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**Catalytic Conversion of Light Alkanes-Proof-of-Concept
Stage - Phase IV**

**Topical Report
February 1, 1994 - January 31, 1995**

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SUMMARY

This report details the research performed on Phase IV of the extended Cooperative Agreement. This Phase, entitled C₁-C₄ Research, provides the research support which accompanies the C₄ Proof-of-Concept Phase (Phase V) as the two major activities of the Cooperative Agreement during calendar 1993. It is the objective of this phase to understand the nature of the catalysts and catalytic activity of perhaloporphyrin complexes uncovered during Phases I-III in order that superior catalytic materials can be made and tested which meet commercial criteria for the oxidation of the C₁-C₄ light alkane gases found in natural gas and other available hydrocarbon streams.

During Phase IV, we have examined the physical and electronic structures of the very active perhaloporphyrin catalysts which we have developed, and have gained an understanding of the properties which make them active. This has led us to design and synthesize materials which are cheaper, more active, more robust and, in general superior for carrying out practical catalysis. Our early generation perhaloporphyrin catalysts, while exhibiting unprecedented catalytic activity, were far too expensive for use in converting natural gas or its C₁-C₄ components. The reason for this is that the perfluorophenyl substituents that occupied the meso positions caused these complexes to be very costly to synthesize. During Phase IV we have found new routes to meso-perfluoromethyl and meso-nitro substituents that are much less costly. Molecular modelling and electrochemical

measurements indicate that these meso-substituents should provide a ligand system which makes the metal center even more active than in our early generation catalysts. Initial screening studies confirm this. Nitroporphyrin complexes have been included in the Phase V studies on the proof-of-concept stage of catalytic conversion of isobutane to t-butyl alcohol.

During Phase IV we have concluded that, although they are good candidates for C₃ and C₄ oxidations, perhaloporphyrin complexes will probably not be active enough to catalyze oxidation of methane or ethane at low temperatures and not robust enough to be effective at elevated temperatures. Our first generation heterogeneous catalyst, iron sodalite, though robust, will not meet the commercial rate and selectivity requirements. During Phase IV we have designed heterogeneous catalysts aimed at incorporating the best aspects of our early generation heterogeneous catalysts while adding important functions designed to impart greater selectivity and rate. A number of new compositions have been successfully synthesized and will be tested in Phase VI of the extended Cooperative Agreement. In addition, a new methane oxidation laboratory was completed and a series of thermal gas phase methane oxidations were done to line out this highly automated and well controlled oxidation facility. This new laboratory will be used to perform the methane oxidation studies in Phase VI of the extended Agreement.

ABSTRACT

During the course of the first three years of the Cooperative Agreement, we uncovered a family of metal perhaloporphyrin complexes which had unprecedented activity for the selective air-oxidation of light alkanes to alcohols. The reactivity of light hydrocarbon substrates with air or oxygen was in the order: isobutane>propane>ethane>methane, in accord with their homolytic bond dissociation energies. Isobutane was so reactive that the proof-of concept stage of a process for producing tert-butyl alcohol from isobutane was begun (Phase V). It was proposed that as more active catalytic systems were developed (Phases IV, VI), propane, then ethane and finally methane oxidations will move into this stage (Phases VII through IX).

Although active, the perhalotetraphenylporphyrin complexes are costly. Generating the perhalophenyl group at the meso position is difficult and it results in a catalyst of high molecular weight. What we learned during the first stage of the Cooperative Agreement is that the important property of a group on the periphery of the porphyrin ring is that it withdraw electrons efficiently. We have now succeeded in introducing nitro groups into the meso positions of octaethylporphyrin in a simple high-yield prep. Nitro groups are among the most electron withdrawing substituents in organic chemistry and indeed the effect of introducing them is to dramatically increase catalytic activity. Cost of the catalyst is also lower due to the ease of the synthesis and the low molecular weight of the complex. We look for materials of this type to be the practical catalysts which may

permit cost-effective production of TBA from isobutane. Process development work on TBA has begun in a dedicated liquid phase reactor facility. An interesting finding has resulted in the ability to get far greater conversions of isobutane while retaining good selectivity.

Although it is likely that catalysts not too dissimilar from those which convert isobutane to TBA could be used to convert propane to IPA, more robust catalysts will be needed for methane and ethane conversion. During the first three years of the Cooperative Agreement, we found that our first generation heterogeneous catalyst, operating between 350 and 450°C produced methanol and ethanol from methane and ethane. Selectivities were not high enough for a practical process, however, and detailed kinetic analysis revealed that we need to build the very same characteristics into a vapor phase catalyst as those which we use in liquid phase. Specifically, binuclear sites having high M(III)/M(II) reduction potential in a hydrophobic environment are necessary. We, therefore, began a major program to design synthesize and characterize materials of this. Considerable synthetic progress has been made and details appear in the body of this report.

The research detailed in this Topical Report covers all of the work done on Phase IV, C₁-C₄ Research, of the extended Cooperative Agreement. Phase IV research made considerable progress toward developing new catalysts. Research done in collaboration with the Caltech laboratories has shed much light on the nature of one of our most active early generation homogeneous catalysts,

$\text{Fe}(\text{TPPF}_{20}\beta\text{-Br}_8)\text{X}$. Structural identification of this material was achieved by single crystal X-Ray crystallography. Spectroelectrochemical determinations have told us to what extent we have tuned the redox potential of this system to make it an active catalyst. Spectroelectrochemistry together with electron paramagnetic resonance spectroscopy and magnetic susceptibility measurements have provided insights into the spin state of the metal and the ease of electron transfer reactions that are critical to catalytic activity. This work together with theoretical studies at Caltech give us a greatly improved understanding of how these exceptional catalysts work and, more importantly, how to improve their performance for ultimate commercial application.

Progress was also made in the area of heterogeneous catalysis in the Phase IV segment of the Cooperative Agreement. Work done in the first stage of the Cooperative Agreement indicated that an active heterogeneous catalyst for direct hydroxylation of difficult substrates such as methane or ethane should have the following properties: a) binuclear metal(iron) centers in which the oxidation active metals had high M(III)/M(II) reduction potentials and b) a hydrophobic support which encouraged expulsion of the oxygenate as formed. We are preparing a novel set of electron deficient binuclear Schiff base complexes which have high M(III)/M(II) reduction potentials. We have prepared a number of hydrophobic surface environments and are ready to support the binuclear complexes on them. We have also tried several other strategies to create binuclear sites on hydrophobic surfaces. We have completed and successfully lined out a new dedicated methane oxidation laboratory which houses a completely automated, reactor facility with on-line total product

analysis for vapor phase methane oxidation. We have conducted non-catalytic oxidations and achieved the predicted 45% selectivity at 10% methane conversion as expected. We are now ready to test new catalyst systems in Phase VI of the Cooperative Agreement.

We have made excellent progress in generating a class of less costly new materials which have the potential for high catalytic activity. Work on new nitro complexes was transferred to the development area while new routes were developed for replacing costly perfluorophenyl groups in the meso-position of metalloporphyrin catalysts with far less expensive and lower molecular weight perfluoromethyl groups. The CF_3 group is more electron-withdrawing than the C_6F_5 group and its effect on catalytic properties is of interest when screening of these new materials begins. Electrochemical and spectroelectrochemical studies as well as determination of gas phase electron affinities, enhanced our understanding of the relationship between electronic and steric properties of metalloporphyrin catalysts and their catalytic activity. Work progressed in the synthesis of binucleating macrocyclic ligands for making both homogeneous and heterogeneous catalysts having proximate metal centers for binding dioxygen. Large rate enhancements for oxygen activation are expected from this novel set of catalysts. In addition to synthesizing new materials with proximate metal centers we continued to prepare new hydrophobic support materials on which to support these complexes. Hydrophobicity is important in order to expel methanol and other alcohols from the surface before they burn and cause low process selectivity.

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1.0 SUMMARY OF PROGRAM INCENTIVES

As petroleum reserves dwindle, all hydrocarbon raw materials which could be converted to usable liquid fuels become more dear. Often the search for oil yields extensive gas reservoirs. Gas availability on a worldwide scale rivals that of crude oil but problems of transportation and differences in end use application often limit its' utility. Most natural gas is found in areas remote to its ultimate use. Currently much of this remote gas is associated with petroleum production. Because it cannot be used at the location where it is produced, it is often flared on a large scale, representing not only a wasted energy resource but also contributing to global warming as a result of carbon dioxide production. Because of its low energy density, methane is relatively costly to transport. Figure 1-1 shows the relative differences between the costs of transporting various liquid and gaseous fuels(1). It is readily seen that the conversion of methane to a liquid fuel such as methanol or a hydrocarbon liquid would both drastically cut the cost of transport of over long distances, and provide an alternative fuel liquid from an abundant, under-utilized resource.

Catalytic alkane conversion science is maturing to the point that one can envision the economically attractive conversion of natural gas to liquid fuels on a commercial scale by the turn of the century. This situation has many international and national implications. Remote accumulations of low value gas such as exist on the North slope of Alaska and various off-shore

Fig. 1.1 Relative cost of transport of liquid and gaseous fuels (LNG = liquified natural gas).

sites could be exploited. Value could be maximized for domestic gas reserves in high value-added products. The National interests would be well served if the U.S. held the technological lead in gas conversion technology and could influence the course of gas conversion abroad. One of the most costly steps in the current technology for converting natural gas to liquid fuels is the energy-intensive steam reforming step. The products of steam reforming are catalytically converted to methanol which has value as an alternative liquid fuel product or which could be converted to gasoline via existing technology.

We have uncovered a new catalytic approach to the direct production of a methanol-rich oxidate from natural gas which avoids costly steam reforming completely. Work conducted in Sun laboratories under the joint sponsorship of the Department of Energy (METC), the Gas Research Institute, and the Sun Company, Inc., has produced a family of new catalytic materials which, if successfully developed, will be effective in the conversion of light alkanes to alcohols or other oxygenates. We have found that it is possible to catalytically convert methane, and the C_2 - C_4 hydrocarbons that are present in smaller but significant amounts in natural gas, to alcohols by direct reaction with air or oxygen. In particular, we have found that the C_4 component of natural gas can be catalytically converted to fuel oxygenates in excellent yield, and significant progress has been made in converting the C_3 component to an oxygenate product without combusting the hydrocarbon substantially. The C_1 and C_2 components can also be converted to alcohol-rich oxygenates but more progress is still required before a practical catalytic route becomes possible.

At the outset of this work we envisioned converting natural gas to an alcohol-rich oxidate which could subsequently be converted to hydrocarbon gasoline via MTG technology. During the period of this research, however, the benefits of oxygenates as clean-burning, high octane, liquid fuel materials has become apparent. Alcohols and the ethers that can be made from them are the oxygenates that are used to replace aromatics, reduce toxicity and reduce ozone and carbon monoxide in the reformulated gasolines of the 90's. As a result it is more reasonable to consider the direct air-oxidation of light alkanes to produce alcohol-rich oxidates for use as components of reformulated gasoline or as liquid fuel alternatives to gasoline in areas where there is non-attainment of CO or ozone limits set forward by the Clean Air Act. Alcohols of the type that can be formed directly from natural gas components: methanol, ethanol and tert-butyl alcohol, TBA, are not only useful as liquid fuel components themselves but are used in the manufacture of ether oxygenates such as MTBE, TAME, and ETBE as well. Table 1-1 shows some of the fuel-related properties of the C_1 - C_4 alcohols and the ethers that can be made from them. It can be seen that these materials have desirable fuel properties in addition to meeting the fuel oxygen-content requirements of the Clean Air Act.

As desirable as it is to convert light alkanes directly to alcohols, doing this in an efficient manner using existing technology is a major problem. The light alkanes: methane, ethane, propane and the butanes, are among the most unreactive of organic substrates. They are also among the most abundant and inexpensive raw materials. They are found not only in natural gas, but in light

PROPERTIES OF ETHERS AND ALCOHOLS

<u>PROPERTY</u>	<u>MIBE</u>	<u>EI BE</u>	<u>GIBA</u>	<u>IPA</u>	<u>EIOH</u>	<u>MeOH</u>
Oxygen, wt %	18.2	15.7	21.6	26.6	34	49.9
Sp. Gravity	0.74	0.74	0.791	0.789	0.79	0.796
Boiling Point, °F	131	163	181	180	172	149
RVP (lbs/in ²)	7.8	2.5	1.8	1.8	2.3	4.6
Blending RVP	9	5	12	14	23	75
RON BV	110-122	117-121	~103	113-119	~122	126
MON BV	98-102	100-105	~91	95-101	~96	104
(R+M)/2 BV	103-110	~110	~97	104-110	~100	115

petroleum fractions, and are being generated in ever-increasing quantities in petroleum refineries due to the increasing severity of catalytic cracking of heavier crudes. There exist few commercial processes for the efficient upgrading of these substrates to high value products and no DIRECT catalytic functionalization of these substrates to produce chemical or fuel alcohols.

During a six-year period in which Sun has invested over six million dollars in research support, coupled with an ongoing program sponsored jointly by Sun, the DOE and GRI, we have formulated and demonstrated a novel catalyst concept which allows the low temperature liquid or vapor phase catalytic conversion of light alkanes, (C_1 - C_4), to their respective alcohols or ketones. This concept grew out of an understanding of biomimetic systems, together with new inorganic and catalytic chemistry. It is known that high oxidation state metal oxo ($M=O$) complexes will react with alkanes to give alcohols under mild conditions. Iron oxo ($Fe=O$) intermediates are, no doubt, involved in the enzymatic hydroxylation of C-H bonds in vivo (Cytochrome P-450). To date no one has been able to synthesize these $Fe=O$ species under mild conditions using ONLY molecular oxygen as oxidant. Even nature requires the stoichiometric consumption of a co-reductant which donates the electrons and protons needed for closing the catalytic oxidation cycle. Nature's co-reductant is NADH which is converted to NAD while donating electrons and proton. Synthetic biomimetic systems add stoichiometric reagents for providing two protons and two electrons for every hydrocarbon molecule which is oxidized. These reagents are regenerated in vivo but, in vitro processes require sacrificial consumption of valuable raw materials in the regeneration

process. This stoichiometric requirement imposes severe and usually prohibitive economic constraints on commercial applications of such a catalytic process.

In our laboratories we have learned how to tune the redox potential of metals in macrocyclic ligand environments to make them active for the selective air-oxidation of alkanes using ONLY molecular oxygen. As we mentioned above, nature uses electrons and protons together with iron to split the oxygen molecule and generate $\text{Fe}=\text{O}$. In so doing half of the oxygen molecule is converted to water while the other half is useful in oxidizing a substrate. We have asked the question whether oxygen can be split between two $\text{Fe}(\text{II})$ centers to make two $\text{Fe}=\text{O}$ species using all of the oxygen as effective oxidant. While Cytochrome P-450 and MMO act as monooxygenases, we are making complexes which may act as synthetic dioxygenases. We have incorporated a number of oxidation-active metal centers into our synthetic catalysts in addition to iron and have found that we are able to convert methane, ethane, propane and the butanes either to the corresponding alcohol or carbonyl compound depending on the nature of the metal center in the macrocyclic ligand system. All-inorganic "macrocycles" such as polyoxometallates and framework substituted zeolites have also been investigated for both liquid and vapor phase catalytic oxidations.

The ease of oxidation of the substrates that we have studied are in the order: isobutane >butane>propane>ethane>methane, which is also the order of increasing C-H bond dissociation energy, Figure 1-2. Isobutane is the easiest of the light hydrocarbons to oxidize. As

FIGURE 1-2

HYDROCARBON REACTIVITY SERIES

ISOBUTANE
(91 Kcal)

PROPANE
(94 Kcal)

ETHANE
(98 Kcal)

METHANE
(104 Kcal)

a result we are close to having achieved a practical catalytic process for isobutane oxidation. High rates, yields and selectivities have been observed. We believe that we are within a factor of three or four of the rate necessary for a practical process. For this reason, it we are proceeding to the proof-of-concept phase for a process that converts isobutane to tert-butyl alcohol. There are many reasons why such a process is of interest. First, sales of field butanes from the gas industry to refiners is down due to the vapor pressure restrictions on automotive transportation fuels. Conversion of C4's to TBA would be a way to put unwanted butanes back into gasoline. TBA is both a commercially tested high octane, clean burning motor fuel component and in addition is the precursor to MTBE, a rapidly growing commodity fuel material which is being used to meet oxygen mandates of the Clean Air Act.

A four year program of work will be undertaken to do this which will involve over 500 man-months of chemist, engineer and technician manpower for a duration of four years at a total cost of approximately 12 MM dollars.

2.0 INTRODUCTION

2.1 MISSION STATEMENT

The mission of the work presented in this proposal is to generate novel catalytic technology which will permit the development of a simple, efficient and economical process for the direct conversion of natural gas to liquid transportation fuels. This process should be simple enough to liquify natural gas economically even at a remote reservoir site.

The most costly and energy-intensive step in currently applied commercial technology for the conversion of natural gas to liquid fuels is the steam reforming of the light hydrocarbons to produce synthesis gas. The synthesis gas is then converted to methanol which is passed over a catalyst to produce gasoline. If it were possible to catalytically transform natural gas into a methanol rich-oxidate rapidly and efficiently in a single step using air or O_2 as oxidant, the economics of the process would be dramatically improved (1-4). In contrast to the energy-inefficient steam reforming process, a direct "methane-to-methanol" process would be highly exoergic and, if properly carried out, would generate usable energy as steam, electricity or both. For these reasons, we are attempting to develop a process for the direct conversion of natural gas to an environmentally superior, methanol-rich liquid fuel oxygenate.

2.2 TECHNICAL OBJECTIVE

The technical objective of this proposal is to synthesize the first effective, practical molecular catalyst and demonstrate its use for the direct air-oxidation of natural gas to a methanol-rich oxidate which can either be used directly or converted into gasoline via known technology.

The light alkanes found in natural gas - methane, ethane, propane, and butane are among the most unreactive of all organic substrates. No effective catalysts are known for the selective partial oxidation of these relatively refractory materials. The development of an efficient catalyst for the smooth and selective oxidation of these light alkanes to alcohols will not only provide a solution to

the problem of liquifying natural gas, but will create new opportunities to utilize the relatively inexpensive and abundant light alkanes for the production of a variety of valuable fuel and chemical products.

Figure 1-2 shows the relative ease of activation of C-H bonds in the kinds of light alkanes that make up natural gas. This trend is reflected in the ease of catalytic air oxidation of the hydrocarbons: isobutane > butane > propane > ethane > methane. The conversion of any major gas component as well as the entire gaseous mixture to an alcohol-rich oxidate has value both to the gas producer and the liquid transportation fuel producer alike. We are currently capable of oxidizing isobutane well and anticipate being ready for proof-of-concept of a propane to IPA process within two years. Ethane and methane oxidation will require more time than this. Thus it is proposed that the proof-of-concept stage proceed in several discrete stages: isobutane to TBA, propane to IPA, (ethane to ethanol - optional), and finally methane to methanol. Concurrent with the developmental aspects of each of these phases will be research phases geared to enable us to produce catalysts active enough for each succeeding phase.

3.0 PROGRAM ELEMENTS

Program elements are reviewed in the first Quarterly Report, (January 1-March 31, 1993), of the Cooperative Agreement. Table 3.1 indicates where Phase IV falls in the original, overall plan for the extended Cooperative Agreement.

TABLE 3.1

COMPONENTS OF NEW COOPERATIVE AGREEMENT

<u>TIME</u>	<u>ACTIVITY</u>	<u>APPROX. LEVEL OF EFFORT</u>
2/93 - 2/94	Phase IV C ₁ -C ₄ Research	\$1.0 MM
	Phase V TBA Development	\$2.0 MM
2/94 - 2/95	Phase V TBA Development	\$2.1 MM
	Phase VI C ₁ -C ₃ Research	\$0.9 MM

4.0 HALOPORPHYRIN COMPLEXES

We have learned much concerning the effects of both electronic and geometric structure of metalloporphyrins on their catalytic oxidation activity by studying halogen substitution on the periphery of the macrocycle. The greater the extent of replacement of hydrogens on the ring periphery, the greater is the catalytic activity. Buckling of the porphyrin ring also affects both selectivity and catalytic activity. Section 4.1 is a compilation of recent work in this area conducted jointly by Sun and the California Institute of Technology. Contributors to this section are:

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4.1 SYNTHESIS AND CHARACTERIZATION OF HALOGENATED METALLOPORPHYRINS

Abstract: Halogenated iron porphyrins are known to catalytically oxidize organic substrates with dioxygen. Perhalogenated iron and ruthenium porphyrins have been synthesized and characterized by NMR and UV-Vis spectroscopies. Partially halogenated iron porphyrins have also been synthesized, and used to create a library of characteristic spectral data for different spin and oxidation states. The reaction of an iron methyl porphyrin with air has been shown to result in the formation of the iron hydroxide porphyrin and methanol, mimicing several steps in the proposed catalytic cycle.

Introduction

Monooxygenases are enzymes responsible for the biological activation of dioxygen. Cytochrome P-450, a monooxygenase capable of metabolizing a wide variety of organic substrates, operates with the stoichiometric use of a sacrificial co-reductant in the form of NADH or NADPH. Only half of the oxygen molecule is utilized in the oxidations catalyzed by cytochrome P-450; the second oxygen atom is released as water.^{1,2} Recent interest has focused on creating a biomimetic model of this enzyme, capable of accomplishing these difficult reactions more efficiently. As well as providing a simpler model for scientific study, the fuel and petroleum industries would be able to adapt a model system for commercial oxidation of inexpensive, abundant hydrocarbons to more useful alcohols.³

Cytochrome P-450, which has a protoporphyrin IX heme center, is believed to catalyze the various substrates through a high oxidation state iron intermediate (Scheme 1).¹ Peroxides, or single oxygen donors such as iodosylbenzene (PhIO),⁴ allow the enzyme to circumvent the dioxygen binding steps via a peroxide shunt pathway. One

¹ McMurray, T. J.; Groves, J. T. "Metalloporphyrin Models for Cytochrome P-450." in Cytochrome P-450, Ortiz de Montellano, P. K., ed. Plenum Press: New York, 1986; p. 1-28.

² White, R. E.; Coon, M. J. *Ann. Rev. Biochem.* 1980, 49, 315.

³ Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* 1990, 105, 181.

⁴ Abbreviations used in this paper: TPP, tetraphenyl porphyrin; TMP, tetramesityl porphyrin; TDCPP, tetrakis(2,6-dichlorophenyl)porphyrin; TFPP, tetrakis(pentafluorophenyl)porphyrin; (FeTFPP)₂O, μ -oxo-bis-tetrakis(pentafluorophenyl)porphyrinatoiron; TFPPCl₈, tetrakis-(pentafluorophenyl)-8-octachloro porphyrin; TFPPBr₈, tetrakis(pentafluorophenyl)-8-octabromo porphyrin. H₂ indicates an

Scheme 1-- This is a proposed catalytic cycle for cytochrome P-450. One molecule of dioxygen is reduced to water and one molecule of oxidized substrate, SO. One molecule of NAD(P)H is also consumed as an energy source during this reaction. The high oxidation intermediate has not been precisely characterized, and could be either a Fe^{V} or Fe^{IV} species. A peroxide or single oxygen donor, XO, allows the protein to operate via the peroxide shunt pathway.¹

of the first synthetic models for P-450 hydroxylation catalysis utilizes this short reaction pathway; tetraphenylporphyrinatoiron(III) chloride, ($\text{Fe}^{\text{III}}\text{TPPCl}$), which has a phenyl ring substituted on each of the four meso carbons, catalyzes the hydroxylation of

Figure 1--The structure of $\text{Fe}^{\text{III}}\text{TPPCl}$

hydrocarbons and the epoxidation of alkenes with PhIO .^{5,6} However, in the presence of hydroxide, the porphyrin forms the unreactive and thermodynamically stable μ -oxo species, TPPFe-O-FeTPP .⁷ The μ -oxo can also form when $\text{Fe}^{\text{III}}\text{TPPCl}$ is exposed to air or water, shutting down the catalytic abilities of the porphyrin. In

cytochrome P-450, a hydrophobic pocket surrounding the active site prevents μ -oxo formation.

unmetallated free base porphyrin, and M indicates a metal coordinated in the porphyrin. PhIO , iodosylbenzene; *m*-CPBA, *meta*-chloroperoxybenzoic acid.

5. Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* 1979, 101, 1032.

6. For a review on porphyrin catalysis, see Meunier, B. *Chem. Rev.* 1992, 92, 1411.

7. a) Dolphin, D. *The Porphyrins*, Vol. 5. Academic Press: New York:1978. b) Cheng, R.J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* 1982, 21, 2412. c) Nanthakumar, A.; Goff, H.M. *Inorg. Chem.* 1989, 28, 4559.

Biomimetic porphyrins must therefore be designed with the inherent ability to avoiding the thermodynamic sink of the iron (III) μ -oxo species. Several elegant means have been developed for synthetic analogs, which function by preventing the two porphyrin molecules from coming into close contact (Figure 2). "Tailed" porphyrins have an imidazole or other nitrogen containing function linked to the porphyrin ring by a flexible hydrocarbon chain, allowing it to swing around and axially bind to the metal center in simulation of histidine coordination.⁸ "Picket fence,"⁹ "basket handle,"^{10,11} and "capped"¹² porphyrins have large organic groups that project perpendicular to the plane of the porphyrin as pickets, or, in the latter two cases, actually bridge across from one side of the porphyrin ring to the other. All of these methods effectively prevent μ -oxo formation.

Figure 2--Representations of tailed, picket fence, basket handle, and capped porphyrins. The bulky ligands create a steric barrier in the plane perpendicular to the porphyrin to prevent μ -oxo dimerization.

8. a) Geibel, J.; Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* 1975, 94, 5924. b) Collman, J. P.; Groh, S. E. *J. Am. Chem. Soc.* 1982, 104, 1391.
9. Gunter, M. J.; McLaughlin, G. M.; Berry, K. J.; Murray, K. S.; Irving, M.; Clark, P. E. *Inorg. Chem.* 1984, 23, 283.
10. Lexa, D.; Mamenteau, M.; Saveant, J. M.; Xu, F. *Inorg. Chem.* 1985, 24, 122.
11. Chang, C. K.; Kuo, M. S. *J. Am. Chem. Soc.* 1979, 101, 3413.
12. a) Zhang, H. Y.; Blasko, A.; Yu, J. Q.; Bruce, T. C. *J. Am. Chem. Soc.* 1992, 114(17), 6621. b) Kim, K.; Ibers, J. A. *J. Am. Chem. Soc.* 1991, 113(16), 6077. c) Lecase, A.; Boitrel, B.; Rose, E. B. *S. Chem Fr.* 1991, 3, 407.

A second consideration in the design of hydroxylation catalysts is the stability of the porphyrin ring in the reaction environment. In the presence of strong chemical oxidants, the porphyrin ring is susceptible to oxidative attack and degradation. Substitution at the meso carbons, as with the phenyl rings on TPP or the linking group in tailed, capped, and bridged porphyrins, is known to help protect the ring from irreversible oxidation.¹¹ Despite this stabilizing effect, $\text{Fe}^{\text{III}}\text{TPPCl}$ is irreversibly oxidized in the presence of dioxygen after catalyzing only a few hundred turnovers of propanal to propionic acid.¹³ Adding substituents to the meso positioned phenyl rings, as with tetramesityl porphyrin (TMP) and *tetrakis*(2,6-dichlorophenyl)porphyrin (TDCPP), allows for even more robust species (Figure 3).^{14, 15} In addition to protecting the

Figure 3-- Free base TMP and TDCPP porphyrins.

porphyrin from self oxidation, the additional steric bulk on the phenyl rings disfavors formation of the μ -oxo species. Although the *ortho* methyl or chloro groups on the phenyl rings create a physical barrier to dimerization, they are not completely prohibitive, and both $\text{Fe}^{\text{III}}\text{TMPCl}$ and $\text{Fe}^{\text{III}}\text{TDCPPCl}$ still form the μ -oxo bis-porphyrin.^{7b}

The relative stability of TMP and TDCPP iron porphyrins in the presence of oxidants has made them useful model compounds for study of the proposed intermediates in the catalytic cycle of cytochrome P-450. A general mechanism for porphyrin catalysis

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14. Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.*, 1983, 105, 6243.

15. Nappa, M. J.; Tolman, C. A. *Inorg. Chem.*, 1985, 24, 4711.

has been suggested. This pathway differs slightly from the proposed enzymatic cycle in that both oxygen atoms are utilized (Scheme 2).^{16,17}

Scheme 2--The proposed catalytic cycle for oxygen activation by metalloporphyrins. The cycle can be halted by the recombination of $P\text{-Fe}^{\text{II}}$ and $P\text{-Fe}^{\text{IV}}\text{=O}$ to form the stable μ -oxo species.

Fe^{II} TMP is known to react with dioxygen along this pathway. The initial reaction of Fe^{II} TMP with dioxygen leads to the formation of the unstable peroxide $\text{TMP-Fe}^{\text{III}}\text{O-OFe}^{\text{III}}$ TMP, which then decomposes to $\text{TMP-Fe}^{\text{IV}}\text{=O}$.^{18,19} The ferryl compound then transfers the oxygen to substrate. These intermediates have been isolated at low temperatures and characterized by UV-Vis and NMR spectroscopies.

If an oxidant such as peroxide is used, higher oxidation state iron-oxo intermediates are produced via the peroxide shunt mechanism. The active intermediates $\text{TMP-Fe}^{\text{IV}}\text{=O}$ and $\text{TDCPP-Fe}^{\text{IV}}\text{=O}$ have been identified from the oxidation of the respective Fe^{III} Cl porphyrins with *meta*-chloroperoxybenzoic acid (*m*-CPBA) by NMR, UV-Vis, EPR, and Resonance Raman.^{20,21} The oxidation state of these compounds is

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19. Arasasingham, R. P.; Cornman, C. R.; Balch, A. L. *J. Am. Chem. Soc.* 1989, 111(20), 7800.

20. a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* 1981, 103, 2884. b) Yamaguchi, K.; Watanabe, Y.; Morishima, I. *J. Chem. Soc., Chem. Comm.* 1992, 1721.

21. a) Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* 1988, 110, 5756. b) Mandon, D.; Weiss, R.; Gold, A.; Jayaraj, K.; Ternier, J.; Bill, E.; Trautwein, A. X. *Inorg. Chem.* 1992, 31, 21.

higher than the intermediates shown in Scheme 2 (the iron(IV) cation radical rather than the iron(IV) porphyrin) because the porphyrins are initially in the iron(III) versus iron(II) oxidation state. Therefore, the reaction path and product distribution are dependent at least in part on the oxidant utilized.²²

With the TDCPP porphyrin, the presence of halogens on the phenyl ring is found to increase the ability of the porphyrin to withstand oxidizing environments.²³ This is likely due to a decrease in electron density on the metal, which helps prevent self oxidation during O₂ activation.²⁴ Therefore, further halogenation of the ring was attempted to create a more robust porphyrin. Both the phenyl rings and the β or pyrrole positions are available for halogenation. The first fluorinated porphyrin, *tetrakis*-(pentafluorophenyl)porphyrin (TFPP), was synthesized as early as 1969, although at the time it was simply noted for its unusual UV-Vis spectra.²⁵ When the catalytic properties were investigated in 1981, Chang, et al. found that in the presence of iodosylbenzene, Fe^{III}TFPPCl hydroxylates cyclohexane and epoxidizes cyclohexene.²⁶ Fe^{III}TDCPPCl, with a partially chlorinated phenyl ring, shows excellent epoxidation activity. Turnovers of over 10,000 molecules of norbornene were found with PhIO as the oxidant, with little loss of hemin to oxidative destruction.²³

The pyrrole halogenated TMP and TDCPP porphyrins (TMP and TDCPP- β -Cl₈ or - β -Br₈) have also been prepared.^{27,28} Manganese derivatives of both the β -halogenated TMP porphyrins show a order of magnitude increase in epoxidation activity over MnTMP, although the rates are dependent on the type of oxidant used. As with Fe^{III}TMPPCl, the intermediate TMP- β -Br₈-Fe^{IV+=O} species can be spectroscopically

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23. Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Comm.* 1984, 279.

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28. Hoffmann, P.; Robert, A.; Meunier, B. *Bull. Soc. Chim. Fr.* 1992, 129, 85.

identified during an oxidation with *m*-CPBA.²⁹ The activity of FeTDCPP- β -Cl₈ doubles upon chlorination, and the electron withdrawing nature of the substituents leads to a greater selectivity for hydroxylation versus epoxidation in competitive substrate experiments.²⁷ FeTDCPP- β -Br₈ is found to be more rugged than the less halogenated porphyrin, Fe^{III}TFPPCl. This is attributed to both electronic and steric effects, as the bulk of the β -halogens helps prevent μ -oxo formation and self oxidation, and the electron deficient porphyrin leads to a more electrophilic oxene complex.³⁰

On the basis of these results, the synthesis of a completely halogenated porphyrin should combine the best aspects of the previous P-450 models, and create a robust, highly active porphyrin. Indeed, halogenated porphyrin systems demonstrate an unprecedented ability to catalytically activate dioxygen without destruction of the heme, removing the industrially limiting requirement of a stoichiometric and often expensive oxidant such as PhIO.^{3, 16, 17, 27, 31, 32} The perhalogenated porphyrins show high selectivity for hydroxylation, and can catalyze thousands of turnovers with little heme destruction (Table 1).

Table 1
Catalytic Abilities of Perhalogenated Porphyrins with Dioxygen.

Porphyrin	Temp (°C)	Time (hr)	Substrate	Selectivity (%-ol)	Turnover numbers	Ref
Fe ^{III} (TFPP- β -Br ₈)Cl	80	3	isobutane	83%	17,150	16
Fe ^{III} (TFPP- β -Br ₈)N ₃	125	4.5	propane	90%	540	3
Fe ^{III} (TFPP- β -Br ₈)Cl	25	71.5	isobutane	95%	12,150	16

a. Reacted under 75 atm of O₂ and N₂. Dioxygen was replaced as consumed.

b. Reacted at 1000 psi of air.

- ²⁹ Austin, R. N.; Jayaraj, K.; Gold, A.; White, P. S.; Weiss, R.; Mandon, D.; Ochsenbeing, P.; Bill, E.; Trautwein, A. X.; Hatfield, W. E. *American Chemical Society Meeting Abstract* #247. Spring, 1992.
- ³⁰ Traylor, T. G.; Shinji, T. *Inorg. Chem.* 1987, 26, 1338.
- ³¹ Ellis, P. E.; Lyons, J. E. *J. Chem Soc., Chem. Comm.* 1989, 1187. b) Ellis, P. E.; Lyons, J. E. *J. Chem Soc., Chem. Comm.* 1989, 1189. c) Ellis, P. E.; Lyons, J. E. *J. Chem Soc., Chem. Comm.* 1989, 1315. d) Ellis, P. E.; Lyons, J. E. *Cat. Lett.* 1989, 3, 389. e) Lyons, J. E.; Ellis, P. E.; Myers, H. K.; Wagner, R. W. *J. Mol. Cat.* In Press.
- ³² a) Wijesekera, T.; Matsumoto, A.; Dolphin, D.; Lexa, D. *Angew. Chem. Int. Eng.* 1990, 29(9), 1028. b) Dolphin, D. H.; Nakano, T.; Kirk, T. K.; Maione, T. E.; Farrell, R. L.; Wijesekera, T. Patent, PCT Int. Appl. # WO88/07 988, 1988.

Although significant catalysis data has been collected, the difficulty in obtaining pure samples of the perhalogenated porphyrins has precluded any detailed mechanism determination. In a collaborative effort with Ellis, et al. at the Sun Company, we have been attempting to better understand these perhalogenated porphyrin systems.

Specifically, several halogenated free base, zinc, iron and ruthenium porphyrins have been prepared and purified. A crystal structure of the free base porphyrin, H₂TFPP- β -Cl₈, has been obtained. Initial mechanistic work has focused on TFPP derivatives, as these compounds are easier to handle and characterize than the perhalogenated compounds. In order to gain an understanding of how the fluorine spectra change with different metals and axial ligands, a series of FeTFPP porphyrins have been carefully characterized by both proton and fluorine NMR. Iron-alkyl porphyrins have also been prepared and their reaction with air monitored, in an attempt to isolate the intermediates during a single turnover reaction. A library of spectral data has been collected which will allow the identification of other intermediates in the catalytic cycle of these porphyrins.

Results and Discussion

Tetrakis(pentafluorophenyl)- β -octachloroporphyrinatozinc (Figure 4) has been synthesized and well characterized by ¹⁹F- and ¹H-NMR, UV-Vis, and mass spectroscopies. ZnTFPP is chosen as the starting material for the chlorination reaction because it is more efficiently halogenated than the free base or iron porphyrin. Chlorination of the pyrrole positions is characterized by a significant red shift in the

Figure 4---- Structure of ZnTFPP-β-Cl₈.

Soret band in the UV-Vis spectra (Table 2), which has been attributed to steric effects (*vide infra*). The β-hydrogen resonance in the ¹H NMR is absent, indicating full chlorination of the porphyrin ring. Substitution with larger, more electronegative chlorine atoms manifests itself in three major ways:

1) electron density is removed from the phenyl rings, 2) general electron density is increased along the perimeter of the porphyrin, and 3) ring current is decreased. These effects apparently counteract one another, thus

Table 2
UV-Vis Values for Halogenated Porphyrins

Porphyrin in CH ₂ Cl ₂	N or MLCT bands (nm)	Soret (nm)	Q bands (nm)
ZnTFPP	318	414	544
H ₂ TFPP	310	412	506
Fe ^{III} TFPPCl	352	410	504
Fe ^{III} TFPPOH		406	563
(FeTFPP) ₂ O	356	398	560
Fe ^{III} TFPPCH ₃ ^a		416	530
Fe ^{III} TFPP-Et ^a		414	526, 548
ZnTFPPCl ₈	364	442	576
H ₂ TFPPCl ₈		440	538, 626
RuTFPPCl ₈	350	412	538, 562
Fe ^{III} TFPPCl ₈	400	440	560
" + pyridine	340	438	542, 574
Fe ^{III} TFPPCl ₈ ^b		426	514, 562

a. UV-Vis taken in a degassed cell, in acetone.

b. Red species from ferrous acetate prep. Soret later red shifts to be in better agreement with the other Soret value of 440 nm.

resulting in only a slight perturbation of the fluorine resonances. The diamagnetic porphyrin spectrum exhibits a complex splitting pattern for the *ortho*, *meta*, and *para*

fluorine atoms (Figure 5). The *ortho* resonances are split into a doublet of doublets, the *para* into a triplet, and the upfield *meta* fluorine resonance is a doubled triplet, similar to the ZnTFPP spectrum. There are only three fluorine signals for the five fluorine atoms due to the D_{2d} symmetry of the porphyrin. (Table 3).

Figure 5: Fluorine NMR of ZnTFPPCl₈. A complex splitting pattern is seen for the *ortho*, *para*, and *meta* fluorine resonances.

The synthesis of β -halogenated porphyrins is a difficult process, as the reaction conditions are extremely harsh and do not easily go to completion. In the synthesis of ZnTFPP- β -Cl₈, a small percentage of partially chlorinated porphyrin molecules remain in the reaction mixture. These are easily detected by fluorine-19 NMR, as a change in electron distribution in the ring causes the fluorine phenyl resonances to shift. In addition to the ZnTFPPCl_xH_{8-x} derivatives, common byproducts such as chlorin (reduced porphyrin) and further degraded porphyrins are present. Chromatography on alumina

with a mixture of polar solvents such as chloroform and methanol will easily separate these degradation products from the intact porphyrins, but the similarly structured porphyrins $\text{ZnTFPPCl}_x\text{H}_{8-x}$ are far more difficult to separate.

Table 3
 ^{19}F and ^1H NMR values for halogenated porphyrins

Porphyrin in CDCl_3	Fluorine NMR ^a			Proton NMR ^b	
	ortho	para	meta	pyrrole	inner H
ZnTFPP	-136.75 (q)	-151.88 (t)	-161.67 (m)	8.99	none
H_2TFPP	-136.97 (q)	-151.67 (t)	-161.78 (m)	8.87	-2.97
$\text{Fe}^{\text{III}}\text{TFPPCl}^{\text{c}}$	-105.4, -107.8	-150.3	-154.0, -156.1	82	none
$\text{Fe}^{\text{III}}\text{TFPPOH}^{\text{c}}$	-105, -115	-152	-156, -158	82	none
$(\text{FeTFPP})_2\text{O}^{\text{c}}$	-133.5, -137.4	-154.9	-163.2, -164.8	13.95	none
$\text{Fe}^{\text{III}}\text{TFPPCH}_3^{\text{c,d}}$	-145.4, -147.4	158.2 (t)	166.8 (m)	-21.5	none
$\text{Fe}^{\text{III}}\text{TFPP-Et}^{\text{c,d}}$	-138, -141	-156, -157	-163, -164 (m)	not seen	none
ZnTFPPCl_8	-137.98 (q)	-150.92 (t)	-162.44 (m)	none	none
$\text{H}_2\text{TFPPCl}_8$	-137.96 (q)	-149.42 (t)	-161.59 (m)	none	-2.14
RuTFPPCl_8	-137.9 (q)	-149.4 (t)	-161.5 (m)	none	none
$\text{Fe}^{\text{III}}\text{TFPPCl}_8$	-143.7	-152	-153	none	none
" + pyridine	-138.2 (q)	-151.8 (t)	-162.9 (m)	none	none

- a. All spectra externally referenced to CFCl_3 (0 ppm) in the same solvent. q = quartet, t = triplet, m = multiplet.
b. Spectra referenced to residual solvent peak.
c. In d_6 -acetone.
d. Degassed sample.

Chromatography on silica gel is the method commonly utilized to separate such porphyrin products. However, with ZnTFPPCl_8 , silica gel chromatography did not remove all traces of impurities. The chromatography was additionally complicated by the fact that the halogenated porphyrins have low solubility in almost all solvents. Attempts with other solid supports, such as florisil, reverse phase silica, and acidic or basic alumina, also met with little success. At this point, high pressure liquid chromatography (HPLC) was attempted. A gradient of 60 to 100% acetonitrile in water was found to give satisfactory separation of the porphyrin products on a C-18 reverse phase column.

However, this was only effective on an analytical scale, as large amounts of porphyrin were not soluble in acetonitrile. The zinc porphyrins are slightly more soluble in acetone, and two runs through the column with an isocratic flow of 80 percent acetone in water allows the isolation of ZnTFPPCl_8 . Even though this is the solvent system in which the porphyrins are the most soluble, the solubility is still limiting and only 20 to 40 mg of pure porphyrin are obtained from each set of runs. Consequently, most experiments were conducted with column chromatographed rather than HPLC purified porphyrin.

HPLC purification, however, had a noticeably positive effect on the properties of the porphyrins. In addition to removing trace impurities from the ^{19}F -NMR spectrum, the Soret and Q bands in the UV-Vis spectrum are considerably sharper (full width-half height dropped from 20 to 13 nm). Additionally, the porphyrins spontaneously formed crystals in solution, rather than the powders previously seen. Mass spectroscopy of the pure porphyrin showed a parent peak at 1313.75 (calculated value: 1313.47) with a distribution of peaks due to chlorine, nitrogen, and zinc isotopes (Figure 6).

Figure 6: Mass spectrum of ZnTFPPCl_8 . The parent peak is at 1313.75, with a distribution mainly due to ^{35}Cl and ^{37}Cl isotopes.

The demetallation of ZnTFPPCl_8 does not occur in concentrated HCl solutions, as with many other porphyrins, but is only accomplished by bubbling HCl gas through the reaction mixture. The UV-Vis Soret shows a small shift, and the free base spectrum shows a splitting in the Q band due to a loss of symmetry in the porphyrin. Purification of this compound by HPLC was problematic, as it appeared to deleteriously insert metal ions from the stainless steel tubing in the instrument. However, the metallated compounds were easily separated from the free base by column chromatography, and a pure sample of $\text{H}_2\text{TFPP-}\beta\text{-Cl}_8$ was obtained.

Crystals of the free base were grown by slow evaporation from a saturated acetone/water solution. The triclinic crystals were long, thin, and green/brown in color. The crystal structure (Figure 7), shows that the porphyrin has the same distortion as evidenced in structures of $\text{CuTFPP-}\beta\text{-Cl}_8$, $\text{NiTFPP-}\beta\text{-Br}_8$, $\text{CuTFPP-}\beta\text{-Br}_8$, and $\text{H}_2\text{TFPP-}\beta\text{-Br}_8$.³³ The closest contact in the porphyrins is the $3.2\text{\AA}$ distance between the β -chlorine and the *ortho*-carbon on the phenyl ring, which is well within the $3.45\text{\AA}$ carbon-chlorine Van der Waals distance. This interaction is likely the driving force for the saddle shaped buckling of the porphyrin.

The free base is not as distorted as the chlorinated copper compound. The unmetallated moiety has a slightly larger core, which results in an overall relaxation of the porphyrin. The chlorine atoms and β -carbons are approximately $0.1\text{\AA}$ further out of the plane for the metallated porphyrin, but even the $1.06\text{\AA}$ out of plane distance for the chlorine atoms in the free base signifies a major distortion of the macrocycle.

Calculations have shown that the distortion contracts the HOMO and LUMO of the porphyrin ligand, resulting in the significant red shift of the Soret for the halogenated porphyrins.³⁴ The electron withdrawing nature of the chlorine substituents lowers the energy of all the orbitals, which has no net effect on the electronic spectra. However, this does contribute to the increased stability of the porphyrin to ring oxidation and the greater

³³. Hodge, J. A.; Hughes, M. E.; Schaefer, W.; Gray, H. B. *Acta Cryst.* In Press.

³⁴. Takeuchi, T. Research Report for PhD Candidacy Examination, Caltech. 1992.

Figure 7: Crystal Structure and Data for $\text{H}_2\text{TFPP-B-Cl}_8$

Atom	Distortion from plane of nitrogen atoms (Å)
C_{meso}	± 0.023
C_8	± 0.625
N	$\pm .088$
Cl	± 1.06
Core size = 2.12 Å	

Dihedral Angle
of phenyl rings:
 107.38°

catalytic efficiency, which is evidenced by increasingly positive shifts in the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple upon halogenation: -0.29 eV for $\text{Fe}^{\text{III}}\text{TPPCl}$, ~ 0 for $\text{Fe}^{\text{III}}\text{TFPPCl}$, and 0.28 eV for $\text{Fe}^{\text{III}}\text{TFPPCl}_8$.³⁵ The electrochemistry of these porphyrins is being further explored.

Ruthenium and iron were inserted into $\text{H}_2\text{TFPPCl}_8$ by several different methods. The insertion of ruthenium with RuCl_3 was a clean reaction, yielding only a single metal derivative and unreacted free base. Unlike other perhalogenated porphyrins, this compound does not show a red shift in the Soret band. Also, the ^{19}F -NMR signals are close to the free base values, indicating that the metal does not greatly perturb the electron density of the ligand. This suggests that the octahedrally coordinated Ru rests squarely in the plane of the nitrogen atoms, reducing the distortion of the ring, and diminishing the characteristic red shift of the Soret band.

There was some concern that this reaction simply dechlorinated the porphyrin, since the UV-Vis Soret band matches that of H_2TFPP . However, there is a significant change in the ruthenium porphyrin Q bands. The split Q_x and Q_y for the free base coalesce into a single, symmetric $Q_{(0,1)}$ band at 538 nm, with the $Q_{(0,0)}$ seen at a slightly higher wavelength (Figure 8).³⁶ This causes the ruthenium compounds to be an intense red color, rather than the green/brown color of the free base compounds. The NMR signals are sharp, and show splittings expected for a diamagnetic Ru^{II} metal center. Diffraction photos of the very fine, stepped crystals indicate a tetragonal crystal type, different from the triclinic free base crystals. Attempts to grow X-ray quality crystals continue.

The insertion of ruthenium was also attempted with a ruthenium carbonyl starting material, $\text{Ru}_3(\text{CO})_{12}$. Surprisingly, the porphyrin isolated from this reaction has identical spectral characteristics as that isolated from reaction with RuCl_3 . Unlike other

³⁵ Electrochemistry data was taken in methylene chloride and TBACl, vs. SCE. FeTPPCl values from Kadish, K. M. in *Iron Porphyrins, Part II*. Lever, A. B. P.; Gray, H. B., eds. Addison-Wesley Pub. Co.: Canada, 1983, 187. Others from unpublished data, Hodge, J. A., Hill, M., and Gray, H. B.

³⁶ Assignments based on Gouterman, M. *J. Mol. Spectr.* 1961, 6, 138.

Figure 8: The UV-Vis spectrum of RuTFPPCl₈. The Soret is blue shifted from other perhalogenated porphyrins.

porphyrins, the insertion with a ruthenium carbonyl precursor into RuTFPPCl₈ did not result in the retention of an axial carbonyl ligand.³⁷ The strong, distinctive CO stretch was not visible by IR spectroscopy, and there were no differences in the UV-Vis spectra between the two syntheses. Perhaps the duration of the reaction (44 hours) was enough to displace a carbonyl from the metal center. The axial ligands do appear to be exchangeable, as the addition of pyridine to a solution of RuTFPPCl₈ slightly shifts the Soret.

Attempts to insert iron into the halogenated porphyrins were not as successful. Insertion with Fe^{II}Cl₂·xH₂O in DMF, as described by Adler, gave a spectroscopically confusing set of products. The UV-Vis showed an extremely broad Soret with a maximum at 440 nm. Fluorine NMR of the initial product gave extremely broad signals, as expected for a high spin Fe^{III} species. However, only three of the predicted five signals were visible, even though a large spectral width was scanned. A pentacoordinate

³⁷. Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P.P. *J. Am. Chem. Soc.* 1978, 100, 3015.

porphyrin would be expected to yield five signals, as the single axial ligand breaks one of the planes of symmetry, causing the five fluorines to be inequivalent. The chemical shifts were distinctly different from other octachloro compounds, and were not assigned.

Upon addition of pyridine to the sample, the noise in the NMR spectrum decreased dramatically, and three signals with typical diamagnetic splittings were seen. This is extremely surprising, for although the coordination of strong field ligand such as pyridine could easily change the metal center from high to low spin, it is not likely to reduce the iron. However, initial electrochemical results suggest that the Fe^{II} state is stabilized, perhaps enough to remain stable in air.

Insertion with ferrous acetate was also attempted, as this route was expected to yield the iron (II) species directly and clarify the nature of the iron species formed upon addition of pyridine in the previous reaction. The product was initially a bright red color, typical of a ferrous porphyrin. However, when exposed to hydrochloric acid or water, as necessary during the work up, or air, it eventually changed to the green ferric porphyrin. The red ferrous species was never characterized by NMR, and the signals for the green compound, although sharp, were extremely messy. Clearly, more than one product was obtained. Further investigation and characterization of the products of these two syntheses is ongoing.

Due to the difficulty in obtaining pure samples of the $\text{Fe}^{\text{III}}(\text{TFPPCl}_8)\text{Cl}$, initial mechanistic experiments have been done with the $\text{Fe}^{\text{III}}\text{TFPPCl}$. Aside from purity and availability, working with the partially halogenated porphyrin has the important advantage that correlations can be made between ^{19}F - and ^1H -NMR signals for various states of the iron porphyrins. Proton NMR values for intermediates such as the ferryl iron or μ -oxo dimer are well documented, and the pyrrole proton resonances of partially halogenated porphyrins used to identify various iron porphyrin species and map the trend in the ^{19}F -NMR.¹⁹⁻²⁴ An understanding of how the fluorine signals change with the oxidation state and spin of the metal center has been achieved for some iron states.

Figure 9: ^{19}F -NMR of $\text{Fe}^{\text{III}}\text{TFPPCl}$ and $(\text{FeTFPP})_2\text{O}$. The resonances shift upfield with the magnetically linked metal centers.

Signals in the ^{19}F -NMR spectrum of $\text{Fe}^{\text{III}}\text{TFPPCl}$ appear over a 70 ppm window, compared to 35 ppm for the corresponding Zn or free base porphyrins. The paramagnetic nature of the metal center has a strong effect on the *ortho* fluorine substituents, and shifts them approximately 32 ppm downfield. The two *ortho* fluorines are now inequivalent, and appear as two broad singlets at -105.4 and -107.8 ppm. The *meta* fluorine signals are also split, and the complete spectrum consists of five broad singlets (Figure 9). The signals do not coalesce below a temperature where the porphyrin would decompose, indicating that the phenyl rings do not have free rotation around the $\text{C}_{\text{meso}}\text{-C}_{\text{phenyl}}$ bond, but are trapped perpendicular to the plane of the porphyrin. A Curie plot of $1/T$ vs. chemical shift demonstrates this effect (Figure 10).

Curie Plot for Phenyl Fluorine Resonances

Figure 10--A Curie plot for the phenyl fluorine resonances of $\text{Fe}^{\text{III}}\text{TFPPCl}$. The linear dependence on temperature indicates that the iron center is paramagnetic. The resonances do not coalesce at any temperature (to 670K shown), indicating the rotation of the phenyl groups is completely restricted.

Metathesis of the chloride ligand for hydroxide does not greatly alter the ^{19}F -NMR spectrum of the porphyrin. The *ortho* fluorines are split by an additional 8 ppm, the *meta* and *para* signals are shifted upfield 2 ppm. The proton spectrum of these two porphyrins have pyrrole resonances at approximately 82 ppm, significantly shifted and broadened due to the paramagnetic iron center. They can be differentiated by the fact that the $\text{Fe}^{\text{III}}\text{TFPPOH}$ resonance is approximately twice as broad as that of $\text{Fe}^{\text{III}}\text{TFPPCl}$.

$\text{Fe}^{\text{III}}\text{TFPPOH}$ will dimerize to form the $\text{FeTFPP } \mu\text{-oxo}$ porphyrin if left in solution several days, or dry in the air over a matter of weeks. The spectroscopy of $(\text{FeTFPP})_2\text{O}$ was significantly different from the other high spin Fe^{III} porphyrins.

Jayaraj, et al. indicated that the metal centers in this porphyrin are antiferromagnetically

coupled, which is supported by the lack of EPR signal for this porphyrin at 77K.³⁸ Both $\text{Fe}^{\text{III}}\text{TFPP-Cl}$ and -OH have a strong EPR signal at this temperature, typical for high spin iron porphyrins.³⁵ ^{19}F -NMR for the μ -oxo porphyrin has five relatively sharp singlets contained in a small window (Figure 9). The *ortho* fluorine signals are at -133.5 and -137.2 ppm, which is far upfield from the monomeric Fe^{III} porphyrins, while the *meta* and *para* fluorines are not greatly shifted. The ^1H -NMR for $(\text{FeTFPP})_2\text{O}$ shows only a single resonance at 13.95 ppm, in agreement with the published value.³⁸

$\text{Fe}^{\text{III}}\text{TFPPCH}_3$ was formed by the treatment of $\text{Fe}^{\text{III}}\text{TFPPCl}$ with CH_3MgBr . The iron alkyl species was identified by the resonance of the pyrrole protons, which shift upfield to -21.5 ppm. A small signal in the proton NMR was also seen at -114 ppm, which is in the area expected for the methyl protons, but this was not seen when the spectrum was repeated and may have been an instrumental artifact.

The lack of an observable EPR signal is consistent with expectations for iron-alkyl porphyrins. Unfortunately, the definitive experiment at 4K, the temperature necessary to see a low spin Fe^{III} center, has not yet been done. However, the ^{19}F -NMR is significantly different from high spin iron porphyrin systems; all signals are shifted upfield into a narrow window, which may result from shielding provided by the electron donating methyl group. The two *meta* resonances partially overlap, yielding a distorted triplet, but the *ortho* resonances are still separated by 2 ppm. These signals are all notably sharper than with the high spin systems.

Other attempts to form iron-carbon bonds were less successful. The reaction of $\text{Fe}^{\text{III}}\text{TFPPCl}$ with butyl grignard yielded only $(\text{FeTFPP})_2\text{O}$. The reaction with phenyl lithium had similar results, although the integrity of the starting material is somewhat in doubt.³⁹ The addition of Super Hydride to a solution of $\text{Fe}^{\text{III}}\text{TFPPCl}$ appeared to result in the formation of $\text{Fe}^{\text{III}}\text{TFPPCH}_2\text{CH}_3$. The fluorine NMR showed four peaks similar in

38. Jayaraj, K.; Gold, A.; Toney, G. G.; Helms, J. H.; Hatfield, W. E. *Inorg. Chem.* 1986, 25, 3516.

39. Shin, K.; Yu, B. S.; Goff, H. M. *Inorg. Chem.*, 1990, 889.

structure and shift to those of the methyl compound, but two other peaks in the spectra were unassignable, and the integration is not consistent with a single product. Pyrrole hydrogen resonances were not observed. Unfortunately, this product degraded before it could be further characterized.

The purpose in synthesizing the iron-alkyl porphyrins was to follow their reaction with air, and probe for intermediates common to the general catalytic cycle (Scheme 2). Once the general spectral characteristics for these intermediates are determined, isolating them from the general catalytic reaction will be simplified. The proposed reaction path is shown in Scheme 3.

Scheme 3
Mechanism of reaction with dioxygen

Scheme 3--A proposed mechanism for the reaction of with air. Several intermediates, such as $\text{Fe}^{\text{IV}}=\text{O}$, are common to the general catalytic mechanism but may be more easily identified here.

To follow the reaction, a degassed sample of $\text{Fe}^{\text{III}}\text{-TFPPCH}_3$ in acetone was cooled to approximately -78°C with a dry ice/acetone bath. A specially constructed metal base held the UV-Vis cell above the bath while maintaining a constant system temperature. However, upon opening the cell to air, an isosbestic conversion to the products, $\text{Fe}^{\text{III}}\text{-TFPP-OH}$ and $(\text{Fe}^{\text{III}}\text{-TFPP})_2\text{O}$, was seen, without the appearance of any

intermediates. The reaction appeared to be diffusion limited by the rate of dioxygen transfer into the solution, and the same products were seen when the reaction was run at room temperature (Figure 11).

Figure 11: UV-Vis spectra taken every 10 minutes upon exposure of an acetone solution of $\text{Fe}^{\text{III}}\text{TFPPCH}_3$ to air. The iron alkyl bands at 416 and 530 nm disappear, and $\text{Fe}^{\text{III}}\text{TFPPOH}$ bands grow in. Residual μ -oxo is present throughout.

This experiment did allow the identification of the iron-alkyl UV-Vis spectra, and demonstrated that the porphyrin is air reactive. This conclusion is also upheld by a similar experiment with ^{19}F -NMR. In figure 12, the peaks due to $\text{Fe}^{\text{III}}\text{TFPPCH}_3$ diminish as $\text{Fe}^{\text{III}}\text{TFPPOH}$ resonances grow in. Peaks due to $(\text{FeTFPP})_2\text{O}$ contamination also appear, but further attempts to synthesize a pure sample have not yet been successful.

Final evidence for this mechanism comes from gas chromatography of the reaction mixture. A small amount of methanol is seen, which would result from the $\text{CH}_3^\bullet$ radical abstracting a hydroxy group from $\text{Fe}^{\text{III}}\text{TFPPOH}$. It would be informative to run

the reaction in the presence of a second substrate such as isobutane, and look for the reaction with the proposed ferryl intermediate to form t-butanol.

Other attempts have been made to directly synthesize intermediates, but without success. In two separate experiments, $\text{Fe}^{\text{III}}\text{TFPPCl}$ was reacted with zinc powder and the benzophenone radical anion to form the Fe^{II} species. The zinc powder appeared to cause

Figure 12: ^{19}F -NMR of $\text{Fe}^{\text{III}}\text{TFPPCH}_3$ with air. Peaks due to $\text{Fe}^{\text{III}}\text{TFPPOH}$ increase with time, while the iron alkyl peaks disappear. The μ -oxo contamination remains constant.

formation of the μ -oxo, and the products from the latter experiment were too complicated to be interpreted. The reduction of $\text{Fe}^{\text{III}}\text{TFPPCl}$ with aza ferrocene has recently been reported.⁴⁰ Use of this reductant may allow the iron(II) species to be characterized.

⁴⁰ Zakrzewski, T.; Cesario, M.; Guilhem, J.; Giannotti, C. *J. Chem. Soc. Dalton Trans.* 1992, 3059.

Conclusions

ZnTFPP- β -Cl₈ and H₂TFPP- β -Cl₈ have been synthesized, purified, and characterized by a number of techniques. A crystal structure of H₂TFPP- β -Cl₈ shows significant distortion of the macrocycle, which leads to a red shift of the Soret band. Iron and ruthenium have been inserted into the free base perhalogenated porphyrin. RuTFPP- β -Cl₈ is believed to be octahedrally coordinated, keeping the metal in the plane, flattening the porphyrin ring, and reducing the characteristic red shift of the Soret band. Different preparations of the iron porphyrin display Soret values ranging from 440 to 426 nm. These may reflect differences in spin or oxidation state, and are being further investigated.

Spectral data has been collected for a series of FeTFPP porphyrins, which has allowed a basic understanding of the fluorine NMR of porphyrins to be achieved. Characteristic shifts for high spin, low spin, and coupled metal centers have been observed.

Finally, FeTFPPCH₃ has been synthesized and reacted with air. Evidence supports a reaction mechanism with intermediates common to the general proposed cycle for catalytic metalloporphyrin oxidation, but none have been directly observed.

Future Work

To further support the Fe^{III}TFPPCH₃ work, this compound needs to be purified before exposure to air. Control reactions with degassed water and dry dioxygen need to be conducted to positively identify the reactive oxygen species. The experimental procedure for the low temperature work will be improved to increase the chance of observing the proposed intermediates.

Now that the synthesis of pure perhalogenated porphyrins is possible, experiments with these derivatives can begin in earnest. Pure FeTFPP- β -Cl₈, as Fe^{II} and Fe^{III}, will be synthesized and fully characterized. The reaction of perhalogenated iron porphyrins with

m-CPBA or other oxidants will be utilized to characterize high oxidation state iron-oxo intermediates. The methods of Balch, et al., will be used to directly probe for various intermediates from the reaction of Fe^{II} porphyrins with dioxygen at low temperature.¹⁸ Further characterization of RuTFPP- β -Cl₈ would also be of interest, including a crystal structure. As a second row transition metal, Ru should be able to form stable oxo-compounds more easily than the iron porphyrins. Experiments to observe these intermediates will be conducted in parallel with the iron porphyrin work.

Methods

Solvents were purchased from EM Science (Omnisol grade), and used as obtained unless otherwise noted. Neutral alumina was purchased from Fluka, and acidic alumina (acidic activity I, 70-230 mesh) and basic alumina (Type T, 150 Basic) from EM Science. Silica (150Å pore, 75-100 μ particle size) was purchased from Analtech. Chlorine gas was from Alphagaz, and a lecture bottle of hydrochloric acid gas was purchased from Matheson. Ruthenium trichloride, triruthenium dodecacarbonyl, iron(II) chloride, Super Hydride, and methyl magnesium bromide were purchased from Aldrich.

¹H- and ¹⁹F-NMR spectra were obtained on a Brüker AM 500 nuclear magnetic resonance spectrometer (500.138 MHz for ¹H). Fluorine spectra were taken with a proton probe tuned down to 470.56 MHz. UV-Vis spectra were taken with a Hewlett Packard 8452 Diode Array or Cary-14 spectrophotometer with an Olis 3820 operating system. Preparative HPLC work was done on a Beckman system with a dual wavelength detector. A Beckman automated Gold system with an autosampler was used for analytical HPLC work. Reverse phase silica gel HPLC columns (C-4 and C-18) were purchased from Vydac. A Perkin Elmer 8400 Gas Chromatograph was used for GC analysis. EPR were taken at Caltech.

Air sensitive samples were handled in a Vac Atmospheres inert atmosphere glove box under nitrogen, or using common schlenk and high vacuum line techniques. NMR samples were made up in tubes equipped with J. Young valves.

Preparation of Porphyrins--

Tetrakis(pentafluorophenyl)porphyrinatozinc (ZnTFPP) was purchased from Porphyrin Products. Samples were purified by chromatography on Fluka alumina, eluting with CHCl_3 + 5% methanol. A single red band was collected, and rotary evaporated to dryness. UV-Vis: CH_2Cl_2 , λ 318, 414 (Soret), 544 nm.

Synthesis of ZnTFPP- βCl_8 -- *Tetrakis*(pentafluorophenyl)- β -octachloro-porphyrinatozinc (ZnTFPP- $\beta\text{-Cl}_8$) was synthesized based on by methods by Ellis et al.^{31e} All glassware was oven dried overnight at 110 °C. Approximately 300 ml of freshly distilled CCl_4 (from P_2O_5 , under Ar) was charged for 10 minutes with Cl_2 gas through a gas dispersion tube. 500 mg of ZnTFPP were added, and the reaction mixture refluxed under a slow, continuous flow of argon. The reaction was monitored by UV-Vis and thin layer chromatography on silica plates with 1:1 hexane: dichloromethane. When no starting material was left (3 to 6 hours) the reaction was allowed to cool, and rotary evaporated to dryness. Occasionally, the addition of more Cl_2 gas was necessary to drive the reaction to completion. The product was redissolved in chloroform, and chromatographed on alumina with chloroform + 5% methanol. The product was then collected and rotary evaporated to dryness. Most samples were further purified by chromatography on a silica column with 3:2 hexane: chloroform elutant to remove partially chlorinated impurities. As this separation proved inadequate, later samples were purified by HPLC (see text). Yields ranged from 40 to 80%. UV-Vis: CH_2Cl_2 , λ 364, 442(Soret), 576.

Demetallation of porphyrins -- Zn porphyrins were demetallated as previously done by Ellis, et al.^{31e} 50 to 300 mg of ZnTFPP or ZnTFPP- $\beta\text{-Cl}_8$ were dissolved in approximately 50 ml chloroform. HCl gas was bubbled through a gas dispersion tube

into the solution for 5 minutes, and the solution allowed to stir for 15 more minutes. The reaction was monitored by TLC on silica in chloroform. The volume of the reaction mixture was reduced, and chromatographed on alumina, eluting with chloroform + 5% methanol. The product, *tetrakis*(pentafluorophenyl)porphyrin (H_2TFPP) and *tetrakis*-(pentafluorophenyl)- β -octachloro porphyrin ($H_2TFPP-\beta-Cl_8$), respectively, were collected and rotary evaporated to dryness, with a yield of approximately 90%. UV-Vis: $CHCl_3$, H_2TFPP , λ 310, 412(Soret), 506, 576; $H_2TFPPCl_8$, λ 440(Soret), 538, 626 nm.

Iron insertion -- The insertion followed the iron(II) chloride in DMF method of Adler et al.⁴¹ With vigorous stirring, 120 mg $H_2TFPPCl_8$ in DMF was heated under Ar to ~ 140 °C. Two equivalents of $Fe^{II}Cl_2 \cdot xH_2O$ were added to the reaction, and heated for 15 minutes. The reaction mixture was then allowed to cool to room temperature, at which point it was added to 70 ml of iced brine to precipitate the porphyrin. The solution was vacuum filtered on a fine frit, and the black, pasty precipitate was redissolved in chloroform and eluted with $CHCl_3$ on an alumina column. The product, *tetrakis*-(pentafluorophenyl)- β -octachloroporphyrinatoiron(III) chloride ($Fe^{III}[TFPP-\beta-Cl_8]Cl$), was collected as broad green-black band. UV-Vis: CH_2Cl_2 , λ 400, 440(Soret), 560 nm.

Insertion was also attempted with iron acetate by Warburg's method⁴². Under Ar, one gram of iron filings was heated to reflux in 50 ml glacial acetic acid to generate $Fe^{II}(OAc)_2$. In a separate flask, 60 mg $H_2TFPP-\beta-Cl_8$ was heated under Ar in 15 ml glacial acetic acid. Carefully keeping all air out of the reaction flask, 1.5 ml of the iron acetate solution was added to the porphyrin with stirring, causing an intense red color. In some preps, 0.5 ml HCl (37%) was added to convert the porphyrin to the $Fe^{III}Cl$ derivative. The porphyrin was then precipitated with water, filtered, and washed with excess water to remove the acid, leaving a powdery, red precipitate. See text for explanation of products.

⁴¹ Adler, A.D.; Longo, F. R.; Kampas, F.; Kim, J. J. *Inorg. Nuc. Chem.* 1970. 32, 2443.

⁴² Warburg, O.; Negelein, E. *Zeit. Biochem.* 1932. 1.

This preparation was also modified to be used with a swivel frit on a high vacuum line. In this case, a slight molar excess of $\text{Fe}^{\text{II}}(\text{OAc})_2$ was synthesized, as above, on one side of the frit, and filtered onto the free base porphyrin (H_2TFPP) on the other side, which was heated to 100°C to insert the iron. At this point, water was added to the reaction, and the precipitated porphyrin isolated. Upon addition of HCl , the product converted cleanly to the iron chloride porphyrin, *tetrakis*(pentafluorophenyl)porphyrinato iron(III) chloride ($\text{Fe}^{\text{III}}\text{TFPPCl}$). UV-Vis: acetone, λ 408(Soret), 502, 628.

Ruthenium Insertion -- Adapted from the methods of Collman, et al.⁴³, and Takagi, et al.⁴⁴. Diethylmonomethyl ether (diglyme, 50 ml) was anaerobically transferred from the Sure Seal™ bottle to a round bottom flask with 160 mg $\text{H}_2\text{TFPPCl}_8$. 600 mg of RuCl_3 was similarly prepared in an additional 40 ml of diglyme, and gently heated and stirred until dissolved. The ruthenium solution was added to the porphyrin, and the mixture allowed to reflux under argon. After 21 hours, UV-Vis showed that insertion had taken place, and the reaction mixture was removed from heat. The product was chromatographed on alumina with chloroform + 5% methanol. A single, but extremely broad, brown band was collected, and run through a silica column with 1:1 CH_2Cl_2 : hexane. The first band proved to be unreacted free base, and a second red-brown band was the product, *tetrakis*(pentafluorophenyl)- β -octachloro porphyrinato ruthenium(II). The axial ligands are undetermined. UV-Vis: CH_2Cl_2 , λ 348, 412(Soret), 538, 568 nm.

A second insertion, based on a prep by Antipas, et al. was also attempted.³⁷ 300 mg $\text{H}_2\text{TFPP}-\beta\text{-Cl}_8$ was heated in benzene under Ar. With continuous stirring, 1 g of $\text{Ru}_3[\text{CO}]_{12}$ was added, and the reaction kept at 80°C for 44 hours. Chromatography of the product on alumina eluting with CHCl_3 and 5% methanol yields a single red-brown band with spectral features identical to the RuCl_3 prep.

⁴³. Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* 1984, 106, 3500.

⁴⁴. Takagi, S.; Miyamoto, T. K.; Hamaguchi, M.; Sasaki, Y.; Matsumura, T. *Inorg. Chim. Acta.* 1990, 173, 215.

Formation of μ -oxo porphyrin -- Prepared as described by Jayaraj, et al.³⁸

Tetrakis-(pentafluorophenyl)porphyrinato iron (III) chloride ($\text{Fe}^{\text{III}}\text{TFPPCl}$) was used as purchased from Aldrich. 100 mg were dissolved in 25 ml CH_2Cl_2 . 25 ml of aqueous 2 N NaOH were added, and the biphasic reaction stirred for 4 hours. The organic phase was washed two times with water in a separatory funnel, and dried with CaSO_4 . The solution was loaded directly onto an alumina column, and eluted with 1:1 benzene: hexane. A small red band moved with the solvent, which proved to be μ -oxo-bis(*tetrakis*-(pentafluorophenyl)porphyrinatoiron), ($[\text{FeTFPP}]_2\text{O}$). By increasing the polarity of the elutant, a second band was pulled off the column. This red-brown material was *tetrakis*-(pentafluorophenyl)porphyrinato iron (III) hydroxide ($\text{Fe}^{\text{III}}\text{TFPPOH}$). UV-Vis agreed with published values, in CH_2Cl_2 , λ μ -oxo 356, 398(Soret), 560; λ hydroxide 406(Soret), 563 nm.

Iron-carbon bond formation -- The synthesis of methyl *tetrakis*-(pentafluorophenyl)porphyrinatoiron (III) ($\text{Fe}^{\text{III}}\text{TFPPCH}_3$) was adapted from a prep by Cocolios, et al.⁴⁵ Under Ar, 200 mg of $\text{Fe}^{\text{III}}\text{TFPPCl}$ was dissolved in 50 ml of benzene, freshly distilled from sodium/benzophenone. One equivalent of methyl magnesium bromide was added dropwise at 0 to 5 °C with vigorous stirring (0.08 ml of 1.4 M CH_3MgBr in toluene/THF). After 10 minutes, 20 ml of deoxygenated water was added. Still under argon, the reaction was washed a second time with water, dried with CaSO_4 . The solvent was removed, and the reaction vessel brought into the box. The mixture was chromatographed with benzene elutant in the dark on basic alumina, and a single product collected. NMR and UV-Vis samples were made up in the box, as the samples had to be kept away from oxygen and light at all times. UV-Vis: acetone, λ 416 (Soret), 530 nm.

Ethyl *tetrakis*(pentafluorophenyl)porphyrinatoiron (III) ($\text{Fe}^{\text{III}}\text{TFPPCH}_2\text{CH}_3$) was prepared by a method designed by Balch, et al.⁴⁶ 100 mg of $\text{Fe}^{\text{III}}\text{TFPPCl}$ was dissolved

⁴⁵ . Cocolios, G.; Lagrange, G.; Guillard, R. *J. Org. Chem.* 1983, 253, 65.

⁴⁶ . Balch, A. L.; Corman, C. R.; Safari, N. *Organometallics*, 1990, 2420.

in freshly distilled CH_2Cl_2 and allowed to stir under Ar for 40 min. A slight molar excess of Super Hydride (200 μl of 1.0 M $\text{LiHB}(\text{CH}_2\text{CH}_3)_3$) was added in the dark, and the reaction allowed to stir for several hours. The reaction mixture was taken into the glove box, and chromatographed on silica with CH_2Cl_2 . A single dark brown band was collected, and NMR and UV-Vis samples were made up from this elutant in the inert atmosphere. Samples had to be kept out of the light, as the iron-carbon bond could be photolyzed. UV-Vis: acetone, λ 414 (Soret), 526, 548.

Reaction with air--

NMR samples of the alkylated iron porphyrins were made up in the glove box in d_5 -acetone. Once the samples had been locked and shimmed on the NMR, and an initial spectrum taken, the air tight cap was removed. Spectra were taken every 20 minutes (256 scans), with air diffusing into the NMR tube. UV-Vis samples were made up in a similar fashion, in acetone in air tight cells. The cells were opened to air, and spectra taken every ten minutes. UV-Vis experiments were conducted at room temperature and -78°C . A specially constructed cell holder with a metal base that rests in a dry ice/acetone bath maintains the temperature of the system.

Crystal Structure--

Crystals of $\text{H}_2\text{TFPP-B-Cl}_8$ were grown by slow evaporation from a saturated water/acetone solution (80%). Triclinic, brown crystals were obtained. The structure was solved at Caltech by Larry Hennling. R value is 0.042.

4.2 STRUCTURE AND SPECTROSCOPY OF TETRAKIS (PENTAFLUOROPHENYL)OCTABROMOPORPHYRINATO IRON (III) CHLORIDE

The investigation of the structure and oxidation activity of the complex, $\text{Fe}(\text{TPPF}_{20}\beta\text{Br}_8)\text{Cl}$, was critical to our understanding of the nature of an active suprabiotic catalyst. This section provides additional details concerning this landmark complex that have been discovered during the phase IV work in collaboration with Caltech. Contributors to this section are:

Harry B. Gray

Eva R. Birnbaum

Julia Hodge

Paul E. Ellis

James E. Lyons

Wayne Langdale

William Schaefer

Figure 1 shows the UV/visible spectrum (402,446,582nm) of pure microcrystalline sample of $\text{Fe}(\text{TPPF}_{20}\beta\text{Br}_8)\text{Cl}$ obtained from a 1:1 hexane/methylene Chloride solution, washed with hexane and dried. Figure 2 shows the expected C^{13} NMR spectrum of the pure compound. Figure 3 shows the X-Ray Crystal Structure of the molecule and Figures 4-6 give three views of the structure including a space-filling molecular model.

Spectroelectrochemical measurements, Figure 7 show the smooth reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ in this complex at 0.31 volts. We have now characterized this important transformation on understanding of which is critical to our proposed oxidation mechanism.

Figure 8 shows the EPR low temperature spectrum of $\text{Fe}(\text{TPPF}_{20}\beta\text{Br}_8)\text{Cl}$. Signals due to high spin (5/2) iron (III) are observed. The spin state of the iron is another critical piece of information in understanding the observed catalytic activity. As the temperature is raised to 80°K there is an apparent change to the spin (3/2) complex which, however, shows no low spin signal (Figure 9). Magnetic susceptibility measurements, Figure 10, 11 are in accord with the EPR measurements.

FIGURE 1

----> WAVELENGTH SCAN REPORT <----

Date : 01-12-1993
Time : 15:28:24
Operator : Not Entered

Sample Name : Fe(TFPPb-Br8)Cl
Solvent Name : ch2cl2
Concentration : 1.0000
Units :

Function : Absorbance
Wavelength Range : 250 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

Annotated Wavelengths:

1 : Wavelength = 576	Result = 0.131699
2 : Wavelength = 442	Result = 0.905716
3 : Wavelength = 404	Result = 0.809280

FIGURE 2

SF 470.597
 SI 29.0
 OI 77.92:155
 SI 65536
 TD 65536
 SM 62500.000
 HZ,PI 1.907
 PM 2.9
 RD 1.000
 AQ 1.524
 RG 40
 NS 512
 TE 29
 FM 78200
 OF 7600.000
 DP PSL PO
 LB 1.000
 GB 0.0
 CY 35.00
 CY 0.0
 I1 -100.8637
 I2 -158.9644
 HZ,CM 91.196
 PPM,CM 1.660
 SR 77688.57

mw61 48 121

ORTEP Diagram of $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$

The ellipsoids drawn at 50% electron density. Selected bond lengths (Å) and angles (degree): Fe-Cl, 2.191(4); Fe-N1, 2.062(11); Fe-N2, 2.066(11); Fe-N3, 2.039(11); Fe-N4, 2.054(11); N1-Fe-N2, 87.1(4); N1-Fe-N3, 146.6(4); N1-Fe-Cl, 108.8(3); N2-Fe-Cl, 98.6(3); N3-Fe-Cl, 104.6(3); N4-Fe-Cl, 103.1(3); N1-C2, 1.391(18); C2-C3, 1.39(2); C2-C1, 1.44(2); C1-C20, 1.35; N1-C2-C3, 122.5(13); N1-C2-C1, 106.4(12); C2-C1-C20, 110.7(13); C1-Br1, 1.891(15); C2-C1-Br1, 123.9(11).

FIGURE 4

Stick Model Illustrating $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$ Saddle Shape Distortion.

Stick Model of Fe(TPP)Cl

FIGURE 6

Space Filling Model of $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$

FIGURE 7

Spectroelectrochemistry of $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$ at
298 K in $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$ for
Reduction at 0.31 V.

EPR at 4.3 K of $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$
in a Toluene Glass (Bruker X-band EPR).

EPR at 80 K of $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$
in a Toluene Glass (Bruker X-band EPR).

FIGURE 10

Plot of U_{eff} vs $T(\text{K})$ for $\text{Fe}(\text{TF}_{20}\text{PPBr}_8)\text{Cl}$ at
a Field Strength of 10,000 Gauss
from 2 to 300 K (Quantum Design MPMS).

Brillouin Fit of the Magnetization
at 2 K versus $H(\text{Gauss})/T(\text{K})$ gives an
 $S=1.68$.

4.3 METAL REDOX CHEMISTRY OF IRON PERHALOPORPHYRINS

(J. E. Lyons, P. E. Ellis, H. B. Gray,

J. Labinger and M. Grinstaff)

Work in our laboratories has shown that iron perhaloporphyrins are highly active catalysts for the oxidation of alkanes (past quarterly reports). This activity has been related to the oxidative stability of the porphyrin ring and the high Fe(III)/Fe(II) reduction potential of the iron center. Continued exploratory research into the nature of the unprecedented activity exhibited by our perhaloporphyrin complexes is ongoing and results of these investigations give the needed insight for preparing the superior catalysts which will ultimately meet commercial criteria.

Table 1 shows the electrochemical properties of the free base, the porphyrinato macrocycle and the iron center. Figure 1 shows the ready electrochemical conversion of Fe(III) to Fe(II) in a peraloporphyrin using UV/visible spectroscopy. Figure 2 shows that the position of equilibrium between Fe(III) and Fe(II) is significantly altered in electron deficient porphyrins and the kinetics of oxygenation of Fe(II) is slow.

We have demonstrated high rates of alkane oxidation using Fe(TPPF₂₀Br₈) complexes and implicate a high oxidation state metal oxo complex as a reaction intermediate, Figure 3. We have now shown that iodosylbenzene, a single oxygen atom donor known to convert ironporphyrins to metal oxo complexes, Figure 4, also oxidizes alkanes to alcohols, Table 2, in the presence of this catalyst.

TABLE 1

METAL REDOX CHEMISTRY OF HALOGENATED PORPHYRINS

Porphyrin. ^a	$E_{+2/+1}^{\text{Porph}}$	$E_{+1/0}^{\text{Porph}}$	$E_{\text{III/II}}$	$E_{+0/-1}^{\text{Porph}}$	$E_{-1/-2}^{\text{Porph}}$
Fe ^{III} (TPP)Cl ^b			-0.29		
Fe ^{III} (TFPP)Cl	> +1.80	+1.65	-0.08	-1.1	-1.5
Fe ^{III} (TFPPBr ₈)Cl	> +1.80	> +1.80	+0.31	-0.63	-0.95
Fe ^{II} (TFPPBr ₈)(py) ₂ ^c	> +1.80	> +1.80	+0.82	-0.75	-0.93
Fe ^{II} (TFPPCl ₈)(py) ₂	> +1.80	> +1.80	+0.84	-0.7	-0.92

Porph. ^a	$E_{+2/+1}^{\text{Porph}}$	$E_{+1/0}^{\text{Porph}}$	$E_{+2/0}^{\text{Porph}}$	$E_{\text{III/II}}$	$E_{+0/-1}^{\text{Porph}}$	$E_{-1/-2}^{\text{Porph}}$
Zn ^{II} (TPP)	+1.18	+0.78			-1.39	-1.6 ^a
Zn ^{II} (TFPP)	+1.57	+1.36			-0.96	-1.38
Zn ^{II} (TFPPCl ₈)			+1.61		-0.48	-0.81
Zn ^{II} (TFPPBr ₈)			+1.55		-0.49	-0.77
H ₂ (TFPP)	+1.78	+1.53			-0.78	-1.07
H ₂ (TFPPCl ₈)	Irr.	+1.66			-0.31	-0.56

^a TBA⁺PF₆⁻ /CH₂Cl₂; Potentials vs AgCl/Ag in 1M KCl; Fc at +0.45 Volts

^b A.B.P. Lever & H. Gray "Iron Porphyrins: Part Two" Addison-Wesley, USA, 1983

^c Metal III/II irreversible at slow potential scans

FIGURE 1

Spectroelectrochemistry of $\text{Fe}(\text{TF}_2\text{PPBr}_8)\text{Cl}$ at
298 K in $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$ for
Reduction at 0.31 V.

FIGURE 2

Oxidation of $\text{Fe}(\text{TFPPBr}_8)$ by Dioxygen

FIGURE 3

FIGURE 4

Alkane Hydroxylation with PhIO

TABLE 2

ISOBUTANE OXIDATIONS USING IODOSYL BENZENE

<u>Fe(porph)^a</u>	<u>Solvent</u>	<u>°C</u>	<u>Oxygen Atom Source</u>	<u>% Yield.^b</u>	<u>Cat. Turn.^c</u>	<u>3-methylpentane(%)</u>					<u>2,4- one</u>
						<u>% Conv 10⁻²d</u>	<u>1-ol</u>	<u>2-ol</u>	<u>3-ol</u>	<u>-diol</u>	<u>2-one</u>
no porphyrin	CH ₂ Cl ₂	23	PhIO	--	--	2.2	--	--	81	--	19
no porphyrin	CH ₂ Cl ₂	23	O ₂ 15 psi	--	--	--	--	--	--	--	--
5 Fe(TF ₂₀ PP)Cl	CH ₂ Cl ₂	23	PhIO	76	0.83	2.4	15	15	61	--	9
Fe(TF ₂₀ PPBr ₈)Cl	CH ₂ Cl ₂	23	PhIO	1721	25	23	7	4	73	--	3

^a 3 hr rxns; PhIO rxns under Argon; approximate molar ratios: alkane/PhIO/Fe 7500/35/1; alkane/oxygen/Fe 7500/10⁶/1.^b based on moles of Fe(porph).^c moles of product/moles of catalyst; ketone formation represents two turnovers.

4.4 OXIDATION PATHWAYS AND SPECTROELECTROCHEMISTRY

(H. B. Gray and M. G. Hill)

In order to formulate conclusions regarding the nature of the interactions between the porphyrin macrocycle and the iron center that give rise to the high activity of electron deficient porphyrin complexes, we must gain understanding into the electronic nature of the porphyrinato macrocycle. In this section we report results of studies of the electrochemistry of halogenated porphyrins with redox-inactive metal centers (e.g. Zn(II)). Figures 1-6, and Table 1 give electrochemical and spectroelectrochemical information from which relative energy levels can be experimentally derived. It can be seen that the experimentally derived energy levels, Figure 7, are in good agreement with the theoretically calculated values.

FIGURE 1

Theoretical Predictions for Electronic Structures of Halogenated Porphyrins

Role of β -halogens:

Electronic Effect: Stabilize both HOMO and LUMO.

Steric Effect: Destabilize HOMO.

FIGURE 2

Electrochemistry of $\text{Zn}(\text{TPP})$, $\text{Zn}(\text{TF}_{20}\text{PP})$, and
 $\text{Zn}(\text{TF}_{20}\text{PPBr}_8)$ in 0.1 M $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

Extracting 1e⁻ Potentials from 2e⁻ Redox Couples

$$K_{\text{disp}} = \frac{[\text{P}^0][\text{P}^{2+}]}{[\text{P}^+]^2}$$

$$E = E^{\circ}_{+/0} + 0.059 \log\left(\frac{[\text{P}^+]}{[\text{P}]}\right) = E^{\circ}_{2+/+} + 0.059 \log\left(\frac{[\text{P}^{2+}]}{[\text{P}^+]}\right)$$

$$\log(K_{\text{disp}}) = \frac{E^{\circ}_{+/0} - E^{\circ}_{2+/+}}{0.059}$$

and

$$E^{\circ}_{2+/0} = \frac{E^{\circ}_{2+/+} + E^{\circ}_{+/0}}{2}$$

FIGURE 4
UV-vis Spectroelectrochemistry of $\text{Zn}(\text{TF}_2\text{PP})$ in
 $0.1 \text{ M TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

FIGURE 5

UV-vis Spectroelectrochemistry of $\text{Zn}(\text{TF}_{20}\text{PPBr}_8)$ in
 $0.1 \text{ M TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

FIGURE 6

Electronic Spectra of $\text{Zn}(\text{TF}_{20}\text{PP})^{n+}$ and $\text{Zn}(\text{TF}_{20}\text{PPBr}_8)^{n+}$
(where $n = 0, 1, 2$)

TABLE 1

Summary of Zn-Porphyrin Redox Potentials

Porphyrin	P+2/0	P+2/+1	P+1/0	P0/-1	P-1/-2
Zn ^{II} TPP		+1.17	+0.78	-1.40	-1.6
Zn ^{II} (TFPP)		+1.58	+1.37	-0.95	-1.37
Zn ^{II} (TFPPCl ₈)	+1.60	(+1.58)	(+1.62)	-0.47	-0.80
Zn ^{II} (TFPPBr ₈)	+1.55	(+1.54)	(+1.56)	-0.48	-0.76

$E_{1/2}$ (in 0.1 M TBAH/CH₂Cl₂) vs. aqueous Ag/AgCl. (Fc⁺/Fc = 0.44 V)

FIGURE 7
Experimentally Determined Relative Energy Levels

4.5 REDOX ACTIVE COBALT PERHALOPORPHYRINS

(J. E. Lyons, H. B. Gray and E. R. Birnbaum)

We have reported that $\text{Co}(\text{TPPF}_{20}\text{Br}_8)$ is an active catalyst for the oxidation of light alkanes (previous quarterly reports). It is highly unlikely that this complex can form a metal oxo bond and yet it catalyzes isobutane oxidation under mild conditions. Though not as active as its iron analogue, perhaps it is exhibiting an alternative pathway for alkane oxidation that we must consider. In this section we discuss the relationship between the redox behaviour of this species and its catalytic activity.

Figure 1 shows the oxidation of $\text{Co}(\text{TPPF}_{20}\text{Br}_8)$ and Figure 2 gives its reduction. The electrochemistry is shown in Figure 3 and compared with that of $\text{Fe}(\text{TPPF}_{20}\text{Br}_8)\text{Cl}$ in Table 1. As indicated below the table, we must consider a Haber-Weiss redox pathway for cobalt-catalyzed alkane oxidations and the question is raised whether this pathway is important for iron as well.

FIGURE 1

Spectroelectrochemical Oxidation of $\text{Co}(\text{TF}_2\text{O}^-\text{PPBr}_8)$ in 0.1 M $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

FIGURE 2

Spectroelectrochemical Reduction of $\text{Co}(\text{TF}_{20}\text{PPBr}_8)$ in 0.1 M
 $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

Electrochemistry of $\text{Co}(\text{TF}_{20}\text{PP})$ and
 $\text{Co}(\text{TF}_{20}\text{PPBr}_8)$ in 0.1 M $\text{TBA}^+\text{PF}_6^-/\text{CH}_2\text{Cl}_2$

Comparison of Co- and Fe-Porphyrin Redox Potentials

Porphyrin	Co ^{I/II}	Cl-Fe ^{II/III}
TPP	-0.97	-0.29
TFPP	-0.55	-0.08
TFPPCl ₈	-0.07	+0.31
TFPPBr ₈	-0.10	+0.32

$E_{1/2}$ (in 0.1 M TBAH/CH₂Cl₂) vs. aqueous Ag/AgCl. (Fc⁺/Fc = 0.44 V)

4.6 REDOX BEHAVIOR OF RUTHENIUM PERHALOPORPHYRINS

(J. E. LYONS, P. E. ELLIS, H. B. GRAY AND E R. BIRNBAUM)

We have demonstrated the activity of perhaloporphyrinatoruthenium complexes in light alkane oxidation (previous progress reports). Ruthenium oxo intermediates may be more accessible than those of iron in catalytic processes. Higher oxidation states may be achieved and these factors may influence their performance as oxidation catalysts. For these reasons we have investigated the redox behavior of ruthenium perhaloporphyrins and report on this topic in this section.

Figure 1 summarizes the synthesis and UV/visible spectra of two perhaloporphyrin ruthenium complexes. Figure 2 shows how the Soret absorption varies with degree of halogenation. Table 1 summarizes current electrochemical information that we have gathered on ruthenium complexes of halogenated porphyrins. Spectroelectrochemistry of two complexes are given in Figures 3 and 4. Figure 5 summarizes spectroelectrochemical experiments in which a perhaloporphyrinatoruthenium(II) species is converted to a ruthenium(VI) dioxo complex by oxygen atom donor substrates. This complex catalyzes the oxidation of an alkane using these substrates as oxidants, Table 2, and the product profile is not dissimilar to that obtained in earlier experiments in which oxygen is used as oxidant. Figures 7 and 8 show how the product profile changes as a function of reaction solvent.

Porphyrin Synthesis

Precipitate and wash with cold hexane

Purify on neutral alumina with $\text{CH}_3\text{Cl}/\text{MeOH}$

Precipitate in water, filter

Chromatograph on silica gel, eluting with 1:1 dichloromethane:hexane to separate from remaining starting material.

FIGURE 2

UV-Vis Spectroscopy of Ruthenium Porphyrins

Porphyrin	UV-Vis Absorbance Max of Soret band (nm)
RuTFPPCl ₈ (CO)	416
RuTFPPCl ₇ (CO)	412
RuTFPPCl ₆ (CO)	410
H ₂ TFPPCl ₈	440

TABLE 1

Electrochemistry of Ruthenium Porphyrins

Porphyrin ^a	$E^{\circ}_{+/0}$	$E^{\circ}_{0/-}$	$E^{\circ}_{\text{Ru(III)/Ru(II)}}$
RuTFPPCl ₈ (CO)L	1.71	-0.64	
RuTFPPCl ₇ (CO)L	1.69	-0.69	
RuTFPPCl ₆ (CO)L	1.64	-0.76	
RuTFPPCl ₈ (py) ₂		-0.94	1.08
RuTFPPCl ₇ (py) ₂		-0.98	1.04
RuTFPPCl ₆ (py) ₂		-1.12	0.89
RuTFPPBr ₈ (CO)L	1.63	-0.84	
H ₂ TFPPCl ₈	1.66	-0.31	
RuTPP(CO) ^b	0.79	-1.32	

- a. All CV's taken in CH₂Cl₂ in vs. AgCl/Ag in 1M KCl.
b. Value from Kadish, K. M., et al. *Inorg. Chem.*, **1982**, 21(10), 3618.

FIGURE 3
 $\text{RuTFPPCl}_8(\text{py})_2$ reduction

FIGURE 4

$\text{RuTFPPCl}_8(\text{CO})$ Reduction

Catalytic Oxidation

Dissolve $\text{Ru}^{\text{II}}\text{TFPPCl}_8(\text{CO})$ in 2 ml benzene or CH_2Cl_2 such that the absorbance of the Q band is ≈ 0.5 .

In cuvette, add $\approx 3\text{mM}$ mCPBA until UV-Vis no longer changes (100-200 μl). The peroxide oxidizes the porphyrin to $\text{Ru}^{\text{VI}}\text{TFPPCl}_8(\text{O})_2$.

Add substrate, flush with dioxygen.

Cap and let stir for 24 hours.

Alternatively, add ≈ 20 equivalents of iodosylbenzene, flush with Ar, and let stir for 24 hours.

TABLE 6

RuTFPPCl₈(CO) Reactivity with 3-Methylpentane

Porphyrin added ^a (Mol x 10 ⁻⁷)	Oxidant added ^b (Mol x 10 ⁻⁷)	substrate added (ml)	Reaction volume (ml)	Moles (x 10 ⁻⁷) product ^c					Total turn-overs ^c	% Distribution				Atmosphere	Solvent
				2-one	3-ol	2-ol	2,4-dione	Total		2-one	3-ol	2-ol	2,4-dione		
1.51	3.84	0.1	2.165	0.48	0.39	2.6		3.38	2.2	14	12	77		O ₂	benzene
1.45	2.92	0.1	1.945	0.21	0.77		1.7	2.64	1.8	8.0	29		63	O ₂	benzene
4.23	8.45	0.5	3.775	2.3	8.3	0.29		10.9	2.6	21	76	27		O ₂	benzene
1.36	3.25	1	4.055	2.2	4.43	3.2	2.9	12.7	9.3	17	35	25	23	O ₂	benzene
241	482	3	18	20	154			174 ^f	0.64	11	89			air	benzene
1.03	2.05	1	6	1.1	32	1.8	6.3	41.2	40	2.8	80	4.5	1.6	O ₂	CH ₂ Cl ₂
—	2.05	1	6	2.5	11		12	25	24	1.2	42		46	O ₂	CH ₂ Cl ₂
3.27	1110 ^e	1	11		20		40	56 ^e	17		36		64	Ar	CH ₂ Cl ₂

- a. Concentration of porphyrin is assumed to be twice the amount of mCPBA used, since two equivalents are need to oxidize Ru^{II} to Ru^{VI}(O)₂.
- b. Calculated from the volume of *m*-chloroperoxybenzoic acid solution used to titrate porphyrin.
- c. As determined by GC analysis at 24 hours.
- d. Based on the amount of porphyrin in solution.
- e. Iodosylbenzene used as the oxidant for this trial, time point taken at 28 hours.
- f. Time point taken at 5 days.

FIGURE 7

Product Distributions in CH_2Cl_2

FIGURE 8

Product Distributions in Benzene

4.7 CORRELATION BETWEEN GAS PHASE ELECTRON AFFINITIES, ELECTRODE POTENTIALS AND CATALYTIC ACTIVITIES OF HALOGENATED METALLOPORPHYRINS

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Abstract

The gas phase electron affinities (EAs) of a series of halogenated iron tetraphenyl porphyrins determined using ion cyclotron resonance mass spectrometry are reported. The EAs of the Fe(II) species vary approximately linearly with their condensed phase reduction potentials. The EAs of the Fe(III) species with axial Cl ligands vary approximately linearly with condensed phase reduction potentials. The lines for the Fe(III) and Fe(II) data sets are quite different, however, suggesting substantial solvent effects on the condensed phase reduction process. Analysis in terms of the Born equation suggests a smaller effective size for the two Fe(III) species with the lowest degree of halogenation which suggests in turn that those species accept an electron into a metal based orbital while the remaining species accept an electron into a ligand based orbital. The available catalytic activities of the various

metalloporphyrins for the oxidation of isobutane to t-butyl alcohol are covariant with the electron affinities. This covariance is discussed in the context of a catalytic mechanism, and it is suggested that the gas phase electron affinity is a useful measure of electronic effects on catalyst activity.

Introduction

Polyhalogenated metalloporphyrins have been the object of a number of recent studies because of their potential as selective oxidative catalysts³⁻⁸. The activity of such heme-based biological oxidation catalysts as cytochrome P-450 suggested that metalloporphyrins might be effective homogeneous oxidation catalysts⁹⁻¹². Readily available iron tetraphenylporphyrin (FeTPP), 1, is essentially ineffective as a catalyst for air oxidation of alkanes to alcohols, but halogenated FeTPPs have been found to be effective and selective catalysts for conversion of isobutane to t-butanol³⁻⁵. Both the stability and activity of the catalysts increase with extent of halogenation. In probing the origin of the dependence of catalytic activity on halogenation it was found that catalytic activity increased with the Fe(III)/Fe(II) electrode potential of the catalyst⁵. The correlation of catalytic activity with the electrode potentials of halogenated FeTPPs led us to measure the gas phase electron affinity (EA) of each of a number of iron porphyrin species. We report the results of those measurements here.

Experimental Section.

The measurements were done using the same methods that were used to measure the EAs of nickel porphyrins¹³. Syntheses of the halogenated porphyrins have been described elsewhere^{4,7}. A selected halogenated FeTPP chloride (FeTPPⁱ-Cl) was introduced into the vacuum chamber of a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer¹⁴ (FTMS 2000,¹⁵ Millipore Extrel, Madison, WI) using a heated probe. The chlorides have an axial

chloride ligand and are formally Fe(III). A reference electrophile such as NO₂ was introduced into the spectrometer through a fixed leak. Combined pressures of the two samples in the vacuum chamber were on the order of 10⁻⁷ torr as indicated by an ionization gauge. The ratio of the pressures of the species present was estimated from their relative ionization cross sections and a 70 eV positive ion mass spectrum of the mixture in the vacuum chamber. When necessary ionization cross sections were estimated from polarizabilities¹⁶ which in turn were estimated using group additivities methods¹⁷. Negative ions formed by a 5 msec, 4 eV electron beam pulse were confined in the ion trap for a variable reaction time after which a spectrum was obtained revealing the relative concentrations of the ions. The ions observed usually included the parent anions of the selected halogenated FeTPP, FeTPP⁻, the halogenated FeTPP-Cl, FeTPP⁻-Cl, and the reference electrophile. These ions grew in over a few tenths of a second reaction time indicating that they were formed as the neutrals present captured slow electrons scattered from the electron beam. The FeTPPⁱ neutral was presumably formed by thermolysis of the FeTPPⁱ-Cl on the heated probe. In some instances the parent anions of only FeTPPⁱ (7 and 9) or only the halogenated FeTPPⁱ-Cl (3, 4 and 6) were observed. EAs could not be obtained for those neutrals corresponding to anions not observed. As reaction time increased the relative concentrations of the various anions changed as a result of charge transfer reactions. At long reaction time either one ion became

predominant or two ions achieved a time independent steady state ratio. In the former case, the neutral corresponding to the ion predominant at long time was taken as the neutral with the highest EA. In the latter case the steady state concentrations were taken as equilibrium concentrations and an equilibrium constant for the charge transfer reaction relating the two ions was determined. By assuming that $\Delta G = \Delta H$ for the charge transfer reaction, the difference between the electron affinities of the neutrals involved in the equilibrium were deduced. These results together with the known electron affinities of the reference electrophiles¹⁸ were used to determine the electron affinities in Table 1.

Electrochemical measurements were made using a conventional three electrode configuration consisting of a reference electrode (a silver wire in contact with a 0.01 M AgNO_3 /0.10 M tetra-n-butylammonium hexafluorophosphate (TBAPF_6) dimethylformamide solution, which was connected to the main cell compartment by a Luggin capillary), a counter electrode (a coiled platinum wire), and a working electrode (a 200 μm diameter platinum electrode). The cyclic voltammograms were run at scan speeds varying from 2 to 200 mV/s. All the reported potentials correspond to $E_{1/2}$ for reversible processes. The potentials were measured relative to $E_{1/2}$ for the ferrocene/ferrocenium couple. For comparison to potentials measured relative to the SCE in the literature the values obtained in the present study were increased (made more positive) by 0.43 V, the difference between our measurement of

the first oxidation potential of tetraphenylporphine in methylene chloride relative to the ferrocene/ferrocenium couple (0.52 V) and a literature value¹⁹ of the same oxidation potential relative to the SCE (0.95 V). This introduces an unknown but probably small (ca. +/- .05 V) systematic error into the numbers.

We note the difference between the potentials of the aqueous SCE and ferrocene/ferrocenium in acetonitrile has been reported to be 0.40 V²⁰.

Results.

The EA measurements are listed in Table 1 and summarized in the ladder illustrated in Fig. 1. The reference electrophiles and the metalloporphyrins are listed in order of decreasing EA as determined in the study. An arrow points down from a reference electrophile to a metalloporphyrin found to have a lower EA in the competitive electron transfer studies described above. An upward pointing arrow connects a reference electrophile to a metalloporphyrin of higher EA as determined by competitive electron transfer. A double-headed arrow connects two species for which equilibrium was observed in competitive charge transfer. The overall consistency of the charge transfer studies is clearly evident from the ladder.

In addition to the EAs Table 1 lists the condensed phase reduction potentials for FeTPPⁱ-Cl (Fe(III) to Fe(II)) and for FeTPPⁱ (Fe(II) to Fe(I)). For some of the species the reduction potentials have yet to be obtained because of the insufficient material, insufficient purity or insufficient solubility. It is

evident from Table 1 that the electron affinities and the reduction potentials vary together. The electron affinities are plotted against the reduction potentials in Figure 1. The Fe(II) to Fe(I) reduction potentials vary approximately linearly with the electron affinities of the neutral halogenated FeTPP. The data for Ni(II) to Ni(I) reduction potentials and the corresponding electron affinities from our earlier study fall approximately on the same line. The Fe(III) to Fe(II) reduction potentials vary approximately linearly with the FeTPPⁱ-Cl electron affinities, but the line through the III-II data is not collinear with the line through the II-I data. Several of the Fe(III) porphyrins are more easily reduced in solution than would be expected from the gas phase electron affinities. This suggests that reduction of the Fe(III) species is mediated by some solvent effect. The solvent effect also decreases the range of reduction potentials for Fe(III) species (0.50 V) relative to the range of their electron affinities (1.25 eV).

Finally we note that for those cases for which we have the III-II reduction potential, the EA and the catalytic activity, all three quantities are listed in Table 1.

Discussion

Reduction Potentials and EAs. The comparison between gas phase electron affinities and the solution reduction potentials of neutral electrophiles has been the subject of recent studies by Heinis, et al.,²¹ by Shalev and Evans²⁰ and by Richardson²². We

follow their lead and discuss the comparison in terms of the standard thermodynamic cycle:

From this cycle it follows that

$$\Delta G^\circ_i = \Delta G^\circ_r + \Delta G_{\text{solv}}^\circ(\text{FeTPP}^i) - \Delta G_{\text{solv}}^\circ(\text{FeTPP}^{i+}). \quad (1)$$

The free energy of electron attachment (ΔG°_i) is approximately the negative of the EA. The free energy of reduction of the neutral halogen substituted Fe(II) porphyrin (FeTPP^i) in solution by a gas phase electron (ΔG°_r) is the negative of the standard electrode potential (E°) of the $\text{FeTPP}^i/\text{FeTPP}^{i+}$ couple plus a constant (C) which depends on the reference electrode. Equation (1) can be recast to give

$$\text{EA} = E^\circ + \Delta\Delta G_{\text{solv}}^\circ + C \quad (2)$$

where the difference ($\Delta\Delta G_{\text{solv}}^\circ$) between the solvation free energy of FeTPP^{i+} and that of FeTPP^i is given by

$$\Delta\Delta G_{\text{solv}}^\circ = \Delta G_{\text{solv}}^\circ(\text{FeTPP}^{i+}) - \Delta G_{\text{solv}}^\circ(\text{FeTPP}^i). \quad (3)$$

Hence, the fact that a plot of the reduction potentials vs. the electron affinities of the Fe(II) and Ni(II) species is linear with slope near unity (1.05) as shown in Fig. 1 indicates that $\Delta\Delta G_{\text{solv}}^\circ$ for those species are all nearly the same. The larger slope of the line through the data for the Fe(III) species indicates that $\Delta\Delta G_{\text{solv}}^\circ$ for these species depends on the ligand.

The degree of charge delocalization in the anion can be important in determining $\Delta\Delta G$. If the charge is more delocalized the average distance of interaction between the solvent and the charge is increased. The addition of electron withdrawing halogen substituents to the ligand could, of course, increase charge delocalization in the anion giving rise to the observed solvent dependent $\Delta\Delta G_{\text{solv}}^\circ$. This effect could make it relatively difficult to reduce the heavily halogenated 5-Cl, 7-Cl and 8-Cl, since the corresponding anions would have delocalized charge not strongly stabilized by the solvent.

The magnitude of the delocalization required to account for the observed potentials of the heavily halogenated species can be estimated by assigning a value to C in Eq. (2) and calculating $\Delta\Delta G$ for a given ion-neutral couple. If we then assume that $\Delta\Delta G$ is equal to the Born energy of the solvated ion, we can estimate an effective radius, r_e , for the ion by rearranging (3) to give

$$E_i - E^\circ - C = \Delta\Delta G_{\text{solv}} = \frac{-e^2(1 - 1/\epsilon)}{2r_e} \quad (4)$$

where e is the ion charge and ϵ is the solvent dielectric constant. We follow the lead of Heinis, et. al.,²⁰ and assign $C = 4.71$ eV for the aqueous SCE and find values for r_e listed in Table 1.

All but two of the r_e values are in the range of 3.2 to 3.7 Å. The two exceptional r_e values are 2.5 Å for 1-Cl and 2.7 Å for 2-Cl. A simple explanation that suggests itself for this

grouping of the values is that the larger r_e values result from adding the electron to a ligand-based LUMO and the smaller r_e values result from adding an electron to a metal-based LUMO. The exceptional FeTPP^i species have an axial Cl ligand and either no halogenation of the ligand (1-Cl, FeTPP-Cl) or only partial halogenation of the ligand's phenyl substituents (2-Cl, $\text{FeTPPoCl}_8\text{-Cl}$). The result is to lower the energy of vacant metal-based orbitals relative to the energy of vacant ligand orbitals.

These results show the extent to which reduction potentials of neutral electrophiles reflect properties other than the intrinsic electronegativity of the electrophile. In combination with the other measured properties, such as the EA, the reduction potentials yield useful information on a variety of molecular properties. On the other hand, the gas phase EA provides a more direct measure of the intrinsic molecular electrophilicity. The EA thus provides a basis for any correlation between reactivity and electrophilicity.

Catalytic Activity. A mechanism proposed for the metalloporphyrin catalyzed oxidation of 3-methyl propane to t-butanol is shown schematically in Fig. 2⁵. Overall reaction velocity will be maximized if equilibrium in

favors the active $(\text{FeTPP}^i)\text{O}$ species and minimizes the amount of catalyst tied up as the inactive mono-oxo dimer. We suggest that as the electron withdrawing capacity of the porphyrin increases

two effects ensue. First the stability of FeTPP^i relative to the oxo-dimer and increases, and second the reactivity of $(\text{FeTPP}^i)\text{O}$ towards substrate increases. The first effect increases the equilibrium constant for (5) and the second decreases the steady state concentration of $(\text{FeTPP}^i)\text{O}$.

The forward reaction is a redox disproportionation reaction in which two Fe(III) centers become an Fe(II) and an Fe(IV) and will be favored to the extent that Fe(II) is stabilized with respect to Fe(III) . Catalytic activity does increase with the stability of Fe(II) relative to Fe(III) as shown by the correlation between catalytic activity and the EAs and reduction potentials of Fe(III) catalysts. Of course, the halogenation that stabilizes Fe(II) might be expected to destabilize Fe(IV) and hence push the equilibrium of (5) to the left toward the unreactive dimer. We surmise from a previous study²³, however, that halogenation increases the reactivity of the mono-oxo Fe(IV) species towards substrate pulling the equilibrium to the right by diminishing the steady state concentration of $\text{Fe(TPP}^i)\text{O}$.

The previous study in question²³ showed that the reaction

proceeds at an observable rate ($k > 10_{.1}^2 \text{ cm}^3 \text{ s}^{-1}$) for $\text{Fe(TPP}^i) = 1, 2, 4$ and 5 while 3^+ was reported not to react at an observable rate. The failure of 3^+ to react was attributed to the coordination of the tethered imidazole to the metal.²⁴ We have subsequently been able to examine the behaviour of 6^+ and 8^+ and find that these highly halogenated species do not react at an

observable rate. This suggests that $D(\text{Fe-O})$ is diminished by a porphyrin ligand with electron withdrawing substituents, particularly if the metal is in a high oxidation state. Hence as halogenation increases, the mono-oxo product of (6) becomes more like the reactive $\text{Fe-O}\cdot$ and less like stable Fe=O , substantiating our assertion above that the reactivity of the mono-oxo Fe(IV) intermediate in the catalytic cycle increases with halogenation.

Whether it be the stabilization of the FeTPP^{I} relative to $\text{FeTPP}^{\text{I}}_2\text{O}$, the activation of $\text{FeTPP}^{\text{I}}\text{O}$ or some other effect, the catalytic activity of the halogenated iron porphyrins increases with their electrophilicity as measured by their gas phase EA. Analysis of the reduction potentials of the neutral Fe(III) complexes reveals that the electron affinities provide a better measure of intrinsic electrophilicity than the electrochemical measurements.

Correlation of the limited data on reactivity with electron affinities is better than with reduction potentials. Assuming a linear free energy type of relationship ($\ln(\text{TON})$ proportional to EA), we would predict from the reactivity of 5 and 8 a very low TON (ca. 150) for the unreactive 1. A similar extrapolation based on the reduction potentials would predict a much higher reactivity of 1 (TON ca. 600). We suggest on the basis of the present admittedly limited set of results that other effects of halogenation, such as steric effects, should emerge from the baseline of electronic effects most clearly if electron affinities are used to measure electrophilicity. Attempts to

generate more extensive data are underway in our laboratories.

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Table 1. Electron Affinities, Reduction Potentials, Radii and Catalytic Activities of Metalloporphyrins

Species ^a	EA(eV) ^b	E _{1/2} (V) ^c	r _c (Å) ^d	TON ^e
NiTPP	1.51±0.01 ^f	-1.370 ^g	3.5	
H ₂ TPP	1.69±0.01 ^f	-1.280 ^g	3.7	
NiTPP-CHO	1.74±0.01 ^f	-1.165 ^g	3.5	
1 FeTPP	1.87±0.03	-1.010 ⁱ	3.5	
2 FeTPPoCl ₈	1.86±0.03	-1.05 ^h	3.6	
3 FeTPP-val	1.97±0.03			
4 FeTPP-piv	2.07±0.03	-0.866 ⁱ		
5 FeTPPF ₂₀	2.15±0.15			
6 FeTPPCL ₂₈	2.59±0.11			
8 FeTPPF ₂₀ βCl ₈	3.21±0.03			
1-Cl FeTPP-Cl	2.15±0.15	-0.221 ^j	2.7	0
2-Cl FeTPPoCl ₈ -Cl	2.10±0.19	-0.221 ^j	2.7	
5-Cl FeTPPF ₂₀ -Cl	3.14±0.03	0.07 ^j	3.9	1160
7-Cl FeTPPoCl ₈ βCl ₈ -Cl	2.82±0.03	0.10 ^h	3.2	
8-Cl FeTPPF ₂₀ βCl ₈ -Cl	3.35±0.03	0.28 ^j , 0.27 ^h	3.7	1800
9-Cl FeTPPCL ₂₀ -Cl	2.93±0.23			

- (a) The species indicated as chlorides (-Cl) correspond to Fe(III) complexes having an axial Cl ligand coordinated to the metal in the numbered structures.
- (b) Present results except as indicated.
- (c) From cyclic voltametry. Potentials for M/M couples where M is the indicated neutral species. Reversible half-wave potentials in CH₂Cl₂ relative to the SCE except as noted.
- (d) Effective radius from Eq. (4).
- (e) Catalyst turnover numbers from ref. 5 for oxidation of isobutane to tertiary butyl alcohol at 60°C under 100 psig of O₂. (moles O₂ consumed in 6 hours)/(mole catalyst used).
- (f) From reference 13
- (g) Measurements done in CH₂Cl₂ from Hagan, T. E., Ph. D. Thesis, University of Delaware, 1992. Potentials measured relative to the ferrocene/ferrocenium couple. Values relative to SCE obtained as described in the text.
- (h) Measurements done in benzonitrile from reference 7.
- (i) Measurements done in 1,2 C₂H₄Cl₂ from Guentin C.; Lexa D.; Momenteau M.; Saveant J-M; and Xu F., Inorg. Chem., 1986, Vol. 25, No. 23, 4294-4306.
- (j) Measurements done in CH₂Cl₂ from reference 5.

- 1: $X=Y=Y'=R=R'=H$
- 2: $R=R'=H, X=Y=Y'=Cl$
- 3: $X=Y=R=R'=H, Y'=C=O$
- 4: $X=R=R'=H, Y=Y'=C=O$
- 5: $X=Y=Y'=R=F, R'=H$
- 6: $X=Y=Y'=R=R'=Cl$
- 7: $X=Y=Y'=R'=Cl, R=H$
- 8: $X=Y=Y'=R=F, R'=Cl$
- 9: $X=Y=Y'=R=Cl, R'=H$
- $$\begin{array}{c}
 C(CH_3)_3 \\
 | \\
 C=O \\
 | \\
 NH \\
 |
 \end{array}$$
- $$\begin{array}{c}
 (CH_2)_4 \\
 | \\
 \text{Pyridine ring}
 \end{array}$$

Compounds

EAs (eV)

FeTPPF ₂₀ βCl ₈ -Cl		3.35 ± 0.03
FeTPPF ₂₀ βCl ₈		3.21 ± 0.03
TCNE		[3.17]
FeTPPF ₂₀ -Cl		3.14 ± 0.03
FeTPPCl ₂₀ -Cl		2.93 ± 0.23
FeTPPoCl ₈ βCl ₈ -Cl		2.82 ± 0.03
F ₄ BQ		[2.70]
FeTPPCl ₂₈		2.59 ± 0.11
2, 6-Cl ₂ BQ		[2.48]
NO ₂		[2.29]
FeTPPF ₂₀ , FeTPP-Cl		2.15 ± 0.15
FeTPPoCl ₈ -Cl		2.10 ± 0.19
FeTPP-pf		2.07 ± 0.03
4-NO ₂ NB		[2.00]
FeTPP-pt		1.97 ± 0.03
BQ		[1.91]
FeTPP		1.87 ± 0.03
FeTPPoCl ₈		1.86 ± 0.05
NPQ		[1.81]
NiTPP-CHO		1.74 ± 0.01
H ₂ TPP		1.69 ± 0.01
3-NO ₂ NB		[1.65]
NiTPP		1.51 ± 0.01
McAn		[1.44]

Figure 1. Electron Affinity Ladder. Bracketed EAs of standards are from ref. 18. TCNE=tetracyanoethylene, F₄BQ=tetrafluorobenzoquinone, 4-NO₂NB=1,4 dinitrobenzene, BQ=benzoquinone, NPQ=naphthaquinone, 3-NO₂NB=1,3 dinitrobenzene, McAn=maleic anhydride. The porphyrins are identified by the codes used in Table 1. Double headed arrows represents an equilibrium constant measurement. Single headed arrows represents determination of an upper or lower limit on an equilibrium constant.

Figure 2. Gas phase electron affinities (EA) vs. reversible half wave one electron reduction potentials ($E_{1/2}$) of metalloporphyrins. The data points marked with an open square are Fe(III)/Fe(II) potentials and EAs of species with an axial chloride. The remaining points are Fe(II)/Fe(I) potentials and EAs of Fe(II) species. The solid line is a fit to data for M(II) species and the dashed line to the M(III) species.

Figure 3. Postulated mechanism of the metalloporphyrin catalyzed air oxidation of alkanes from ref. 5. Dioxygen first adds to the reduced catalyst (a). The resulting dioxo species reacts with a second molecule of catalyst (b) giving two molecules of mono-oxo complex (c) which oxidizes the alkane ((d) and (e)). The mono-oxo complex equilibrates with reduced catalyst to give the inactive oxo dimer (f).

4.8 ELECTRONIC STRUCTURES OF HALOGENATED PORPHYRINS:
SPECTROSCOPIC PROPERTIES OF $ZnTFPPX_8$ (TFPPX₈ =
TETRAKIS(PENTAFLUOROPHENYL)- β -OCTAHALOPORPHYRIN; X=Cl,Br).

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Abstract

Ellis and Lyons (*Coord. Chem. Rev.* **1990**, *105*, 181) have shown that tetrakis(pentafluorophenyl)- β -octahaloporphyrinatoiron(III) ($FeTFPPX_8$; X = Cl, Br) complexes have unprecedented catalytic activity for the oxygenation of alkanes to alcohols. We report here spectroscopic and theoretical (AM1) studies on $ZnTFPPX_8$ that show a red shift in the Soret and Q absorption bands attributable to substituent-induced saddling of the porphyrin (not to electronic effects of halogenation). The electronic effect of the halogens is to reduce the energies of both the HOMOs and LUMOs, which accounts in part for the increased resistance of the porphyrin to ring oxidation.

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I. Introduction

Halogenated porphyrins are unusually effective catalysts for the oxygenation of alkanes.¹⁻⁵ Thus, chloro[tetrakis(pentafluorophenyl)- β -octabromoporphyrinato]iron(III) (denoted ClFeTFPPBr₈) catalyzes the room-temperature conversion of isobutane to *tert*-butyl alcohol in the presence of oxygen at a rate of 190 mol-product per mol-catalyst per hour with over 90% selectivity to the alcohol. Remarkably, this activity is unchanged after 74 hours.³

Halogenation induces large changes in both the *geometric structure* (leading to highly nonplanar porphyrins) and the *electronic structure* (shifts in both the Q and Soret absorption bands).⁴ Because there is a general correlation of catalytic activity with halogen content, Lyons and Ellis suggested that electron withdrawal from the ring enhances the reactivity of these iron porphyrins.³ In order to gain insight into whether it is the change in geometric structure or electronic structure that is the more important factor affecting the catalytic activity and spectroscopic properties, we have done theoretical and experimental work on a ZnTFPPX₈ (X = H, Cl, Br) model system.⁶

The standard model for the interpretation of porphyrin spectra is due to Gouterman (the Four Orbital Model, or FOM).⁷ This model involves two nearly degenerate MOs (b₁ and b₂ with a_{2u} and a_{1u} symmetries in D_{4h}) occupied in the ground state (HOMOs) and two nearly degenerate MOs (c₁ and c₂ with e_g symmetry in D_{4h}) unoccupied in the ground state (LUMOs).

Thus the ground state (b₁)²(b₂)² and the excited states are defined in terms of the transitions:

$$\begin{matrix} B_x \\ Q_x \end{matrix} = [(b_1c_2) \mp (b_2c_1)] / (2)^{1/2} \quad (1)$$

$$\begin{matrix} B_y \\ Q_y \end{matrix} = [(b_1c_1) \pm (b_2c_2)] / (2)^{1/2} \quad (2)$$

where Q_x, Q_y correspond to the visible bands and B_x, B_y correspond to the Soret bands. This is illustrated in Figure 1. Elsewhere⁸ we will report extensive *ab initio* HF, GVB-

MCSCF, and configuration-interaction calculations that confirm the principal aspects of the FOM. Here we will use this model with semiempirical (AM1) calculations.^{9,10} Figure 1 and Eqs. 1 and 2 show how the one-electron transitions within the four orbitals mix to give the observed transitions; Figure 2 shows the four orbitals for ZnTFPPBr₈.

Previous studies have shown that each bromine at a pyrrole position causes a spectral shift of 6 nm to the red relative to the bands observed for tetraphenylporphyrin (TPP).¹¹ Bhyrappa and Krishnan (BK)¹² attempted to explain these shifts in terms of a parameterized version of the FOM, considering only the electronic effects of the bromine substituents in their analysis of the absorption spectra. However, crystal structures of these halogenated compounds have shown that significant distortion of the porphyrin ring occurs,^{6,13,14} forcing the BK explanation to be reexamined.

The magnitude of ring distortion from a planar geometry is given in Table 1 for a series of copper porphyrins.^{6,13} It is clear that the degree of out-of-plane bending increases with the steric bulk of the substituents on the ring. In this paper, we examine the effect of such distortions on the absorption spectra of porphyrins.

II. Computational Details

In order to assess the changes in spectra with halogenation of the porphyrin, we carried out AM1⁹ calculations using MOPAC.¹⁰ These calculations include full configuration interaction (CI) within the orbitals of the FOM.

The calculations were performed on a series of halogenated porphyrins, ZnTFPP, ZnTFPPCl₈, and ZnTFPPBr₈, where in each case perfluorophenyl groups are attached to each methine carbon (TFPP). The halogen atoms (Cl or Br) are at the eight C β (or pyrrole) positions. The geometries of the Zn porphyrins are derived from the crystal structures^{6,13} of the analogous Cu compounds.

III. Experimental Section

H₂TFPP obtained from Aldrich was purified using techniques described earlier.¹⁵ H₂TFPPCl₈¹⁶ and H₂TFPPBr₈² were prepared according to literature procedures. All zinc-metallated species were prepared by refluxing the appropriate porphyrin with Zn(OAc)₂·2H₂O in methanol. All porphyrins were purified on a silica gel column (150 Å pore size and 75-150 μ particle size). ZnTFPP was eluted using dichloromethane/hexane (1/1 v/v), while ZnTFPPCl₈ and ZnTFPPBr₈ were eluted with dichloromethane/hexane (2/1 v/v).

Absorption spectra were measured using a Cary 14 spectrophotometer. The porphyrin solutions were prepared by dissolving approximately 1.25 mg of porphyrin in 50 ml of methylcyclohexane followed by 20:1 solvent: solution dilution. Spectra were obtained at 25 °C.

IV. Results and Discussion

Examination of Table 2 shows that the calculations reproduce the experimental trends. The absorption spectrum shifts to the red as the size of the Cβ substituents increases (H to Cl to Br). Thus, porphyrins with hydrogen at the beta (pyrrolic) positions exhibit the highest-energy transitions, whereas those compounds with bromine in the pyrrolic positions have the lowest-energy transitions.

In order to separate the steric component of the ring distortion from electronegativity effects, the following calculations were performed. The bromines of ZnTFPPBr₈ and the chlorines of ZnTFPPCl₈ were removed and replaced with hydrogens while retaining the geometries of the respective compounds (and using the correct C-H bond distances). The effects of these replacements on the total excitation energies are given in parentheses in Table 2; and they are plotted in Figure 3. If electronic effects due to the halogens caused the red-shifting, then replacement of the halogens with hydrogens should have significantly reduced the shifts. However, replacement of Cl or Br by H leads to little reduction in the

red-shifting. Thus we conclude that the sterically induced porphyrin saddling is the main factor in the decrease of the Q and Soret transition energies.

In order to ascertain the electronic perturbations associated with this red-shifting, the FOM-MO transition energies were examined (Table 3). Note that these are simple MO excitation energies, whereas the theoretical values in Table 2 include CI. The effect of the electronegativity of the substituents is determined by the substitution of Cl $\rightarrow$ H and Br $\rightarrow$ H *without* changing geometry. Here we see that the energies of both the filled orbitals (b1, b2) and the unfilled orbitals decrease by about the same amount as the electronegativity is increased. Thus an increase in electronegativity at the C β positions stabilizes both the HOMOs and LUMOs, with negligible effect on the excitation energies. However, saddling of the porphyrin stabilizes the LUMOs much more than the HOMOs, decreasing the gap (red-shifting the spectrum).

The spectral red-shift with increased bending of the porphyrin ring can be attributed to a loss in orbital overlap within the porphyrin ring. As the porphyrin ring buckles, the p_z-derived molecular orbitals cannot overlap as efficiently, thereby decreasing both bonding and antibonding interactions. (This loss in overlap is displayed in Figure 4, which shows the changes in the b1 orbital with different substituents.) However, antibonding interactions are more significant in the unoccupied orbitals, leading to a much greater effect on the LUMOs than the HOMOs.

VI. Conclusions

Red shifts in the absorption spectrum of a halogenated porphyrin are due to a substituent-induced saddle distortion that causes a contraction of the energy gap between the HOMOs and LUMOs. The electron-withdrawing effect of the halogen substituents stabilizes both the porphyrin HOMOs and LUMOs, but does not markedly perturb the spectrum. Accordingly, the UV-visible spectrum can be used as a probe of porphyrin

geometry; the greater the red-shift of porphyrin absorption bands, the greater the distortion of the porphyrin macrocycle.

This electron-withdrawing effect appears to be responsible for the relatively high reduction potential of ClFeTFPPBr₂; and this enhanced reduction potential may play a significant role in the catalytic activity of the porphyrin.³ Lowering the energy of the porphyrin HOMOs likely is an important factor in increasing catalyst lifetimes, because this type of electronic stabilization strongly disfavors oxidative destruction of the macrocycle.

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Table 1. Distortion of CuTFPPX₈.^a

Distortion (Å)	X = H	X = Cl	X = Br
N	0.000	0.12	0.15
C _{meso}	0.006	0.13	0.18
C _β	0.008	0.80	1.25
X	0.01 ^b	1.19	1.99

^a From Cu plane, see references 10 and 11.

^b The hydrogens were optimized using MOPAC.

Table 2. Excitation energies for ZnTFPPX₈ from theory (AM1) and experiment.

	ZnTFPP	ZnTFPPCl ₈	ZnTFPPBr ₈
	λ (nm)	λ (nm)	λ (nm)
Q (visible)			
Exper	544	575	596
Theory (Q _x)	517	535 (527) ^a	553 (552) ^b
(Q _y)	516	533 (524) ^a	548 (547) ^b
B (Soret)			
Exper	412	442	464
Theory (B _x)	317	329 (324) ^a	345 (343) ^b
(B _y)	317	328 (323) ^a	344 (342) ^b

^a Using same geometry as ZnTFPPCl₈ but with H replacing Cl.

^b Using same geometry as ZnTFPPBr₈ but with H replacing Br.

Table 3. Energies (ev) from AM1 calculations.

	ZnTFPP	ZnTFPPCl ₈		ZnTFPPBr ₈	
Orbital Energies	ϵ_i	ϵ_i	ϵ_i^a	ϵ_i	ϵ_i^b
b2	-8.40	-8.87	-8.39	-8.77	-8.39
b1	-8.05	-8.67	-8.07	-8.64	-8.03
c1	-2.71	-3.34	-2.73	-3.36	-2.85
c2	-2.66	-3.30	-2.68	-3.34	-2.81
Excitation Energies	E_{ij}	E_{ij}	E_{ij}^a	E_{ij}	E_{ij}^b
b1 $\rightarrow$ c1	5.35	5.33	5.34	5.28	5.18
b1 $\rightarrow$ c2	5.39	5.37	5.39	5.30	5.22
b2 $\rightarrow$ c1	5.69	5.53	5.66	5.42	5.54
b2 $\rightarrow$ c2	5.74	5.57	5.71	5.44	5.58

^aChange due to Cl $\rightarrow$ H at the same geometry.

^bChange due to Br $\rightarrow$ H at the same geometry.

Figure Captions

Figure 1. The Four Orbital Model for porphyrin spectra (see Figure 2 for illustrations of the orbitals).

Figure 2. The Gouterman orbitals for ZnTFPPBr₈ from AM1 calculations.

Figure 3. Effect of saddling on Q-band absorption energies.

Figure 4. The b₁ orbital for ZnTFPPX₈ (X = H, Cl, Br) from AM1 calculations.

FIGURE 1

(a) ground state

(b) excited states

FIGURE 2

$e_g(c2)$

unoccupied

$e_g(c1)$

$a_{2u}(b1)$

occupied

$a_{1u}(b2)$

FIGURE 3

FIGURE 4

(a) **ZnTFPP**

(b) **ZnTFPPCl₈**

(c) **ZnTFPPBr₈**

4.9 ELECTRONIC STRUCTURES OF PERHALOGENATED RUTHENIUM PORPHYRINS

Work reported in previous Quarterlies has shed light on the electronic structure of iron perhaloporphyrin complexes which had a bearing on catalytic activity. This information together with alkane oxidation results, electrochemistry and kinetics enabled us to understand some of the aspects of the behavior of the iron porphyrin catalysts. It seems at this time that these catalysts operate by homolyzing the C-H bond of the alkane resulting in the formation of coordinated and free radical species. Radicals react with oxygen to form peroxy species which can give rise to hydroperoxides - possible intermediates in the oxidation process. From this level of understanding we showed that ironperhaloporphyrins catalyzed rapid conversion of tert-butyl hydroperoxide, TBHP, to tert-butyl alcohol, TBA, and devised a two step processs which may have commercial utility if properly developed. Although iron oxo species are no doubt present in the isobutane oxidation reaction media, significant amounts of TBA come from radical processes as well. Thus, the direct oxidation of isobutane to TBA can be accomplished in a selective manner catalyzed by perhaloporphyrin iron complexes through radical processes. Oxidation of propane in this way would give rise to acetone as a coproduct together with isoprophyl alcohol, IPA. Although this by-product might not be critical to a propane oxidation process, we know that ethane or methane oxidation processes that proceed through radical processes are not selective enough to be commercially viable. Thus, it is of interest to generate catalysts in which metal oxo insertion into the C-H bond is the predominant catalytic mechanism, and radical processes are minimal. We feel that perhaloporphyrinatoruthenium complexes may be able to achieve this and thus are studying them.

The following is a discussion of the electronic structure of a set of perhaloporphyrinato ruthenium complexes analogous to the iron complexes which we have discussed previously.

This section was prepared by Eva Birnbaum, Jay Labinger, John Bercaw and Harry Gray.

Abstract

Ruthenium(II) β -octahalo-tetrakis(pentafluorophenyl)porphyrins ($\text{RuTFPPX}_8(\text{CO})$, $\text{RuTFPPCl}_8(\text{py})_2$; $\text{X} = \text{Cl}, \text{Br}$) exhibit unusually positive oxidation potentials ($> 1 \text{ V}$ vs. AgCl/Ag). The relatively high energies of the Soret bands in the electronic spectra of RuTFPPX_8 complexes are consistent with an electronic structural model involving Ru^{II} backbonding to the $\epsilon\pi^*$ orbitals of the perhalogenated porphyrin. The reduction potential of $\text{RuTFPPCl}_8(\text{py})_2$ is 0.3 V more negative than that of $\text{RuTFPPCl}_8(\text{CO})$, indicating that the $\text{Ru}^{\text{II}} - \epsilon\pi^*(\text{TFPPCl}_8)$ interactions are stronger in the py derivative.

Results and Discussion

We are investigating the structures and properties of metal complexes containing β -octahalo-tetrakis(pentafluorophenyl)porphyrins (TFPPX₈; X = Cl, Br) and related halogenated ligands.^{1,9} Iron derivatives of the saddle-shaped TFPPX₈ molecules are of special interest, owing to their ability to catalyze the oxygenation of alkanes at relatively low temperatures and pressures.^{1,9} The Fe^{III/II} reduction potentials are unusually high in Fe(TFPPX₈)X complexes, and both Fe^{III} and Fe^{II} are believed to play an active role in the catalytic reactions.^{9,10}

We have extended our work on perhalogenated metal porphyrins to include RuTFPPX₈(CO) and RuTFPPCl₈(py)₂.¹¹ Electrochemical measurements show that Ru^{II} is stabilized in these species, thereby confirming that β -octahaloporphyrins are powerful π -acceptor ligands (Table 1).¹² The oxidation potentials of RuTFPPX₈(CO) complexes are much higher than those of RuTPP(CO);^{13,14} indeed, they are within 0.07 V of those of the unmetallated H₂TFPPX₈ molecules, indicating that a porphyrin-based electron is removed.

The oxidation of RuTFPPCl₈(py)₂ at 1.08 V (vs. AgCl/Ag) is metal-based (Ru^{II} $\rightarrow$ Ru^{III}). The shift of the RuTFPPCl₈(py)₂ oxidation to higher potential relative to that of RuTPP(py)₂¹⁵ is evidence for extensive Ru^{II} to TFPPCl₈ backbonding in the halogenated compound.¹⁶ Nevertheless, the magnitude of the shift, ~ 0.8 V, is surprisingly high; it indicates that the electronic coupling of Ru^{II} to the porphyrin is unusually strong.

The electronic structures of perhalogenated Ru^{II} porphyrins can be interpreted in terms of a Gouterman four-orbital model^{8,17} modified by the inclusion of the Ru $d\pi$ orbitals. The reduction potentials confirm that the $e\pi^*$ orbitals of RuTFPPCl₈(py)₂ are destabilized relative to those of RuTFPPCl₈(CO) (Table 1), owing to enhanced Ru^{II} - TFPPCl₈ backbonding (Figure 1). Further reductions of both compounds are irreversible; it is probable that the irreversibility is associated with reductive dehalogenation processes.¹⁸

The blue shift of the Soret band of RuTFPPCl₈(CO) (418 nm) from that of H₂TFPPCl₈ (440 nm)⁷ is larger than the normal shift attributable to metal binding.¹⁹⁻²¹ Increased backbonding in the TFPPX₈ complexes promotes mixing of $\pi \rightarrow e\pi^*$ and Ru^{II} $\rightarrow e\pi^*$ excited states, with the result that the Soret (mainly $\pi \rightarrow e\pi^*$) transition falls at higher energies than would be predicted by a simple one-electron (HOMO-LUMO) model.²¹ Additional support for this electronic structural picture is our finding that the Soret bands for both RuTFPPCl₈(CO) and RuTFPPCl₈(py)₂ (416 nm) are only slightly red-shifted from those of RuTPP(CO) (412 nm) and RuTPP(py)₂ (413 nm) (Figure 2).²²

As expected from established trends,²³⁻²⁵ the Soret transition energy decreases according to RuTFPPCl₆(CO) (410) > RuTFPPCl₇(CO) (413.5 nm) > RuTFPPCl₈(CO) (Figure 2c). The Soret band of RuTFPPBr₈(CO) is further red-shifted to 424 nm; as predicted,⁸ the larger halogen atoms generate a greater distortion of the porphyrin, thereby producing a smaller HOMO-LUMO gap. Porphyrin saddling also is responsible for the red shifts of the Q(0,1) bands of RuTFPPX₈ complexes from those of the corresponding TPP derivatives (Figure 2ab).

Relatively weak bands at 670 ($\epsilon \approx 800$) and 792 nm ($\epsilon \approx 300 \text{ M}^{-1}\text{cm}^{-1}$) are observed in the spectrum of RuTFPPCl₈(py)₂ (not shown in Figure 2). Low-lying Ru^{II} $\rightarrow e\pi^*$ (TFPPCl₈) transitions are expected, since the electrochemical data show that both Ru^{II} oxidation and TFPPCl₈ reduction are accessible. Extensive backbonding to $e\pi^*$ (TFPPCl₈) orbitals would stabilize d_{xz} , d_{yz} relative to d_{xy} (Figure 1); it is likely, then, that a d_{xy} electron is involved in both electrochemical and the 792-nm spectroscopic oxidation of Ru^{II} to Ru^{III}. No bands above 650 nm were observed in the spectrum of RuTFPPCl₈(CO), consistent with the absence of any Ru^{II} oxidations in the electrochemical experiments.

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(11) $H_2TFPPX_8 = 2,3,7,8,12,13,17,18$ -octahalo-5,10,15,20-

tetrakis(pentafluorophenyl)porphyrin ($X = Cl, Br$; prepared by standard methods).^{1,6,7} $Ru_3(CO)_{12}$ (Aldrich) reacts with $H_2TFPPCl_8$ (40 h, refluxing benzene) to form $RuTFPPCl_8(CO)$. $RuTFPPCl_7(CO)$ and $RuTFPPCl_6(CO)$ also were isolated from the reaction mixture. $RuTFPPCl_{8-x}H_x(CO)$ ($x = 0,1,2$) complexes were purified by HPLC, and the identity of each fraction was confirmed by mass spectroscopy. The parent peak in each mass spectrum appears at the mass for $RuTFPPCl_{8-x}H_x$ ($x = 0,1,2$), with a smaller peak appearing at the mass for the monocarbonyl complex. Parent peaks appeared at $m/z = 1351.2$ ($RuTFPPCl_8$), 1315.8 ($RuTFPPCl_7$), and 1280.1 ($RuTFPPCl_6$). Pyridine solutions of $RuTFPPCl_{8-x}H_x(CO)$ exposed to a 1000W mercury lamp for several hours lose a carbonyl ligand to form $RuTFPPCl_{8-x}H_x(py)_2$. Photolysis of the carbonyl was confirmed by the disappearance of the CO stretch (IR, CCl_4 solution) and by ^{19}F -NMR spectroscopy ($CDCl_3$ solution): δ ($RuTFPPCl_8(py)_2$) = -138.7 (2F, q, ortho); -152.3 (1F, t, para); -163.2 (2F, m, meta). $RuTFPPBr_8(CO)$ (mass spectrum; $m/z = 1703$) was synthesized from $Ru_3(CO)_{12}$ and $H_2TFPPBr_8$ (50 h refluxing benzene).

(12) IR data also indicate that halogenated porphyrins are π acceptors: the peak attributable to the CO stretch decreases according to $RuTFPPCl_8(CO)$ (1989.8) > $RuTFPPCl_7(CO)$ (1986.6) > $RuTFPPCl_6(CO)$ (1984) > $RuTFPPBr_8(CO)$ (1973 cm^{-1}). For reference, the CO stretch in the IR spectrum of $RuTPP(CO)$ is at 1945 cm^{-1} : Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* 1971, 1, 57.

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Table 1. Electrochemistry of Halogenated Ruthenium Porphyrins.^a

Porphyrin	$E''_{+/0}$	$E''_{\text{Ru(III)/Ru(II)}}$	$E''_{0/L}$
RuTFPPCl ₈ (CO)	1.71	—	-0.64
RuTFPPCl ₇ (CO)	1.69	—	-0.69
RuTFPPCl ₆ (CO)	1.64	—	-0.76
H ₂ TFPPCl ₈	1.66 ^b	—	-0.32
RuTFPPBr ₈ (CO)	1.63	—	-0.84
H ₂ TFPPBr ₈	1.56 ^b	—	-0.31
RuTFPPCl ₈ (py) ₂	—	1.08	-0.94
RuTFPPCl ₇ (py) ₂	—	1.04	-0.98
RuTFPPCl ₆ (py) ₂	—	0.89	-1.12

a. Potentials in CH₂Cl₂ solution at room temperature (V vs. AgCl/Ag, 0.1M TBAPF₆).

b. E_{pa} .

Figure 1: Molecular orbital diagram of the Gouterman orbitals for H_2TFPPX_8 modified by inclusion of interactions with the $d\pi$ orbitals of carbonyl and bis(pyridine) ruthenium fragments (D_{2d} labels). Extensive π -backbonding to the carbonyl ligand strongly stabilizes the d_{xz} , d_{yz} orbitals (and, to a lesser extent, the d_{xy} orbital, owing to the reduction in electron density at the Ru center), resulting in a ligand-based HOMO for $\text{RuTFPPX}_8(\text{CO})$. Weaker π -backbonding in the Ru(py)_2 fragment leaves the $d\pi$ orbitals at higher energies, consistent with stronger d_{xz} , $d_{yz} \rightarrow e\pi^*$ (TFPPX_8) interactions and a Ru-based HOMO in $\text{RuTFPPX}_8(\text{py})_2$. The lowest energy $\pi \rightarrow e\pi^*$ transition (Q band) is shown with a dotted line.

a) RuTPP(CO) and RuTFPPCl₈(CO); b) RuTPP(py)₂ (in pyridine) and RuTFPPCl₈(py)₂; and c) RuTFPPX₈(CO), RuTFPPCl₇(CO), and RuTFPPCl₆(CO).

4.10 ELECTRON DEFICIENT PORPHYRINS VIA DIPYRROMETHANES: MESO-(PERHALOCARBYL)-METALLOPORPHYRINS FOR OXIDATION OF LIGHT ALKANES AND DECOMPOSITION OF ALKYL HYDROPEROXIDE

This work provides access for the first time, to catalytically active metalloporphyrins carrying perhalocarbyl groups at two opposite *meso* positions (e.g. 5,15) and perhalocarbyl or other electron-withdrawing groups (e.g. nitro-NO₂) at the other two *meso* (10,20) positions. The novel catalytic species reported here, have been shown to be highly active for both alkane hydroxylation and hydroperoxide decomposition. Workers who contributed to this section are:

Tilak P. Wijesekera

Richard W. Wagner

Floyd A. Moore

Paul E. Ellis, Jr.

Ronald A. Merrill

James E. Lyons

Electron deficient metalloporphyrins 1 (e.g. R=C₆F₅, X=F,Cl,Br,M=Fe) have been shown to be efficient catalysts for the highly selective air oxidation of light alkanes to alcohols (Ellis and Lyons, Cat. Lett., 3, 389; Lyons and Ellis, Cat. Lett., 8, 45, 1991; U.S. Patents 4,900,871; 4,970,348) as well as for efficient decomposition of alkyl hydroperoxide (Lyons and Ellis, J. Catalysis, 141,311 1993; Lyons and Ellis, U. S. Patent 5,120,886). They are prepared by the co-condensation of pyrrole with the appropriate aldehyde (Badger, Jones and Leslett, Aust. J. Chem., 17, 1028, 1964; Lindsey and Wagner, J. Org. Chem., 54,828, 1989; U.S. Patents 4,970,348; 5,120,882) followed by metal

insertion (Adler, Longo, Kampos and Kim, J. Inorg. Nucl. Chem., 32, 2443, 1970) and β -halogenation (U.S. Patents 4,892,941; 4,970,348; U.S. Pat. Appl. 568116), *meso*-Tetrakis(perhaloalkyl)porphyrins have also been prepared by the self-condensation of the corresponding 2-(hydroxyperhaloalkyl)pyrrole by prior activation of the hydroxy leaving group (U.S. Pat. Appl. (18/005/702).

Dipyrromethanes (2; see J. B. Paine in "The Porphyrins," D. Dolphin Ed., Academic Press, New York, Vol. 1, 1978) are the most commonly used precursors to a wide variety of symmetrical and unsymmetrical porphyrins. The use of dipyrromethanes for the synthesis of porphyrins carrying electron-withdrawing groups in all peripheral positions has been limited by the inaccessibility of 5,5-unsubstituted dipyrromethanes (2; $R^1=R^2=H$) in which *beta* and *meso* positions either carry electron-withdrawing groups or are unsubstituted for appropriate post-cyclization functionalization. Our recent work has provided access to the hitherto unknown *beta* unsubstituted *meso*-perhalocarbyldipyrromethanes (2; $R^1=R^2=R^3=R^5=R^6=R^7=H$; $R^4=\text{perhalocarbyl}$), which are highly useful synthetic intermediates for variety of polypyrrolic macrocycles. The present work describes the synthesis of a series of catalytically active, highly electron deficient 5,15-(bis)perhalocarbylmetalloporphyrins with the 10, 20 *meso* positions unsubstituted or carrying electron withdrawing groups).

Acid-catalyzed co-condensation of 5,5' diunsubstituted dipyrromethanes 3 with aldehydes 4

has been shown to give porphyrins 5 ($M=2H$) in high yield. (Ogoshi, Sugimoto, Nisiguchi, Watanabe, Matsuda and Yoshida, Chemistry Lett., Osuka, Nagata, Kobayashi and Maruyama, J. Hetrocyclic Chem., 27 1657 1990). However, since the precursor dipyrromethanes 3 used are generally *beta* alkyl *meso*-unsubstituted systems ($R^1=R^2=R^4=R^5=alkyl; R^3=H$), the resulting porphyrins 5 are 5,15-diaryl ($R^5=aryl$)-10,20-diunsubstituted ($R^3=H$), with alkyl substitution at the *beta* positions ($R^1=R^2=R^4=R^5=alkyl$). The fully unsubstituted dipyrromethane 3 ($R^1=R^2=R^3=R^4=R^5=H$) has also been condensed with substituted aromatic aldehydes to give *beta* unsubstituted 5,15-diarylporphyrins which are also unsubstituted at the other two *meso* positions 10 and 20 (5; $R^1=R^2=R^3=R^4=R^5=H; R^6=aryl$; Manka and Lawrence. Tetrahedron Lett., 30 6989 1989). Since the syntheses described in this work use *meso*-substituted-*beta*- unsubstituted dipyrromethanes (e.g. 3; $R^1=R^2=R^4=R^5=H; R^3=perhalocarbyl$), porphyrins 5 produced by co-condensation with appropriate aldehydes will carry electron-withdrawing groups in all four *meso* positions, while the *beta* positions will still be available for substitution by other such groups. By using $R^6=H$ (HCHO or synthetic equivalent), 10,20-diunsubstituted porphyrins (5; $R^1=R^2=R^4=R^5=R^6=H; R^3=perhalcocarbyl$) are synthesized, which can be substituted by electron-withdrawing groups (e.g. NO_2) according to prior art (Gong and Dolphin, Can. J. Chem., 63 401 1985; U.S. Patent 5,120,882). Any unsubstituted *beta*-position on the porphyrin macrocycle could then be halogenated according to standard methods.

1

2

R^6CHO

4

$OHCR^6$

4

4.10.1 NEW SYNTHETIC ROUTES TO 5,5'-UNSUBSTITUTED-*meso*-HYDROCARBYL (OR SUBSTITUTED HYDROCARBYL) DIPYRRROMETHANES

Porphyrin synthesis is a condensation reaction which often suffers from low yields causing metalloporphyrin manufacturing costs to be high. One alternative to the cyclization of four pyrroles with four aldehydes is to first make a dipyrromethane which can be cyclodimerized in much higher yield. This technique also provides greater flexibility in catalyst structure. We report herein on progress toward making active electron deficient metalloporphyrin catalysts for the first time by this technique.

The work provides new synthetic routes to 5,5'-unsubstituted-*meso*-hydrocarbyl dipyrromethanes which are useful precursors to di-,tri-,tetra- and polypyrrolic compounds as well as cyclic polypyrrolic compounds such as porphyrins, azaporphyrins, expanded polypyrrolic macrocycles and their metal derivatives.

Cyclic polypyrrolic compounds such as porphyrins, azaporphyrins and expanded polypyrrolic compounds have found many uses both as their non-metallated free-base form as well as their metallated forms. Porphyrins in their metallated form (particularly as Fe, Co, Mn and Cr) have been used as catalysts for air oxidations of hydrocarbons (Ellis and Lyons, Catalysis, Lett., 3, 389 1989; Lyons and Ellis, Catalysis Lett., 8 45 1991; U.S.Patents 4,900,871; 4,970,348) as well as degradation of lignin in the pulp and paper industry (U.S.Patents 4,892,941; 5,077,394). Variation of the type and position of the peripheral substituents of these macrocycles are known to change their photophysical, photochemical and electrochemical properties which in turn alter their activity.

Catalytic activity of metalloporphyrins is known to increase with the introduction of electron-withdrawing substituents at all peripheral positions, *beta* as well as *meso*. Although some useful substituents can be introduced on to the macrocycle after its formation e.g. halogens; F, Cl or Br (U.S. Patents 4,892,941; 4,970,348; U.S. Pat. Appl. Serial No. 07/568116), nitro NO₂ (U.S. Patent 5,120,882) and cyano CN (U.S. Patent 5,118,886), certain groups e.g. hydrohalocarbyl, halocarbyl (Lindsey and Wagner, J. Org. Chem., 54 828 1989; U.S. Pat. Appl. Serial No. 08/005,702) have to be introduced at the appropriate position of the precursor fragments during cyclization. Therefore if a porphyrin is to be modified to produce an efficient oxidation catalyst, it is preferable to have unsubstituted peripheral positions or have appropriate carbon bonded substituents (e.g. perhaloalkyl, perhaloaryl etc.) already in place.

Dipyrromethanes (2; see J. B. Paine in "The Porphyrins", D. Dolphin Ed. Academic Press, New York, Vol. 1, 1978) are the most commonly used precursors for porphyrins. In addition, they are used to prepare tripyrrins and a,c-biladienes in the step wise build-up of unsymmetrically substituted porphyrins, azaporphyrins and expanded polypyrrolic macrocycles. The use of dipyrromethanes for the synthesis of porphyrins carrying electron-withdrawing groups in all peripheral positions has been limited by the inaccessibility of 5,5'-unsubstituted dipyrromethanes (2; R¹=R²=H) in which *beta* and *meso* groups (R²-R⁶) are electron-withdrawing. Dipyrromethanes carrying electron-withdrawing *beta* substituents are synthetically less useful since the presence of

such groups renders the dipyrromethane highly unreactive at the 5,5'-positions. However, if the *beta* positions are unsubstituted ($R^2, R^3, R^5, R^6 = H$) and the *meso* position carries an electron-withdrawing substituent (e.g. $R^4 = \text{halohydrocarbyl}$ or halocarbyl), the macrocycle derived from it will carry electron-withdrawing groups at the bridging carbons and will also have the *beta* positions available for subsequent functionalization with electron-withdrawing substituents (e.g. halogens).

This work provides two routes to 5,5'-unsubstituted dipyrromethanes (1; $R^1 = R^7 = H$) which may or may not be substituted at the *beta* positions, but carry *meso*-perhalocarbyl groups (for example; perfluoroalkyl), which have hitherto not been reported. With pyrrole itself as the starting material, one obtains dipyrromethanes with unsubstituted *alpha* and *beta* positions (2; $R^1 = R^2 = R^3 = R^5 = R^6 = R^7 = H$).

Scheme 1 depicts the general reaction used to make dipyrromethanes and Scheme 2 shows the synthesis of *bis*-(pyrrol-2-yl) trifluoromethylmethane, 6.

Scheme 1

Scheme 2

A Two-Step Route to Bis-(pyrrol-2-yl)trifluoromethylmethane, 6

Pyrrole was reacted (over a 4h period), with an equimolar quantity of trifluoroacetic anhydride in benzene under an inert atmosphere at 2-3°C. The reaction mixture was diluted with water, the organic phase washed with aqueous sodium bicarbonate and water and the trifluoroacetylpyrrole 4 isolated in over 75% yield by evaporation of the solvent; m.pt. 45-46°C, mass spectrum: $m/z=163(M^+)$.

Trifluoroacetylpyrrole in methanol was reacted with solid sodium borohydride (in positions) at 0-5°C. The reaction mixture was treated with a saturated solution of sodium bicarbonate and the product [2-(2-hydroxyl-1.1.1-trifluoroethyl)pyrrole] was extracted into ether. The ether solution was washed with aqueous sodium bicarbonate, water, dried and the product isolated in over 90% yield by evaporation of the solvent; mass spectrum: $m/z=165(M^+)$.

Equimolar quantities of pyrrole 2 and 2-(2-hydroxyl-1.1.1-trifluoroethyl)pyrrole (5mmol each) in tetrahydrofuran (30mL) were refluxed with catalytic amounts of hydrochloric acid for 2h under an inert atmosphere. GC analysis of the reaction mixture indicated the presence of the desired dipyrromethane, bis-(pyrrol-2-yl)trifluoromethylmethane 6 in up to 65%. The pure product was isolated by neutralization of the acid, extraction into chloroform and chromatography. GCMS m/z ; 214 (M^+ , 55%); 145 (100%); 1H NMR (8, $CDCl_3$, at 7.24); 4.80 (q, 1H), 6.24 (m, 4H), 6.73 (s, 2H), 7.96 (bs, 2H).

A One-Step Route to Bis-(pyrrol-2-yl)trifluoromethylmethane, 6

Pyrrole (150mmol) and trifluoroacetaldehyde as the methyl hemiacetal, 75 mmol) in tetrahydrofuran are heated at reflux with catalytic amounts of hydrochloric acid for 2h under an inert atmosphere. GC analysis of the reaction mixture indicated the presence of the desired dipyrromethane in up to 80%. Neutralization of the acid followed by work up and chromatography gave the pure product in 65% yield. GCMS and ^1H NMR of this material was identical to the material prepared by the previous method.

Bis-(pyrrol-2-yl) heptafluoroprop-1-ylmethane, 7

Pyrrole (50mmol) and heptafluorobutyraldehyde (as the hydrate, 25 mmol) were condensed in tetrahydrofuran in the presence of acid catalyst as described above to give *bis*-(pyrrol-2-yl)heptafluoroprop-1-ylmethane) in >50% isolated yield. GCMS m/z ; 314 (M^+ , 22%), 145 (100%); ^1H NMR (CDCl_3 , at 7.24): 4.92 (t, 1H), 6.22 (d, 4H), 6.75 (s, 2H), 8.07 (bs, 2H).

4.10.2 SYNTHESIS OF 5,15-BIS(PENTAFLUOROPHENYL)-10,20-BIS(TRIFLUOROMETHYL)PORPHYRIN

Bis(pyrrole-2-yl)-trifluoromethylmethane (1.07g; 5mmol) and pentafluorobenzaldehyde (982mg; 5mmol) were placed in a 2L 3-neck rb flask containing freshly distilled chloroform (1L) and degassed by bubbling argon for 30 minutes at room temperature. Hydrobromic acid (1mL) was

added, and the reaction mixture allowed to stir for 20 hours in the dark under a closed argon atmosphere.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 2.2g) was added in small portions (500mg every hour), stirred for 3 hours exposed to light and air and evaporated to dryness. Redissolved the residue in chloroform (300mL), and reevaporated. The crude reaction mixture, dissolved in chloroform (25mL) was filtered through alumina (neutral, activity I; 30g), which retains excess oxidant and most of the impurities. The pure product is obtained by evaporation of the filtrate to dryness and recrystallization of the residue in dichloromethane/methanol. Yield 389mg (20%). Spectroscopic data were given in an earlier report.

4.10.3 INSERTION OF IRON TO 5,15-BIS(PENTAFLUOROPHENYL)-10,20-BIS(TRIFLUOROMETHYL)PORPHYRIN

The porphyrin ($F_{16}PH_2$; 118mg; 0.15mmol), sodium acetate, trihydrate (400mg) and glacial acetic acid (45mL) were placed in a 100mL 3-neck rb flask fitted with a reflux condenser and an argon inlet tube. The solution was degassed for 15 minutes, heated to 80°C and treated with a solution of ferrous chloride (600mg) in water (1mL). The system was closed under argon and heating continued at 100°C for 20 minutes. A uv spectrum in acetic acid indicated the four band spectrum in the visible region (characteristic of the free-base porphyrin (504, 538, 584, 638nm) had disappeared producing an almost featureless spectrum (weak 504, 604nm bands). The Soret band appeared at 404nm together with another absorption near 350nm, the latter being due to the excess ferrous/ferric

chloride. The reaction mixture was allowed to cool to room temperature and exposed to air overnight to complete the oxidation of any coordinated ferrous to ferric.

Hydrochloric acid (3M; 45mL) was added to the reaction mixture, allowed to stir for 30 minutes and the precipitated solid was filtered using a 30F sinter funnel. The crude product was washed thoroughly with water to remove any remaining acid and was allowed to dry under suction. The solid was redissolved in chloroform (UV: split Soret at 350/406nm), the volume reduced to ca. 10-15mL and passed through alumina (65g; neutral; Brockman Activity V) using chloroform for elution. The product eluted out as a greenish-purple dichroic solution (uv spectrum shows 332/sh, 388/br-Soret, 424/sh, 562 and 602).

The volume was adjusted to approximately 75mL, transferred to a separatory funnel and extracted with 6M hydrochloric acid (40mL). The absorption spectrum reverted back to the previous one with a split Soret (350/408nm) and weak visible bands near 508, 622nm. The chloroform layer was washed with water (3x40mL), dried (sodium sulfate), filtered and evaporated to dryness. Yield, 121mg (92.4%).

4.10.4 CONVERSION OF THE HEMIN ($F_{16}PFeCl$) TO THE μ -OXO DIMER

Meso-Tetrakis(pentafluorophenyl)porphyrinatoiron(III) [$F_{20}TPPFeX$], is known to form both a hydroxo species ($F_{20}TPPFeOH$) and a μ -oxo dimer on treatment with base.

FIGURE 1; Absorption Spectra of $F_{16}PFeX$

A: $X=Cl$; Hemin

B: $X=O-Fe(P)$; μ -oxo Dimer

FIGURE 2; FABMS of $F_{10}PFeCl$

FIGURE 3; FAB/MS of $F_{16}PF_6-O-FePF_6$

However, for $F_{16}PFeX$, with less steric hindrance for dimer formation (two bulky C_6F_5 groups substituted by CF_3 groups), the μ -oxo dimer was thought to be the predominant or even the only product from base interaction of the hemin ($F_{16}PFeCl$). This indeed was the case.

The most convenient method for the conversion of the hemin to the μ -oxo dimer was to pass a solution, in chloroform, through alumina (neutral, Brockman activity V). The red-brown solution changed to a green-purple color with the eluting material exhibiting a distinctly different absorption spectrum [UV: 334 (sh), 388 (Soret/br), 428 (sh), 562 (wk), 602 (wk)]. The highly non-polar nature of this material ($r_f = 0.8$; silica/dichloromethane-hexane 1:1) and the strong parent peak at $m/z=1679$ ($M-1$) or 1680 (M) in the FABMS strongly suggest that this is the μ -oxodimer and not the hydroxo species. A weak peak at 1697 ($M+17$) suggest the ligation of a hydroxide to a metal center of the dimer. This same material may be obtained by stirring a toluene solution of the hemin with aqueous sodium hydroxide.

4.10.5 CONVERSION OF THE HEMIN TO THE AZIDE

A sample of the hemin (40mg) dissolved in acetone (6mL) was treated with solid sodium azide (40mg) and allowed to stir under an inert atmosphere for a total of 47 hours. At the end of this period, the excess salt was filtered, evaporated the filtrate to dryness, redissolved the

metalloporphyrin residue in dichloromethane and refiltered. The solid material obtained by evaporation of the filtrate [UV: 368 (sh), 400 (br)nm] exhibited a strong infrared absorption at 2045 cm^{-1} , which is the characteristic IR stretching frequency for azides. This material was submitted for isobutane oxidation studies without further purification and analysis, because of the known liability of the azide ligand. It is interesting to note that the catalyst solution recovered from isobutane oxidation studies exhibited an absorption spectrum different from that of the azide sample used but similar to that of the μ -oxo dimer.

4.10.6 TESTING OF F_{16}PFeX FOR ISOBUTANE OXIDATION

Preliminary isobutane oxidation studies carried out with the dimeric trifluoromethylated catalyst $(\text{F}_{16}\text{PFe})_2\text{O}$ indicated that it is less active than the analogous oxo-bridged dimer of tetrakis(pentafluorophenyl)porphyrinatoiron(III) $(\text{F}_{20}\text{TPPFe})_2\text{O}$, although the CF_3 group is known to be a superior electron-withdrawing group (cf. C_6F_5). This may be due to the stronger Fe-O-Fe bond of $(\text{F}_{16}\text{PFe})_2\text{O}$ preventing the monomer from being made available for catalysis. The overlap of the two smaller CF_3 groups with the two C_6F_5 groups allows a closer approach of the two iron centers (and a stronger Fe-O-Fe bond) as compared with the molecule that has four bulky C_6F_5 groups. This is supported by the presence of strong bands at $877, 889\text{ cm}^{-1}$ in the IR (cf. $878, 892\text{ cm}^{-1}$ for Fe-O-Fe of unsubstituted $[\text{TPPFe}]_2\text{O}$ while the oxo-bridged dimer $(\text{F}_{20}\text{TPPFe})_2\text{O}$ exhibits the IR stretch at 850 cm^{-1} . The greater relative increase in catalytic activity of $(\text{F}_{16}\text{PFe})_2\text{O}$ with

increase in temperature (compared with other catalysts) also tends to support this hypothesis. See Table 1 for details.

The halide was not active at either 60°C or 80°C for isobutane oxidation. We have noticed in the past that porphyrinatoiron(III) chloride complexes can be either inactive or may exhibit a prolonged induction period.

Porphyrinatometal azide complexes have been shown by us to be active catalysts for isobutane oxidations ($\text{F}_{16}\text{PFe})\text{N}_3$ is also active but slightly less so at low temperatures than the μ -oxo dimer, Table 1. This may be due to the presence of significant quantities of $(\text{F}_{16}\text{PFe})\text{Cl}$ in the catalyst.

TABLE 1

OXIDATION OF ISOBUTANE TO TBA USING F₁₆P IRON
COMPLEXES AS CATALYSTS^a

<u>CATALYST</u>	<u>ACTIVITY^b</u>	
	<u>60°C</u>	<u>80° C</u>
[F ₁₆ Fe] ₂ O	530	1270
(F ₁₆ Fe)Cl	0	0
(F ₁₆ Fe)N ₃	310	1330

^a Isobutane, 7 grams, was added to a solution of 0.013 mmoles in 25 mls benzene. Oxygen was added to the stirred solution at temperature (total pressure = 100 psig). Reaction was run for 6 hours with O₂ added as used. Products were analyzed by glpc (in all cases TBA selectivity exceeded 85%).

^b Activity = moles O₂ reacted/mole catalyst used.

Testing of $(F_{16}PFe)Cl$ for Propane Oxidation

The complex $(F_{16}PFe)Cl$, 0.020 gram was dissolved in 48 ml benzene to which 1.13 moles propane was added. Air, 1500 psig, was pressed onto the solution which was stirred in a glass lined autoclave, heated to $125^{\circ}C$ for 13.5 hours. After this time the vessel was cooled, gases released and analyzed and the liquid analyzed by standardized glpc. Acetone and isopropyl alcohol were formed in a 2/1 ratio. Liquid product (acetone + IPA) was formed to the extent of 312 moles/mole catalyst.

Testing of $F_{16}PX$ Complexes for tert-Butyl Hydroperoxide Decomposition

Both $(F_{16}PFe)Cl$ and $(F_{16}PFe)_2O$ were found to be very active catalysts for the conversion of tert-butyl hydroperoxide to tert-butyl alcohol, TBA. Table 2 compares the activity of these catalysts with that of the very active $(TPPF_{20}Cl_8)FeCl$.

**EFFECT OF SOLVENT AND REACTION CONDITIONS^{a,b} ON THE
CATALYZED DECOMPOSITION OF TBHP TO TBA**

<u>Catalyst</u>	-	<u>PPM</u>	<u>Solvent</u>	<u>T, °C</u>	<u>T, HR.</u>	<u>RO₂H Conv., %</u>	<u>O₂ Yield %</u>	<u>TBA^d Sel., %</u>	<u>1 Hour TO^e (Thousands)</u>
Fe(TPP)Cl	-	16	BzH	23	23	>99	97	87	3.9
Fe(TPPF ₂₀ Cl ₈)Cl	-	16	BzH	22 ^c	3.8	>99	100	87	9.5
[Fe(F ₁₆ P)] ₂ O	-	16	BzH	22	25	>99	NA	87	2.0
<hr/>									
Fe(OEP)Cl	-	22	TBA	80	3.7	11	13	NA	1.3
Fe(TPP)Cl	-	16	TBA	80	18.0	48	50	84	5.6
Fe(TPPF ₂₀)Cl	-	19	TBA	80	4.2	99	85	85	11.4
Fe(TPPF ₂₀ Cl ₈)Cl	-	19	TBA	80	3.6	99	86	86	14.7
Fe(F ₁₆ P)Cl	-	19	TBA	80	4.0	97	87	90	13.4
[Fe(F ₁₆ P)] ₂ O	-	19	TBA	80	3.5	96	86	88	13.4

a) Reactions in Benzene: The catalyst was added in a boat to a stirred solution of 9.03g of TBHP in 41.6g of benzene with stirring at T.
(O₂ determined manometrically).

b) Reactions in TBA: 13.83g of TBHP in 18.13g TBA.

c) Brief Exotherm to 31°C.

d) Molar selectivity of the hydroperoxide decomposition reaction.

e) (2 X moles O₂ produced X M.W. RO₂H)/grams catalyst grams RO₂H reacted/grams catalyst used, in the first hour of each reaction X 10³.

4.10.7 Reaction Optimization Studies - Bis(pyrrol-2-yl)trifluoromethylmethane

The synthesis of bis(pyrrol-2-yl)-trifluoromethylmethane was re-investigated in order to optimize the yields since it is the key dipyrromethane intermediate in the 2+2 synthesis of all porphyrins carrying trifluoromethyl groups in the meso-positions. GC analysis of the reaction mixture during the reaction as well as during the work up revealed several stages at which the product yields dropped. The best conditions used prior to this study were, to reflux pyrrole (0.15mol) and trifluoroacetaldehyde methyl hemiacetal (0.075mol) with conc. HCl (4.0mL) in THF (200mL) for 1h, neutralize the acid with a NaHCO₃ solution and isolate the product by extraction into petroleum ether. The following observations were made during this study:

1. The optimum reaction time was found to be 2h, beyond which significant quantities of higher molecular weight by-products were formed.
2. Concentration of the reaction mixture prior to complete neutralization of the acid resulted in the formation of dark colored by-products, lowering the isolated yields.
3. Neutralization of the acid by extraction with aqueous NaHCO₃ appeared to reduce the isolated yields probably due to the hydrolysis of the acid/water sensitive product.

Stirring the reaction mixture vigorously with solid NaHCO₃ (with subsequent filtration of the salts) was found to result in minimum decomposition of the product as determined by the improved isolated yields. Extremely low solubility of bicarbonate in THF usually leads to extended times for

neutralization but a pH greater than 7 is essential prior to addition of water in order to minimize decomposition.

The use of ethanol as the reaction solvent was also investigated. Under the same reaction conditions, GC yields >80% were obtained, with the neutralization made easier by the higher solubility of NaHCO₃ in this solvent. Furthermore, absolute ethanol was found to be better than 95% ethanol, and as such, the possibility of using gaseous hydrogen chloride as the catalyst in this reaction will be investigated.

4.10.8 Improvements in the Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis(trifluoromethyl)porphyrin [F₁₆PH₂]

The acid catalyzed 2+2 coupling of bis(pyrrol-2-yl)trifluoromethane and pentafluorobenzaldehyde was reinvestigated during the preparation of new samples for catalytic studies. One important change that was made in the procedure was to use Montmorillonite K-10 clay instead of homogeneous acids to catalyze the reaction. Onaka and co-workers recently reported the use of K-10 clay to prepare meso-tetraalkylporphyrins in good yields by the co-condensation of pyrrole and aliphatic aldehydes (Porphyrin Synthesis in Clay Nanospaces, M. Onaka, T. Shinoda, Y. Izumi and E. Nolen, Chemistry Lett., p 117, 1993) although its use in the coupling of dipyrromethanes and electron-deficient aldehydes has not yet been established.

Commercially available Montmorillonite K-10 clay (Aldrich) was activated at 120°C for 24h and stored in a screw-cap bottle for 3 months without significant loss of activity. XRD analysis indicated that this material contains some quartz and muscovite as impurities. The highlights of this study are:

1. Substitution of hydrobromic acid (30-32% in acetic acid; 1.0mL) by 7.5gK-10 clay as the acid catalyst of the reaction, led to improved yields; 24% (isolated) reproducibly. This also eliminated the variation of isolated product yields, associated with the purity of hydrobromic acid (% bromine).
2. Work-up and product isolation was made easier by the adsorption of a significant quantity of polymeric by-products on the clay catalyst. Filtration of the hot reaction mixture (after an initial DDQ oxidation) gave the porphyrin in >70% purity.
3. It is now possible to omit the prepurification step (filtering the crude reaction mixture through a pad of alumina) and crystallize the porphyrin directly from dichloromethane/methanol to obtain a >95% pure product.
4. The reactant concentrations have been doubled and the reaction time has been reduced with no apparent loss of yield.

The details of the new procedure are given in the experimental section.

4.10.9 Synthesis of meso-Tetrakis(trifluoromethyl)porphyrin [$F_{12}PH_2$] via Dipyrrromethane Coupling and Insertion of Iron

In order to have access to reasonable quantities of the catalyst $F_{12}PFeX$, the research efforts for the synthesis of the free base porphyrin $F_{12}PH_2$ were expedited during this quarter. Since the generation of a carbocation (reactive intermediate of an aldehyde) adjacent to a trifluoromethyl group is known to be difficult, the coupling of trifluoroacetaldehyde with the dipyrrromethane was expected to give lower yields of product, compared to the corresponding reaction with pentafluorobenzaldehyde. The highlights of this work are:

1. The 2+2 coupling of bis(pyrrol-2-yl)trifluoromethylmethane with trifluoroacetaldehyde methyl hemiacetal under the standard conditions used for $F_{16}PH_2$ synthesis (0.032% HBr in CH_2Cl_2 at room temperature for 48h) produced only small quantities of $F_{12}PH_2$ with by-products that could not be easily removed.
2. Montmorillonite K-10 clay catalyzed cyclization at room temperature (successful for $F_{16}PH_2$ synthesis) produced only minor quantities of the desired porphyrin.
3. Attempted cyclization at higher acid concentrations (0.8% HBr in ethanol at reflux for 2h) produced only polymeric material although this method had been used successfully to prepare other porphyrins by reacting pyrroles with appropriate aldehydes.

4. Use of Montmorillonite K-10 clay in refluxing CHCl_3 (24h) produced the porphyrin in low yields but reasonable quantities of pure material could be isolated without complicated purification procedures.

Since the primary objective was to make available, sufficient quantities of F_{12}PFeX for screening, yield optimizations were not attempted at this stage, although some changes were made to the original procedure in order to reduce a major by-product that was chromatographically quite similar to the porphyrin. The synthetic procedure and the analytical data are given in the experimental section. The use of other heterogeneous acid catalysts for the cyclization is also being investigated.

Insertion of iron to F_{12}PH_2 was first attempted in THF using FeCl_2 . Insertion was not complete even after 2h at reflux, but some decomposition had already set in. The desired product $\text{F}_{12}\text{PFeCl}$ was isolated in >70% yield, with some unreacted porphyrin being recovered. However, when glacial acetic acid was used as the solvent, with the reaction temperature being $>100^\circ\text{C}$, iron insertion was complete in less than 30min. The isolated yields were near quantitative.

4.10.10 Montmorillonite K-10 Catalyzed Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis(trifluoromethyl)porphyrin

Activated Montmorillonite K-10 (7.5g) and chloroform (distilled from CaH_2 ; 180mL) were placed in a 500mL 3-neck rb flask and degassed for 10min. Bis(2,2'-pyrrolyl)-trifluoromethylmethane (1.07g; 5mmole) dissolved in chloroform (10mL) was added followed immediately by pentafluorobenzaldehyde (989mg; 5mmol; washed with 10mL solvent) and argon bubbling continued for a further 5min. The system was closed under argon and the reaction mixture stirred at room temperature for 24h. A solution of DDQ (500mg) in benzene (30mL) was added dropwise (within 20min) while heating the solution gently and continued heating for a further 1h.

The clay was removed by filtration [directly into a flask containing DDQ (500mg) in benzene (20mL)] and was washed thoroughly with hot chloroform in small portions (200mL total) until the filtrate was only faintly colored (most of the dark impurities were adsorbed onto the clay). The filtrate was refluxed for 90min, solvent removed, residue redissolved in chloroform and passed through alumina (90g; A-950); chloroform was used to elute the porphyrin. The solution was evaporated to dryness, the residue redissolved in dichloromethane and the porphyrin crystallized from methanol; the product was filtered and washed with methanol. Yield: 478mg; 24.1%. Analytical data for this material have been reported earlier.

4.10.11 Synthesis of meso-Tetrakis(trifluoromethyl)porphyrin Using Montmorillonite K-10 Catalyst

Bis(pyrrol-2-yl)trifluoromethylmethane (2.14g; 10mmol) and trifluoroacetaldehyde methyl hemiacetal (2.2g; 16.9mmol-excess) were placed in chloroform (500mL; dried and distilled from CaH_2) and degassed for 20min. Montmorillonite K-10 clay (10g; activated at 120°C for 24h) was added, the system closed under argon and heated at reflux for 20h. The reaction mixture was allowed to cool to room temperature a solution of DDQ (2g) in benzene (60mL) added over a 30min period and heated at reflux for a further 1h. The hot solution was filtered to remove the clay which washed with hot chloroform (100-150mL). More DDQ (1g) in benzene (60mL) was added and the solution was refluxed overnight (18-20h).

The solvents were removed under reduced pressure, the residue redissolved in chloroform (50-100mL), and evaporated once again to dryness to remove the residual solvents. The solid was dissolved in minimum hot chloroform and the solution was passed through neutral alumina. The forerunning porphyrin was eluted with chloroform and the solvent was evaporated under reduced pressure to give the pure porphyrin. UV: 404 (Soret), 510, 544, 594, 648nm. MS: m/z , 582 (M^+).

4.10.12 Iron Insertion to meso-Tetrakis(trifluoromethyl)porphyrin Synthesis of $(\text{CF}_3)_4\text{PFeCl} [\text{C}_{24}\text{H}_8\text{N}_4\text{F}_{12}\text{FeCl}]$

meso-Tetrakis(trifluoromethyl)porphyrin (30mg), sodium acetate, trihydrate (100mg) and acetic acid (12mL) were placed in a 25mL 3-neck rb flask fitted with, a reflux condenser and an argon inlet. The contents were degassed for 30min and heated to ca. 100°C using a temperature controlled oil-bath. A solution of ferrous chloride (150mg) in water (1mL) was added, the system closed under argon and heating continued at 110-120°C for 30min. The reaction mixture was allowed to cool to room temperature, exposed to air and allowed to stir overnight to complete the oxidation of iron to its ferric state.

Hydrochloric acid (3N) was added to the reaction mixture which was allowed to stir at room temperature for 30min. The precipitate was filtered, washed with 1N HCl and allowed to suck dry. The solid was redissolved in chloroform, the solution extracted once with 6N HCl, the organic layer separated and evaporated to dryness. The residual solvent was removed by connecting to a vacuum-line. The product was isolated by redissolving in dichloromethane and crystallizing from n-hexane. UV: 348/404 (split Soret), 506, 640nm. MS: m/z, 671/673 (M+), 636 (M-Cl).

4.10.13 **Iron Insertion to meso-Tetrakis(trifluoromethyl)porphyrin Synthesis of**
 $(\text{CF}_3)_4\text{PFeCl} [\text{C}_{24}\text{H}_8\text{N}_4\text{F}_{12}\text{FeCl}]$

meso-Tetrakis(trifluoromethyl)porphyrin (30mg), sodium acetate, trihydrate (100mg) and acetic acid (12mL) were placed in a 25mL 3-neck rb flask fitted with, a reflux condenser and an argon inlet. The contents were degassed for 30min and heated to ca. 100°C using a temperature controlled oil-bath. A solution of ferrous chloride (150mg) in water (1mL) was added, the system closed under argon and heating continued at 110-120°C for 30min. The reaction mixture was allowed to cool to room temperature, exposed to air and allowed to stir overnight to complete the oxidation of iron to its ferric state.

Hydrochloric acid (3N) was added to the reaction mixture which was allowed to stir at room temperature for 30min. The precipitate was filtered, washed with 1N HCl and allowed to suck dry. The solid was redissolved in chloroform, the solution extracted once with 6N HCl, the organic layer separated and evaporated to dryness. The residual solvent was removed by connecting to a vacuum-line. The product was isolated by redissolving in dichloromethane and crystallizing from n-hexane. UV: 348/404 (split Soret), 506, 640nm. MS: m/z, 671/673 (M+), 636 (M-Cl).

Isobutane oxidation studies using $F_{16}PFeX$ systems as catalysts have shown that smaller CF_3 groups (compared to C_6F_5 groups), though more powerful in electron-withdrawing capability, may cause structure related problems. While the tetrakis(pentafluorophenyl)porphyrinatoiron system $[F_{20}OPFe]$ is capable of forming both the monomeric hydroxo and the oxo-bridged dimer species, $F_{16}PFe$ system forms only the oxo-bridged dimer when treated with base. Furthermore, the infrared spectra of the oxo-bridged dimers suggest that the Fe-O-Fe bond in $[F_{16}PFe]_2O$ ($\nu = 877, 889\text{ cm}^{-1}$) is stronger than that in $[F_{20}PFe]_2O$ ($\nu = 850\text{ cm}^{-1}$). The smaller CF_3 groups in the opposite meso-positions of $F_{16}PFe$ allow for a closer approach, and hence stronger bonding of the two macrocycles (Figure 1), which probably leads to the lower isobutane oxidation rates observed experimentally. Introduction of bulky groups at the β -positions was therefore considered to be a reasonable way of reducing the Fe-O-Fe bond strength of dimeric systems.

An earlier report presented the work carried out to achieve this goal by bromination of the β -positions. The synthetic approach employed involved the bromination of the zinc complex $F_{16}PZn$, demetallation of the bromo derivative and insertion of iron to give the catalytic species $BrnF_{16}PFeX$. Although this route had been successful in the case of tetrakis(pentafluorophenyl)porphyrin, it had to be abandoned due to incomplete bromination and difficulties arising at the iron insertion step. Furthermore, if one considers the commercial implications, this route would lead to a higher cost for the final product since it adds two extra steps, i.e., insertion of a secondary metal (zinc) and its removal after bromination. During the

fourth quarter, direct bromination of the iron complex $F_{16}PFeCl$ was investigated as an alternative.

Four different procedures were employed, each leading to a different extent of bromination:

1. $F_{16}PFeCl$ was brominated in refluxing CCl_4 using liquid bromine. No significant red shift of the Soret band (usually associated with halogenation) could be observed even after 30h (some broadening only). The reaction mixture was stirred with a 2M NaOH solution, the organic layer separated, washed with water and the product (1011549C) isolated after chromatography on neutral alumina (Fisher A-950; 15% water added). The uv spectrum (Figure 2a) is typical of an oxo-bridged dimer, with the Soret being ca. 10nm red shifted. FABMS data (Figure 2b) suggest that this sample consists of monomeric hydroxo species ($Br_3F_{16}PFeOH$ - major) as well as oxo-bridged dimer species brominated to a lesser extent.
2. When the above bromination was repeated in the presence of N-bromosuccinimide (NBS), only a 4nm red shift was observed after 30h. The product (1011546B) isolated after work up and chromatography (as before), exhibited a uv spectrum (Figure 3a) different from that of 1011549C above with the Soret band red shifted by a further 10nm. FABMS data (Figure 3b) suggest that the predominant component of this

material is the monomeric tetrabrominated iron (III) hydroxide, while the dimer content is either minimal or the weak Fe-O-Fe bond leads to facile bond cleavage. In either case, the formation of the monomer appears to be favoured.

The next two procedures involved the use of pyridine as a co-solvent for bromination. Pyridine is known to bind to the iron center and, in the case of electron-deficient systems, reduce the Fe(III) to the Fe(II). Since β -halogenations of porphyrins have been most successful with metals in the +2 oxidation state [e.g. Zn(II), Ni(II)], the use of pyridine was expected to assist the bromination of the iron complex by generating the Fe(II) state. Furthermore, pyridinium hydrobromide perbromide, which is formed in situ, is known to be a superior brominating agent (electrophilic) than bromine itself, particularly in low polar aprotic solvents.

3. $F_{16}PFeCl$ (118mg) was refluxed in CCl_4 (40mL) and pyridine (2mL) in the presence of bromine (0.2mL) and NBS (157mg). The Soret band shifted from 408nm to 435nm in 5h and remained at that point even after 24h. The supernatant green solution was decanted from the insoluble salts and the residue, combined with $CHCl_3$ washings and extracted with 6M HCl to remove any excess free or ligated pyridine. Washing with 2M NaOH followed by water changed the uv spectrum to 420 (broad Soret), 664 (wk) nm, which when chromatographed on neutral alumina (Fisher A-950; 15% water added; elution with $CHCl_3$) changed to 407 (broad Soret), 655 (wk) nm. Major components of

the material isolated (1011568; UV: Figure 4a) were deduced (by FABMS; Figure 4b) to be monomeric $\text{Br}_4\text{F}_{16}\text{PFeCl}$, $\text{Br}_5\text{F}_{16}\text{PFeCl}$ and $\text{Br}_6\text{F}_{16}\text{PFeCl}$, with the dimer content being minimal. Once again, it is possible that the dimers are not observed in MS due to the facile cleavage of weak Fe-O-Fe bonds.

4. The above bromination was repeated with $\text{F}_{16}\text{PFeCl}$ (121mg) in CCl_4 (40mL) and pyridine (2mL) in the presence of bromine (0.5mL) and no added NBS. The Soret band shifted from 408 to 436nm within 1h at reflux and remained for 7h. The acid (6M HCl) wash followed by the base (2M NaOH) wash of the isolated CCl_4 solution (as above) moved the Soret down to 424nm. The material isolated (1011573) after chromatography (as above) exhibited a uv spectrum (Figure 5a) with a broad Soret at 418nm and a FABMS (Figure 5b) that suggests the major components to be monomeric $\text{Br}_6\text{F}_{16}\text{PFeCl}$ and $\text{Br}_7\text{F}_{16}\text{PFeCl}$ with lesser amounts of $\text{Br}_5\text{F}_{16}\text{PFeCl}$ and $\text{Br}_8\text{F}_{16}\text{PFeCl}$.

It is clear from the FABMS analysis of the variously brominated materials that with a higher degree of bromination, the oxo-bridged dimer would either not form or it will not have strong Fe-O-Fe bonds. This of course has been the primary objective of β -bromination, although increased electron-deficiency created would be an added advantage.

Axial Group Modification Studies of $F_{12}PFeCl$

During this quarter, sufficient quantities of tetrakis(trifluoromethyl)porphyrin ($F_{12}PH_2$) were prepared by a non-optimized procedure that consumed relatively larger amounts of the dipyrromethane intermediate. Reaction optimization studies were not undertaken at this time since it was considered more important to establish the catalytic activity of the iron derivative and, if necessary, subject it to any minor structural modifications that may be required to enhance activity. Iron insertion using $FeCl_2$ in acetate buffered glacial acetic acid was complete in less than 30 min, with the hemin ($F_{12}PFeCl$) being isolated consistently in near quantitative yield. It should however be noted that unlike in the case of tetrakis(pentafluorophenyl)porphyrin ($F_{20}PH_2$), the use of N,N-dimethylformamide (DMF) as the solvent for iron insertion led to rapid decomposition of the porphyrin. This is probably due to the nucleophilic attack by dimethylamine (decomposition product of DMF) at the less-hindered meso positions of $F_{12}PFeX$.

The $F_{12}PFeX$ system differed from the analogous iron complex $F_{16}PFeX$ in many ways, primarily in the solubility aspects of the hydroxo/oxo-dimer species. Some interesting observations are:

1. The monomeric hemin $F_{12}PFeCl$ is moderately soluble in both $CHCl_3$ and benzene.
2. Extraction of a $CHCl_3$ solution of the hemin with water produces a green colored less soluble material (hydroxo and/or μ -oxo dimer?).

3. Attempted purification by chromatography on neutral alumina (Act. I or V) leads to the loss of significant quantities of material which adsorb strongly at the origin: possible aggregation!

A sample of $F_{12}PFeCl$ dissolved in $CHCl_3$ was chromatographed on neutral alumina (Fisher A-950; Act I) and by varying the polarity of solvent (from $CHCl_3$ to 5% CH_3OH in $CHCl_3$), three green fractions were eluted from the column leaving behind green material at the origin. Their optical spectra correspond to hydroxo monomer, oxo-bridged dimer and mixtures thereof. The fractions were combined and evaporated to dryness and crystallized from CH_2Cl_2 -hexane to give a green solid stored as 1011536C (UV: Figure 6).

In an attempt to prepare an active hydroxo/ μ -oxo dimer species while minimizing the loss of material on alumina (due to aggregation), reduction of Fe(III) to Fe(II) with subsequent exposure to air was investigated. Although the use of $NaBH_4$ (in $CHCl_3/CH_3OH$) led to instantaneous decomposition of the hemin, sodium dithionite ($Na_2S_2O_4$) appeared to be a suitable reagent for this purpose. The following experiments were carried out with $Na_2S_2O_4$:

1. A uv sample of $F_{12}PFeCl$ in $CHCl_3/CH_3OH$ was treated with solid $Na_2S_2O_4$ and the progress of the reaction was followed by uv spectroscopy (Figure 7). The kinetic run (Figure 7; center) clearly indicated the change from the hemin (top) to the μ -oxo dimer (bottom).

2. A degassed solution of $F_{12}PFeCl$ (43mg) in $CHCl_3$ (40mL) was stirred with an aqueous solution of $Na_2S_2O_4$ (1g in 50mL) for 30 min, treated with 1mL CH_3OH and continued stirring for 3h. The organic layer was separated and exposed to air for 24h and the product (1011587) isolated by evaporation of the solvent. The uv spectrum (Figure 8; in $CHCl_3$), with a Soret at 398nm, shoulder ca. 364 and a featureless visible region suggests that this material may be a 5-coordinate Fe(III) species and not a μ -oxo dimer. The mass spectrum exhibited no peak corresponding to the starting hemin [$Fe(III)Cl$], but peaks at 636 ($F_{12}PFe$), 652 ($F_{12}PFeO$) and 653 ($F_{12}PFeOH$).
3. A degassed solution of $F_{12}PFeCl$ (40mg) in $CHCl_3$ (40mL) and CH_3OH (2mL) was stirred with solid $Na_2S_2O_4$ (300mg) for 20min. Since no spectral change was observed, 1.5mL of CH_3OH-H_2O (2:1) was added resulting in an immediate color change. After 2h stirring, water was added to dissolve the excess solids and the product (1011589) isolated from the organic layer. The uv spectrum (Figure 9a) resembled that observed in 1 above (Figure 7) suggesting that this material may correspond to a dimer. The laser desorption MS (Figure 9b) once again showed peaks corresponding to $F_{12}PFe$, $F_{12}PFeO$ and $F_{12}PFeOH$ species, which can arise from either monomer (hydroxo ?) or dimer.

The 3 samples 1011536C, 1011587 and 1011589 have been submitted for screening.

oxo-Dimer

Figure 1

$$\lambda_{\max} = 320, 396 \text{ (Soret)}, 430, 572, 610, 664\text{nm}$$

Figure 2a

Figure 2b

$\lambda_{\text{max}} = 320, 406 \text{ (Soret), } 446, 640, 686\text{nm}$

Figure 3a

Figure 3b

monomer region

1068: $\text{Br}_3\text{F}_{16}\text{PFe}$

1085: $\text{Br}_3\text{F}_{16}\text{PFeOH}$

1129: $[\text{Br}_4\text{F}_{16}\text{PFe}] - \text{F}$

1148: $\text{Br}_4\text{F}_{16}\text{PFe}$

1165: $\text{Br}_4\text{F}_{16}\text{PFeOH}$

1228: $\text{Br}_5\text{F}_{16}\text{PFe}$

1243: $\text{Br}_5\text{F}_{16}\text{PFeOH}$

Figure 4a

Figure 4b

1182: $\text{Br}_4\text{F}_{16}\text{PFeCl}$

1226: $\text{Br}_5\text{F}_{16}\text{PFe}$

1262: $\text{Br}_5\text{F}_{16}\text{PFeCl}$

1306: $\text{Br}_6\text{F}_{16}\text{PFe}$

1341: $\text{Br}_6\text{F}_{16}\text{PFeCl}$

$\lambda_{\max} = 418$ (Soret), 684

Figure 5a

Figure 5b

1262: $\text{Br}_5\text{F}_{16}\text{PFeCl}$

1306: $\text{Br}_6\text{F}_{16}\text{PFeCl}$

1341: $\text{Br}_6\text{F}_{16}\text{PFeCl}$

1385: $\text{Br}_7\text{F}_{16}\text{PFe}$

1422: $\text{Br}_7\text{F}_{16}\text{PFeCl}$

1455: $\text{Br}_7\text{F}_{16}\text{PFeCl (Cl)}$

1501: $\text{Br}_8\text{F}_{16}\text{PFeCl}$

$$\lambda_{\max} = 342, 370, 392, 418, 570, 600$$

Figure 6

λ_{max} : 350, 402, 506, 640

λ_{max} : 344, 386, 434, 574, 608

Figure 7

$\lambda_{\text{max}} = 364, 398 \text{ (Soret)}, 562, 600\text{nm}$

Figure 8

$$\lambda_{\text{max}} = 340, 380, 418, 572, 604$$

Figure 9a

Figure 9b

5.0 MOLECULAR DESIGN OF NEW MACROCYCLIC METAL COMPLEXES FOR LIQUID PHASE OXIDATION OF ALKANES

5.1 SUMMARY

We have found that metals in the coordination sphere of electron-deficient macrocycles have extraordinarily high activity for oxidizing the relatively refractory light alkanes under mild conditions. Porphyrins, phthalocyanines and other macrocycles can be made electron-deficient by replacing peripheral hydrogens by halogen substituents. In the case of porphyrin complexes, meso-perfluorophenyl substituents are the most effective electron-withdrawing groups. However the perfluorophenyl group renders the catalyst too expensive for use as an industrial alkane oxidation catalyst so we have been searching for cheaper substituents such as the trifluoromethyl or nitro groups.

During the period of the Cooperative Agreement we have screened a number of macrocyclic metal complexes for their activity as catalysts for the oxidation of isobutane and propane. These catalysts are complexes of electron-deficient macrocycles from two families: porphyrins and Schiff bases. In both cases it has been demonstrated that electron withdrawal from the macrocycle results in large and positive shifts in the $M(III)/M(II)$ reduction potential. The observation of high $M(III)/M(II)$ reduction potential has in the past indicated that the macrocyclic complex has high alkane oxidation activity.

The new porphyrin complexes which we have screened have used nitro or trifluoromethyl groups for the first time as electron withdrawing substituents. Not only are these groups very

electronegative, the catalysts bearing them are far less costly than the perhaloporphyrin catalysts which we have used up till now. Catalyst cost is a major factor in providing practical processes. Our synthetic goal was to make a catalyst having only CF_3 or NO_2 groups in the meso-position of a porphine ring. Catalyst design criteria aided by molecular modelling techniques indicated that high activity should result from such systems. Although we have not succeeded in synthesizing those structures that we believe will be the most active, we have made complexes with CF_3 or NO_2 groups in them. These materials are active catalysts and this indicates that the desired catalysts, once made, will be highly active.

Schiff base complexes have been synthesized which also bear nitro groups. These materials have been shown to have higher M(III)/M(II) reduction potentials than their un-nitrated analogs. Their solubility in organic solvents is very low, however, and this has hampered their testing as alkane oxidation catalysts. We are working both to find suitable solvent systems and to modify catalyst structure in order to confer organic solubility. Schiff base catalysts are of further interest because we are able to readily prepare both binucleating and mononucleating macrocycles. Binuclear complexes hold the possibility of binding the dioxygen molecule between two metal centers in the same molecule. This may provide catalysts with increased activity as well.

5.2 INTRODUCTION

Research in Sun laboratories has demonstrated that a series of perhaloporphyrin complexes are uniquely active catalysts for the oxidation of light alkanes to an alcohol rich oxidate. If it were possible to convert light alkanes such as those found in natural gas or in light refinery streams to an

alcohol, one would have the means to convert the abundant hydrocarbon gases into a clean-burning high-octane liquid fuel material that could serve as an alternative transportation fuel or fuel precursor or as an oxygenate of the type that is mandated by the Clean Air Act to meet environmental standards for air quality.

The only perhaloporphyrin complexes which initially proved effective as alkane oxidation catalysts were those which had a perfluorophenyl group in each of the four meso- positions of the porphyrin ring - the tetrakis(pentafluorophenyl)porphyrinato metal complexes, $M(TPPF_{20}X_8)X$. The oxidation of isobutane using $Fe(TPPF_{20}Cl_8)N_3$ as the catalyst occurs at a rate only about one-third that required of a practical process to produce tert-butyl alcohol for fuel use, provided that the catalyst could be manufactured for under \$50/lb. $TPPF_{20}X_8$ complexes were made via a condensation reaction between perhalobenzaldehyde and pyrrole, followed by further halogenation at the pyrrolic carbons to produce a perhaloporphyrin. Insertion of an oxidation-active metal such as iron, cobalt, chromium, manganese, ruthenium, and the like produced the active catalyst. However, perfluorobenzaldehyde is an extremely expensive catalyst precursor and is made in many steps using costly raw materials. The cost of a catalyst containing four perfluorophenyl groups could be an order of magnitude greater than required. Therefore, although a relatively modest enhancement in reaction rate could result in a practical isobutane oxidation catalyst, a much lower catalyst cost is needed.

For the reasons stated above, it was clear at the outset that if an electron withdrawing group more powerful than the C_6F_5 group could be substituted into the meso- position of a porphyrinatometal complex, rates of oxidation should be enhanced. If, in addition, this group could be introduced far more cheaply, we would be well along toward solving this problem.

5.3 RESULTS AND DISCUSSION

Molecular Modeling and Catalyst Design

During the research stage of this work we found that two factors led to increased catalytic activity of macrocyclic metal complexes. Electron withdrawal from the macrocycle was one. The interpretation of this effect was relatively straightforward - the greater the electron withdrawal, the greater the activity of the complex for alkane oxidation. A good measure of the effectiveness of electron-withdrawing groups on the activity of the metal center was the M(III)/(II) reduction potential measured by cyclic voltametry.

As reported in previous Quarterly Reports, another factor also appeared to be at work. This factor was related to the steric bulk of groups on the periphery of the macrocycle which resulted in varying degrees of saddling of the macrocyclic structure. A good measure of the degree of saddling was the position of a set of structure-sensitive marker bands in the Resonance Raman spectrum of the complex. Steric bulk was interpreted as affecting the position of the multiple equilibria, eq. 1, involving metal superoxide, μ -peroxo dimer, and μ -oxo dimer which may exist in the catalytic cycle. A certain amount of bulk may allow reductive binding of dioxygen, 1a, but may retard μ -oxo dimer

formation, eq. 2, allowing a greater standing concentration of the presumed $M=O$ intermediate.

Because of the importance of steric effects on the structure of macrocyclic complexes, we have begun a molecular modeling study on the new metal complexes referred to above having NO_2 , CF_3 , and other electron withdrawing groups. We have completed initial theoretical studies of several tetranitroporphyrin complexes including: iron(III)meso-tetranitroporphine, $Fe(TNP)X$, and iron(III)meso-tetranitrobeta-octaethylporphyrin, $Fe(TNOEP)X$. It is of interest to note that while $Fe(TNP)X$ is flat, the complex, $Fe(TNOEP)X$, is highly saddled. Investigators in this study were:

Wilbert Tsao

Paul E. Ellis, Jr.

James E. Lyons

Tilak Wijesekera

PURPOSE OF THE STUDY

To investigate the effect of meso- tetranitro groups on the structure and electronic spectrum of metalloporphines using the ZINDO semi-empirical QM program. The metals included in this study were Fe(+2), Cu(+2) and Zn(+2).

THE ZINDO PROGRAM

Since the ZINDO program in the CAChe system was used for this study, brief comments on the ZINDO program and its limitations are discussed here first.

ZINDO (Zerner's Intermediate Neglect of Differential Overlap program) provides two different valence-electron-only semi-empirical procedures: a method for computing spectroscopic properties (electronic spectra) and a method of computing molecular geometries. The ZINDO program in the CAChe system is limited to 60 atoms and a maximum of 210 basis functions.

ZINDO uses the theoretically-based INDO parametrization and therefore contains parameters for transition metals. ZINDO's prediction on structures, in general, is not as reliable as MOPAC's which uses experimentally-based parameters. However, MOPAC does not deal with transition metals.

ZINDO has an alternative parameterization for electronic (UV/visible) spectra which produces only fair results. It is not expected that ZINDO-created spectra will be identical to UV-visible spectra obtained experimentally.

Computational Chemistry at this level often provides only approximate results. However all things being equal, trends can often be established for a given series of compounds. In this study, it was found that tetranitro-porphyrin-Cu is quite different from Zn or Fe homologs in structural shape (buckled vs. planar). To confirm the ZINDO results requires experimental study and/or higher level calculations. It is of interest to mention that a recent crystal structure determination shows the porphyrin plane to be severely buckled in $H_2(OEP)(NO_2)_4$ (N. Zhu, Y. Li, G. Wu, and X Liang, Acta Chimica Sinica, 50,249(1992)).

SIMULATION METHOD

Compounds of porphine and its derivatives (Figure I) were "synthesized" using the Molecular Editor program in the CACHÉ system. Structures were initially optimized using the Molecular Mechanics program, and the optimized structures were further fine tuned using the ZINDO semi-empirical Quantum program. Based on the ZINDO outputs, a theoretical electronic spectrum of each compound was generated using the configuration interaction (CI) option with CI=14 which means that one electron is excited from any of the fourteen HOMOs into any of the fourteen LUMOs.

<u>Compound</u>	<u>X</u>	<u>Metal</u>	
I	H	H, H	P
II	NO ₂	H, H	free-base TNP
III	NO ₂	Zn(+2)	TNP-Zn
IV	NO ₂	Cu(+2)	TNP-Cu
V	NO ₂	Fe(+2)	TNP-Fe
VI	H	Fe(+2)	Porphyrin-Fe
VII	H	Cu(+2)	Porphyrin-Cu

Note: TNP = tetranitro-porphyrin
p = porphine

FIGURE I

CONCLUSIONS

1. In most cases (except TNP-Cu), the ZINDO predicts that the two oxygens of the nitro group are out of the porphyrin ring plane, suggesting that the steric problem of the nitro group could be eased by tilting the two oxygens.
2. ZINDO results indicate that metals play a key role in determining the porphyrin ring structure, e.g. buckled vs. planar.

In the case of tetranitro-porphyrins, TNP-Cu (Fig. IIIa) is buckled, TNP-Zn (Fig. Va) much less buckled, and TNP-Fe (Fig. IVa) flat. The buckled TNP-Cu results in a shorter distance (3.658 Å) between the two opposite nitrogens of the porphyrin ring as shown in Table I.

Most buckled ----> Flat

In the case of porphyrins (without the nitro group), porphyrin-Cu (Fig. VIIIa) is slightly buckled and porphyrin-Fe (Fig. VIIa), again, flat.

3. From the HOMO and LUMO energy gap listed in Table II, the following trends are observed:

- * The energy gap between HOMO and LUMO of metalloporphyrins is usually larger than the corresponding free base porphyrins. For example, either porphyrin-Fe (5.199 ev) or porphyrin-Cu (5.105 ev) has a larger energy gap than porphine (4.858 ev). The HOMO/LUMO energy gap of TNP-Zn (4.501 ev) or TNP-Fe (4.575 ev) is larger than tetranitroporphine (4.283 ev). Tetranitroporphyrin-Cu (4.078 ev). is an exception.
- * The tetranitro groups tend to decrease the HOMO and LUMO energy gap of porphine or a given metal porphyrin system. This is illustrated with the following examples:

porphine (4.858 ev) > free-base TNP (4.283 ev)

porphyrin-Fe (5.199 ev) > TNP-Fe (4.574 ev)

Again, in the case copper, the reverse was found, porphine-Cu (5.105 ev) vs. TNP-Cu (4.078 ev).

4. The calculated Q bands (500-600 nm) and B Bands (380-420 nm) of tetranitroporphyrins are listed in Table III. For B bands, wavelength decreases along the series Zn>Fe>Cu and for Q bands, Cu>Zn>Fe, noticing the peak of 694 nm of TNP-Fe not included. Again, in the case of TNP-Cu the shift of the Bond Q bands is in the opposite direction.

Nitro groups cause a red shift for both Q and B bands as illustrated in the cases of porphine vs. tetranitro-porphine, porphyrin-Fe vs. tetranitro-porphyrin-Fe, and porphyrin-Cu vs. tetranitro-porphyrin-Cu.

5. Graphic representation of HOMOs and LUMOs is not included in this report. However, each MO involved in the UV/visible absorption can be generated if needed. It is observed that the iron center in TNP-Fe participates in many Q and B bands but Zn and Cu do not.

RESULTS

Porphine, P (I)

The simulated porphine structure and its electronic spectra are shown in Fig. VIa and VIb respectively. The tabulated absorption peaks are given below.

<u>MOs</u>	<u>Energy GAPS</u>	<u>Peak Wavelength</u>	<u>Molar Absorptivity</u>
HOMO -> LUMO	4.858 ev	661 nm	5450 l/mol-cm
HOMO -> LUMO+1	4.966	653	5450
HOMO-2 -> LUMO	7.230	364	240570
HOMO-3 -> LUMO	7.230	362	256608
HOMO-3 -> LUMO	7.251	361	256608
HOMO-2 -> LUMO	7.338	353	288684
HOMO-3 -> LUMO+1	7.359	352	288684
HOMO-2 -> LUMO+1	7.338	353	-
HOMO-1 -> LUMO	5.311	345	275684
HOMO -> LUMO+2	6.566	343	269438

Tetranitro-porphine, Free-Base TNP (II)

The porphine ring of the free-base TNP is predicted to be flat with the nitro groups (actually, the two oxygens of the nitro group) out of the porphine ring (Figure IIa). The structural information such as bond length, bond angle and dihedral angle is listed in Table I.

The theoretically predicted electronic spectrum of the free-base TNP is shown in Figure IIb. The most intense absorption peaks and the lowest energy absorption peaks are listed below.

<u>MOs</u>	<u>Energy GAPS</u>	<u>Peak Wavelength</u>	<u>Molar Absorptivity</u>
HOMO -> LUMO	4.283 ev.	701 nm	50 l/mol-cm
HOMO -> LUMO+1	4.525	655	50
HOMO-1 ->LUMO	5.227	369	280900
HOMO-4 -> LUMO+4	8.244	262	112360

Tetranitro-porphyrin-Zn, TNP-Zn (III)

Figures Va and Vb show the structure and electronic spectrum of TNP-Zn respectively. Some of its structural data are listed in Table I. The most intense absorption peaks and the lowest energy absorption peaks are listed below.

<u>MOs</u>	<u>Energy GAPS</u>	<u>Peak Wavelength</u>	<u>Molar Absorptivity</u>
HOMO -> LUMO	4.501 ev	656 nm	13750l/mol-cm
HOMO -> LUMO+1	4.529	653	13750
HOMO -> LUMO+4	6.224	393	112500
HOMO -> LUMO+5	6.230	392	105750
HOMO -> LUMO+3	6.179	388	105750
HOMO-2 -> LUMO+1	7.134	357	195000
HOMO-4 -> LUMO	7.172	335	195000
HOMO-2 -> LUMO+5	8.855	193	90000

Tetranitro-porphyrin-Cu, TNP-Cu (IV)

According to ZINDO calculations, TNP-Cu has a saddle shape structure (Fig IIIa). Its structural information and calculated electronic spectrum are listed in Table I and Fig. IIIb respectively. The most intense absorption peaks and the lowest energy absorption peaks are listed below.

<u>MOs</u>	<u>Energy</u> <u>GAPS</u>	<u>Peak</u> <u>Wavelength</u>	<u>Molar</u> <u>Absorptivity</u>
HOMO -> LUMO	4.378 EV	722 nm	26250 l/mol-cm
HOMO-1 -> LUMO	5.643	378	70000
HOMO-1 -> LUMO+2	6.400	297	133345
HOMO -> LUMO+8	7.417	268	175000
HOMO-11 -> LUMO+2	8.320	225	75000
HOMO-1 -> LUMO+10	9.084	188	170000

Tetranitro-porphyrin-Fe, TNP-Fe (V)

The structure of TNP-Fe and its electronic spectrum are shown in Fig. IVa and IVb respectively. Some of its structural data is listed in Table I. The most intense absorption peaks and the lowest energy absorption peaks are listed below.

<u>MOs</u>	<u>Energy</u> <u>GAPS</u>	<u>Peak</u> <u>Wavelength</u>	<u>Molar</u> <u>Absorptivity</u>
HOMO-8 -> LUMO+8	10.812 ev	694 nm	7800 l/mol-cm
HOMO -> LUMO	4.575	638	12000
HOMO -> LUMO+1	4.589	636	12000
HOMO-1 -> LUMO+1	5.538	380	158000
HOMO -> LUMO+5	6.380	340	183000
HOMO-3 -> LUMO+8	9.775	252	80000
HOMO-8 -> LUMO+2	8.837	210	68900
HOMO-2 -> LUMO+9	9.725	187	190000

Porphyrin-Fe (VI)

A flat ring of porphyrin-Fe (Fig. VII) is predicted by ZINDO. The most intense and the lowest energy absorption peaks are listed below.

<u>MOs</u>	<u>Energy</u> <u>GAPS</u>	<u>Peak</u> <u>Wavelength</u>	<u>Molar</u> <u>Absorptivity</u>
HOMO -> LUMO	-5.167 ev	573 nm	7800 l/mol-cm
HOMO -> LUMO+1	-5.171	572	7800
HOMO-2 -> LUMO+4	10.006	426	20
HOMO-9 -> LUMO+4	11.728	421	20
HOMO-1 -> LUMO	5.629	332	350000
HOMO-1 -> LUMO+1	5.633	323	350000
HOMO-6 -> LUMO+3	6.856	320	348900
HOMO-3 -> LUMO	7.398	318	275000

Porphyrin-Cu, (VII)

A slightly out of plane structure (Fig. VIIIa) is predicted with ZINDO. The most intense and lowest energy absorption peaks of the electronic spectra (Fig. VIIIb) are listed below.

<u>MOs</u>	<u>Energy</u> <u>GAPS</u>	<u>Peak</u> <u>Wavelength</u>	<u>Molar</u> <u>Absorptivity</u>
HOMO -> LUMO+2	5.272 ev	716 nm	50 l/mol-cm
HOMO -> LUMO+1	5.111	547	36558
HOMO -> LUMO	5.105	546	36558
HOMO-1 -> LUMO+2	6.617	371	50
HOMO -> LUMO+3	6.803	324	146233
HOMO-1 -> LUMO	6.45	319	164512

TABLE I

Structural Data

Compounds

	II <u>Free Base TNP</u>	III <u>TNP-Zn</u>	IV <u>TNP-Cu</u>	V <u>TNP-Fe</u>
Dihedral Angle				
C O				
C N				
C O				
1234	143	-152.930	-179.148	-153.264
1235	-37	28.278	1.004	28.840
Diagonal Distance				
N N	4.126	3.929	3.658	4.068
N N	4.139	3.929	3.681	4.054
Distance				
N-M		1.983	1.921	2.029
Bond Angle				
O-N-O	120.853	121.750	111.432	121.398
Bond Length				
N-O	1.232	1.231	1.211	1.232

TABLE II

HOMO-LUMO Energy Gap

	<u>HOMO</u>	<u>LUMO</u>	<u>HOMO-LUMO</u>
porphine	-6.341 ev	-1.483 ev	4.858 ev
Tetranitroporphine	-7.547	-3.264	4.283
Tetranitroporphyrin-Zn	-7.461	-2.960	4.501
Tetranitroporphyrin-Cu	-7.819	-3.741	4.078
Tetranitroporphyrin-Fe	-7.617	-3.042	4.575
Porphyrin-Fe	-6.448	-1.281	5.199
Porphyrin-Cu	-6.322	-1.217	5.105

TABLE III

	<u>Q Bands</u>	<u>B Bands</u>
	(nm)	(nm)
porphine	661, 653	364,362,361
Tetranitroporphine	701, 655	369
Tetranitroporphyrin-Zn	656,653	393,392,388
Tetranitroporphyrin-Cu	722	378
Tetranitroporphyrin-Fe	638,636	380,340
Porphyrin-Fe	573,572	426,421,332,323
Porphyrin-Cu	716,547,546	371,324

Figure IIa

Molar Absorptivity (l·m d·cm)

Electronic Spectra

Figure IIb

Figure IIIa

Electronic Spectra

Molar Absorptivity (l/m d-cm)

Electronic Spectra

Figure IIIb

Tetranitro-porphyrin-Fe

Figure IVa

Electronic Spectra

Figure IVb

Molar Absorptivity (l/m d-cm)

Electronic Spectra

Figure Va

Molar Absorptivity (l/mol-cm)

Electronic Spectra

Figure Vb

Figure VIa

Molar Absorptivity (l·m d-cm)

Electronic Spectra

Figure VIb

Figure VIIIa

Electronic Spectra

Molar Absorptivity (l/m d-cm)

Electronic Spectra

Figure VIIIb

Using coordinates from the crystal structure determined by Zhu, Li, Wu, and Liang [Acta Chimica Sinica, 50,249 (1992)] we constructed a model of the highly saddled tetranitrooctaethylporphine molecule shown in stick, ball-and-stick, and space filling forms in Figures IX, X, and XI.

FIGURE IX

SKELETAL STRUCTURE OF TETRANITROOCTAETHYLPORPHINE

FIGURE X

MOLECULAR MODEL OF TETRANITROOCTAETHYLPORPHINE

FIGURE XI

SPACE-FILLING MOLECULAR MODEL OF TETRANITROOCTAETHYLPORPHINE

6.0 SYNTHESIS OF ELECTRON DEFICIENT SCHIFF BASE COMPLEXES

6.1 SUMMARY

We have found that metals in the coordination sphere of electron-deficient macrocycles have extraordinarily high activity for oxidizing the relatively refractory light alkanes under mild conditions. Porphyrins, phthalocyanines and other macrocycles can be made electron-deficient by replacing peripheral hydrogens by halogen substituents. In the case of porphyrin complexes, meso-perfluorophenyl substituents are the most effective electron-withdrawing groups. However the perfluorophenyl group renders the catalyst too expensive for use as an industrial alkane oxidation catalyst so we have been searching for cheaper substituents such as the trifluoromethyl or nitro groups.

During the past quarter we have screened a number of macrocyclic metal complexes for their activity as catalysts for the oxidation of isobutane and propane. These catalysts are complexes of electron-deficient macrocycles from two families: porphyrins and Schiff bases. In both cases it has been demonstrated that electron withdrawal from the macrocycle results in large and positive shifts in the $M(III)/M(II)$ reduction potential. The observation of high $M(III)/M(II)$ reduction potential has in the past indicated that the macrocyclic complex has high alkane oxidation activity.

Schiff base complexes have been synthesized which also bear nitro groups. These materials have been shown to have higher $M(III)/M(II)$ reduction potentials than their un-nitrated analogs. Their solubility in organic solvents is very low, however, and this has hampered their testing as alkane oxidation catalysts. We are working both to find suitable solvent systems and to modify

catalyst structure in order to confer organic solubility. Schiff base catalysts are of further interest because we are able to readily prepare both binucleating and mononucleating macrocycles. Binuclear complexes hold the possibility of binding the dioxygen molecule between two metal centers in the same molecule. This may provide catalysts with increased activity as well. Workers who contributed to this section are:

Shalid N. Shaikh
Joseph Klein
James E. Lyons

6.2 INTRODUCTION

The mono-nuclear Schiff base complexes have been used to oxidize different substrates mostly, alkenes by using iodosylbenzene as an oxidant¹. It has also been reported that electron-deficient Schiff base complexes not only enhance the rate of the reaction but better yields are also achieved. Reaction rates can be correlated with reduction potential of the metal centers in the Schiff base complexes. The more positive the potential of the metal center is, the faster is the oxidation rate of the substrate². High M(III)/M(II) reduction potentials are achieved by introducing electron withdrawing groups into the periphery of the macrocycle. The greater the number of electron withdrawing groups, the higher is the M(III)/M(II) reduction potential.³

It has been reported in the literature⁴, that bi-nuclear complexes in which the two metal centers are in close proximity have the ability to serve as simple models for multi-metal-centered

catalysts⁵. In our study, we want to synthesize binuclear metal complexes which are based on ligands having bridging xylene moieties. These are flexibly bridged binuclear metal systems in which metal centers are separated by distances that vary from a minimum of 4°A to a maximum of 12°A. The metal centers bound to these ligands may activate dioxygen which could then be transferred to a substrate, (in our case a light alkanes) and convert it to oxygenates as proposed in **Scheme 3**. Indeed, Martell and co-workers⁶, Karlin⁷ and Kitajima, et. al⁸ have shown that interactions of the type we envisioned do occur in dioxygen adducts of Co(II), Cu(I) complexes, where the dioxygen molecule bridges two metal centers in an intramolecular fashion.

The electron-deficient complexes (vide supra) have been chosen on the basis of literature citations which show that nitro- groups on the aromatic rings greatly enhance the reduction potential of metal centers in Schiff base complexes relative to their non-derivative analogs^{3,4} (see **Table 1-4**). Also, studies of metallo porphyrins developed at Sun for light alkane oxidations showed that the greater the number of electron withdrawing groups that are on peripheral carbons of porphyrins, the higher was the catalytic activity and the catalyst life. Thus, we are attempting to increase catalytic activity of Schiff base complexes by electron withdrawal from the macrocycle.

6.3 RESULTS AND DISCUSSION

A. Synthesis of Schiff bases

The Schiff base ligands are prepared by condensation of the appropriate salicylaldehyde and

phenylenediamine in pure refluxing ethanol. The ligands **1**, **3**, **6** and **12** were isolated as orange to pale-yellow precipitates, and subsequently crystallized from the appropriate solvents (Experimental section). Each of the ligands have been characterized by Mass, IR and NMR spectroscopies where deemed necessary. The mass spectra of ligands **1**, **3**, and **6** display a m/e (M^+) pattern of 316, 406 and 496 respectively which correspond to their structural formulations. The mass spectral analysis of **12** could not be determined because of its decomposition in the probe.

The infra-red spectra of all four ligands show a broad band in 3450 cm^{-1} region which has been assigned to the hydroxyl stretching frequency region. The broadness may also indicate the presence of some moisture. The very weak band at 3090 and 3085 cm^{-1} of the ligands **3** and **6** can either be assigned to the slight impurity of the starting material i.e. phenylenediamine or to the amine residue (H-bonded to the π -electron of the $-\text{CH}=\text{N}-$ bond). By examining the NMR resonance peaks of **3** and **6** at around 9.0 and 14.0 ppm, these may be assigned to the azomethine proton and the hydroxyl group of salicylaldehyde. Broad multiplets assignable to phenyl protons are also observed in the range of 6.7 - 8.9 ppm for all the Schiff bases. Deuterium exchange of hydroxyl protons of the ligands was not carried out at this stage, because the literature data⁹ supports the given assignments. The strong infra-red bands near 1610 - 1620 cm^{-1} are doubtless associated with $\nu(\text{HC}=\text{N})$ stretching frequencies which are derived from salicylaldehyde¹⁰. The 1500 cm^{-1} region bands can be assigned to $\nu(\text{C}=\text{C})$ stretching frequencies. The infra-red spectrum of **12** is quite complicated and its exact

interpretation will be made in the future by carefully examining its NMR, MS spectra and elemental analysis.

B. Synthesis of mono- and bi-nucleating ligands

The mono- and binucleating ligands (Schiff bases) which will be utilized to make metal complexes are synthesized in five steps as shown in **Scheme 2**. The mono- and binucleating Schiff bases are obtained by the condensation of 2/4 equivalent of salicylaldehyde with 1 equivalent of 2-benzyl (1,3-diaminopropane) **8** or m-xylylenebis[2-(1,3-propanediamine)] **9**. The synthesis of diamine **8** and tertaamine **9** is accomplished by the condensation of benzaldehyde/isophthalaldehyde with an equivalent of malononitrile to produce benzylidenemalononitrile **4** and m-xylylidenebis(malononitrile) **5**. The reduction of **4** and **5** by TEAF, followed by BH_3 .THF reduction produces the desired amines **8** and **9** respectively. Each of the above intermediates were characterized by proton and carbon-13 NMR, infra-red and mass spectroscopy. The detailed assignments are given in the experimental section. The diamine **8** and tetramine **9** were not pure. The impurities could not be separated due to the close R_f values in several mixed solvent systems. Distillation at lower pressure had the same effect. The compound **9** probably decomposed at higher temperature as its color changed from light brown-yellow to tar brown. The distilled product (~2.0%) from 5.0 g crude also showed impurities determined by ^1H , ^{13}C -NMR and mass spectroscopy.

The mono- and binucleating ligands (Schiff bases) were synthesized in five steps as shown in **Scheme 2**. The diamine **8** and tetraamine **9** reported previously were not pure. The impurities

could not be separated by column chromatography even in different solvent systems. It was opined that the side products¹¹ were formed due to partial reduction of parent nitriles giving rise to imines or secondary amines or higher oligomers (?), as shown below:

It was decided to run these reactions under ammonia atmosphere to avoid the undesired side products. The BH_3 reductions of parent nitriles, **6** and **7** under the above conditions went very smoothly and no apparent precipitate was formed in case of diamine **8**. The BH_3 reduction of **7** produced a yellow precipitate but the quantity was far less as compared to the reaction without ammonia. In both cases, the acidification of the crude products followed by base hydrolysis and subsequent workup gave pale-yellow oil. The crude amine **8** was distilled at reduced pressure to produce a colorless oil in 30 % yield. The ^1H -NMR in deuterated chloroform showed peaks at 7.2 aromatic protons, 2.5 - 2.8- overlapping doublets due to methylene and benzylic protons, 1.6 - 1.8- and a sharp peak at 1.4 ppm- due to methine and amine protons respectively. Also, there were small peaks which are due to minor impurities (5 % see **Figure 1**). The IR spectrum showed a band at 3250 cm^{-1} due to NH_2 stretch confirming the formation of desired product.

To confirm the formation of the compound **8**, the ligand was reacted with nitro-salicylaldehyde in refluxing ethanol to get an orange precipitate with a green tinge. The compound

10, less metal, was characterized by IR, ^1H -NMR and mass spectroscopy. The mass spectrum, **Figure 2** showed its parent m/e peak at 462 and the DIP/MS fragmentation pattern is shown in **Figure 3**. The mass spectrum of **10**, less metal, showed no impurities related to side products. The m/e peaks at 149 and 167 are due to plasticizer which was present in the solvent bottle and was confirmed independently.

SCHEME 1

SCHEME 2

SCHEME 2

LINKED SCHIFF BASE LIGAND
FOR O₂ BINDING

SCHEME 3

TABLE 1

REDUCTION POTENTIALS OF (SALEN)Mn^{III} CATIONS^a

(Salen)Mn ^{III}	E°, V vs. SCE	(Salen)Mn ^{III}	E°, V vs. SCE
Unsubstituted	-0.44	5,5'-dichloro	-0.34
3,3'-dimethoxy	-0.42	5,5'-dinitro	-0.07
7,7'-diphenyl	-0.47	3,3',5,5'-tetranitro	+0.25

^a CV measurements performed on 1×10^{-3} M [(Salen)Mn] PF₆ in DMSO containing 0.1 M tetra-n-butylammonium hexafluorophosphate at 25°C. Potentials calibrated with respect to ferrocene E° 0.31 V.

TABLE 2^{3c}REDUCTION POTENTIALS OF (SALEN)Co^{II} COMPLEXES^a

(Salen)Co ^{II}	E°, V vs. Fc/Fc ⁺	(Salen)Co ^{II}	E°, V vs. Fc/Fc ⁺
Unsubstituted	-0.466	5,5'-dimethoxy	-0.432
5,5'-dichloro	-0.454	5,5'-dinitro	-0.337

^a CV measurement performed in DMF containing 0.1 M tetra-n-butylammonium hexafluorophosphate using Pt electrode at 25°C.

TABLE 3^{3a,b}REDUCTION POTENTIAL OF Fe^{III}/Fe^{II} IN SALOPH COMPLEXES^a

(Saloph)Fe ^{II}	E°, V vs. SCE	(Saloph)Fe ^{II}	E°, V vs. SCE
Unsubstituted	-0.28	5,5'-dichloro	+0.19
4,4'-dimethoxy	-0.32	5,5'-dinitro, Y-nitro	+0.06
5,5'-dimethoxy	-0.32	5,5'-dinitro	-0.02

Saloph = N,N'-1,2-phenylenebis(salicylideneimine)

^a CV measurement performed on 1.8 mmol complex in DMSO containing 0.1 M tetraethylammonium perchlorate at 25°C, using mercury/Pt electrode.

TABLE 4⁴ELECTROCHEMICAL DATA FOR THE BINUCLEAR
AND MONONUCLEAR COMPLEXES OF Mn^{IIa}

Complex	E°, V vs. SCE	Complex	E°, V vs. SCE
1,2-phenylenebis[Mn(Salpm)] ^b	-0.25	Mn[(Salpm)] ^b	-0.24
1,2-phenylenebis[Mn(5,5'-NO ₂ -Salpm)]	-0.11	Mn(5,5'-NO ₂ -Salpm)	-0.12

^a DMSO solution; complex concentration ~ 10⁻³ M in 0.1 M (TBA)PF₆.

^b Salpm - 1,3-propanedisalicylaldimine

Figure 1 - ^1H -NMR of compound 8

Mass/Charge

Figure 2

DIP/MS FRAGMENTATION PATTERN OF SAL-Bz-Pm

Figure 3

C. Synthesis of Schiff base complexes:

The Schiff base complexes of Mn^{2+} and Fe^{2+} , 1, 2, 3, 4, 1a, 2a, were prepared by the reaction of appropriate ligands, synthesized previously, with the metal acetates in dried ethanol and isolated as powders. Each of the complexes have been characterized by IR and elemental analysis.

EXPERIMENTAL SECTION

Manipulations involving air-sensitive materials were performed under prepurified N_2/Ar by using modified Schlenk techniques. Isophthalaldehyde, phenylenediamine, 3/5 and 3,5-dinitrosalicylaldehydes, malononitrile, benzaldehyde, $\text{BH}_3\cdot\text{THF}$ complex (1.0 M solution in THF) were purchased from Aldrich, malononitrile was distilled from P_2O_5 at reduced pressure and stored under N_2 prior to use. Benzylmalononitrile¹², triethylamine-formic acid azeotrope (TEAF)¹³, 2-benzyl-1,3-diaminopropane⁴ and m-xylylenebis(2-(1,3-propanediamine))⁴, were prepared by literature methods. TEAF azeotrope was distilled at 80°C and 124°C at ~25 mm pressure and was standardized with 0.1 N NaOH prior to use. Phenylenediamine was recrystallized from hot toluene and its purity confirmed by NMR spectroscopy. All solvents used were HPLC grade except where otherwise noted. THF was distilled from Na-benzophenone ketyl under N_2 prior to use.

A. SYNTHESIS OF SCHIFF BASES

General Procedure: In a typical example, phenylenediamine (0.0185 mol) was dissolved in hot ethanol (50 mL) to get a clear yellow solution. Appropriate un-/ substituted salicylaldehyde (0.037 mol) in hot ethanol (50 ml) was added to the above solution. Immediately, an orange/pale yellow precipitate formed depending upon the substituent on salicylaldehyde. The reaction contents were refluxed for an hour, cooled down to room temperature, filtered, the precipitate washed with ethanol followed by ether and then aspirated to dryness yielding Schiff base ligands. The volume of ethanol in reaction medium can vary according to the amount of the reactants.

Saloph-H (1): Shining orange oblong crystals. Yield: 73 %. M.P. 164°C. Mass spectrum: m/e 316 (M^+). (KBr, cm^{-1}): $^1\text{H-NMR}$ (DMSO-d_6): 6.8-7.8 (aromatic), 9.1 ($=\text{CH}$), 13.3 ($-\text{OH}$). IR (KBr, cm^{-1}): 3450 br, 1610 vs, 1580 s, 1530 s, 1460 s, 1440 m, sh, 1380 m, 1310 w, 1175 m, 1150 m, 900 w, 645 s.

3,3'-(NO_2)₂-Saloph-H (3): Orange powder. Yield: 75 %. M.P. 260°C (decomposed). Mass spectrum: m/e 406 (M^+). IR (KBr, cm^{-1}): 3450 br, 3090 vw, 1620 vs, 1590 m, 1570 m, 1520 m, 1480 m, 1340 vs, 1300 s, 1095 m, 930 w, 820 m, 740 m, 630 w.

3,3',5,5'-(NO_2)₄-Saloph-H (6): Orange powder, recrystallized from hot DMF/ ethanol to get thin hair-like orange crystals. Yield: 70 %. M.P. $201 \pm 1^\circ\text{C}$. $^1\text{H-NMR}$ (DMSO-d_6): 7.6-8.0

(aromatic), 9.1 ($\text{CH}=\text{N}$), 13.9 ($-\text{OH}$). IR (KBr, cm^{-1}): 3440 br, 3085 vw, 1615 vs, 1585 w, 1560 m, 1450 vs, 1350 m, 1290 m, 1270 w, sh, 1200 s, 1180 vs, 855 w,d, 830 m, 750 s, 735 s.

3,3',5,5'-(NO₂)₄-Sal-o-ph-3-NO₂ (12): Pale-yellow powder. Yield: 60 %.M.P. 280°C (decomposed). Recrystallized from hot DMF/ ethanol. ¹H-NMR (DMSO-d₆): 12.8 ($-\text{OH}$), 9.1 ($\text{N}=\text{CH}$), 6.7-8.25 (m, aromatic). Shows some impurities and requires further crystallization.

B. SYNTHESIS OF MONO- AND BI-NUCLEATING LIGANDS

Benzylidenemalononitrile (4)

Method A: Malononitrile (6.23 g, 9.42 mmol) was dissolved in 50 ml of ethanol (200 proof) and added to a solution of isophthalaldehyde (10.0 g, 9.42 mmol) in hot ethanol (150 mL, 55°C). Piperidine (6 drops) was added to catalyze the reaction. The color changed to dark orange. Heated at 70°C temperature to obtain long colorless needles. Filtered, washed the crystals with cold diethyl ether (5°C) and aspirated to dryness. Yield: 17.8 g; 77 %, M.P. 83± 1°C.

Method B: Same as above except t-amyl alcohol was used as a solvent. Yield: 17.1 g; 73%. M. P. 84-85°C (lit. M.P. 83.5-84°C)¹⁴.

Method C: Benzaldehyde (10.0 g, 0.094 mol) and malononitrile (6.23 g, 0.0942 mol) were partially dissolved in 275 mL of ethanol water mixture (1:4.5) and heated to 65°C for 15 minutes. White precipitate floated in the mixture and was stirred for an additional 30 minutes. Cooled down to room temperature. Colorless needle like crystals formed. Filtered through coarse frit, washed

with 5°C cold ethanol (30 mL) followed by cold ether and aspirated to dryness. Yield = 9.8 g; 67%. M.P. $85 \pm 1^\circ\text{C}$. (Caution: Run reaction in well ventilated hood. Compound has pungent odor and irritates the skin). Mass spectrum $m/e = 154 (M^+)$. IR: $\nu_{\text{C}\equiv\text{N}}$ 2262 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): 7.52, 7.62, 7.90 (t,t,d,4 H, aromatic), 7.77 (s,1 H, benzylidene).

Benzylmalononitrile (6)

The compound 4 (6.8 g, 0.04 mol) was dissolved in HPLC grade DMF (80 mL) and heated to $40 \pm 5^\circ\text{C}$ over an oil-bath. TEAF (10.4 g) was added and the reaction mixture was stirred at this temperature for 2 hours. The color changed from light yellow to green. The mixture was then poured into 100 mL of ice water to get very light green powder. Filtered, dried under vacuum and then dissolved in hot ethanol (50 mL) and allowed to cool to room temperature until the incipient formation of colorless crystals. Cooled at $5\text{--}10^\circ\text{C}$ overnight to get complete crystallization. Filtered, washed with cold ether and aspirated to dryness, giving 5.3 g (77%) of colorless crystals. IR $\nu_{\text{C}\equiv\text{N}}$ 2224 cm^{-1} . Mass Spectrum = m/e 156 (M^+). $^1\text{H-NMR}$ (CD_3COCD_3): 7.4 (m, aromatic), 3.44 (d, -H), 4.79 (t, α -H). $^{13}\text{C-NMR}$ (CD_3COCD_3): 25.33 [$\text{CH}_2\text{-CH(CN)}_2$], 36.36 [-CH(CN)_2], 114.3 [-CH(CN)_2], 128.9 (4-aromatic), 129.58 (3,5-aromatic), 130.23 (2,6-aromatic), 135.43 (1-aromatic).

m-Xylylidenebis(malononitrile) (5)

Malononitrile (10.56 g, 0.164 mol) dissolved in ethanol (40 mL) was added to a solution of isophthalaldehyde (11.04 g, 0.082 mol) in hot ethanol (140 mL). The solution was heated at 70°C for 30 minutes, cooled down to room temperature, filtered, washed with cold ethanol (5°C, 2 X 20 mL) followed by ether (2 X 25 mL), yielding **5** as an off-white crystalline solid (17.1 g, 93%). M.P. $179 \pm 1^\circ\text{C}$ (lit. value $177 - 179^\circ\text{C}$). IR (KBr): $\nu_{\text{C}\equiv\text{N}}$ 2231 cm^{-1} . Mass Spectrum = m/e 230 (M^+). $^1\text{H-NMR}$ (CD_3COCD_3): 8.3 - 8.4 (m, 3 H, 2,4,6-aromatics), 8.5 (s, 2 H, vinyl), 7.92 (t, 1 H, 5-aromatic). $^{13}\text{C-NMR}$ (CD_3COCD_3): 85.8 [$=\text{C}-(\text{CN})_2$], 113-25, 114.3 [$\text{C}-(\text{CN})_2$], 131.6 (2-aromatic), 133.52 (1,3-aromatic), 133.57 (5-aromatic), 135.1 (4,6-aromatic), 160.25 [$\text{C}=\text{C}(\text{CN})_2$].

m-Xylylbis(malononitrile) (7)

The compound was synthesized according to the literature procedure with slight modification. The compound **5** was dissolved in DMF (150 mL) and warmed up to 45°C over an oil bath to get light yellow solution. TEAF (46.0 g) was added and the reaction mixture was stirred at 45°C for two hours. The color changed to red wine. Poured into 450 mL of ice cold water to get light yellow precipitate. Filtered, washed with water and suction dried. Recrystallized from hot ethanol (150 mL) yielding (16.5 g, 81%) of light yellow crystals. If the color is dark, add activated charcoal to hot ethanol solution and filtered to get crystals. M.P. $121 \pm 1^\circ\text{C}$ (lit. value $120.5 - 122^\circ\text{C}$). IR (KBr): $\nu_{\text{C}\equiv\text{N}}$ 2262 cm^{-1} . Mass spectrum: m/e 234 (M^+). $^1\text{H-NMR}$ (CD_3COCD_3): 3.46 [d, $\text{CH}_2-\text{CH}(\text{CN})_2$], 4.8 [t, $\text{CH}(\text{CN})_2$], 7.46 (s, 4,5,6-aromatic), 7.51 (s, 2-aromatic). $^{13}\text{C-NMR}$ (CD_3COCD_3): 25.24 [$\text{CH}_2-\text{CH}(\text{CN})_2$], 36.32 [$\text{CH}_2-\text{CH}(\text{CN})_2$], 114.22 [$\text{CH}(\text{CN})_2$], 130.07 (2,4-aromatic), 130.17 (3-aromatic),

131.35(1,5-aromatic), 136.17(6-aromatic).

2-Benzyl-1,3-diaminopropane (8)

Under N_2 , $BH_3 \cdot THF$ (85 mL, 0.082 mol) was added to the refluxing solution of **6** (5.0 g, 32.0 mmol) in THF (25 mL) over a period of an hour. The reaction mixture was refluxed for 4 hours and then cooled down to room temperature. Added concentration and 6.0 M HCl (4.5 and 5 mL ea) to get light yellow precipitate and solvent was removed in vacuo. To the solid residue was slowly added aqueous NaOH (16.0 M, 25 mL). The slurry was heated over an oil-bath at $90^\circ C$ for an hr to get translucent solution. Transferred to a separatory and let it cool to room temperature. Upon standing, the solution formed two layers. The top pale-yellow (sometimes light brown) layer was removed, dissolved in methanol (100 mL), and filtered. Removal of solvent gave pale-yellow oil with some particulates in it. Distillation under vacuum gave **8** as colorless oil (0.5 g, 9 %). B.P. $90-94^\circ C$ (mm Hg): 1H -NMR ($CDCl_3$): 7.2(s, 5 H-aromatic), 2.4-2.7(m, 6 H, methylene, benzylic), 1.8 (m, methine), 0.95 (s, 4 H, NH_2). The compound seems to be impure (see results and discussion).

m-Xylylenebis[2-(1,3-propanediamine)] (9)

$BH_3 \cdot THF$ (140.0 mL, 0.14 mol) was added to a refluxing solution of **7** (6.4 gm, 27.3 mmol) in THF (100 mL) under N_2 atmosphere over a period of 5-6 hours. After addition of 20.0 mL $BH_3 \cdot THF$ solution, a yellow precipitate formed which became thick as addition continued. Refluxed the reaction contents for 9 hours and then cooled down to room temperature. Conc. HCl (12 mL) was cautiously added to the reaction mixture to get light yellow solid. The solvent was removed over

rotavac to obtain yellow solid. Basic hydrolysis with 16.0 M NaOH (45 mL) and workup was carried out similar to the workup of **8** to obtain 6.8 g of crude product. Distillation at 220°C at 0.1 Hg pressure gave **9** as colorless oil. Yield: 0.4 gm, (6%). $^1\text{H-NMR}$ (CDCl_3): 7.1 (m, aromatic), 2.6 (m, methylenes), 1.8 (m, methine). The compound is impure. (See Results and Discussion - Page 3).

C. Synthesis of Schiff Base Complexes

General Procedure, Mn-complexes: In a typical example, the appropriate ligand (1.23 m mol) was suspended in Ar purged distilled ethanol (40 mL) followed by the addition of KOH (2.46 m mol) solution in Ar purged distilled ethanol (25 mL). The mixture was heated until the ligand completely dissolved. To this solution, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.23 m mol) in 20 mL of Ar purged HPLC grade water was added dropwise to get orange/pale precipitate. refluxed the reaction contents for an hr, cooled down to room temperature, and then filtered under Ar to get desired products. each product was washed with deaerated HPLC water (2 x 20 mL) followed by washing with deaerated ethanol (2 X 20 mL). The Complexes were dried under vacuum at $\sim 50^\circ\text{C}$ for overnight and then stored in a Ar-filled glove-box.

Mn(Saloph) (1): Shining orange-red powder. Yield: 80 %. M.P. Decomposed. IR (KBr, cm^{-1}): 3450 br, 1610 vs, 1580 s, 1530 s, 1460 s, 1440 m,sh, 1380 m, 1310 w, 1175 m, 1150 m, 900 w, 645 s. Analysis: Calcd for Mn, 14.88. Found: Mn, 14.5.

Mn[3,3'-(NO₂)₂-Saloph].CH₃OH (2): Orange powder. Yield: 81 %. M.P. 260°C

(decomposed). IR (KBr, cm^{-1}): 1610 vs, 1580 s,sh, 1550 s, 1500 s, 1475 s,sh, 1335 vs,sh, 1300 vs, 1100 s, 940 m, 750 s, 640 m. Analysis: Calcd for Mn, 11.2. Found: Mn, 11.4.

Mn[3,3',5,5'-(NO₂)₄-Saloph] (3): Orange-green powder. Yield: 100 %. IR(KBr, cm^{-1}): 1615 vs, 1585 s, 1515 s, 1450 vs, 1430 s, 1380 m, 1315 w, 1160 s, 855 m, 750 s. Analysis: Calcd for Mn, 10.0. Found: Mn, 10.0.

Mn[3,3',5,5'-(NO₂)₄-Sal-o-ph-3-NO₂] (4): Pale-yellow powder. Yield: 60 %. IR Analysis shows some impurities and requires fresh prep.

Fe[Saloph] (2a) and Fe[3,3'-(NO₂)₂-Saloph] (3a):

In an Ar filled glove-box, anhydrous Fe(OAc)₂ (2.87 m mol) was placed in a Schlenk flask. This flask was fitted with a powder-addition tube containing the desired ligand. The assembly was taken out of the glove-box and fitted with an addition funnel under Ar atm and connected to the vac line. Pure ethanol deaerated with argon (75 mL) was added. The slurry was stirred, and Saloph ligand (2.87 m mol) was slowly added from a powdered-addition tube. A dark olive-green product was formed and the reaction contents were refluxed for 36 hours. The dark olive-green product was filtered, washed twice with deaerated pure ethanol (2 x 10 mL), washed with two 10-mL portions of pure deaerated methanol, and finally dried in vacuo for overnight. Yield in both cases was around 85%.

Analysis: Calcd for $C_{20}H_{14}N_2O_2Fe \cdot C_2H_5OH$ (2a): Fe, 13.41. Found: 13.3 Analysis:
Calcd for $C_{20}H_{12}N_4O_6Fe \cdot 0.5 C_2H_5OH$ (3a): C, 52.2; H, 3.12; N, 11.59; Fe, 10.55. Found: C,
51.54; H, 3.34; N, 11.54; Fe, 10.4.

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7.0 SYNTHESIS OF HIGH SPIN MIXED VALENCE BINUCLEATED IRON COMPLEXES USING A SEPTADENTATE POLYIMIDAZOLE LIGAND

INTRODUCTION

Electronically tuned Porphyrinatometal complexes have been used as light alkane oxidation catalysts that are in some ways analogous to the biological cytochromes P-450. It has been demonstrated at SUN that transition metals in electron-deficient porphyrins have exceptional activity towards light alkanes under mild conditions. Porphyrins and other macrocycles e.g. Schiff bases can be made by derivatizing the peripheral hydrogens by halogen substituents or other electron-withdrawing groups, notably, nitro-, cyano- or carbonyl groups. Halogenated or nitrometalloporphyrins show remarkably positive $M(III)/M(II)$ redox potentials due to the -value of the electron withdrawing groups. These positive potentials may further be enhanced if the metalloporphyrin skeleton is modified. On the other hand, although, metalloporphyrins are very active catalysts for light alkane oxidations, they are difficult to synthesize and expensive to use as an industrial oxidation catalysts under present circumstances.

Another biological catalyst system is methane monooxygenase which catalyzes conversion of methane to methanol. MMO is a non-heme binuclear oxygenase and models of this would not require expensive porphyrin ligands. For this reason we have undertaken the synthesis of a series of binuclear metal complexes which may be able to activate and split oxygen. Electron deficient analogs will be synthesized as part of the Phase VI programs. Investigators carrying out this research were Vincent A. Durante and Brett Ullman.

7.1 Preparation of the Binucleating Polyimidazole Ligand: HBIMP, (2,6-Bis((bis((1-methylimidazol-2-yl)methyl)amino)methyl)-4-methylphenol)

This compound was previously reported in published literature (cited below) and was successfully prepared from the BMIMA intermediate according to the procedure of Mashuta. Several precursors to this BMIMA intermediate were synthesized utilizing literature procedures differing from those of Mashuta, however. Synthetic methodology is detailed below along with appropriate literature references for each step. Spectra associated with each species appear in the appendix.

A. Preparation of 1-methyl-2-imidazole-carboxaldehyde(**1**) (1000746).

The procedure of Oberhausen was followed (J. Oberhausen, J.F. Richardson, and R.M. Buchanan, Polyhedron (1989) **8**, 659) as follows:

1. 8.2g of 1-methylimidazole was dissolved in 250ml of ether and cooled to -45°C in an acetone dry ice bath.
2. 68ml of 1.6M n-butyllithium was cautiously added (the key to this reaction was to use fresh butyllithium) and the mixture stirred for 1 hour.
3. After stirring, 12.5ml of DMF was dissolved in 20ml of ether and quickly added via an addition funnel. The mixture was stirred overnight and the temperature was allowed to slowly rise to 0°C .
4. 10ml of water was added over a period of 15 min. and was followed by 65ml of 4N HCl.
5. The layers were separated and the ether was washed with 5*15ml. portions of HCl.
6. The acid extracts were combined and saturated with potassium carbonate (this had to be added slowly) and extracted 4*30ml of chloroform.
7. The chloroform extracts were dried over magnesium sulphate, filtered and evaporated at reduced pressure.
8. The resulting residue was distilled under vacuum.

The procedure was straight forward, the key to success being the use of fresh butyllithium. The product was isolated by distillation under a vacuum of approximately 40 torr; the product distilled over at approximately 70°C. ^1H NMR (CDCl_3) shows peaks at 4.01, 7.16, 7.27, 9.79. Although the reaction was run several additional times (1000748, 1000757), experimental yields were always found to be lower than those reported by Oberhausen.

SAFETY NOTE: A FIRE EXTINGUISHER SUITABLE FOR BURNING METAL AND PYROPHORIC SOLIDS WAS KEPT IN THE VICINITY OF THE HOOD DURING THIS PROCEDURE.

B. Preparation of 1-methyl-2-imidazole carboxaldehyde oxime

The next step in the synthesis of the binucleating ligand was to prepare 1-methyl-2-imidazole carboxaldehyde oxime (**2**) (1000750, 1000758). The procedure of Oberhausen, cited above, was followed:

1. A solution was made of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.4g) and Na_2CO_3 (1.06g) in 20ml of water (cooled to 0°C), then a solution of **1** ((2.20g) in 10ml of ethanol) was added.
2. A precipitate immediately formed upon mixing of the two solutions. The precipitate was filtered and washed with 30% ethanol (cold) to yield the product (**2**) (~80%).
3. The mother liquor and the washings were combined and evaporated down to ~30ml, cooled to -20°C, and the precipitate (if any) was filtered and washed to yield additional product (usually less than 0.5g).

An improvement to the published procedure involved the vacuum drying of the product prior to the next step. ^1H NMR(CDCl_3) spectra showed peaks at 3.8, 6.95, 7.2, 8.0, 10.1.

C. Preparation of 1-methyl-2-aminomethylimidazole dihydrochloride (3)

1-methyl-2-aminomethylimidazole dihydrochloride was the next compound made in the sequence to the desired ligand (1000751, 1000752, 1000759). The procedure is as follows:

1. A solution of **2** (1.0g in 50ml of methanolic hydrochloride (95:5)) was hydrogenated with 10% Palladium on activated charcoal at 65°C for at least 3 hours.
2. The catalyst was filtered off and washed with 10ml of MeOH•HCl.
3. The filtrate was evaporated to ~30ml and cooled to -20°C and the resulting crystals were filtered and washed with 2 10ml portions of MeOH•HCl to yield ~80%.

The key to the recovery of the product was to evaporate the solvent effectively. The crystals also should be dried in a vacuum oven. ¹H NMR (d₆-DMSO) spectra showed peaks at 4.0, 4.43, 7.75, 7.77, 8.25.

D. Preparation of Bis(2-(1-methylimidazolyl)methyl)amine trihydrochloride

Bis(2-(1-methylimidazolyl)methyl)amine trihydrochloride (**4**) (100753, 1000761) was synthesised by the procedure outlined by Oberhausen. The procedure is as follows:

1. A solution was made of **3** (2.0g) and KOH (0.6g) in 50ml of methanol. It was added to a solution of **1** (1.2g) in 50ml of methanol.
2. The mixture of solutions was hydrogenated at room temperature over 10% Pd/C for 4 hours.
3. The catalyst was filtered off and the solvent was reduced to 25ml, then the KCl was filtered off.
4. 100ml of MeOH•HCl was added to the filtrate and the combined solution was cooled to -20°C, the precipitate was

filtered and washed twice with 10ml portions of MeOH•HCl to give a yield of ~50%.

E. Synthesis of Bis(2-(1-methylimidazolyl)methyl)amine, (B-MIMA) (5)

(B-MIMA), bis(2-(1-methylimidazolyl)methyl)amine, was the last compound synthesised according to the Oberhausen procedures. The procedure is as follows:

1. 1.88g of **4** was dissolved in a saturated K_2CO_3 solution and extracted 5 times with 50ml of chloroform.
2. The combined chloroform extracts were dried with magnesium sulphate and the solvent was removed to give a yield of ~30%.

The low yield of product may have been caused by a poor extraction. A second attempt to prepare this compound, 1000762, was unsuccessful. Run number 1000755 generated the correct product but with the low yield reported above.

F. Synthesis of 2,6-(hydroxymethyl)-p-cresol

2,6-bis(chloromethyl)-4-methylphenol was synthesised by first making 2,6-(hydroxymethyl)-p-cresol according to a procedure by Ullmann and Brittner,

(Chemische Berichte (1909), 2539-2548). Brett Ullmann translated the procedure from German, and it is as follows:

1. 10.8g of p-cresol and 5.07g of NaOH were added to 20ml of distilled water.
2. 22.84g of formaldehyde (32.94%) were added to the solution, and the mixture was allowed to set for 4 days. Crystals began to fall out of solution after the first day.
3. The crystals were filtered off and washed with brine.
4. The crystals were dissolved in water and the solution was neutralized with glacial acetic acid and colorless crystals fell out of solution. The solvent was filtered off and the crystals were recovered, to give a yield of ~90%.

G. Synthesis of 2,6-bis(chloromethyl)-4-methylphenol

This synthesis was first performed by Dave Kisailus of our laboratory (1000732). His work was repeated successfully by Brett Ullmann (1000774) according to a procedure outlined in E. Ziegler, Ber., (1944), **77B**, 731-735. The procedure was as follows:

1. Dissolved 10g of 2,6(hydroxymethyl)-p-cresol in 50ml of benzene and stirred well.
2. Added 100ml of 12N HCl and stirred at room temperature until the aqueous phase (lower) was clear.
3. The layers were separated and the benzene layer was dried with non-indicating Drierite.
4. The Drierite was filtered off and the benzene solution was evaporated to dryness to give a yield of ~90%.

Synthesis of this product was also attempted by another route, unsuccessfully.

The alternative procedure had been suggested in the literature, Borovik, J. Am. Chem. Soc., (1989), **111**, 6183-6195. The reaction involved the addition of thionyl chloride (instead of HCl) in methylene chloride. The mixture was stirred for 24 hours and then neutralized with $\text{NaOH}_{(\text{aq})}$. The aqueous solution then was extracted with methylene chloride. The methylene chloride solution was dried and evaporated to yield the product. In our attempts at using this procedure, it is possible that too much NaOH had been added which consequently caused a polymerization of the product.

H. Synthesis of 2,6-Bis((bis((1-methylimidazol-2-yl)methyl)amino)methyl)-4-methylphenol, (Hbimp)

The compound 2,6-Bis((bis((1-methylimidazol-2-yl)methyl)amino)methyl)-4-methylphenol, (Hbimp) (1000763) was synthesised by a procedure outlined by Mashuta in J. Am. Chem. Soc. (1992), **114**, 3815-3827:

1. 0.925g of BMIMA was dissolved in 55ml of THF with 0.718g of triethyl amine.
2. A solution of 2,6 Bis(chloromethyl)-p-cresol (0.458g in 15ml THF) was added to the BMIMA soln. and mixture was stirred for 4 hours.
3. The crystals were filtered off, the filtrate dried on a rotoevaporator, and the crude oil dissolved in ~100ml of H_2O and made alkaline with KHCO_3 .
4. The solution was extracted 3 times with 50ml of methylene chloride, dried over MgSO_4 , and dried under reduced pressure to give a yield of ~60%.

^1H NMR (CDCl_3) spectra showed peaks at 2.20, 3.30, 3.69, 3.70, 6.76, 6.83, 6.90.

The ligand was also characterized by, electronic spectroscopy, Pyroprobe mass spectroscopy, and FTIR spectroscopy.

7.2 Synthesis of Metal Complexes using HBIMP Ligand

This ligand, HBIMP, was used for the synthesis of several coordination complexes and derivatives which remain only partially characterized at this time. Attempts were made to prepare diiron, diruthenium, and mixed iron-ruthenium complexes in various permutations of oxidation state. One of these had been previously reported in the literature, $(\text{Fe}(\text{II}), \text{Fe}(\text{III}) (\text{BIMP}) (\mu\text{-carboxalato})_2)(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$, and was prepared as a reference compound. A zinc salt was also prepared which was used for an attempted chlorination of the ligand. These attempts are described below according to the expected products.

A. Preparation of $(\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}(\text{bimp})(\mu\text{-O}_2\text{CCH}_3)_2)(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$

$(\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}(\text{bimp})(\mu\text{-O}_2\text{CCH}_3)_2)(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared according to the procedure described by Mashuta, (Mashuta, "Electron Transfer in $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ Model Complexes of Iron-Oxo Proteins", *J. Am. Chem. Soc.*, (1992), **114**, 3815-3827) as follows:

1. A solution of 0.010g of Hbimp and 0.0038g of sodium acetate in 10ml of methanol was slowly added to a solution of

$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10ml of methanol, and the solution was stirred for several hours.

2. The solution was reduced and filtered to yield blue crystals.

3. The crude product was dissolved in acetonitrile and layered with toluene and evaporated off with argon to yield dark blue crystals.

The successful preparation of this complex is presumed since characteristic NMR spectra and quantitative elemental analysis of iron have not been completed as of this time.

The mixed valence nature of the iron gives rise to an intervalence charge transfer absorption band in the near IR; samples will be sent to California Institute of Technology for measurement of this band. FAB-mass spectra will also be conducted.

8.0 NEW SUPPORTED CATALYSTS

Workers who contributed to this section are:

Bonnie Marcus

Vincent Durante

James E. Lyons

Walter Seitzer

8.1 Catalyst Design Criteria and Background

We have demonstrated that oxidation-active first-row transition metals in the framework of zeolitic structures catalyze the oxidation of methane to methanol if certain criteria are met. We have put high loadings of iron - up to 15% - in the sodalite framework, Figure 1. If no extra framework iron were present, catalytic activity was low, but if, in addition to high framework loadings, iron also occupied exchange sites, $\text{Fe}_x[\text{Fe}]\text{SOD}$, an active catalyst resulted, Table 1. This behavior was rationalized on the basis that framework iron could not readily reduce to iron(II) - its Fe(III)/(II) reduction potential was too low. This is due to the constraints of the sodalite system which accepts Fe(III) but not Fe(II) . Iron in the exchange site can be reduced to Fe(II) and activate oxygen. Cooperative Fe(II)/Fe(III) sites can bind and cleave dioxygen, Figure 2. An iron aluminophosphate was then prepared and tested which, though active, was inferior to $[\text{Fe}]\text{SOD}$.

We have made many attempts to incorporate manganese into hydroxysodalite in our laboratories but they have not yet met with success. We reported recently, however, that we were able to get up to 8% manganese into an aluminophosphate structure. This catalyst has activity comparable to

$\text{Fe}_x[\text{Fe}]\text{SOD}$ although it has far less metal. Manganese(II) has been shown to be capable of incorporation into aluminophosphate structures so it may not be necessary to use extra framework manganese to get methane oxidation activity provided that manganese loadings are high enough to encourage cooperative oxygen binding between Mn sites. We are in the process of making a number of aluminophosphates with high loadings of manganese to test in the near future. With the ability of certain zeolites to accept Mn(II) into the framework we are nearing the kind of catalyst which will exhibit C-H bond homolysis activity needed to activate methane.

FIGURE 1

LIGHT ALKANES TO LIQUID OCTANE
METHANE TO METHANOL

CATALYST = 15% Fe IN SODALITE

CONDITIONS: T = 420°C, G HSV~600, 3/1 METHANE/AIR

TABLE 1**VAPOR PHASE AIR OXIDATIONS OF METHANE TO METHANOL^a**

Catalyst	GHSV h ⁻¹	Bed T °C	CH ₃ OH Sel., %	CH ₄ Conv., %	O ₂ Conv., %
[Fe]SOD	530	407	64	4.6	76
		416	70	5.7	90
		418	68	5.4	91
		422	65	5.4	92
		432	63	5.5	90
		442	64	6.1	90
SOD	530	404	-	0.0	0
		430	9	0.3	4
		445	24	5.1	84
Fe _x O _y /SiO ₂ (12.5%)	530	431	26	5.1	85
		700	10	0.5	11
		409	18	1.2	15
		420	20	2.7	74
		428	23	3.9	83

^a A 3/1 methane/air mixture (800psig) was passed over the catalyst

FIGURE 2
METHANE OXIDATION PATHWAYS OVER $\text{Fe}_x\text{Fe}[\text{SOD}]$

Whether active solid iron, manganese or chromium catalysts are used, we have envisioned the reaction as occurring by homolytic scission of the C-H bond of methane on the surface. Methyl radicals leave the surface and initiate gas phase oxidation to form methanol, Eq. 9-12.

In-depth kinetic analysis of this process indicates that it is unlikely that selectivities as high as 80% to methanol at methane conversions in excess of 20% could be realized by a catalyst that operates exclusively by this mechanism. Figure 3 shows the drop in methanol selectivity predicted to occur for uncatalyzed gas phase methane oxidation under a representative set of conditions as conversion is increased. An hypothetical catalytic reaction which forms methyl radicals in greater abundance than the catalytic reaction will give higher selectivity. Figure 4 shows that as methyl radical flux increases, selectivity goes through a maximum. Our kinetic model predicts that this maximum is less than 70% under all conditions which we examined, when methane conversion was 10% or higher. Proprietary economic analysis carried out in-house suggests that this performance would not produce a highly attractive commercial process.

FIGURE 3

METHANE OXIDATION

815 psia , 430° C, METHANE : AIR MIXTURES
EMPTY REACTOR
COMPLETE CONSUMPTION OF OXYGEN

FIGURE 4

METHANE OXIDATION
 CATALYZED $\text{CH}_4 + \frac{1}{4} \text{O}_2 \rightarrow \text{CH}_3 + \frac{1}{2} \text{H}_2\text{O}$
 815 psi, M: AIR = 3:1, 400° C

For this reason we have now embarked on the synthesis of a series of catalysts which are designed to have oxidation-active metals capable of homolytic scission of C-H bonds but which retain the intermediates on the surface long enough to form methanol. It is our intent to place these metals into a hydrophobic environment in order that methanol be expelled from the surface as formed. Such a catalytic process if successfully carried out will not have the yield limitations of the gas phase autoxidations. Ideal temperatures will be in the 250°-300°C range which puts demands on the metal centers for higher activity than we have observed to date.

It will be necessary that these new catalysts, therefore, meet the same suprabiotic criteria, as their homogeneous counterparts, Figure 5.

FIGURE 5

PROPERTIES OF A SUPRABIOTIC CATALYST

- COOPERATIVE IRON (II) SITES

- LIPOPHILIC ENVIRONMENT

- HIGH $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ REDUCTION POTENTIAL^I

* HYDROPHOBIC ENVIRONMENT

- SUPPRESSED μ -OXO FORMATION

- STABILITY TO OXIDATION

8.2. Recent Results on Characterization of Iron Sodalite - a Methane Oxidation Catalyst

Iron sodalite which has been synthesized so that there are iron centers in both the framework and ion exchange sites has been shown by us to be an active catalyst for converting methane to methanol, U.S. Patent 4,918,249,1990. Methanol could be obtained in up to 70% selectivity at up to 7% methane conversion.

On the other hand, improperly prepared iron sodalite as well as other iron-containing zeolites are not active methane oxidation catalysts. We suspect that access to appropriate iron oxidation states may be the determining factor in this and a high Fe(III)/Fe(II) reduction potential may facilitate surface activation of oxygen. For this reason, we have undertaken a program of work to begin to understand surface oxidation states and their interconvertability.

Workers who have contributed to this section are

Mark Davis

James E. Lyons

Vincent A. Durante

Cyclic voltammetry of iron zeolites

CV traces may be obtained from solid zeolite samples bound in a paste with carbon and coated onto electrodes. As-synthesized Fe sodalite having no exchanged Fe, following the approximate conditions used by Sun, exhibits a reversible waves around +0.05V Table 1, (Figure 1), quite different from the literature dta for Fe^{III}-exchanged Y (peaks around +0.5V), but similar to that found for Fe-ZSM-5. (Calcined Fe sodalite shows no CV at all.) This suggests CV may be useful for characterization of redox-active ions in zeolites, particularly in distinguishing between exchange and framework sites.

TABLE 1

CV Data on Fe³⁺-Exchanged and Fe³⁺-Incorporated Molecular Sieves

Sample	Si/Fe in the gel	Co-Cations	Electrolyte (pH)	Formal potential, E ⁰ (V vs. SCE)	Ref.
Fe ³⁺ -NaY	-	Na ⁺	0.1 M NaCl in CH ₃ CN	+0.48	a
Fe ³⁺ -NaX	-	Na ⁺	aq. 0.1 M NaCl (< 2)	+0.5	b
Fe-SOD	7.5	Na ⁺ , TMA ⁺	aq. 0.1 NaCl (5.75)	+0.04	this work
Fe-MFI	30	TPA ⁺	aq. 0.1 NaCl (5.75)	+0.04 (E _{p,c})	this work

^a Phani, K. L. N.; Pitchumani, S. *Electrochim. Acta* **37**, 2411 (1992).

^b Iwakura, C.; Miyazaki, S.; Yoneyama, H. *J. Electroanal. Chem.* **246**, 63 (1988).

FIGURE 1

**Cyclic Voltammetry
of Iron-Containing Molecular Sieves**

8.3 SYNTHESIS OF NEW SUPPORTED CATALYSTS

A systematic study of the material properties that are useful in this process has been started. This study will include complete characterization of the materials of interest. To be successful, the catalytic materials should cleave C-H bonds, hold on to the methyl radicals until they react, make methanol and expel it into the vapor phase. In addition to the necessary surface properties, the catalyst should have binuclear metal sites that can cleave oxygen in such a way that the oxygen atoms are available for reacting with the radicals to form alcohol. The metal sites must be at the O-O bonding distance, and the framework must accommodate changes in oxidation state of the metals.

8.3.1 Hydrophobic Zeolites Carbons and Silicas

Based on these requirements, the initial surface property that is being studied is hydrophobicity which will enhance the rebound of the alcohol into the vapor phase after formation. A series of materials including zeolites, carbons and silicas with different degrees of hydrophobicity have been chosen and are being loaded with metal complexes to determine if their hydrophobicity improves the catalytic activity. Two zeolites, silicalite and fluoride silicalite, have been synthesized and loaded with a phthalocyanine. Fifteen carbons and silicas have been tested for hydrophobicity, and five materials have been chosen for loading with metal complexes of interest: PQ CS1231G silica, Cab-o-Sil fumed silica, Degussa W54 carbon, Calgon Xtrasorb Carbon, F graphite. These materials have also been loaded with phthalocyanine. A total of seven loaded and four unloaded

materials have been submitted for testing.

INTRODUCTION

The initial surface property studied was the effect of hydrophobicity to enhance rebound of the alcohol after formation. A series of materials with different levels of hydrophobicity were chosen for study and were loaded with various metal complexes to determine if the hydrophobicity enhances the catalytic activity.

The materials chosen for the hydrophobicity study include two zeolites: silicalite and fluoride silicalite. Silicalite is an all-silica polymorph of ZSM-5 and is quite hydrophobic. When silicalite is prepared with fluoride in the reaction gel, the terminal OH groups are replaced by F atoms, and the material becomes extremely hydrophobic. A series of silicas and carbons were also studied, and those that had different degrees of hydrophobicity were identified.

Metals in framework sites have been extensively studied. Due to the limitations on the amount of metal that can be incorporated into a framework, other materials that have potentially higher metal levels are being studied. The system of interest being investigated first is hydrotalcite and hydrotalcite-like clays. These materials are anionic clays that have ion exchange capacity that can be varied by changing the framework composition. In addition, the size of the gallery where the exchangeable anion is located can be changed by varying the anion. It is hoped that the metals in the

layers and the metal ligands exchanged into the galleries will form catalytically active sites.

The silica and carbon supports are available commercially, and the zeolites can be synthesized in-house with relative ease; the hydrotalcite materials are a synthetic challenge. It is not possible to use one standard preparation method and vary the framework composition; each preparation requires different synthesis conditions (temperature, order of addition, pH, post treatment, etc.), and therefore this area represented a longer term synthesis project.

RESULTS AND DISCUSSION

Hydrophobic Supports

Zeolites - The silicalite and fluoride silicalite were both synthesized in-house to assure similarity in particle size and composition. The fluoride silicalite was prepared following USP 4,073,865 Example 1; the details are in the Experimental Section. The first preparation digested at 150°C, did not appear to be fully crystalline when examined under an optical microscope, and the XRD showed the presence of amorphous material and a poorly crystalline F-silicalite. The second preparation was digested at 200°C and had excellent crystallinity (Figure 1). The sample was calcined at 600°C for two hours in air to remove the organic template.

The silicalite was prepared following the same patent example. Under the optical microscope, the material appeared to be very crystalline, and the XRD was consistent with a well crystallized silicalite (Figure 1). The sample was calcined for 3 hours at 600°C in air to remove the organic template. It was then treated with a 10% aqueous HCl solution at 80°C for one hour to remove the residual alkali. The XRD of the post calcined and acid washed sample showed excellent crystallinity.

F-silicalite displays a high degree of hydrophobicity due to the replacement of the external hydroxyl groups with fluorine atoms. IR's of the terminal silanol region (3720 cm⁻¹) were done. The F-silicalite as synthesized and calcined showed no band present; the silicalite did have a band present.

A method to perform 950°C loss on ignition (LOI) on small quantities of sample was developed and is detailed in the Experimental Section. The LOI's of the silicalite and F-silicalite were:

F-Silicalite (as-synthesized)	10.98%
F-Silicalite (calcined)	1.01
Silicalite (as-synthesized)	13.92
Silicalite (calcined, acid washed)	0.45

Chemical analyses of the materials is pending, but the materials were used as a support for Fe(FPc)Cl, a phthalocyanine supplied by Paul Ellis.

Fe(FPc)Cl was tested for solubility with a number of organic solvents, and was found to be the

most soluble in THF. Loadings were done on a standard weight/cc basis because the test reactor uses a fixed volume of material. Each impregnation was done by incipient wetness of clear phthalocyanine solution; after each loading THF was added to dissolve additional material. This was continued until all of the phthalocyanine was dissolved and added to the support. The zeolites were dried at 90°C after each treatment. The 4.66 grams of silicalite required ten impregnations which yielded .05mmols/cc (0.079mmols/g). The F-silicalite (4.12g) also required ten impregnation resulting in .055 mmols/cc (0.095mmols/g).

The zeolites were loaded as powders; the optimum particle size for the reactors is 18/35 mesh. Normally, the powders would be bound with a material such as silica to provide hardness and then meshed to the proper size. In this case, the surface characteristics of the materials should not be changed by binding them with a material that would alter the hydrophobic properties, so self-supported meshes were made. These meshes were extremely friable.

The silicalite sample was different shades of green, indicating uneven coverage of the phthalocyanine onto the material. The F-silicalite appeared to have green material present that looked liked recrystallized phthalocyanine. The pore size of silicalite is 6 Å, and the phthalocyanine is not expected to go into the opening. The uneven coverage could be an indication that the level of coverage attempted was too high.

Carbons and Silicas - A series of commercial carbons and silicas was tested for hydrophobicity by calculating their loss on heating (LOH) and their water uptake upon hydration. The procedure is detailed in the Experimental Section. The materials tested, their properties and the results are listed in Table 1.

The materials loaded with Fe(FPc)Cl were: PQ CS-1231G, Cab-o-Sil, Degussa W54, Calgon Xtrasorb 700, F-Graphite. The procedure used was the same as that used for the zeolite loadings. The number of impregnations needed varied from 6 to 12. The materials that were powder were made into self-supporting mesh that was very friable. A total of 7 samples loaded with Fe(FPc)Cl were submitted for testing as oxidation catalysts; 4 materials were supplied unloaded as blanks for testing.

TABLE 1

Material	Reported S.A. m²/g	Determined S.A. m²/g	LOH %	Water Gain %
Anderson Carbon Super A	2800 - 3500	2200	0	92
Degusorb W54	1300 +/- 50	1300	3.7	49
Nuchar WV-B	1600 - 1800	1500	9.7	63
Calgon Xtrasorb 700	---	612	0.8	41
Aldrich (CF _x) _n		179.2	0	6.1
Huber Amorphous Precipitated Silica				
CH650-60-3			8.7	29
CH650-60-5			7.7	25
CH650-60-1			11.1	25
CH650-60-2			12.5	36
CH650-60-4			11.8	33
PQ CS-10-20			30.0	33
PQ CS-12-31	220		6.1	48
PQ CS-21-33	333		0	30
PQ CS-1231G			0	2.3
Cab-o-Sil Fumed Silica			0	0.22

DATA AND EXPERIMENTAL PROCEDURE

F-Silicalite (USP 4,073,865, Ex. 1)

Gel Ratio: $0.166\text{NH}_4\text{F} \cdot 0.791\text{SiO}_2 \cdot 0.02(\text{TPA})_2\text{O} \cdot 0.063\text{Na}_2\text{O} \cdot 11.2\text{H}_2\text{O}$

Reagents: NH_4F , Nyacol Silica, NaOH , TPABr

Procedure: Dissolve NH_4F in approximately 1/3 of the water

Add to silica + 1/3 of the water using a mechanical stirrer

Add NaOH in 1/6 of the water with stirring

Add TPABr in 1/6 of the water with stirring

Stir for 3 to 4 minutes and measure the pH

Put the gel into a Teflon-lined stainless steel pressure vessel and digest at 200° for 4 days. The bombs are heated quiescently under autogeneous pressure.

The reaction mixture was cooled, removed from the bomb, the pH was measured and the sample filtered and washed with distilled water.

Silicalite (USP 4,073,865, Ex. 1)

Gel Ratio: $2.0(\text{TPA})_2\text{O} \cdot 6.5\text{Na}_2\text{O} \cdot 0.80\text{SiO}_2 \cdot 1105\text{H}_2\text{O}$

The reagents and procedure are the same as above, but the digestion temperature is 150°C .

Loss on Ignition (LOI) Procedure

Heat crucibles to 400°C , remove at 200°C and store in desiccator.

When cool, weigh crucibles without handling.

Add sample and re-weigh without handling.

Heat for 2 hours at 950°C .

Remove at 200°C and store in desiccator.

When cool, weigh without handling crucibles.

The difference in the weight divided by the starting weight x 100 = LOI

Hydrophobicity Procedure

Place the sample into a crucible and weigh.

Heat at 250°C for 24 hours under vacuum.

Remove at 80°C, cool in desiccator and weigh; weight loss divided by the starting weight $\times 100 =$ Loss on drying (LOD).

Place into a hydrator at approximately 85% relative humidity (saturated Na_2CO_3).

Weigh the sample every day until the weight stabilizes. The gain on hydration (GOH) is calculated by the weight gain divided by the LOD weight $\times 100$.

The LOD is repeated on the hydrated sample to assure accuracy.

Characterization of Catalyst

Samples that were supplied for catalytic testing were characterized. The measured surface areas were:

Calgon Xtrasorb 700 carbon	612 m ² /gm
Fluoride Graphite	179 m ² /gm
Fluoride Graphite	168 m ² /gm calculated from the dry weight
AX 21 Carbon	2207 m ² /gm
XS700 Carbon	1142 m ² /gm

The relative hydrophobicity of the zeolites was determined:

Calcined, acid washed silicalite	5.56% Loss on Drying
	11.8% Gain on hydration
Fluoride Silicate, as synthesized	0% Loss on Drying
	0% Gain on Hydration

Fluoride Silicalite, calcined

6.67% Loss on Drying

0% Gain on Hydration

The chemical analyses of the zeolites were obtained:

Silicalite, as synthesized

SiO ₂	95.01 wt. %
Na ₂ O	1.52
L.O.I.	3.14

Fluoride Silicalite, as synthesized

SiO ₂	85.81 wt. %
Na ₂ O	0.51
L.O.I.	11.14

Fluoride Silicalite, calcined

SiO ₂	101.22
Na ₂ O	0.32
L.O.I.	1.01

REFERENCES

1. USP 4,073,865, Flanigen, E. M., Patton, R. L., "Silica Polymorph and Process for Preparing Same", Feb. 14, 1978.
2. Petrosius, S.C., Drago, R. S., "Decomposition of Chlorinated Hydrocarbons Using Metal Oxides Supported On carbonaceous Adsorbents", J. Chem. Soc. Chem. Comm., 1992, 344.
3. Huber Silicas are experimental products from J. M. Huber Corporation.
4. PQ Silicas are catalyst supports from PQ Corporation.

Figure 1

FN: BM1002828.NI

ID: #10028-28 SILICALITE 48-516 BKM

SCINTAG/USA

DATE: 02/25/93

TIME: 14: 24

PT: 0.60000

STEP: 0.02000

WL: 1.54060

Characterization of the hydrophobic supports described above was completed. The loaded materials were not homogeneous; the metal agglomerated on the surface even with low loadings.

8.3.2 Hydrotalcites as Hydrophobic Supports of Oxidation-Active Metal Centers

In the oxidation of an alkane to an alcohol one important property that is being studied is the presence of binuclear metal sites that can cleave oxygen in such a way that the oxygen atoms are available for reacting with methyl radicals to form alcohol. It is necessary to have a greater number of sites per unit volume than was found in previously studied materials, and they must be at the O-O bonding distance. In addition, the framework of the materials must be able to accommodate changes in the oxidation state of the metal.

The amount of metal that can be incorporated into a zeolite framework is limited, therefore other materials of interest are being investigated. The first materials of interest are the anionic clays that have exchange capacity that can be varied by varying the composition. Anionic clays can be considered to be positively charged sheets of metal hydroxides between which are charge balancing anions and water. The positively charged sheets must contain two different metals in different oxidation states:

The main features of HTlcs are determined by the nature of the brucite-like sheet of metal hydroxides, by the position of the anions and the water in the interlayer space and by the type of stacking of the brucite-like sheets.

The clays are homogeneous, have a large surface area and are stable to thermal treatments. It is possible to synthesize HTlcs with different stoichiometries and hence, different exchange capacities. However, there is a maximum capacity that can be achieved, and that is approximately 4.4 meqs/g. Post synthesis treatments to increase the amount of aluminum in the brucite layer without having it be in the interlayer space would be difficult; the treatment would have to remove Mg and re-insert Al into the layer. There is also a maximum amount of aluminum that can be in the layer regardless of the technique employed. At high levels of aluminum, adjacent aluminum atoms

become octahedral and form $\text{Al}(\text{OH})_3$ which pops out of the layer. An analogous situation exists with magnesium. Levels of aluminum at the reported maximum are also difficult to ion exchange due to the increased electrostatic interactions between the brucite layer and the interlayer cations. Therefore, the upper limit of exchange capacity may be too low for our catalytic purposes.

Other methods that could increase the amount of metal include having it present in the interlayers and/or in the brucite layer. The Mg/Fe analogue of HTC is pyroaurite which has the Fe and Mg in the layers.

RESULTS AND DISCUSSION:

Hydrotalcite Preparation

Gel Ratio: $6.4\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 1.6\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 3.2\text{Na}_2\text{CO}_3 + 1.5 \text{NaOH}$

Procedure: Addition of Mg and Al solutions separately to a $\text{NaOH}/\text{Na}_2\text{CO}_3$ solution ($\text{Al}/\text{CO}_3^{2-}=2$).

Maintenance of the pH at 8 to 10 during addition by changing the addition rate.

Addition at 60°C .

Stir at 60°C for one hour.

Filter, wash with hot distilled water.

Reslurry with water and treat hydrothermally under autogeneous pressure
in stainless steel reactor vessels.

Filter, dry.

Results: pH of this preparation was too low, and required the addition
of 2M NaOH to maintain it at approximately 8.

10028-38-1: Dried at 100°C - HTC, hydromagnesite

10028-38-2: HT at 200°C - HTC and magnesite

Gel Ratio: $6.4\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 1.6\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 3.2\text{Na}_2\text{CO}_3 + 4\text{NaOH}$

Procedure: Add the Mg and Al solutions together and add to NaOH/Na₂CO₃ solution.
Rest of procedure the same.

Results:

10028-45-1: 150°C - HTC, magnesite

10028-45-2: 115°C - HTC, magnesite, hydromagnesite

10028-45-3: Dried 90°C - HTC, hydromagnesite

These preparations of hydrotalcite-like (HTlc) clays produced a mixture of HTlc and magnesium carbonates. We then attempted to identify synthetic routes that would produce pure materials with a range of ion exchange capacities. The first preparation followed a procedure published by Reichle¹ and used the nitrates. The HTlc properties were reported to be: $\text{Mg}/\text{Al} = 2.49$, $x = 0.286$, $[\text{Mg}_{5.71}\text{Al}_{2.29}]$. Using the gel ratios reported, a precipitate did not develop, and

the final pH was too high. No hydrothermal treatment was done on the sample. The final product was a mixture of HTlc, magnesite and an unidentified impurity.

A method reported by Miyata² using chlorides, was used to try to prepare HTlc with $x = 0.33$, $Mg/Al = 2.03$, $[Mg_{5.36} Al_{2.64}]$. In this preparation, anhydrous aluminum chloride was used. The final pH of the prep was higher than desired. The precipitate was hydrothermally treated at 125° and 150°C for 18 hours. The x-ray patterns of both products was consistent with HTlc. Hydrothermal treatment is a common synthetic route in the production of zeolites. In the clays, it was used to attempt to produce a materials with slightly larger particle size that was easier to filter, was more crystalline and had an XRD that was easier to interpret.

In an attempt to make very pure material with an easier synthetic route, a modification of the preparation was done that involved lowering the pH and using hydrated $AlCl_3$. The final pH of the gel was low and was adjusted with aqueous NaOH. Hydrothermal treatment was done at 125° and 150°C, and both temperatures produced excellent HTC after 20 hours (Figure 1).

A further modification of the preparation was done to attempt to increase the pH, decrease the water and increase the available carbonate for pillaring. This prep was hydrothermally treated at 150° and 170°C

for 24 hours. These preps were extremely difficult to filter and produced HTlc that showed some peak splitting and line broadening at higher 2θ values in the XRD indicating short range disorder. There was also one extra peak that was not able to be identified.

Additional modification of the preparation scheme was used to prepare an HTlc at the upper limit of the amount of aluminum that can be incorporated, $x = 0.35$. It was prepared using more base to increase the final pH and with a high level of carbonate. Hydrothermal digestion at a lower temperature was attempted (125°C) in addition to 150°C for 18 hours. Both produced excellent HTC, but the crystallinity of the 150°C prep appeared to be better.

Based on the data from these and the previous preparations, a procedure was developed that produced excellent HTlc reproducibly; it is detailed in the Experimental Section. Details of the HTlc preparations are in Appendix 2.

The literature values for the Mg/Al ratios that are considered to have all of the Al in the brucite layer are 2.03 to 4.0. A prep with a Mg/Al outside of that range (1.70) was attempted in order to try to produce a material with a large ion exchange capacity. The product was HTlc with numerous impurity peaks that could not be identified using JCPDS. An attempt to make a low ion exchange material (Mg/Al = 4.0) produced poorly crystalline HTlc.

Characterization of the materials made was undertaken. From the XRD, it is possible to determine the interlayer spacing that is available for the exchanged anions. The thickness of the unit layer which includes one brucite layer and one interlayer space is the d_{003} spacing. A brucite layer in the $\text{Mg}^{+2}\text{Al}^{+3}\text{CO}_3^{-2}$ at 26°C is 4.769 Å. The thickness of the interlayer space is the difference between the unit layer and the basic layer. In the carbonate system, this value is generally around 2.8 - 2.9 Å; the values for the materials produced this quarter fall within this range.

The interlayer spacing can also be determined from the cell dimensions. Hydrotalcite $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4] \cdot 7\text{H}_2\text{O}$ is rhombohedral; varying the Mg/Al gives hexagonal symmetry, and the c dimension is three times the d_{003} spacing. The XRD hkl assignments were used to calculate the cell dimensions, using two different programs (LATCON, Nelson-Riley) available. The best match with the XRD data was the LATCON program.

Changes in cell dimensions that occur are due to both brucite and interlayer changes. The value of the interlayer space changes as the size of the anion is changed, and calculating the space from the cell dimensions is a way to measure the efficiency of ion exchange. The c dimension also changes as the amount of aluminum is changed: it decreases as the aluminum content of the brucite layer increases. This is due to the electrostatic interaction between the aluminum and the interlayer anions. It is possible to correlate this change in cell dimension with aluminum insertion into the brucite layer.

Anions and water are randomly located in the interlayer region and are free to move by bond breakage and formation. In order to determine the amount of interlayer and structural water present, loss on ignition (L.O.I.), loss on drying (L.O.D.) and DSC/TGA were used. The L.O.I. measures the total weight loss after heating to 900°C which includes the physadsorbed and interlayer water and carbonate and should agree with the total weight loss seen in the TGA. The L.O.D. at 105°C gives an approximate amount of physadsorbed water.

The HTlc literature lists three endothermic peaks in the DTA: approximately 127°C due to physadsorbed water and interlayer water (~11 wt. %); 367°C and 437°C due to dehydroxylation of structural water and the loss of CO_3^{2-} (~35wt%). The DSC's of the materials synthesized all had three peaks at approximately 225-235°C, 310-315 and 405-420; the weight losses from the TGA were 13-15% for the first peak and 18-29% for the other two. These data can be used to determine the interlayer and structural water: the weight loss from the first peak - LOD = interlayer water; total weight loss - first peak loss = structural water.

Chemical analyses of the clays produced were done to assure that the materials matched the gel ratios. The results are found in the Appendix 3. Generally, they were in agreement, but in several cases the mass balance of the reported data was not good.

Another goal of this study was to make HTlcs with different ion exchange capacities and then

exchange metal ligands into the interlayer spaces to form catalytically active materials. One sample of high aluminum content ($x=0.34$, $Mg/Al=1.73$) was exchanged with iron(III)-tetra-(4-sulfanato-phenyl)-porphyrin, Na salt. The exchange capacity of the clay was 4.38 meqs/g. The exchange was done under nitrogen to minimize the amount of carbonate that could be formed. A self-supported mesh was submitted for testing. The results were not good, and a second sample was prepared using multiple exchanges on a clay sample that had an $Mg/Al = 1.84$ ($x=0.35$); the exchange capacity was 4.41 meqs/g. The sample was exchanged twice and bound with 20% silica (a second preparation did not require a binder). An x-ray of the material showed no increase in the interlayer spacing, and this indicates that the exchange was not complete. This could be due to diffusional limitations since the anion that is being exchanged is larger than the one being replaced. Clays with larger interlayer anions would be a solution. One attempt was made to ion exchange in a larger cation, terphthalic acid, that would then be exchanged for the ligand of interest. Again, there was no increase in the interlayer spacing. Direct synthesis of materials with larger cations is necessary for incorporation.

Metals of interest can also be placed into the interlayer spaces during synthesis. Miyata and Hirose³ reported the preparation of $[(Mg_{0.741}Al_{0.259})(OH_2)](Fe^{II}(CN)_6)_{0.067}(CO_3)_{0.002}(H_2O)_{1.05}$. This material has a structure that is a repetition of a positively charged brucite-like layer and an interlayer consisting of $(Fe^{II}(CN)_6)^{4-}$ anions and water. In the HTlc system, the anion is generally carbonate, and it is difficult to prepare it without carbonate because CO_2 is readily adsorbed from the air during

preparation. However, higher valence anions are more readily incorporated, and this should decrease the amount of CO_2 that is incorporated.

The material is of interest because the iron is in the layers, and the interlayer spacing is 3.52 Å greater than that of HTC allowing more room for reactions to occur. It also would make it easier to ion exchange other anions of interest into the interlayer space.

The first preparation was done with no hydrothermal treatment, and the produced the desired product with low crystallinity on the XRD. The prep was repeated with 125 and 150°C hydrothermal treatment and produced the desired product at both temperatures, but the 150°C treated material was more crystalline. One interesting observation was that the preps prepared without hydrothermal treatment produced a green solid indicative of Fe(III). The prep prepared hydrothermally was reddish when removed from the digestion vessel and green brown after drying. It would appear that during the hydrothermal treatment, the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ was oxidized to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ in the alkaline medium. The DSC of the material had a peak consistent with the loss of the iron cyanide group, and a peak at 445°C that was due to the decomposition of the material. This material was submitted as synthesized for catalytic testing.

Pyroaurite

Pyroaurite is the Fe(III) Mg(II) analogue of HTC; iron is present in the brucite layers and imparts the same positive charge that Al(III) does in HTC. This material would be of particular

interest because iron that is ion exchanged into the interlayers would be in proximity with the iron in the layers and could produce catalytically active sites; the limitation in this material is the same as that of HTlc: the amount of exchange capacity. The synthesis of this material was attempted using the preparative method for HTlc. The product was a mixture of impurities.

Work was undertaken on the iron-magnesium analogue of hydrotalcite (pyroaurite). In pyroaurite, iron (III) is present in the brucite layers and imparts the same positive charge that Al (III) does in HTC. This material has the same limitation that HTlc materials do: the low level of exchange capacity. Pyroaurite is a synthetic challenge since there is very little literature on the system. The synthesis used the same preparative methods as HTlc and produced a mixture of impurities. Attempts to make pure pyroaurite were done, and the materials were studied.

A preparation with terephthalic acid as the anion in the layer was done. Terephthalic acid is of interest because it would produce a larger gallery between the brucite layers resulting in an easier ion exchange or loading of the metal complexes of interest. The gel ratio used was:

0.67 Mg 0.33 Fe 2.5 NaOH 0.66 TA

It was hoped that the mixture of terephthalic acid and sodium hydroxide would produce a pH

high enough to synthesize pyroaurite. The chlorides were used and the synthesis was done in air. When the prep was done, it was found that the terephthalic acid would not dissolve even in boiling water. In order to get a clear terephthalic acid solution, the final gel amounts were 2.5 NaOH, 0.22 TA. The method of simultaneous addition previously described (Second Quarter Report 1993) was used. Hydrothermal digestion was done at 125 and 150° C for twenty hours.

The 125° C digestion produced good pyroaurite with an x-ray powder pattern that had low intensity peaks. The low intensity of the peaks could be due to the presence of iron. Based on the d spacings, there was no increase in the interlayer space due to the presence of terephthalic acid. The 150° C digestion also produced pyroaurite with a low intensity powder pattern. The d003 spacing appeared to be a doublet which could be due to the presence of terephthalic acid and CO₂ in the interlayer space.

A second prep using the nitrates of the metals and a higher NaOH level was attempted. The terephthalic acid did not dissolve even with the additional NaOH, and the reaction was run by adding the clear Fe/Mg solution to the turbid terephthalic acid solution; it was heated under reflux rather than hydrothermally digested. Under the optical microscope, the material was composed of small platelet-like particles that birefringed; there were also some brown particles that did not birefringe. The sample was stored wet to try to minimize exposure to CO₂.

An XRD study of the material was done under different conditions: a portion was dried at 125° C, one portion was run wet and a preferred orientation zero background plate was prepared. The sample dried at 125° C had an XRD pattern consistent with a mixture of pyroaurite, brucite and material that could not be identified using JCPDS. The d003 spacing of the pyroaurite was consistent with CO₃⁻ as the interlayer anion. The wet sample was primarily pyroaurite with some brucite impurity. The d003 spacing was consistent with CO₃⁻. The POXRD had very few impurity peaks, but the interlayer spacing was still consistent with carbonate present as the interlayer anion and not terephthalic acid. There appears to be a second phase that crystallizes out when the sample is dried. This prep also did not result in the desired larger interlayer spacing that would be necessary for anion exchange of the materials of interest. The crystallization of impurity materials upon drying also presents a problem, since the metal complexes of interest are not water soluble.

A solubility study of the terephthalic acid was done to try to determine if it could be used as an interlayer anion in this system. To get the amount of terephthalic acid into solution that is necessary to balance the charge requires a Na/TA greater than 15; the amount of water necessary is four times greater than that used in the prep. Because of the problems in synthesizing this material and the limitations of the system, this work was abandoned.

EXPERIMENTAL

Synthesis of HTlc Materials (Mg/Al):

Preparation of $\text{Mg}_{0.67}\text{Al}_{0.33}$; other materials made by made by calculating the reagent amounts from the product ratio.

1. Heat 400 ml. of distilled water to 40 -60°C.
2. Dissolve 4.3 g of Na_2CO_3 (0.2 M) in H_2O . Add 16.02 g NaOH (2M) and q.s to 200 ml.
3. Dissolve 16.06 g $\text{AlCl}_3 \cdot 76\text{H}_2\text{O}$ (0.32 M) in H_2O . Add 27.64 g $\text{MgCl}_2 \cdot 76\text{H}_2\text{O}$ and q.s. to 200 ml.
4. The solutions are placed into a separate biurets and added simultaneously to the heated water with vigorous stirring. The solution addition rate is adjusted to maintain the pH at approximately 10.
5. If the final pH after addition is less than 10, add 2 M NaOH to increase to 10.
6. Allow to stir at temperature for approximately one half hour.
7. Filter and wash with 1000 ml of deionized water.
8. Resuspend in 300 ml of deionized water with vigorous mixing to get a homogeneous mixture.

9. Place into teflon liner, measure weight, pH.
10. Place into digestion vessel and heat quiescently under autogenous pressure for 18 to 24 hours at 150°C.
11. Remove vessel and allow to cool to room temperature. When opened, measure weight and pH. Under an optical microscope, the material will be very fine, even spheres.
12. Filter, wash, dry at 80°C.
13. Determine dry yield.

REFERENCES

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APPENDIX 2

HTlc CLAY PREPARATIONS

PREP. NO.	GEL RATIO					X	TREATMENT	XRD RESULTS
	Mg	Al	Na ₂ CO ₃	NaOH	M _{II} /M _{III}			
10028-37/38 ^a	6.4	1.6	3.2	1.5	4.0	0.20	Dried 100 °C HT, 200°C, 18 Hours	HTc, Hydromagnesite HTc, Magnesite
10028-45	6.4	1.6	3.2	4.0	4.0	0.20	Dried 90°C HT, 115°C, 18 Hours HT, 150°C, 18 Hours	HTc, Hydromagnesite HTc, Magnesite, Hydromagnesite HTc, Magnesite
10028-57	5.71	2.29	3.5	5.0	2.49	0.286	Dried 90°C	HTc, Magnesite, Al Mg Carbonates
10028-58 ^b	5.36	2.64	0.2	2.0	2.03	0.33	HT, 125°C, 18 Hours HT, 150°C, 18 hours	HTc - Good HTc - Good
10028-60	5.36	2.64	0.2	2.0	2.03	0.33	HT, 125°C, 20 Hours HT, 150°C, 20 Hours	HTc - Excellent HTc - Excellent
10028-62	5.30	2.70	0.3	2.0	1.96	0.34	HT, 150°C, 24 Hours HT, 170°C, 24 Hours	HTc - Peak Splitting plus one unidentified peak
10028-68	5.20	2.80	0.3	2.5	1.86	0.35	HT, 125°C, 18 Hours HT, 150°C, 18 Hours	HTc - Excellent HTc - Very Excellent
10028-72	5.93	2.07	-	2.0 ⁺	2.86	0.26	Dry @ 80°C	HTc - Not well xlied
10028-73	5.93	2.07	[Fe(CN) ₆] ⁴⁻	2.0 ⁺	2.86	0.26	HT, 125°C, 18 Hours HT, 150°C, 18 Hours	HTc - Excellent HTc - Very Excellent
10028-78	5.04	2.96	0.3	2.0 ⁺	1.70	0.37	HT, 125°C, 18 Hours HT, 150°C, 18 Hours	HTc + Impurity HTc + Impurity
10028-80	6.40	1.60	0.3	2.0 ⁺	4.0	0.20	HT, 125°C, 18 Hours HT, 150°C, 18 Hours	Low Xlinity Poor Pattern of HTc

^a Prep Nos. 10028-37 thru 57 are Nitrates.

^b Prep Nos. 10028-58 thru 80 are Chlorides.

APPENDIX 3:

HTlc Clay Data

	<u>Sample Number</u>					
	10028-58-1	58-2	60-1	60-2	62-1	62-2
L.O.I.	52.7%	42.9%	48.3%	42.7%	41.5%	41.45
L.O.D.		0.20%	0.74%	0.37%	0.26%	0.03%
MgO	32.83	33.33	33.33	33.16	31.01	30.51
Al ₂ O ₃	19.65	20.02	22.10	22.10	21.91	22.29

	10028-68-1	68-2	80-2
L.O.I.			
L.O.D.	0.46%	0.45%	
MgO	31.01	32.85	31.67
Al ₂ O ₃	21.16	22.48	4.72

	Gel Ratio	Chemical Analysis
10028-58-1	Mg _{0.67} Al _{0.33}	Mg _{0.678} Al _{0.32}
58-2	Mg _{0.67} Al _{0.33}	Mg _{0.678} Al _{0.32}
60-1	Mg _{0.67} Al _{0.33}	Mg _{0.66} Al _{0.34}
60-2	Mg _{0.67} Al _{0.33}	Mg _{0.66} Al _{0.34}
62-1	Mg _{0.66} Al _{0.34}	Mg _{0.64} Al _{0.36}
62-2	Mg _{0.66} Al _{0.34}	Mg _{0.63} Al _{0.37}
68-1	Mg _{0.65} Al _{0.35}	Mg _{0.65} Al _{0.35}
68-2	Mg _{0.65} Al _{0.35}	Mg _{0.65} Al _{0.35}
80-2	Mg _{0.80} Al _{0.20}	Mg _{0.90} Al _{0.10}

Figure 1

FN: B10028602.NI

ID: #10028-60-2 HYDROTALCITE B.K.MARCUS

SCINTAG/USA

DATE: 04/08/93

TIME: 09: 08

PT: 0.60000

STEP: 0.02000

WL: 1.54060

8.3.3 Cloverite as a carrier for Metals Porphyrins

During the second quarter, a large pore zeolite, cloverite, was synthesized in order to study the feasibility of using it as a carrier for porphyrins in order to provide stability and allow them to maintain structural integrity during catalysis. In addition, the size of the cloverite pore and the supercage could allow the formation of a porphyrin dimer in situ.

In the second quarter, cloverite was successfully synthesized on a small scale and its properties were studied. A scale-up of the prep produced cloverite and AlPO_4 tridymite; calcination of the material produced total structure collapse due to oven malfunction. This quarter, a scale up was prepared using the gel ratio:

This is a low water gel that was digested for 24 hours at 150°C . The XRD of the product was consistent with well crystallized cloverite; the yield was 24.9 grams.

A sample of the cloverite was calcined under vacuum at 220°C for two days; the sample was tan after calcination. Calcined samples of cloverite exposed to moist air at room temperature show complete structural collapse over time, therefore the calcined material was immediately used as a support. The amount of solvent necessary for incipient wetness addition was determined to be 0.2 cc

of methylene chloride per gram of cloverite, and the porphyrin of interest ($\text{Fe(III)(TPP-F}_{20}\text{)Cl}$) is soluble in methylene chloride at a level of 1.8 mgs./gram. The sample was impregnated a total of six times; the solvent was removed by heating at 50°C under vacuum for 2 to 3 hours between impregnations. The final loading on the cloverite was 5.50×10^{-3} mmols/gram of cloverite, and the sample was an even greenish color.

The dimer of the F_{20}Cl monomer may be formed by treatment with base or acid, and a portion of the cloverite impregnated with the monomer was treated with 1M NaOH to determine if the dimer could be formed on the support. The cloverite turned brown and dissolved.

Cloverite is an acidic material with dangling OH groups present in the openings of the pores, and it is possible that the dimer had formed in contact with the support. A portion of the sample was treated with methylene chloride to try to dissolve off the porphyrin to determine if the dimer was present. A UV of the dissolved material had a max of 406 nms; the neat porphyrin had a max of 410 nms. The 406 peak could be due to the hydroxy form of the porphyrin. The literature value of the dimer max is 393 nms.

Another way to add base to the treated material is by utilizing a silica binder; the silica solution used in a binder is quite basic and could form the dimer. A potential problem is that the water needed to dilute the silica binder could destroy the crystallinity of the cloverite. A portion of

the sample was bound with 20% silica using Nyacol silica and dried at 80° C. The sample was meshed to 18/35 and submitted to V. A. Durante for testing. An XRD of the fines gave an excellent cloverite pattern; it appears that liquid water added to the cloverite does not affect the structure.

Figure 2

Cloverite, a large pore gallosilicate molecular sieve, and Cab-o-Sil, a hydrophobic fumed silica were loaded with F_{20} Cl porphyrin monomer; it was hoped that the dimer could be formed by treatment with base or acid. The cloverite dissolved during the treatment. However, cloverite is an acidic material, and there was the possibility that the dimer had formed during the deposition process. Diffuse reflectance IR studies of cloverite and Cab-o-Sil and the porphyrin loaded materials were performed during this quarter to try to determine the nature of the porphyrin.

The dimer is necessary for the iron centers to be at the optimum distance to allow the cleavage of oxygen and the formation of Fe - O - Fe centers without the formation of Fe -O - O - Fe. A paper by Jayarj, et. al.⁽¹⁾ assigned the Fe- O - Fe IR peak in $(FeF_{20})_2O$ to the band at 850 cm^{-1} . The difference IR did show a peak in the base treated porphyrin loaded Cab-o-Sil at 846.8 cm^{-1} , but the results were not definitive. The loaded cloverite had peaks consistent with the porphyrin, but none that could be attributed to the dimer. Diffuse reflectance IR of the loaded cloverite did not show any peak at 850 cm^{-1} . Cheryl Jones did additional work on the samples including collecting numerous scans at slow speed, subtracting out the differences and analyzing the results using several programs. None of them were able to determine if there was dimer present on the cloverite or the Cab-o-Sil. This is probably due to the low level of loading on the materials. Silicalite molecular sieve was also loaded with the F_{20} monomer; diffuse reflectance IR was unable to determine if the dimer was present on that material either. Other methods to determine if the dimer has been formed will have

to be investigated, and they will have to be able to detect very low levels of the dimer and distinguish it for the monomer.

The first material attempted was Fe(FPc) on Cab-o-Sil. The synthesis procedure followed for the pthalocyanine was Jones and Twigg ⁽²⁾ with some modifications; the amount of solvent, 1-methyl naphthalene, was increased to allow the silica to be fully in solution and the wash amounts were increased to re full dissolution of unreacted materials and by-products on the solid. The final product was a green solid that appeared to be uniform in color. A portion of the materials was dissolved off the support and examined by UV-VIS. The spectra was consistent with the material provided by P. Ellis previously. The L.O.I. of the sample was 36.8%; after calcination at 600° C, the sample was brick Red. The chemical analysis of the sample showed 2.71 weight percent iron present "as-is"; on a dry basis it was 3.71 weight percent. (6.64×10^{-4} mols/gram). This preparation was successful, and additional ones will be attempted during the Phase VI program.

Supporting Oxidation Active Complexes on Hydrophobic Materials

As we have described in past reports, the goal of the vapor phase component of this research is to prepare, characterize and support oxidation active electronically tuned binuclear metal centers on hydrophobic support materials for light alkane oxidation in the gas phase. These catalyst design criteria emerged from analysis of the mechanism of operation of vapor phase oxidations of methane

and ethane using catalysts having proximate metal centers in regular oxidic arrays which were able to homolyze C-H bonds but not able to bind substrates, assemble alcohols and rapidly eject them from the surface before substantial burn occurred. The new design is aimed at retaining the best characteristics of the first generation catalyst but adding the new functions mentioned above. Our current synthesis program puts stable mononuclear metal systems proximate to one another in one set of catalysts and makes binuclear centers in a binucleating macrocycle in another set. Both sets are then supported on hydrophobic materials which will encourage desorption of methanol or light alcohols after formation on the surface. During the past quarter we have made good progress in the synthesis of binucleating macrocycles, but since characterization data is still being generated we will defer discussing this subject until next quarter. In the next section we will discuss our initial work on supporting mononuclear complexes in a proximate manner on hydrophobic support materials.

Summary

Supported Porphyrin Complexes:

Materials other than cloverite were used as supports for metal complexes of interest. Cab-o-sil TS720 fumed silica was loaded with the $F_{20}Cl$ porphyrin using the technique described above. The loading level was 1.8×10^{-5} mols/gram of cab-o-sil. The sample was different shades of green with some white particles indicating that the loading of this material was not uniform.

An attempt was made to dimerize the porphyrin with 1M NaOH. The cab-o-sil was very difficult to wet with the aqueous solution due to its hydrophobicity. When filtered, the initial filtrate was brownish; subsequent water rinses were colorless. After treatment, there was a large loss in weight indicating that the silica was dissolved by the base treatment. Some of the porphyrin was washed off the surface with chloroform for UV analysis; the max was 404 nms. which is high for the dimer. Samples were submitted for IR, but the results were inconclusive. Additional work is being done using diffuse reflectance IR. The sample was meshed to 18/35 without a binder and submitted to V. Durante for testing.

The F₂₀Cl was loaded onto silicalite and fluoride silicalite. Fluoride silicalite was calcined at 500° C for three hours to remove the organic template (LOI = 10.91%). A portion was dried under vacuum at 200° C for two days and submitted to V. Durante for testing. Silicalite that had previously been calcined and acid washed was back washed with NaCl to eliminate acidity, dried at 200° C under vacuum for two days and submitted to V. Durante for testing. Both of these unloaded materials were used as blanks.

Subsequently, V. Durante reported that amines had been detected in the TPR when the fluoride silicalite was tested and that there was a possibility that the sample was not fully calcined. The sample was recalcined at 600° C for three hours; the LOI was 0.22%. It seems unlikely that there was any amine left in the sample after the original calcination. The recalcined sample was also

submitted for testing.

A sample of the silicalite was loaded with $F_{20}Cl$ using the described procedure. The total loading was 1.38×10^{-5} mols/gram. The final material was brownish-green and uniform. Samples were given to V. Durante for testing and were submitted for diffuse reflectance IR. A portion of the sample was treated with 0.1 M NaOH to try to form the dimer. The treatment was milder than that used before in an effort to prevent dissolution of any silica. After treatment, there was a small loss of weight. Samples were given for testing and submitted for diffuse reflectance IR.

Fluoride silicalite was loaded with $F_{20}Cl$ in a similar manner. The loading was 1.28×10^{-5} mols/gram, and the sample was a uniform brownish-green in color. A portion was treated with 1.0 M NaOH; after treatment, the initial filtrate was faintly brown and UV analysis showed some F_{20} present in the filtrate. Samples of the monomer and dimer materials were sampled for testing and for diffuse reflectance IR.

The non-fluorinated porphyrin, $(Fe(III)TPP)Cl$ was also loaded onto silicalite for testing. The loading was 1.238×10^{-5} mols/gram.

Samples loaded with porphyrins were extensively studied by diffuse reflectance IR to determine if the dimer had been formed. The dimer is the preferred material due to the optimum

distance of the iron centers. The tests were not able to distinguish the dimer; this is probably due to the low loadings of the porphyrin on the support. Other tests will have to be investigated to distinguish the monomer and dimer.

Supported Phthalocyanines

Phthalocyanines were found to give potentially interesting results in heterogeneous reactions with propane. Additional samples with higher loadings were needed for testing. The use of impregnation techniques was impractical for high loadings; direct synthesis techniques were attempted and were successful. This technique will be expanded to other materials.

A sample of iron sodalite catalyst on stream for fifty hours was examined. There was an 80% loss in sodalite crystallinity and other unidentified phases were seen in the XRD. This sample was examined previously after fewer hours on stream; a correlation between structural collapse and activity could be interesting.

Phthalocyanines are known to be inactive in homogenous catalysis being investigated at SUN. However, they may be useful in obtaining the optimum iron distances, and samples with low loadings have produced some interesting results when tested by V. Durante. A sample loaded with approximately 50 micromols of Fe(FPc)Cl was requested.

A sample of Fe(FPc)Cl was received from P. Ellis (976314A). Dissolution studies were done to determine what solvent could be used for incipient wetness impregnation. In several solvents, the material formed a suspension rather than a solution, and crystals could be seen under the microscope. The only solvent tested that showed some solubility was THF; the solubility was <1.6 mgs./g THF. To load 50 micromols on 10 grams of silica would require 4.6 grams of phthalocyanine, which is an impractical amount to add in this way. However, an attempt was made to try this technique.

To load, 4.6 grams of Fe(FPc)Cl was added to a jar, and 16 grams of THF was added. The mixture was well shaken and allowed to settle; the clear blue solution was examined under a microscope, and if no crystals were present, was used for the impregnation. As the clear solution was used up, additional THF was added to dissolve more of the solid. The amount of THF required for incipient wetness was 1.6 g/g of silica, and each addition took approximately 30 to 45 minutes of slow stirring by hand followed by 1 to 2 hours of drying at 90°C to achieve full dryness for the next addition. After 33 treatments, approximately of the phthalocyanine had been loaded, and the Cab-o-Sil was showing signs were fully saturated. Chemical analysis of the sample gave 5.2×10^{-5} mol Fe per gram. "as-is"; the L.O.I. was done and was 13.7% giving 5.87×10^{-5} mols iron/gram on a dry basis. The sample was submitted to V. Durante for testing, but this method of forming loaded materials is not practical for high loading levels.

The direct synthesis of the phthalocyanine onto the support is one method for producing a material with higher loadings. There are several potential problems with this approach: the support may change the reaction conditions and prevent the synthesis of the material of interest, the phthalocyanine may form as an admixture with the support rather than on the support, the reagents used in the synthesis may destroy the support. Each material that is synthesized presents a different problem, and each support reacts differently during the reaction.

9.0 NEW METHANE OXIDATION LABORATORY

During Phase IV we completed a modern new methane oxidation laboratory. The work station of this laboratory is a highly automated versatile methane oxidation unit described in past reports. We have developed and implemented a chloride guard bed system for removing unwanted halide from methane streams since the presence of trace chloride profoundly affects methane oxidation results. We have lined out the unit and achieved results comparable to published work on non-catalytic oxidations (45% Sel, 10% conv.) We are now ready to screen catalysts in this unit. Results will be reported in the Phase VI activity reports.

Workers responsible for this work in this section are:

Margaret Nemet

Kevin Boyer

Vincent A. Durante

James E. Lyons

9.1 DISCUSSION

A. Chloride Guard bed System

We used the existing feed mixing vessel (RDP #1409) as a chloride oxidation reactor. 46 mls of catalyst #1028-24, prepared by Bonnie Marcus were loaded into this vessel. The preblended methanol reactor feeds (methane, oxygen, and neon) were passed over this bed, held at 300°C. The chromia catalyst is first reductively deoxygenated to a Cr 3+ specie. Organic chlorides are first converted to catalytically active surface chloride species (1), which is followed, after an apparent induction period (2) by desorption of hydrochloric acid. Hydrochloric acid was then adsorbed in a separate 75 ml bed (RDP #1315) of Alcoa's Selexsorb-SPCL adsorbent, held at ambient temperature.

We operated the adsorbent system in the course of our homogeneous chemistry screening runs (item below) for over ten 24 hour days. Hydrochloric acid generation in the methanol reactor was monitored by Draeger tubes installed in the off-gas line. Completely chloride free operation was maintained throughout.

B. On-Line GC Method Improvement

We evaluated our on-line GC methods and identified areas of potential improvement. We found that our inability to reproduce GC operation stemmed from a flow imbalance in the external sample splitter we developed earlier, with assistance from Shimmer Scientific Instruments Co. This flow imbalance caused erratic splitter performance, and varying sample size reaching the detector. We replumbed the instrument (Shimadzu GC 14A) so that the sample valve now injects the sample

directly into the instrument's built-in capillary splitter. This way much higher split ratios became possible, which allowed us to go to larger external sample loops (from 5 microliter to 100 microliter sample loops). The larger sample loops are less prone to plugging and pressure drop change. The modifications will also enable us analyze product from either stage reactor without any additional hardware.

We trained an operator the point where now he is comfortable with the instrument, and made up a diagnostic checklist for troubleshooting and maintenance.

We explored several ways of calibrating the GC for compounds of very different volatilities, e.g. carbon oxides, methanol and water on the same capillary column. Among others we tried: (a) making up a gaseous standard in a large Whitey sample cylinder, and slowly bleeding the standard into the GC sample loop, (b) pumping into the reactor pure methanol while metering in a mixture of light gases. We learned, while trying to implement these methods, that methanol dehydrates readily, even at 200°C, in the heat traced GC sample loop, possibly mediated by SS tubing. We ended up injecting with a microsyringe a liquid standard at the same time as we injected a gaseous standard via the GC sampling valve. We will verify the methanol factor when we collect and measure the methanol separately.

We also went through a selection process for the best overall internal standard inert gas. Even though xenon was technically superior, for economic reasons we chose neon, which separated very well from nitrogen, oxygen, and carbon monoxide on a "true" Poraplot Q capillary column. (The first Poraplot Q column we received was a product of poor quality control by Chrompack, the manufacturer).

C. Noncatalytic Oxidation Screening Runs

We completed four cycles of oxidation, all at the same pressure, temperature, and feed composition, but residence times (based on feed flow rates at reactor temperature and pressure) from 3 to 19 sec. The feed contained about 7 mol% neon, and 5 mol % oxygen in methane. Each of these gases was metered in with separate Brooks mass flow controllers. Reactor pressure was maintained at about 800 psig, and the reactor internal temperature at 420-430°C. The active reactor volume was assumed to be 1.5 mls, based on earlier measurements of the reactor temperature profile.

At the highest residence time (equivalent to about 4300 GHSV) methane conversion was in excess of 20%, and deep oxidation predominated. Methanol selectivity was only 15-20 mol%. As the residence time decreased, or the GHSV increased to about 26,000 methane conversion decreased to 5-6%, and methanol molar selectivity surpassed 40%. Detailed run conditions and conversion-selectivity data are shown in Table 1. The data were calculated assuming that the neon balance closed. This was done because of some uncertainties in flow rate measurements, which are currently being addressed. For these reason it should be understood that the data could be subject to revision.

Just as soon as we resolve the flow question and compare on-line data with methanol collection data we will be able to have more confidence in our numbers.

Despite the uncertainties these screening data still clearly indicate that complete oxygen conversion at the pressure, temperature, and feed composition of our work occurs at about 3 sec residence time. We will use these conditions as a starting point for our future work.

D. Lotus 1-2-3 Database

We set up a first generation data base in Lotus 1-2-3. The rationale behind selecting Lotus was continued support from the Systems Group, whereas future support for RS-1 will be less and less. The data files can be stored on the common O: drive of the PC network, and accessed by anybody with a PC connected to the network.

Presently all data files are set up. Raw GC data are transferred from Shimadzu to the network where they are edited and processed using the latest calibration factors. Additionally, since the raw data are stored, we can go back and reedit them without much effort, and automatically update the processed data files. We can also transfer the raw Labtech process data to Lotus, but the macro to extract averaged process parameters for material balance calculations has not yet been set up. We are currently doing the matching of the GC and process data manually. Plans are to fully automate all data base operations.

E. Methane Conversion Process Evaluations

The methane conversion economic comparison based on more recent, and more rigorous, capital cost estimates was updated. Details are available in a soon to be issued proprietary internal memo. Non-proprietary aspects will appear in the Phase VI Topical Report.

TABLE 1

NONCATALYTIC OXIDATION OF METHANE

5 VOL % OXYGEN, 800 PSIG 420-430°C

<u>Run No.</u>	<u>TOS,Hrs</u>	<u>RT,Sec</u>	<u>C1 Conv</u>	<u>O₂ Conv</u>	<u>CO Sel</u>	<u>CO₂ Sel</u>	<u>Meol Sel</u>
995116	26	19.3	23	100	51	36	13
995116	45	19.3	25	100	55	39	6
995117	24	6.8	7	100	43	23	34
995119	21	3.3	8	100	23	33	44
995119	24	3.4	10	100	31	24	45

F. DATA PROCESSING

The flow of analytical and process data into material balance files is shown on Figure 4.

Gas chromatography report files, after integration and baseline correction are transferred as ASCII files to the R&D PC network by the technician, Kevin Boyer. The Labtech process logs consist of flows, pressures and temperatures recorded vs. the Time of Day. These logs are compatible with spreadsheet programs, such as Lotus 1-2-3, and are also transferred by Kevin to the R&D PC network. The GC and process files are processed by M. Nemet on the office PC, which is, like all office PC's connected to the network. Selected features of the data processing mechanisms are described below:

G. GC Files

The ASCII files are read as numbers by Lotus. After editing, the retention times and peak areas are used to calculate, with the most up to date chromatographic factors, the component weight and mole % concentration. The concentrations are then stored in the chromatography database, which also contains information on the date and time of the analysis, and key run identifiers, such as type of analysis (total reactor effluent vs. light off-gas analysis), the Run Number, the reactor type, the catalyst, if any, etc.

H. Process Data Files

The Labtech logs are read by Lotus as text files. The text is then parsed, to convert it to

numerical data, i.e. process variable vs. Time-of-Day. The file is then searched for process information around the time of the GC. The process information is averaged and stored in process files similar in construction to the GC data files: i.e. key identifiers, and process variables at time-on-stream.

REFERENCES

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FIGURE 1

METHANE OXIDATION REACTOR PRODUCT COLLECTION

FIGURE 2

METHANE OXIDATION BENCH-SCALE REACTOR
DATA PROCESSING FLOW SHEET