's method.[21] A listing of the equilibrium constants and forward rate constants obtained for the reaction of NCr(OEP) with a variety of phenyl ring substituted chlorochromium(III) tetraphenylporphyrins is given in Table I.

Table I. Summary of Equilibrium Constants and Forward Rate Constants for the Reaction of NCr(OEP) with ClCr(4-substituted TPP) in Benzene.

Acceptor	K_{eq} (at 298 K)	k_f ($M^{-1}s^{-1}$)
ClCr(4-benzyloxy-TPP)	2.1 ± 0.22	6.8 ± 0.6
ClCr(4-methoxy-TPP)	1.6 ± 0.20	16 ± 2
ClCr(4-methyl-TPP)	1.5 ± 0.18	60 ± 6
ClCr(TPP)	1.4 ± 0.15	94 ± 9
ClCr(4-fluoro-TPP)	0.70 ± 0.10	120 ± 12
ClCr(4-chloro-TPP)	0.50 ± 0.06	470 ± 50
ClCr(4-trifluoromethyl-TPP)	0.37 ± 0.04	1420 ± 100

The equilibrium constant magnitude increased slightly (a Hammett-Taft rho of -0.20) with an increase in the electron-donating ability of the phenyl ring substituent. However, the forward rate constant increased by over three orders of magnitude with an increase in the electron-withdrawing ability of the phenyl ring substituent (a Hammett-Taft rho of 0.72). This trend is consistent with the hypothesis of nucleophilic attack by the nitride on the chromium(III) center. The presence of pyridine in molar ratios as low as 2:1 (with respect to chlorochromium(III) porphyrin) halted the reaction. Also, no reaction was observed between NCr(OEP) and any ClCr(2,6-disubstituted-TPP). When the reaction of NCr(OEP) with ClCr(TPP) was carried out in 1,2-dichloroethane, the measured values of K_{eq} and k_f were 1.1 and 440 $M^{-1}s^{-1}$, respectively. Thus, increasing solvent dielectric enhanced both the forward and reverse reaction rates, resulting in an essentially unchanged equilibrium distribution.

We have also found reversible reactivity between NMn(OEP) and ClMn(TPP), but the rate of the forward reaction is significantly slower than that observed for the chromium to chromium N atom transfer. Interestingly, Woo[22] and Takahashi[23] have reported N atom transfer concomitant with the transfer of three electrons between manganese(V) and manganese(II).

Intermetal nitrogen atom transfer reactivity is not limited to metalloporphyrin based substrates.[20,24] We have shown that the nitride from NMn(OEP) can be transferred to ClCr(Sal$_2$en), ClMn(Sal$_2$en) and ClMn(TMTAA). The manganese(V) to manganese(III) N atom transfers were reversible reactions with K_{eq} values of 0.050 $\pm$ 0.009 and 0.69 $\pm$ 0.05 and k_f values of 12 and 22 $\pm$ 3 $M^{-1}s^{-1}$, respectively. We have hypothesized that the nitrogen atom transfer reactivity observed for both nitridomanganese(V) and nitridochromium(V) porphyrin donors to manganese(III) and chromium(III) macrocyclic acceptor complexes proceeds through a common mechanism, generalized in Fig. 2. This hypothesis invokes backside nucleophilic attack by the nitride on the metal(III) center. The concomitant two-electron transfer is mediated by a N bridged, binuclear intermediate. The proposed preparation of novel nitrido metalloporphyrins (specific aim one) will provide a straightforward means for evaluation of the scope and generality of the N atom transfer reaction. Additional support for the proposed mechanism will be provided by the isolation and structural characterization of novel binuclear N-bridged complexes. These binuclear complexes should be analogs of the proposed intermediates. Thus, the novelty of the N atom transfer reaction, the variation in number of electrons involved and the general lack of information concerning non-oxygen heteroatom transfer reactions provide strong incentives for our continued research in this area.

Functionalized Nitrogen Atom Transfer. Preliminary studies on functionalized nitrogen atom transfer other than with the metal-acylimido complexes detailed above have been carried out by the Mansuy, Breslow, Ortiz de Montellano and
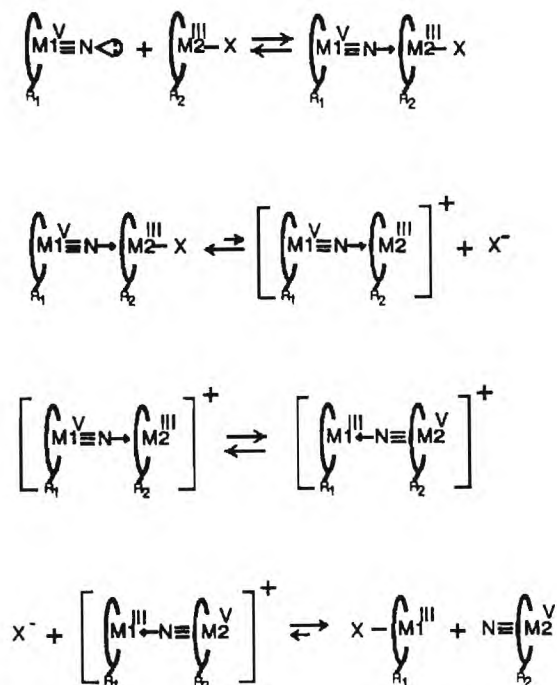

Figure 2. Proposed mechanism for intermetal nitrogen atom transfer.

White research groups. Mansuy has shown that chloro or perchlorato tetraphenylporphinatoiron(III) can catalyze the transfer of the tosylnitrene moiety of N-tosyliminoaryliodinane (the functional equivalent of iodosylbenzene) to olefins.[25,26] However, the catalytic cycle is limited by (a) the presence of adventitious water in the reaction mixture, (b) "progressive" oxidative destruction of the iron(III) porphyrin catalyst and (c) the chemically irreversible insertion of the tosylnitrene into the iron-pyrrole nitrogen bond. He has proven that the initial product in the reaction of N-tosyliminoaryliodinane with ClFe(POR) is a coordinated tosylnitrene complex.[27] In the absence of added nitrogen atom acceptors, the tosylnitrene insertion reaction is facilitated. The presence of water in the reaction hydrolyzed the iron-nitrene intermediate and resulted in the production of significant quantities of tosylamine and epoxide. When chloro-tetrakis(2,6-dichlorophenyl)porphinatoiron(III) was used as the catalyst, no oxidative decomposition of the catalyst or irreversible formation of a tosylnitrene bridged species was observed. Yields of aziridination of aromatic olefins ranged from 36 % to 90 % with this catalyst. It is presently undetermined whether the improved performance of the octachloro-substituted catalyst was due to the inductive or steric influence of the phenyl ring substituents.

Interestingly, chemoselectivity was observed when the functionalized nitrogen atom transfer of tosylnitrene to olefins was catalyzed by manganese porphyrins in place of iron.[25] Reaction of N-tosyliminoaryliodinane with olefins gave both N-tosylaziridines and allylic N-tosylamides. The combined yield of functionalized nitrogen atom transfer products was similar to that obtained for the corresponding reaction with the iron catalyst. Remarkably, the ratio of tosylamide to tosylaziridine products for the manganese porphyrin catalyst was between 6 and 20 times that of the corresponding iron porphyrin catalyst. Thus, the chemoselectivity of tosylnitrene transfer to olefins varies greatly with the identity of the metalloporphyrin catalyst. The origin of this chemoselectivity is presently undetermined.

Breslow[28] has catalyzed the tosylamidation of cyclohexane with both iron and manganese porphyrins. In the presence of these catalysts, he demonstrated intermolecular functionalized nitrogen atom transfer of cyclohexane with N-tosyliminoaryliodinane and intramolecular functionalized nitrogen atom transfer with 2,5-diisopropylbenzenesulfonamide (see top of next page).
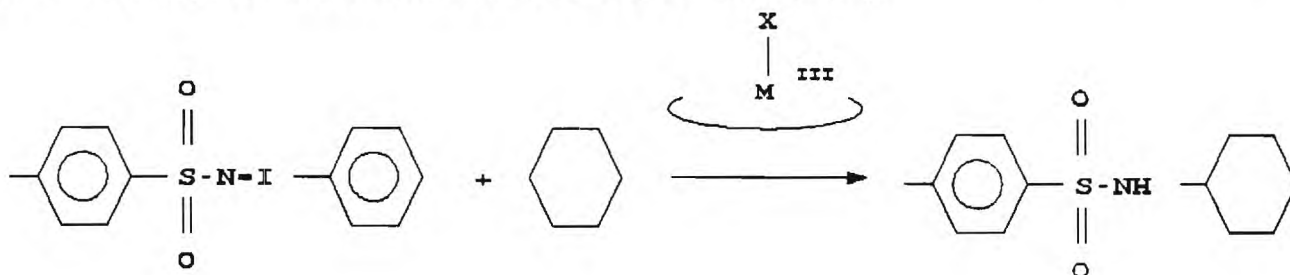
Dawson and Breslow have shown[29] that this reactivity is not limited just to monooxygenase model compounds. Liver microsomal cytochrome P-450-LM3,4 catalyzes the intramolecular functionalization of 2,5-diisopropylbenzenesulfonamide. Both Ortiz de Montellano[30] and White[31] have shown that this catalytic activity is strongly dependent upon the enzyme formulation and thus, the microenvironment of the active site. Hydroxylated products are observed for most enzymes and are a result of hydrolysis of
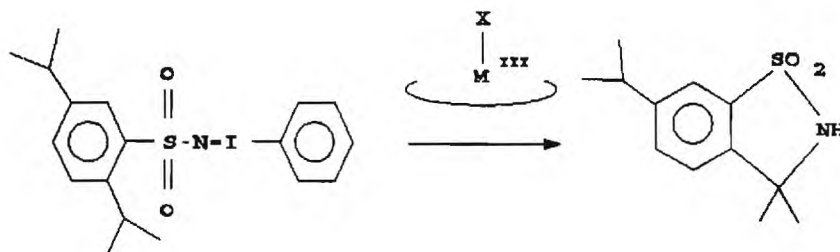
the coordinated nitrene (or metal-imido) intermediate. Indeed, coordinated nitrene-heme adducts are intermediates in the reaction of monosubstituted hydrazines with hemoglobin, myoglobin, lactoperoxidase and horseradish peroxidase producing partial inhibition or destruction of the enzyme.[32]

The proposed preparation and reactivity of new metal-imido and metal-acylimido porphyrins will test the scope and generality of the observed aziridination versus amidation chemoselectivity, as described above. The elucidation of the mechanism of both nitrogen atom transfer and functionalized nitrogen atom transfer (i.e. imido and acylimido group transfer) will lead to the development of novel synthons and improved catalytic performance. It is anticipated that the mechanistic studies proposed herein will provide straightforward synthetic avenues to substituted aziridines as well as other imido and nitrene group transfer products. Even though the development of high yield and selective routes to substituted aziridines is not the primary goal of this research program, this avenue will be explored because of its potential payoff. The regio- and stereo-specific ring-opening of epoxides is an important synthetic pathway in organic chemistry.[33] Ring-opening reactions for aziridines are also known, but the use of aziridines as nitrogen analogs of epoxides is not widespread.[34] Aziridination can be accomplished by the direct insertion of nitrenes into olefins, but this route suffers from low yields and/or lack of stereospecificity.[35] Intermolecular nitrene insertion is known for only a few nitrenes. However, the chiral aziridination of alkenes has been recently demonstrated.[36] The discovery of an improved aziridination catalyst would have a major impact on the design of new drugs and pro-drugs. Thus, our preliminary investigation into the chemistry of nitrogen atom transfer coupled with the functionalized nitrogen group transfer reactivity of both the synthetic porphyrins and the native enzymes, provides strong impetus for further investigation into the reactivity of nitrido, imido and acylimido metalloporphyrins proposed herein.

EXPERIMENTAL DESIGN AND METHODS

Specific Aim One: Novel Nitrido Metalloporphyrins. Prior to the discovery of the intermetal N atom transfer pathway, three synthetic avenues existed for the preparation of nitrido metalloporphyrins: photolysis or thermolysis of azido-metal(III) porphyrins,[37,38] oxidation of either the acetato-metal(III) or hydroxo- metal(III) porphyrins in the presence of ammonia,[39,40] or treatment of the cis- or trans-dioxo-metal(VI) with hydrazine followed by peroxyacetic acid.[41] Cr(POR) and NMn(POR) complexes have been prepared from both the azido-metal(III) and hydroxo-metal(III) porphyrins. To date, nitridoiron porphyrins have been made exclusively from the azido-Fe precursor. Both mononuclear nitridoiron(V)[42] and binuclear nitridoiron(III,IV) complexes[15,38] are known. Nitridomolybdenum(VI) and nitridoosmium(VI) porphyrins have been prepared via the hydrazine-peroxyacetic acid route.[41,43] Trimethylsilylazide has been used as a synthon for the preparation of a variety of second and third row transition nitrido-metal complexes.[44,45] Although there

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PROGRESS REPORT AND PRELIMINARY RESULTS

This section of the proposal details progress achieved during the period 09/15/85 through 05/30/89. This work was accomplished by the P.I. in collaboration with six graduate students at various levels of support. The goal of the research during the previous four years was the complete characterization of the redox chemistry of synthetic oxygen-carrying hemoprotein model compounds which possess metal coordination geometries found *in vivo*. This goal was largely achieved. The specific aims were:

1) to synthesize a series of functionalized derivatives of Baldwin's "capped" porphyrin containing Co(II), Fe(III), Ru(II) and Os(II) central metal ions and to investigate, in detail, the electrode reactions of these species in nonaqueous media.

2) to react each of the above capped metalloporphyrins with a series of Lewis bases to form pentacoordinate derivatives.

3) to demonstrate that the pentacoordinate metallo derivatives of Baldwin's "capped" porphyrin remain pentacoordinate during all electron transfer steps.

4) to synthesize Fe(II), Ru(II) and Os(II) capped porphyrin complexes with CO, CS, CSe, or dioxygen axially coordinated under the cap, and to investigate, in detail, the electrode reactions of these species in nonaqueous media.

Electrochemical and spectroelectrochemical studies on the Zn, Cr, Mn, Fe and Co derivatives of Baldwin's capped porphyrin, abbreviated $M(C_2Cap)$, have been carried out. These studies revealed two intriguing aspects. First, the potentials for electrooxidation of the $M(C_2Cap)$ complexes were not those predicted from consideration of the phenyl ring substituent effect alone. This suggested that the cap causes a significant change in solvation of the porphyrin as compared to sterically unencumbered porphyrins. Second, the kinetics of the heterogeneous rate of electron transfer were comparable to that of the uncapped homologs.
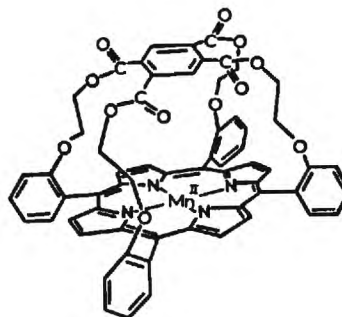
Spectroelectrochemical experiments were also performed in coordinating media. Salient features of this phase of the work include the following points: The electroactivity of the capped

porphyrins with central metal ions which favor only one axial ligand, such as (nitrogeneous base)Zn(C_2Cap), was comparable, in all respects, to that of other unencumbered porphyrins possessing the same central metal ion. From this observation, we concluded that the supporting electrolyte cation, tetra-n-butylammonium, is probably too large to fit under the cap. For capped porphyrins possessing central metal ions which possess a strong thermodynamic driving force for diadduct formation, such as $Co^{III}(C_2Cap)$, the presence of the capping functionality severely impeded completion of the Co(III) coordination sphere. Electrooxidation of $Co^{II}(C_2Cap)$ in the presence of a one-thousand-fold excess of nitrogenous base proceeded reversibly whereas the corresponding oxidation of the unhindered homologs did not. For the unencumbered Co porphyrins, the Co(III) to Co(II) electron-transfer occurred concomitantly with changes in the number of ligands coordinated to the Co center. Under these conditions, the $Co^{II}(C_2Cap)$ complex exhibited only outer sphere redox reactivity and gave oxidation products whose spectra were markedly different from that of the unhindered homologs. Similar findings were obtained for Mn(C_2Cap). Further details concerning the electrochemistry and spectroelectrochemistry of both the Co and Mn derivatives of Baldwin's capped porphyrin can be found in reprints #1 and #2 included in the Appendix section.

Our spectroelectrochemical studies of Fe(C_2Cap) in the presence of excess nitrogenous base demonstrated that its redox reactivity also differs markedly from that of the Fe porphyrins without steric encumbering groups. The latter complexes readily form nitrogenous base diadducts under the conditions investigated. Formal potentials for the reduction of the $\{Fe^{III}(C_2Cap)\}^+$ complexes were shifted to higher potentials by up to 300 mV compared to the unencumbered $(L_2)Fe(POR)$ complexes. Significant differences in the electrode reaction pathways were observed. We have postponed publication of our results on the Fe(C_2Cap) complexes until conclusive proof of the structure of redox pathway intermediates has been provided.

During the second year of the grant, we completed our characterization of chalcocarbonyl Fe porphyrins. Our objectives were to determine the cis-trans effects operative for chalcocarbonyl Fe porphyrin complexes, and to test the possibility of forming novel binuclear Fe porphyrins by reaction of the chalcocarbonyl Fe porphyrins with exo-bidentate ligands. An understanding of the cis-trans effects was deemed essential in the design of synthetic routes for attainment of original aim #4 (vide supra). The porphyrins studied were the thiocarbonyl and seleno-carbonyl adducts of 2,3,7,8,12,13,17,18-octaethylporphinatoiron(II) and 5,10,15,20-tetraphenyporphinatoiron(II), hereafter abbreviated S=C-Fe(OEP), Se=C-Fe(OEP), S=C-Fe(TPP) and Se=C-Fe(TPP), respectively. All four compounds underwent as many as three electrooxidation and two electroreduction process at a Pt electrode, without · loss of the diatomic axial ligand. This

reactivity contrasted with the structurally analogous OC-Fe(POR) complexes which readily lose the diatomic upon electrooxidation. Reaction of S=C- or Se=C- Fe porphyrins with a series of monodentate nitrogenous bases produced exceptionally stable six-coordinate complexes which could also be sequentially oxidized or reduced with complete retention of the chalcocarbonyl ligand. Further details concerning the electrochemistry and spectroelectrochemistry of thiocarbonyl and selenocarbonyl derivatives of Fe(OEP) can be found in reprint #3 in the Appendix section.

In general, when Fe^{II} porphyrins are treated with exobidentate nitrogenous bases, L-L, polymeric materials are produced. This has been recently exploited by Collman et.al.[23] in their preparation of novel metalloporphyrin-based conducting polymers. During the first year of the grant, we hypothesized that the polymerization reaction could be inhibited either by a) prior installation of a nonlabile axial ligand such as CS or CSe, or b) placement of groups with a high degree of steric hindrance onto one side of the porphyrin. Reaction of chalcocarbonyl Fe(TPP) complexes with L-L afforded hexacoordinate mononuclear and binuclear complexes in dynamic equilibrium (as shown by nuclear magnetic resonance studies of these reactions). The predominant species in solution could be controlled by varying both the temperature and the relative concentration of L-L to Fe. The redox reactivity of these complexes mirrored that observed with monodentate nitrogenous bases. No evidence inferring metal-metal interaction in the binuclear species was obtained. Further details can be found in reprint #4 in the Appendix section.

When $Fe(C_2Cap)$ was treated with a series of exo-bidentate nitrogenous bases, *no evidence of polymer formation was observed*. Similar to our findings for the chalcocarbonyl Fe porphyrins, both mononuclear and binuclear complexes were obtained in the reaction of $Fe(C_2Cap)$ with L-L. However, a small but measurable degree of ligand-mediated metal-metal interaction was observed with the $[Fe(C_2Cap)]_2$L-L complexes. Structurally, the binuclear "capped" porphyrin dimers should possess Fe centers which are displaced from the nitrogen core of the porphyrin (toward the bridging ligand) whereas the binuclear complexes with the nonlabile axial ligand blocking group should possess in-plane Fe centers. We have hypothesized that significant ligand-mediated metal-metal interaction will only be observed for binuclear metalloporphyrins possessing metal centers significantly displaced from the nitrogen core of the porphyrin. This displacement should maximize the metal-ligand pi-orbital overlap and minimize the coulostatic repulsion between the porphyrin and the L-L bridging moiety. Although NMR studies indicate that the Fe centers are out of the plane of the capped porphyrin, we wish to confirm our hypothesis with a crystal structure of at least one of the binuclear complexes. Attempts at growing a suitable crystal have, to date, been unsuccessful.

Preliminary Studies on Nitrogen Atom Transfer. During the end of the second year of the grant, we initiated a study of the chemistry of capped porphyrins containing high valent metal centers and soon focused our attention on the chemistry of nitrido Mn(V) porphyrins. Since the nitrido-Mn(V) core is isoelectronic with the ferryl moiety, we hypothesized that atom transfer reactions might be possible with these complexes. The capability and propensity of oxo-Cr, oxo-Mn and oxo-Fe porphyrins for oxygen atom transfer to olefins and paraffins was well documented.[1,2] This reactivity mimicked that of the monooxygenases, especially cytochrome P-450. Indeed, Groves and Takahashi[24] had demonstrated that nitrido Mn tetramesitylporphyrin, $NMn^V(TMP)$, could be activated and the nitrogen subsequently transferred to cyclooctene, producing the corresponding aziridine and $\{Mn^{III}(TMP)\}^+$. First, we set out to determine if nitrido derivatives of capped metalloporphyrins could be prepared with complete maintenance of the capping functionality. Second, we sought to place the nitrido metalloporphyrins within the general framework of high valent metalloporphyrin chemistry.

We found that the nitrido Mn(V) capped porphyrin can be prepared quantitatively from the Mn(III) capped porphyrin by treatment with aqueous ammonia and sodium hypochlorite. The ester linkages holding the cap above the metalloporphyrin core are not cleaved. Our investigation of the spectroelectrochemistry of $NMn(C_2Cap)$ as well as other phenyl ring substituted nitrido Mn TPP's found that each complex underwent two, chemically reversible, single-electron oxidations and reductions with full retention of the nitrido function. All electron transfer reactions occurred solely at the porphyrin ring. No discernible solvent effect was observed. Details of this study can be found in reprint #5 in the Appendix.

We initiated studies leading to functionalized N atom transfer by converting $NMn(C_2Cap)$ to a coordinated nitrene complex by reaction with trifluoroacetic anhydride. The coordinated nitrene-$Mn(C_2Cap)$ species reacts with olefins at rates at least one order of magnitude faster than its unencumbered porphyrin counterpart. To ascertain whether this increase in rate was due to the presence of the capping group or due to the increased porphyrin basicity produced by the ether substituents on the phenyl rings, we explored the effect of porphyrin substituents on the rates of formation of the coordinated nitrene complexes. We found that the rate of nitrene formation and, consequently, the rate of nitrogen atom transfer from NMn(POR) to olefins is markedly dependent upon the basicity of the porphyrin ring and upon the steric environment of the NMn(POR) reactant. We demonstrated that the rate of Mn-nitrene formation can be varied over three orders of magnitude through appropriate selection of the porphyrin ring structure. Porphyrins with strongly electron-donating substituents enhance the rate of coordinated nitrene formation. This trend is opposite to that observed for oxygen atom transfer reactivity of oxo-Fe and oxo-Mn porphyrins. *The highest rates observed for the formation of*

coordinated nitrene Mn porphyrins were with NMn(C_2Cap). Although the rate observed for the reaction of this porphyrin was close to that required for utilization as an aziridine synthon, the synthetic complexity in preparing the capped porphyrin will preclude its widespread use. A reprint providing additional details is included in the Appendix (reprint #6).
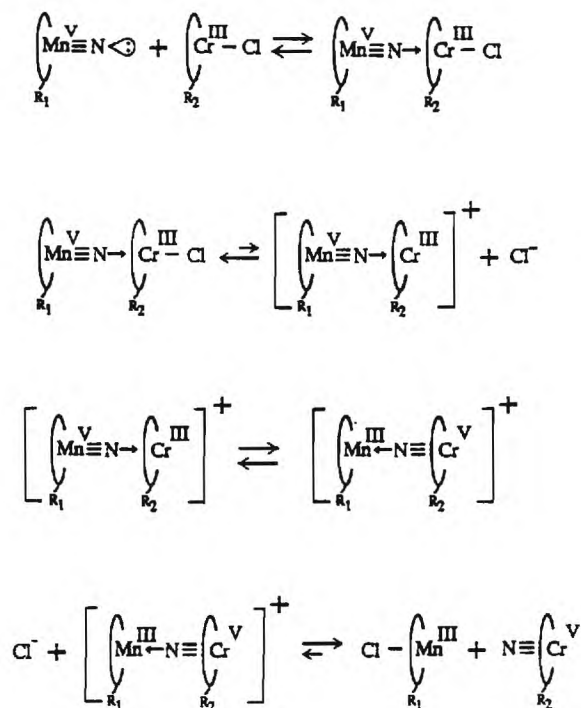
Various nitrido Cr(V) porphyrins were also prepared. The redox reactivity of these complexes was investigated by the voltammetric and spectroelectrochemical (electronic and EPR) techniques utilized in the study of the nitrido-Mn analogs. Each NCr(POR) complex investigated underwent two, single electron reversible oxidation and two, single electron reversible reduction reactions at a Pt electrode. The site of each charge transfer reaction was centered on the porphyrin ring. This compares with our findings on nitrido Mn porphyrins but contrasts with the general redox behavior of Cr porphyrins. The reactivity of NCr(POR) with olefins in the presence of substituted acetic anhydrides was also explored in an attempt to promote nitrogen atom transfer chemistry analogous to that observed for nitrido Mn porphyrins. The reaction of NCr(POR) with substituted acetic anhydrides was observed at rates at least an order of magnitude faster than the corresponding Mn complexes. However, the subsequent transfer of the coordinated nitrene from the Cr center to olefins was not observed. A spectroelectrochemical investigation revealed that the nitrenoid Cr porphyrins are best described as Cr(IV) cation radicals. This is in contrast to the Mn complexes which formally possess Mn(V) centers and may account for the unreactivity of the nitrenoid Cr porphyrins with olefins. This work has been submitted for publication in *Inorg. Chem.* A preprint is included in the Appendix (see reprint #7).

In the course of subsequent studies of the reactivity of NMn(POR) with other electrophiles, we attempted the reaction of NMn(POR) with ClCr(POR) is hopes of obtaining novel heterobinuclear mu-nitrido complexes. The extensive literature on [Fe(TPP)]$_2$N indicated that mu-nitrido linkages can be quite stable.[25] Also, West and coworkers[26] had shown that homo- and hetero-binuclear oxo-bridged complexes were easily prepared by reaction of oxo-Cr^{IV} porphyrins with M(II) macrocyclic complexes. Holm has described the formation of mu-oxo or mu-nitrido dimers as evidence for partial intermetal atom transfer.[1] When the partial transfer of the nitrido group from NMn(OEP) to ClCr(TPP) was attempted, we found that the following reaction proceeded rapidly, irreversibly and quantitatively. Note that the porphyrin ring is depicted as an oval about the central metal atom in all illustrations contained herein.
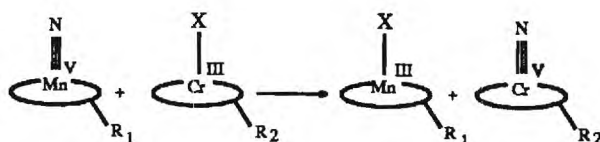
This reaction is the first example of a net, two-electron process involving nitrido metalloporphyrins. More importantly, this reaction pathway is the first example of complete, intermetal, nitrogen atom transfer. The rate law was shown to be first order in each of the reactants. The rate can be significantly diminished either by the placement of steric groups on the porphyrin periphery or by addition of nitrogenous bases capable of axial ligation with the Cr(III) reactant. Our preliminary findings are currently in press for publication in the *J. Am. Chem. Soc* (see preprint #8 in the Appendix). A systematic study of the stereoelectronic aspects of this reaction has shown that the reaction rate is dependent upon the electronic and steric effects of the porphyrin ring substituents, the identity of the anion coordinate-covalently bound to the Cr(III) reactant and also, upon the solvent dielectric constant and donor strength.

In very recent experiments, we've shown that this unusual reactivity is not limited to the transfer of the nitride from Mn(V) to Cr(III). This reaction pathway is operative for Mn to Mn and Cr to Cr transfer as well. We have proposed that the mechanism of this reaction involves backside nucleophilic attack of the nitrido metalloporphyrin donor on the metal(III) porphyrin acceptor facilitating a net, two-electron transfer process mediated by a binuclear mu-nitrido intermediate. The mechanism proposed for the N atom transfer between NMn(POR) and XCr(POR) is depicted in figure to the right. Justification for this mechanism and its applicability to the Mn to Mn and Cr to Cr N atom transfer reactions is given in preprint #9 of the Appendix.

PROPOSED MECHANISM

$$
\left(Mn^V \equiv N\right) + \left(Cr^{III} - Cl\right) \rightleftharpoons \left(Mn^V \equiv N \rightarrow Cr^{III} - Cl\right)
$$

$$
\left(Mn^V \equiv N \rightarrow Cr^{III} - Cl\right) \rightleftharpoons \left[\left(Mn^V \equiv N \rightarrow Cr^{III}\right)\right]^+ + Cl^-
$$

$$
\left[\left(Mn^V \equiv N \rightarrow Cr^{III}\right)\right]^+ \rightleftharpoons \left[\left(Mn^{III} \leftarrow N \equiv Cr^V\right)\right]^+
$$

$$
Cl^- + \left[\left(Mn^{III} \leftarrow N \equiv Cr^V\right)\right]^+ \rightleftharpoons Cl - \left(Mn^{III}\right) + N \equiv \left(Cr^V\right)
$$

Publications:

a) Published during the grant period:

   "Spectroelectrochemistry of Cobalt Capped Porphyrins" by L. A. Bottomley, J.-N. Gorce and W. M. Davis, *J. Electroanal. Chem.* **1986**, 202, 111-124.

"Spectroelectrochemistry of a Urea-Linked Oxo-Bridged Iron Porphyrin Dimer" by L. A. Bottomley, J.-N. Gorce and J. T. Landrum, *Inorg. Chim. Acta* **1986**, <u>125</u>, 135-142.

"Spectroelectrochemistry of (u-Oxo)bis[(phthalocyaninato)-iron(III)]" by L. A. Bottomley, C. Ercolani, J.-N. Gorce, G. Pennesi and G. Rossi, *Inorg. Chem.* **1986**, <u>25</u>, 2338-2342. This work was partially supported by this grant.

"The Electrochemistry of Thiocarbonyl and Selenocarbonyl Iron Octaethylporphyrins" by L. A. Bottomley and J.-N. Gorce, *Polyhedron* **1988**, <u>7</u>, 589-596.

"Redox Reactivity of Manganese Capped Metalloporphyrins" by L. A. Bottomley, F. L. Neely, J. F. Luck and J. S. Quick, in "Redox Chemistry and Interfacial Behavior of Biological Molecules" G. Dryhurst and K. Niki, eds. Plenum Press, **1988**.

"Spectroelectrochemical Studies of High Valent Nitrido Metal-loporphyrins" by L. A. Bottomley, F. L. Neely and J.-N. Gorce *Inorg. Chem.* **1988**, <u>27</u>, 1300-1303.

"The Reactivity of Pentacoordinate Ferrous Porphyrins with Exo-bidentate Nitrogenous Bases. Mononuclear and Binuclear Complexes in Dynamic Equilibrium" by L. A. Bottomley and J.-N. Gorce, *Inorg. Chem.* **1988**, <u>27</u>, 3733-3739.

"Nitrogen Atom Activation: The Influence of Porphyrin Ring Structure on the Kinetics of the Reaction of Trifluoroacetic Anhydride with Nitrido Manganese(V) Porphyrins" by L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc.* **1988**, <u>110</u>, 6748-6752.

"The Nitrogen Atom Transfer Reactivity of Nitrido Manganese(V) Porphyrins with Chromium(III) Porphyrins" L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc.*, in press.

b) Manuscripts Currently in Review:

"Spectroelectrochemical Characterization of Nitrido Chromium(V) Porphyrins and Their Reactivity with Substituted Acetic Anhydrides." L. A. Bottomley and F. L. Neely, submitted for publication in *Inorg. Chem.*

"Nitrogen Atom Transfer. Stereoelectronic Aspects of the Reaction of Nitrido Manganese(V) Porphyrins with Chromium(III) Porphyrins." L. A. Bottomley and F. L. Neely, submitted for publication in *J. Am. Chem. Soc.*.

EXPERIMENTAL DESIGN AND METHODS

Novel Nitrido Metalloporphyrins. Until our discovery of the intermetal N atom transfer pathway, three synthetic avenues existed for the preparation of nitrido metalloporphyrins:
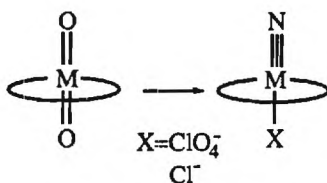
a) photolysis or thermolysis of azido-metal(III) porphyrins,[27,28]
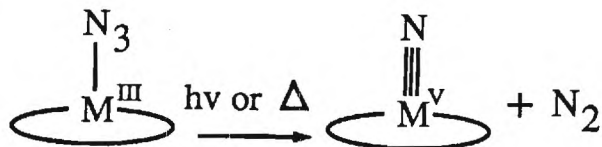
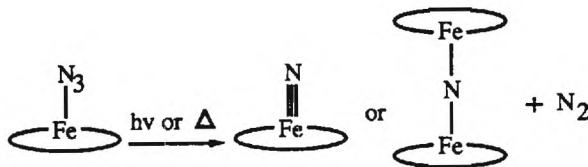$$\underset{M^{III}}{\overset{N_3}{|}} \quad hv \text{ or } \Delta \quad \underset{M^V}{\overset{N}{|||}} + N_2$$

b) oxidation of either the acetato-metal(III) or hydroxo-metal(III) porphyrins in the presence of ammonia.[29,30]

$$\underset{M^{III}}{\overset{OR}{|}} \quad \xrightarrow[\text{[OX]}]{NH_3} \quad \underset{M^V}{\overset{N}{||}} + HOR$$

$$R = H, CH_3$$
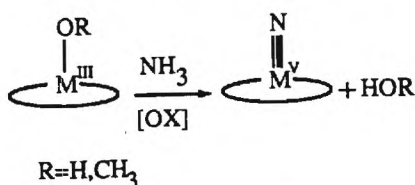
c) treatment of the *cis*- or *trans*-dioxo-metal(VI) with hydrazine followed by peroxyacetic acid.[31]

$$\underset{O}{\overset{O}{\underset{||}{\overset{||}{M}}}} \quad \longrightarrow \quad \underset{X}{\overset{N}{\underset{|}{\overset{|||}{M}}}} \qquad X = ClO_4^- \\ Cl^-$$

Cr(POR) and NMn(POR) complexes have been prepared by both avenues a and b. To date, nitrido-Fe porphyrins have been exclusively prepared by avenue a. Two different products have been isolated and characterized.

$$\underset{Fe}{\overset{N_3}{|}} \quad hv \text{ or } \Delta \quad \underset{Fe}{\overset{N}{|||}} \quad or \quad \underset{Fe}{\overset{Fe}{\underset{|}{\overset{|}{N}}}} \quad + N_2$$

The binuclear product is obtained except when the substituents on the porphyrin sterically prevent its formation. The published preparations of nitrido-Mo and nitrido-Os porphyrins have utilized avenue c. We have recently used route c in the preparation of a novel nitrido-Ru porphyrin.

As detailed in the Preliminary Results section, the nitrogen atom transfer route to nitrido metalloporphyrins is novel. At present, this pathway has been documented only with nitrido Mn and

nitrido Cr porphyrin as N atom donors and Mn(II), Mn(III) and Cr(III) porphyrins as acceptors. However, we have recently succeeded in preparing a novel mononuclear nitrido Cr macrocyclic complex by this route and are confident of its utility, at least with metalloporphyrins which are capable of oxygen atom transfer chemistry, i.e. metalloporphyrins possessing central metal ions with a d^1 to d^4 electronic configuration.[1]

The aim of this phase of the research program is the preparation of novel nitrido metalloporphyrins by one or more of the above routes. Initial efforts will focus on Re, Tc, W, Ti and V porphyrins in hopes of preparing their nitrido derivatives. We intend to isolate and characterize as many different nitrido-metal complexes as possible. We anticipate both mononuclear and binuclear complexes, depending upon the synthetic route used as well as the steric bulk of the porphyrin. In an effort to determine the limitations of each of the above synthetic avenues, we will attempt to elucidate the kinetics and mechanism of each using the techiques, methods and approaches employed in acquiring our preliminary results i.e. tandem and sequential electrochemical and spectroscopic (UV-vis, infrared, EPR, NMR and Raman) experiments. Accomplishment of this aim will provide us with an array of nitrido metalloporphyrins with which we can evaluate N atom and functionalized N atom transfer reactivity.

Nitrogen Atom Transfer With Nitrido Metalloporphyrins. The aim of this phase of the research program will be the evaluation of the reactivity of NM(POR)'s as N atom donors. In our preliminary results, we've shown that nitrido-M(V) porphyrins donate the N atom to M(III) porphyrins in a net, two-electron process. Woo has reported[32] the NMn(V) to Mn(II) transfer, a net, three-electron process. It is intriguing to consider the possible reactivity of nitrido Os, Mo and Ru metalloporphyrins with M(III) acceptor porphyrins since N atom transfer with these donor-acceptor pairs would also be a net, three-electron process. However, we anticipate that the reduced nitrido-metal(V) form of these porphyrins will be more reactive. Detailed voltammetric and spectroelectrochemical experiments will be performed on solutions containing these and similar N donor-acceptor pairs in an effort to promote the transfer reaction with one or more metal valence state. Special attention will be placed on determining the mechanism of N atom transfer involving a net three-electron process. We will endeavor to stabilize and characterize long-lived intermediates.

We will explore the reactivity of a variety of M(II) and M(III) porphyrin complexes as potential N atom acceptors. All reaction mixtures will be chromatographed and each fraction characterized. We anticipate the discovery of novel mononuclear and binuclear nitrido metalloporphyrins. Reactions with nonporphyrinic metallomacrocyclic complexes will also be explored to fully catalog the generality of the N atom transfer reaction.