1994

Metalloporphyrin sulfido, selenido, and imido complexes: synthesis, characterization, and transfer reactions

Lisa Mary Berreau
Iowa State University

Recommended Citation

Berreau, Lisa Mary, "Metalloporphyrin sulfido, selenido, and imido complexes: synthesis, characterization, and transfer reactions " (1994). *Retrospective Theses and Dissertations*. 11029.
https://lib.dr.iastate.edu/rtd/11029

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Metalloporphyrin sulfido, selenido, and imido complexes:
Synthesis, characterization, and transfer reactions

by

Lisa Mary Berreau

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1994

UMI Number: 9606636

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

Metalloporphyrin sulfido, selenido, and imido complexes:
Synthesis, characterization, and transfer reactions

Lisa Mary Berreau

Major Professor: L. Keith Woo
Iowa State University

Metalloporphyrins containing metal-oxygen multiple bonds have been the focus of numerous studies. In contrast, the chemistry of species containing multiple bonds to the heavier chalcogenides or the Group 15 elements is underdeveloped. In general, this has been the result of a lack of suitable synthetic precursors for the preparation of non-oxo containing derivatives.

A new simple method for the preparation of early transition metal porphyrin halide complexes, starting from a porphyrin dianion and a metal halide species, provides a high yield route to metalloporphyrin halides of vanadium, molybdenum, titanium, and tungsten. Utilizing the molybdenum halide complex, (TTP)MoCl$_2$, we have found a number of synthetic routes for the preparation of the first terminal sulfido and selenido molybdenum porphyrins, (TTP)Mo=X (X = S, Se). The molybdenum chalcogenides may also be generated by treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=X, formally an intermetal two-electron redox process mediated by sulfur or selenium atom transfer. In an analogous manner, treatment of (TPP)Sn=X (X = S, Se) with (TTP)Sn(II) results in the reversible exchange of a sulfur or selenium atom. For this Sn(IV)/Sn(II) exchange, we have found that the rate of selenium atom transfer is over 200 times faster than that of sulfur atom transfer.

Employing early transition metal porphyrin halide complexes as precursors, we have also been able to prepare novel imido complexes of titanium and molybdenum porphyrins. In a reaction analogous to atom transfer, treatment of (TTP)Mo=NPh with (TTP)Ti(PhC≡CPh) results in complete imido group transfer to give (TTP)Mo(PhC≡CPh) and (TTP)Ti=NPh. This dissertation focuses on the synthesis, characterization, and transfer reactions of these sulfido, selenido, and imido metalloporphyrins.

DEDICATION

To my mother and father

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

anis	anisole
biph	biphenyl
BM	Bohr magnetons
^{t}Bu	tertiary butyl
bdt	benzenedithiolate
cal	calorie
cm	centimeter
COT	cyclooctatetranyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp^{Et*}	ethyltetramethylcyclopentadienyl
Cy	cyclohexyl
dmbpz	tris(3,5-dimethylpyrazolyl)borate
DME	dimethoxyethane
dppe	diphenylphosphinoethane
EPR	electron paramagnetic resonance
Et	ethyl
eq	equation
IR	infrared
kcal	kilocalorie
Me	methyl

mg	milligram
MHz	megahertz
mL	milliliter
mmol	millimole
mol	mole
MS{EI}	mass spectrometry by electron impact
nm	nanometer
NMR	nuclear magnetic resonance
OAc	acetate
OEP	octaethylporphyrinato dianion
OEt_2	diethylether
Ph	phenyl
POR	general porphyrinato dianion
ppm	parts per million
py	pyridine
pz	pyrazolyl borate
solv	solvent
THF	tetrahydrofuran
THT	tetrahydrothiophene
TMEDA	tetramethylethylenediamine
tmtaa	dibenzotetramethyltetraaza[14]annulene
TMP	*meso*-tetramesitylporphyrinato

TmTP	*meso*-tetra-*m*-tolylporphyrinato dianion
TMS	trimethylsilyl
Tol	tolyl
TPP	*meso*-tetraphenylporphyrinato dianion
Ts	tosylate
TTP or TpTP	*meso*-tetra-*p*-tolylporphyrinato dianion
μ_{eff}	magnetic moment
UV-vis	ultaviolet-visible

GENERAL INTRODUCTION

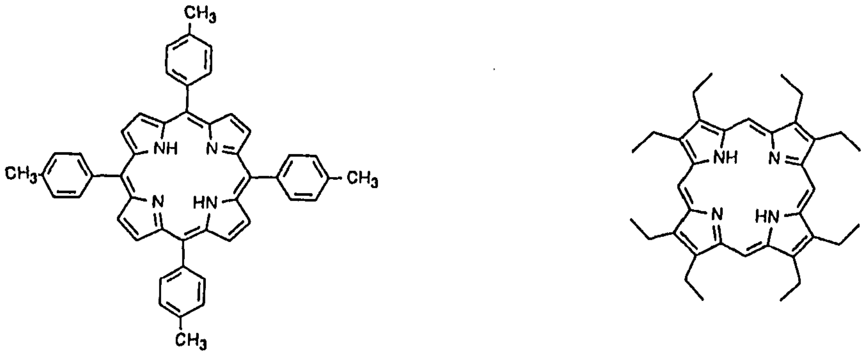
Dissertation organization

This dissertation contains three chapters of literature review. Chapter 1 concerns metalloporphyrin halide complexes. Chapter 3 deals with recent advances in the chemistry of heavier chalcogenide complexes of the early transition metals as well as the main group elements. Examples of atom transfer reactions involving sulfur and selenium are also discussed. Chapter 6 discusses recent advances in the synthesis and reactivity of early transition metal complexes containing imido ligands. The remaining chapters constitute individual papers that have been published, submitted for publication, or are being prepared for submission. Following the last paper is a general conclusions chapter.

Porphyrins as ligands

Porphyrins have been used as a supporting ligand for numerous organometallic and coordination complexes. The doubly deprotonated porphyrin is a tetradentate chelating dianion with the four pyrrole nitrogen atoms defining an equatorial plane with four fold symmetry. Two examples of commonly used porphyrins, *meso*-tetra-*p*-tolylporphyrin and octaethylporphyrin, are shown in Figure 1. The macrocyclic core contains 11 double bonds and therefore is a planar 4n + 2 π aromatic system. The porphyrinato ligand may coordinate a metal ion in the central cavity. It is important to note that not all metals fit into the hole of the porphyrin ligand. Notable exceptions include the heavier early transition elements of Groups 4-6. As an example, titanium fits into the porphyrin hole. Therefore, titanium metalloporphyrins may coordinate two additional ligands in trans axial coordination sites. However, zirconium does not fit into the cavity and instead has two cis coordination sites available (Figure 2).

Porphyrin ligands possess numerous advantages over other ligand systems. Important to atom transfer studies is the fact that metalloporphyrin complexes do not undergo rearrangements of the supporting ligand. Secondly, steric and electronic factors may be varied by



(a) (b)

Figure 1. a) *meso*-tetra-*p*-tolylporphyrin b) octaethylporphyrin

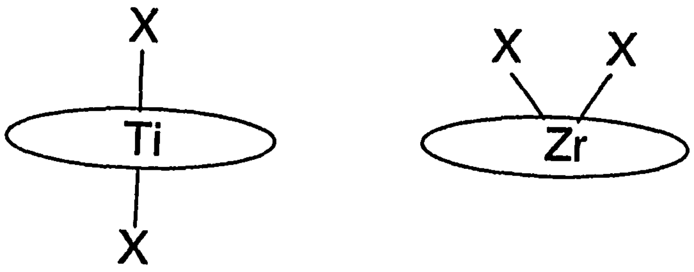


Figure 2. Geometry of titanium and zirconium porphyrin complexes

simply changing the peripheral substitution of the porphyrin ligand. However, a key factor is that porphyrins are excellent spectroscopic tags in both UV-vis and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra reflect the symmetry of the ligand and is therefore very structurally diagnostic. For example, when the four-fold symmetry of the porphyrin is maintained on the NMR time scale, a typical metalloporphyrin complex utilizing TTP^{2-} as the ligand exhibits only four resonances, corresponding to the β-pyrrole, *o*-tolyl, *m*-tolyl, and tolyl-CH_3 protons. Ligands coordinated in the axial positions above and below the porphyrin plane are readily distinguished as ^{1}H NMR signals for the ligand are often shifted dramatically upfield due to the ring current of the porphyrin π-system.

Metalloporphyrins containing multiply bonded ligands

Terminal oxo complexes dominate the known metalloporphyrins species containing metal-ligand multiple bonds. This is due in part to the fact that metallation of the porphyrin ligand often results in formation of the very stable terminal oxo species. This is especially true for the early transition metals where terminal oxo complexes are generally the most stable form of metalloporphyrin. Examples of metalloporphyrins stabilizing other metal-ligand multiple bonds are significantly fewer in number. Metalloporphyrin complexes containing nitrido ($M{\equiv}N$), imido ($M{=}NR$), sulfido ($M{=}S$), selenido ($M{=}Se$), carbene ($M{=}CR_2$), and silylene ($M{=}SiR_2$) moieties are of interest in terms of both synthetic and possible catalytic applications and are the subject of a number of continuing studies. The work presented here centers on the preparation and applications of metalloporphyrins containing sulfido, selenido and imido ligands.

Metal-ligand multiple bonds

The chemistry of species containing metal-ligand multiple bonds has been the subject of a recent book by Mayer and Nugent.[1] Topics such as electronic structure, synthesis, reactivity, spectroscopy, and catalytic applications of metal-ligand multiple bonds are discussed. This book is an excellent general reference for the topics to be covered in this dissertation.

CHAPTER 1: METALLOPORPHYRIN HALIDE COMPLEXES OF THE EARLY TRANSITION METALS: A LITERATURE REVIEW

Porphyrin ligands have been used to stabilize a wide range of coordination and organometallic complexes.[2] While the chemistry of late transition metal porphyrins has been studied immensely, the chemistry of early transition metal porphyrins remains relatively undeveloped. This is due in part to the facile oxidation, high oxophilicity and/or ease of hydrolysis of early transition metal porphyrin species. This chapter will highlight recent developments in the area of preparation and reactivity of early transition metal porphyrin halide complexes.

The greatest problem encountered in the preparation of early transition metal porphyrin complexes was the lack of a clean, high-yield preparative route to suitable starting materials. Published procedures often required the use of very high-boiling solvents, followed by purification using column chromatography, and typically produce unreactive oxo complexes. Recent advances in early transition metal porphyrin chemistry have largely involved development of new synthetic routes for the preparation of metalloporphyrin halide complexes. Of particular importance has been the development of alkali metal porphyrins, which may be used as starting materials for the preparation of a number of different metalloporphyrins. Arnold, et al. have found that treatment of free base porphyrins, H_2POR (POR = OEP, TPP, TTP, TBPP, TMPP), with a metal silylamide ($MN(SiMe_3)_2$; M = Li, Na, K) in the presence of either THF or DME, cleanly gives isolable dialkali metal porphyrins, $M_2(POR)(solv)_n$ where n = 2-4.[3] The lithium derivatives, studied using ^7Li NMR and conductivity measurements, have been shown to be a 1:1

electrolyte in polar solvents. However, in nonpolar solvents, a symmetrically bound ion-paired structure is postulated. Derivatives of Li, Na, and K have all been characterized using single-crystal X-ray diffraction.

Similar alkali metal porphyrin complexes containing diethyl ether as the donor solvent molecules have also been reported.[4] These species, $Li_2(POR)(ether)_2$, are quite soluble in nonpolar solvents and, unlike the THF and DME derivatives, possess a well-defined stoichiometry. Dilithium porphyrins of the formula $(POR)Li_2$ were also prepared by treatment of the free-base porphyrin with $LiN(SiMe_3)_2$ in toluene. Arnold has reported that use of the diethyl ether derivatives as the porphyrin transfer reagent greatly increases the yield of dihalogenozirconium porphyrins.

Prior to 1988, only three scandium porphyrins had been reported.[5] These complexes, reported by Buchler, were all derivatives of OEP and contained acetate, acetylacetonate, and oxo axial ligands. Haushalter subsequently reported the preparation of (TTP)ScCl and a μ-oxo species, $O[(Sc(TTP))]_2$.[6] However, Arnold and coworkers found a more general and simpler route to the scandium halide species starting with a porphyrin dianion and a scandium halide (eq

$$Li_2(OEP)(THF)_2 + ScCl_3(THF)_3 \longrightarrow (OEP)ScCl + 2\ LiCl + 5\ THF \qquad (1)$$

1).[7] This porphyrin halide complex is an excellent starting material for the preparation of a number of organometallic and coordination complexes. For example, organometallic complexes with σ- and π-bonded ligands have been isolated and fully characterized. These include (OEP)ScR (R = Me, $CH(SiMe_3)_2$, CH_2CMe_3, (η^5-C_9H_7), (η^5-C_5H_5), (η^5-C_5H_4Me), and (η^5-

C_5Me_5)). Additional derivatives with R = $OCMe_3$, $O(2,4,6\text{-}Me_3C_6H_2)$, $N(SiMe_3)_2$, and triflate were also reported. Hydrolysis of (OEP)ScCl yielded the dimeric bridged hydroxide $[(OEP)Sc(\mu\text{-}OH)]_2$.

Dihalogeno titanium porphyrins have recently been found to be valuable starting materials for the preparation of the first Ti(II) porphyrin complexes.[8] Treatment of $(POR)TiCl_2$ with $LiAlH_4$ in the presence of an alkyne, gave (POR)Ti(RC≡CR) (R = aryl, alkyl), a titanium(II) porphyrin with the alkyne acting as a four electron donor to the titanium center.

Arnold and coworkers have recently reported a synthetic route for the preparation of zirconium dihalide porphyrins.[9] Multigram quantities of $(OEP)ZrCl_2$ were obtained from the reaction of $Li_2(THF)_4(OEP)$ with $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene) in refluxing dimethoxyethane. However, a second product, the metalloporphyrin sandwich complex $(OEP)_2Zr$, was also isolated in about 25% yield. Note that when the dimethoxyethane porphyrin derivative, $Li_2(OEP)(DME)_n$, was treated with $ZrCl_4(DME)$ in CH_2Cl_2 at room temperature, virtually none of the sandwich compound was generated. The dihalide species is an excellent precursor to several new metalloporphyrin derivatives. Treatment with a variety of nucleophiles produced the corresponding disubstituted zirconium porphyrins, $(POR)ZrR_2$ (R = triflate, acetate, alkoxide, alkyl, aryl). A metalloporphyrin π-complex was synthesized by treatment of the dihalide complex with K_2COT. A second example of a π-complex was prepared by treatment of $(OEP)ZrCl_2$ with $Na_2C_2B_9H_{11}$ in refluxing THF to give the zirconacarborane porphyrin species.[10]

The organometallic derivatives readily undergo protonolysis, hydrogenolysis, and insertion of CO_2 and acetone into the Zr-C bonds. $(OEP)ZrCl_2$, $(OEP)Zr(O^tBu)_2$, and $(OEP)ZrMe_2$ have been characterized using single crystal X-ray diffraction analysis. In all three cases, the nonporphyrin ligands are coordinated in a cis orientation due to the out-of-plane nature of the zirconium.

Kim, *et al.* have independently reported the synthesis of porphyrin zirconium and hafnium dihalide complexes.[11] Again, treatment of a porphyrin dianion, $Li_2(THF)_4(POR)$ (POR = OEP, TPP), with a metal halide complex, $ZrCl_4(THF)_2$, in toluene resulted in the formation of the zirconium porphyrin dihalide species. The authors report that recrystallization of (TTP)$ZrCl_2$ from THF/dichloromethane/heptane gave the THF adduct (TPP)$ZrCl_2$•THF, which they have been able to characterize using single crystal X-ray diffraction. Because the zirconium atom is displaced 1.064 Å out of the mean N_4 plane, the two chloride ligands as well as the donor THF molecule are all bonded on the same face of the porphyrin ligand. This is reflected in the ^1H NMR signals of the THF adduct which exhibits significant broadening of the resonances due to the decrease in symmetry of the molecule. Kim and coworkers also have reported that treatment of the zirconium dihalide porphyrin with MeLi results in the formation of the dimethyl complex, with the methyl resonance at -3.26 ppm in the ^1H NMR spectrum. They also report the independent synthesis of the organometallic π-complex (η^5-1,2-$C_2B_9H_{11}$)Zr(OEP), formed by treatment of (OEP)$ZrCl_2$ with $Tl_2C_2B_9H_{11}$.

In a completely analogous manner, dichloro hafnium porphyrin complexes were prepared from $Li_2(POR)(THF)_2$ (POR = TPP or OEP) and $HfCl_4(THF)_2$.[12] The structure of (OEP)$HfCl_2$•H_2O has been reported and is similar to that of (TPP)$ZrCl_2$•THF: a 4:3 piano stool with the square base occupied by the porphyrin nitrogen atoms and the legs formed by the two chlorine atoms and a water or THF molecule. The source of the H_2O molecule was postulated to be moisture in the benzene used for crystallization. Treatment of the dichloro hafnium complex

(POR = OEP or TPP) with tetrabutylammonium trimetaphosphate in CH_2Cl_2 gives $[NBu_4][(POR)Hf(P_3O_9)]$. This complex has also been structurally characterized and has a 4:3 piano stool-type geometry. A benzenedithiolate hafnium porphyrin, (TPP)Hf(bdt) (bdt = benzenedithiolate) has also been reported by Kim, *et al.*.[13] It is the first structurally characterized six-coordinate hafnium porphyrin complex.

A catalytic application of zirconium porphyrins has recently been reported by Inoue and coworkers.[14] Treatment of $(TPP)ZrX_2$ ($X = O_2CCH_3$, $O_2CC(CH_3)_3$, O_2C^tBu, Cl) with monosubstituted alkynes in the presence of Et_3Al results in the highly regio- and stereo-selective ethylalumination of the terminal alkyne.

Organometallic derivatives of zirconium porphyrins have also been isolated using the diacetate complex $(TPP)Zr(OAc)_2$ as a starting material.[15] Treatment of $(TPP)Zr(OAc)_2$ with organo-lithium or organo-magnesium compounds gave the corresponding σ-bonded organozirconium(IV) porphyrins $(TPP)ZrR_2$ (R = Me, Et, *n*-Bu, and Ph). Of particular interest is the reported clean photoreduction of $(TPP)ZrMe_2$ to form a low-valent zirconium(II) species. The authors report that after 3 hours of irradiation (λ>420 nm), a C_6D_6/Et_2O solution of $(TPP)ZrMe_2$ gradually changed color from red to green. In the ^1H NMR spectrum, the signal attributed to the methyl groups disappeared, while the resonances due to the ortho-protons of the phenyl rings became a single resonance, indicating that the two sides of the porphyrin plane are now equivalent. The authors suggested that the product is in fact a six-coordinate zirconium porphyrin with trans diethyl ether molecules. Upfield signals of coordinated ether are visible in the ^1H NMR spectrum. The ether ligands were readily displaced upon addition of 1-methylimidazole. Addition of trimethylphosphine or *tert*-butylacetylene did not displace the coordinated diethyl ether.

Zirconium bis(porphyrinato) complexes have been synthesized by treatment of $Zr(NEt_2)_4$ with the free-base porphyrins H_2TPP or H_2OEP.[16] The hafnium analogue $Hf(OEP)_2$ may be similarly prepared from $Hf(NEt_2)_4$. The same double decker porphyrins were reported by Buchler from the treatment of $Li_2(POR)$[17] (POR = TPP or OEP) with the appropriate metallocene dichloride in refluxing 1,2,4-trichlorobenzene.[18]

The following chapter discusses our work involving the synthesis of early transition metal porphyrin halide complexes.

References

1. Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience, New York, **1988**.
2. (a) Dolphin, D. *The Porphyrins*; Academic: New York, 1978; Vols. 1-4. (b) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975.
3. (a) Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976. (b) Arnold, J.; Dawson, D. Y.; Hoffman, C. G. *J. Am. Chem. Soc.* **1993**, *115*, 2707.
4. Brand, H.; Capriotti, J. A.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 4334.
5. Buchler, J. W. In *The Porphyrins*; Dolphin D.; Ed.; Academic: New York, 1978; Vol. 1, p. 390.
6. Sewchok, M. G.; Haushalter, R. C.; Merola, J. S. *Inorg. Chim. Acta* **1988**, *144*, 47.
7. (a) Arnold, J.; Hoffman, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics*

1993, *12*, 3645. (b) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620.

8. (a) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102. (b) Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. *Inorg. Chem.* **1993**, *32*, 4186.
9. (a) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (b) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.
10. Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996.
11. Kim, H. J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360.
12. Ryu, S.; Whang, D.; Kim, J.; Yeo, W.; Kim, K. *J. Chem. Soc., Dalton Trans.* **1993**, 205.
13. Ryu, S.; Whang, D.; Yeo, H.; Kim, K. *Inorg. Chim. Acta* **1994**, *221*, 51.
14. Shibata, K.; Aida, T.; Inoue, S. *Tetrahedron Lett.* **1992**, *33*, 1077.
15. Shibata, K; Aida, T.; Inoue, S. *Chem. Let.* **1992**, 1173.
16. Kim, K.; Lee, W. S.; Kim, H. J.; Cho, S. H.; Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. *Inorg. Chem.* **1991**, *30*, 2652.
17. Li_2(POR) was prepared from the treatment of free base H_2POR with butyllithium in hexane.
18. (a) Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, D.; Weiss, R. *Chem. Ber.* **1991**, *124*, 1051. (b) Buchler, J. W.; De Cian, A.; Elschner, S.; Fischer, J.; Hammerschmitt, D.; Weiss, R. *Chem. Ber.* **1992**, *125*, 107.

CHAPTER 2: SYNTHESIS OF EARLY TRANSITION METAL PORPHYRIN HALIDE COMPLEXES: FIRST STRUCTURAL CHARACTERIZATION OF A VANADIUM(III) PORPHYRIN

A paper published in Inorganic Chemistry[1]

Lisa M. Berreau, J. Alan Hays, Victor G. Young, Jr., and L. Keith Woo*[2]

Abstract

A general method for the preparation of early transition metal porphyrin halide complexes using a porphyrin dianion, $(THF)_2Li_2(POR)$ (POR = OEP, TTP; OEP = octaethylporphyrinato, TTP = *meso*-tetra-*p*-tolylporphyrinato), and the appropriate metal halide complex, MX_n (MX_n = $VCl_3(THF)_3$, $TiCl_4(THF)_2$, $TiCl_3(THF)_3$, $MoCl_4(CH_3CN)_2$, WCl_4), is described. The structure of $(TTP)V^{III}Cl{\bullet}THF$ (**2•THF**) has been determined by single-crystal X-ray diffraction analysis. Complex **2•THF** crystallizes in the centrosymmetric space group $P2_1/m$ with a = 11.968(2) Å, b = 17.072(3) Å, c = 12.649(2) Å, β = 98.62(2)°, V = 2555.2(8) Å^3, Z = 2, R = 4.6%, and R_w = 6.7%. The V-Cl bond length is 2.272(1) Å, the V-N bond lengths range from 2.040(4) to 2.050(4) Å, and the V-O bond distance is 2.141(3) Å.

---

[1] Reprinted with permission from *Inorg. Chem.* **1993**, *33*, 105. Copyright © 1993 American Chemical Society.

Introduction

Recently, there has been renewed interest in the synthesis of early transition metal porphyrin halide complexes.[3] Such compounds have led to the development of new organometallic complexes.[3a,3b,3d,4] Furthermore, we have shown that low valent metalloporphyrin halides, in particular those of titanium, chromium, and manganese serve as good oxygen or nitrogen atom acceptors in inner sphere electron transfer reactions.[5]

Typically, synthetic routes to the dihalogeno metalloporphyrins have involved treatment of high valent oxo complexes, (POR)M=O (M = Ti, V, Mo; POR = OEP, TTP, TPP, or TmTP)[6], with HX (X = F, Cl, Br), SOX_2, or $(COX)_2$ to produce $(POR)M^{IV}X_2$.[7] Also, reduction of (TTP)W(O)(Cl) with Si_2Cl_6 followed by treatment with HCl(g) produced the $(TTP)W^{IV}Cl_2$ complex.[8] Lower valent compounds, such as $(TPP)Ti^{III}F$, have been prepared by Zn/Hg reduction of $(POR)M^{IV}$ complexes, eg. $(TTP)Ti^{IV}F_2$.[9] Recently, the electrochemical generation of a vanadium(III) porphyrin, $X\text{-}V^{III}(TTP)(THF)$, by reduction of $(TTP)V^{IV}X_2$ (X = Cl, Br) was reported.[10]

Because of our interest in using metalloporphyrin halide complexes as starting materials for the synthesis of low valent derivatives and as atom acceptor species, we have developed a more general means of preparing such vanadium, titanium, molybdenum, and tungsten compounds using a modified porphyrin dianion method first reported by Arnold.[11] In addition, the first structural characterization of a vanadium(III) porphyrin complex is reported here.

Experimental

General. Toluene, THF, d_6-benzene, and hexanes for glovebox use were distilled from their purple sodium benzophenone ketyl solutions. $CDCl_3$ was distilled from phosphorus pentoxide. CH_3CN and CH_2Cl_2 were distilled from CaH_2. Dry solvents were subsequently degassed on a vacuum line (10^{-5} torr) with three successive freeze-pump-thaw cycles. VCl_3, $TiCl_3$, $TiCl_4$, $MoCl_5$, and $LiN(TMS)_2$ were purchased from Aldrich and used without further purification. $VCl_3(THF)_3$,[11] $TiCl_4(THF)_2$,[12] $TiCl_3(THF)_3$,[11] $(THF)_2Li_2(TTP)$,[10] $(THF)_2Li_2(OEP)$,[10] H_2TTP,[13] $MoCl_4(CH_3CN)_2$,[14] and WCl_4[15] were prepared according to literature procedures.

All manipulations were performed either in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV-visible data were obtained using a Hewlett-Packard HP 8452A diode array spectrophotometer. ^1H NMR spectra were recorded on a Nicolet NT300 spectrometer. Room temperature magnetic susceptibilities were measured at ambient temperature by Evans' method.[16] Elemental analyses were obtained from Desert Analytics, Tucson, AZ.

Chloro(2,3,7,8,12,13,17,18-Octaethylporpyrinato)vanadium(III). General Method. $(THF)_2Li_2(OEP)$ (87.3 mg, 0.105 mmol) was stirred with $VCl_3(THF)_3$ (45.3 mg, .0121 mmol) in toluene (20 mL) with mild heating for 8 h. During this time the color of the solution gradually changed from claret to brown with the formation of (OEP)VCl. The solution was then filtered, concentrated to ca. 3 mL, layered with ca. 8 mL hexane, and was cooled to -20 °C for 24 h. Filtration and washing with hexanes produced a brown solid. This crude solid was then dissolved in 10 mL CH_2Cl_2 and was filtered. The volume of CH_2Cl_2 was reduced to ca. 3 mL. The solution was layered with ca. 6 mL hexanes and was cooled to -20 °C for 12 h. Filtration, washing with hexanes, and drying in vacuo produced a brown solid (30.6 mg, 47%). UV-vis (Toluene): 406 (Soret), 534, 576 ^1H NMR (C_6D_6): 40.26 (s, 4H, *meso*-H), 10.91 (br, 8H, -

CH_2CH_3), 7.02 (br, 8H, -CH_2CH_3), 2.17 (br, 24H, -CH_2CH_3). ^{1}H NMR ($CDCl_3$): 45.18 (s, 4H, *meso*-H), 11.45 (br, 8H, -CH_2CH_3), 6.81 (br, 8H, -CH_2CH_3), 2.27 (br, 24, -CH_2CH_3). μ_{eff} = 2.51 B.M. MS{EI} Calcd. (found) m/e: 618 (618) $[M]^+$, 583 (584) $[M + H - Cl]^+$. IR (KBr): $\nu_{V\text{-}Cl}$ = 392 cm^{-1}. Anal. Calcd. (found) for $C_{36}H_{44}N_4VCl$: C, 69.87 (68.60); H, 7.17 (6.51); N, 9.06 (9.91).

Chloro(5,10,15,20-Tetratolylporphyrinato)vanadium(III). Using the general method outlined for preparation of (OEP)VCl, (TTP)VCl was prepared from $(THF)_2Li_2(TTP)$ (330.4 mg, 0.400 mmol) and $VCl_3(THF)_3$ (196.6 mg, 0.527 mmol) in 92% yield. UV-vis (Toluene): 424 (Soret), 548. ^{1}H NMR (C_6D_6): 8.73 (m, 8H), 7.30 (m, 8H), 5.77 (m, 8H), 2.22 (s, 12H).

Dichloro(5,10,15,20-Tetratolylporphyrinato)titanium(IV). $(THF)_2Li_2(TTP)$ (128.2 mg, 0.155 mmol) and $TiCl_4(THF)_2$ (57.1 mg, 0.171 mmol) were stirred in toluene (25 mL) with mild heating for 4 h, resulting in a color change from blue-green to dark green. The solution was then allowed to cool to room temperature and was subsequently filtered. The filtrate was evaporated to dryness, redissolved in a minimum of toluene, and was cooled to -20 °C for 16 h. A green solid was isolated (72.9 mg, 60%). UV-vis: 320, 376 (Soret), 420, 492. ^{1}H NMR (C_6D_6): 9.02 (s, 8H, β-H), 7.88 (d, 8H, -$C_6H_4CH_3$), 7.20 (d, 8H, -$C_6H_4CH_3$), 2.37 (s, 12H, -$C_6H_4CH_3$). Anal. Calcd. (found) for $C_{48}H_{36}N_4TiCl_2$: C, 73.20 (72.26); H, 4.61 (4.38); N, 7.11 (7.30).

Chloro(5,10,15,20-Tetratolylporphyrinato)titanium(III). $(THF)_2Li_2(TTP)$ (124.0 mg, 0.150 mmol) and $TiCl_3(THF)_3$ (57.0 mg, 0.154 mmol) were stirred in toluene (15 mL) with mild heating for 6 h resulting in a color change form blue-green to dark purple. Following the procedure described for the isolation of $(TTP)TiCl_2$, a purple microcrystalline solid was obtained (90.5 mg, 81%). UV-vis(toluene): 428 (Soret), 552. ^{1}H NMR (C_6D_6): 2.37 (br, -$C_6H_4CH_3$).

Anal. Calcd. (found) for $C_{48}H_{36}N_4TiCl$: C, 76.65 (76.08); H, 4.82 (4.73); N, 7.45 (7.51).

Dichloro(5,10,15,20-Tetratolylporphyrinato)molybdenum(IV). $(THF)_2Li_2(TTP)$ (104.1 mg, 0.126 mmol) was stirred with $MoCl_4(CH_3CN)_2$ (107.0 mg, 0.334 mmol) in toluene (20 mL) with mild heating for 12 h. After allowing the solution to cool to room temperature, the solution was filtered producing a purple precipitate. The solid was redissolved in CH_2Cl_2 (15 mL) and was filtered. After the filtrate was evaporated to dryness, the product was recrystallized from CH_2Cl_2/hexane (1:3) to produce a green solid (50.0 mg, 48%). UV-vis (Toluene): 366, 398, 420, 496, 578. ^1H NMR($CDCl_3$): 17.69 (s, 8H, β-H), 10.09 (d, 8H, $-C_6\mathit{H}_4CH_3$), 7.71 (d, 8H, -$C_6\mathit{H}_4CH_3$), 2.46 (s, 12H, $-C_6H_4C\mathit{H}_3$). MS{EI} Calcd. (found) 836 (836) $[M]^+$, 801 (801) $[M\text{-}Cl]^+$.

Dichloro(5,10,15,20-Tetratolylporphyrinato)tungsten(IV). $(THF)_2Li_2(TTP)$ (131.4 mg, 0.159 mmol) was stirred with WCl_4 (88.8 mg, 0.273 mmol) in toluene (20 mL) with mild heating for 12 h. After allowing the solution to cool to room temperature, the solution was filtered producing a green precipitate. The solid was redissolved in CH_2Cl_2 (15 mL) and was filtered. After the filtrate was evaported to dryness, the product was recrystallized from CH_2Cl_2/hexane (1:2) to produce a black solid (58.6 mg, 40%). UV-vis (Toluene): 336, 370, 388, 420, 466, 558. ^1H NMR ($CDCl_3$): 14.39 (s, 8H, β-H), 9.12 (d, 8H, $-C_6\mathit{H}_4CH_3$), 8.07 (d, 8H, $-C_6\mathit{H}_4CH_3$), 2.85 (s, 12H, $-C_6H_4C\mathit{H}_3$). ^1H NMR (C_6D_6): 14.31 (s, 8H, β-H), 8.82 (d, 8H, $-C_6\mathit{H}_4CH_3$), 7.68 (d, 8H, $C_6\mathit{H}_4CH_3$), 2.49 (s, 12H, $-C_6H_4C\mathit{H}_3$). μ_{eff} = 1.75 B.M. MS{EI} Calcd. (found) m/e 924 (924) $[M]^+$. Anal. Calcd. (found) for $C_{48}H_{36}N_4WCl_2$: C, 62.92 (62.44); H, 3.93 (3.77); N, 6.07 (5.85).

X-ray Crystal Structure Determination of (TTP)VCl. Crystals of (TTP)VCl•THF suitable for single-crystal X-ray diffraction were grown by layering a benzene/THF solution of (TTP)VCl with hexane. A brown platelet (0.50 X 0.45 X 0.15 mm) was attached to the tip of a glass fiber and mounted on a Siemens P4/RA diffractometer for data collection at -60 ± 1 °C using Cu K_α radiation ($\lambda = 1.54178$ Å). Cell constants were determined from a list of reflections found by a rotation photograph. Pertinent data collection and reduction information is given in Table I. Lorentz and polarization corrections were applied. A correction based on non-linear decay in the standard reflections was applied to the data. An absorption correction was deemed unnecessary for this study. The agreement factor for the averaging of observed reflections was 2.9% (based on F).

The centric space group $P2_1/m$ was indicated initially by systematic absenses and intensity statistics. The structure was solved in $P2_1$ and after completion transformed to the centrosymmetric space group. All atoms were located by a Patterson interpretation technique. All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least-squares converged all hydrogen atoms were placed at calculated positions 0.96 Å from the attached atom with isotropic temperature factors set equal to the isotropic equivalent of the host atom. Two solvent molecules of benzene were found in the lattice.

The porphyrin ring is bisected by a crystallographic mirror in this space group. This requires that the THF ligand be disordered over two equivalent sites with 50% occupancy. The normal "puckering" of the THF was not found in this analysis, but rather the ligand is dynamically disordered over the two "puckered" geometries for an averaged local structure.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. VaxStation 3100 computer using the SHELXTL PLUS version 4.0 programs.[17]

Results

Preparation and Characterization of Vanadium(III) Porphyrins. As illustrated in eq 1, vanadium(III) porphyrin halide complexes were prepared using a porphyrin dianion and the appropriate metal halide complex. The vanadium complexes, (POR)V^{III}Cl, (POR = OEP or TTP) were isolated as brown solids which have good solubility in toluene, benzene, THF, dichloromethane, and chloroform, but have low solubility in n-hexane. Complexes **1** and **2** are both extremely air sensitive and are converted to the corresponding vanadyl complexes on exposure to oxygen.

$$(THF)_2Li_2(POR) + MX_n \longrightarrow (POR)MX_{n-2} + 2\ LiCl + THF \qquad (1)$$

1, POR = OEP; $MX_n = VCl_3(THF)_3$

2, POR = TTP; $MX_n = VCl_3(THF)_3$

The electronic absorption spectra of **1** and **2** are characteristic of porphyrin complexes with an intense Soret peak at 406 nm for (OEP)V^{III}Cl and 426 nm for (TTP)V^{III}Cl in toluene. Dilute solutions of both complexes are yellow while more concentrated solutions are brown. The absorption spectra are similar to those of vanadium(IV) porphyrins.[6b]

The ^{1}H NMR spectrum for (OEP)V^{III}Cl in d_6-benzene shows broad resonances for the meso protons at 43.3 ppm, for the methylene protons at 11.3 and 6.5 ppm, and for the methyl protons at 2.1 ppm. The proton assignments were made on the basis of intensity. The large chemical shift range is indicative of the paramagnetic character of the compound. The magnetic moment of (OEP)V^{III}Cl, determined at ambient temperature by Evans' method, was found to be

2.51 B.M.[15] The TTP analogue, 2, was also found to be paramagnetic.

X-Ray Structure of (TTP)VCl•THF. The molecular structure of the TTP complex 2 was determined by single-crystal X-ray diffraction. The molecular structure and atom numbering scheme are shown in Figure 1. Crystallographic data for the structure determination is listed in Table I. Atomic positional parameters are given in Table II. Table III presents selected bond distances and angles. Tables I-III are found in Appendix A.

Complex 2 crystallizes in the centrosymmetric space group $P2_1/m$ with 2 molecules per unit cell. The 24 atoms of the porphyrin core are nearly coplanar, with the largest out-of-plane displacement of 0.10 Å by C(8). In addition, the vanadium ion is displaced from the mean porphyrin plane 0.15 Å toward the Cl ligand. The V-N distances range from 2.040(4) to 2.050(3) Å and are typical of those observed for other vanadium porphyrin complexes.[18] The phenyl rings form dihedral angles with the porphyrin plane of 63.4 and 85.4°.

The V-O(1) distance, 2.141(3) Å, is similar to that reported for $(OEP)V(THF)_2$ (2.174(4) Å).[17c] However, this distance is much shorter that that observed in $(TPP)Fe(THF)_2$ (Fe-O 2.351(3) Å at room temperature and 2.288(1) Å at liquid-nitrogen temperature).[19] The iron(II) complex is high spin, S = 2. Similarly, the Zn-O distance of 2.380(2) Å in $(TPP)Zn(THF)_2$ suggests that the THF molecules are bound weakly to the zinc atom. In both the iron and zinc complexes, population of the dz^2 orbital, which is partially metal-THF antibonding, is reflected in the long metal-oxygen distance.[20] In $(OEP)V(THF)_2$ and (TTP)VCl·THF this orbital is empty and results in a stronger V-O interaction.[17c] The V-Cl bond length in **2**•THF (2.272(1) Å) is similar to that reported for other vanadium(III) macrocycles with nitrogen donor ligands. For example, a compound utilizing the

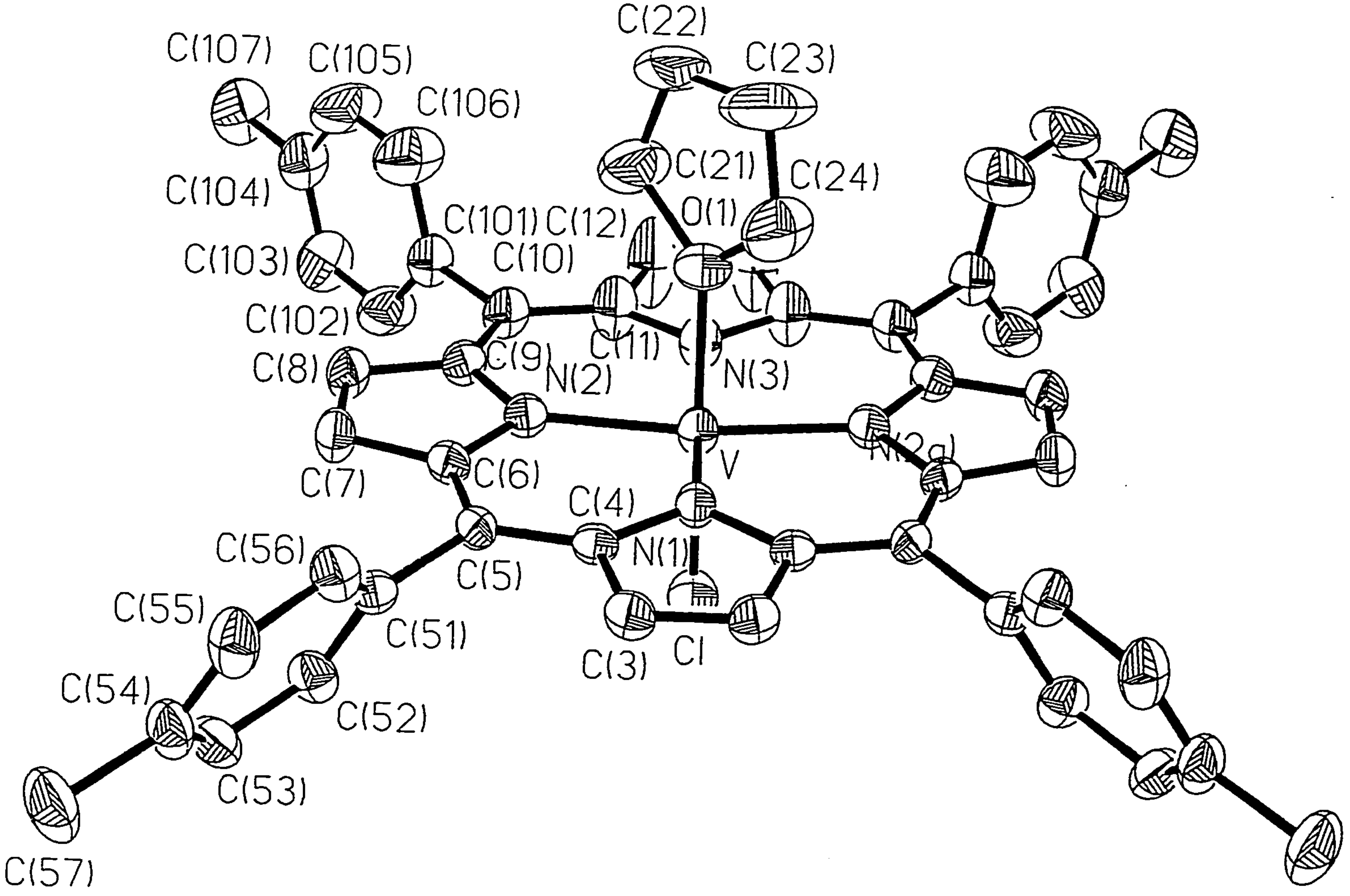


Figure 1. Molecular structure and atom numbering scheme for (TTP)VCl•THF. Only one of two possible orientations of the coordinated THF ligand is shown. Thermal ellipsoids are shown at the 50% probability level.

dibenzotetramethyltetraaza-[14]-annulene ligand (tmtaa), $[(tmtaa)V(Cl)]\cdot 0.5C_7H_8$, has a V-Cl bond length of 2.221(5) Å.[21] Schiff base complexes have slightly longer V-Cl bond lengths, generally in the range of 2.34-2.37 Å.[22]

Preparation and Characterization of Titanium, Molybdenum, and Tungsten Porphyrin Halide Complexes. Titanium, molybdenum, and tungsten porphyrin halide complexes were also obtained by treating porphyrinato dianions with the appropriate metal halide complex (eq 2). $(TTP)Ti^{IV}Cl_2$ (**3**) and $(TTP)Ti^{III}Cl$ (**4**) were isolated in 60% and 81% yields respectively after recrystallization from toluene/hexane (1:2). Both complexes have good solubility in halogenated solvents but low solubility in n-hexane. In aromatic solvents, $(TTP)Ti^{IV}Cl_2$ has low solubility whereas $(TTP)Ti^{III}Cl$ is more soluble. Spectroscopic characterization of complexes **3** and **4**, using ^1H NMR and UV-vis, was consistent with that previously reported for $(TPP)Ti^{IV}Cl_2$ and analogous $(TPP)Ti^{III}$ complexes.[23,24]

$(TTP)Mo^{IV}Cl_2$ (**5**) and $(TTP)W^{IV}Cl_2$ (**6**) were isolated after recrystallization from CH_2Cl_2/hexane (1:3). Both complexes have good solubility in dichloromethane,

$$(THF)_2Li_2(POR) + MX_n \longrightarrow (POR)MX_{n-2} + 2\,LiCl + THF \qquad (2)$$

3, POR = TTP; $MX_n = TiCl_4(THF)_2$

4, POR = TTP; $MX_n = TiCl_3(THF)_3$

5, POR = TTP; $MX_n = MoCl_4(CH_3CN)_2$

6, POR = TTP; $MX_n = WCl_4$

chloroform, and THF, but limited solubility in toluene, benzene, and n-hexane. The ^1H NMR of 5 and 6 were similar to reported spectra.[6d,7]

Discussion

The synthetic method we have employed to prepare early transition metal porphyrin halide complexes of vanadium, titanium, molybdenum, and tungsten has many advantages over previously reported methods. For example, this simple route provides a convenient means of synthesizing vanadium(III) porphyrins, species previously prepared only by electrochemical methods.[9] These complexes are paramagnetic as evidenced by the large chemical shift range and broadness of the resonances in the ^1H NMR. The paramagnetic character of $(TTP)V^{III}Cl$ is in sharp contrast to the diamagnetic behavior reported earlier.[9] $(TTP)V^{III}Cl$ is the first vanadium(III) porphyrin to be structurally characterized. The V-O(1), V-Cl, and V-N bond lengths are similar to those in other vanadium porphyrins and vanadium containing macrocycles.[17,20,21]

Most insertions of titanium into a porphyrin free base ultimately result in the formation of very stable oxotitanium compounds.[25] However, such complexes cannot be directly converted to low-valent titanium porphyrin compounds.[26] Previously, preparation of dihalogenotitanium(IV) porphyrins involved treatment of the oxo complexes with hydrogen halides, SOX_2, or $(COX)_2$.[6] Titanium(III) porphyrin halide complexes were synthesized by reduction of the dihalogenotitanium(IV) porphyrins using Zn/Hg.[8] The synthetic method reported here provides the titanium(IV) and titanium(III) complexes in high purity under mild conditions.

The one-pot metathesis reaction (eq 2) simplifies the preparation of $(TTP)Mo^{IV}Cl_2$ and $(TTP)W^{IV}Cl_2$, useful precursors to the low-valent chemistry of molybdenum and tungsten porphyrins. The previous route to the tungsten complex, involved reduction of the W^{V}(POR)(O)(Cl) species with Si_2Cl_6 and resulted in a mixture of paramagnetic W^{IV}(POR)(X)(X') complexes where X or X' = Cl^-, Cl_3Si^-, or Cl_3SiO^-.[7] Subsequent treatment of the mixture of products with HCl(g) produced (TTP)$W^{IV}Cl_2$.[7] In contrast to this method, synthesis of (TTP)$W^{IV}Cl_2$ using $(THF)_2Li_2$(TTP) is rather simple because of the low solubility of (TTP)$W^{IV}Cl_2$ in toluene. As the reaction proceeds, (TTP)$W^{IV}Cl_2$ precipitates out of solution. After filtration to remove the crude product from the toluene solution, the resulting solid is redissolved in CH_2Cl_2, filtered, and isolated by evaporating the filtrate to dryness. Recrystallization from CH_2Cl_2/hexane provides (TTP)$W^{IV}Cl_2$ in high purity.

References

1. Reprinted with permission from *Inorg. Chem.* **1994**, *33*, 105. Copyright © 1993 American Chemical Society.
2. Presidential Young Investigator, 1990-1995; Camille and Henry Dreyfus Teacher-Scholar 1993-1998.
3. (a) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.*, **1990**, *112*, 8620. (b) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (c) Ryu, S.; Whang, D.; Kim, W.; Yeo, W.; Kim, K. *J. Chem. Soc. Dalton Trans.* **1993**, 205. (d) Kim, H. J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360.
4. (a) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

(b) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996.

4. (a) Woo, L. K.; Czapla, D. J.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3915. (b) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916. (c) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. (d) Woo, L. K.; Goll, J. G.; Berreau, L. M.; Weaving, R. *J. Am. Chem. Soc.* **1992**, *114*, 7411.

6. Abbreviations: OEP is the octaethylporphyrinato dianion, TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion, TPP is the *meso*-tetraphenylpophyrinato dianion, and TmTP is the *meso*-tetra-*m*-tolylporphyrinato dianion.

7. (a) Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87. (b) Nakajima, M.; Latour, J. M.; Marchon, J. C. *J. Chem. Soc. Chem. Commun.* **1977**, 763. (c) Richard, P.; Poncet, J. L.; Barbe, J. M.; Guilard, R.; Goulon, J.; Rinaldi, D.; Cartier, A.; Tola, P. *J. Chem. Soc. Dalton Trans.* **1982**, 1421. (d) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.*, **1979**, *18*, 1193. (e) Guilard, R.; Latour, J. M.; Lecomte, C.; Marchon, J. C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1225.

8. Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.

9. Latour, J. M.; Marchon, J. C.; Nakajima, M. *J. Am. Chem. Soc.* **1979**, *101*, 3974.

10. (a) Reeb, P; Mugnier, Y.; Guilard, R.; Laviron, E. *Inorg. Chem.* **1987**, *26*, 209. (b) Reeb, P.; Mugnier, Y. *J. Organomet. Chem.* **1988**, *339*, 89.

11. (a) $(THF)_2Li_2(TTP)$ was prepared according to the literature method for the preparation of $(THF)_2Li_2(OEP)$. Arnold, J. *J. Chem. Soc. Chem. Commun.* **1990**, 976. (b) Spectroscopic data for $(THF)_2Li_2(TTP)$: ^{1}H NMR (C_6D_6): 9.27 (s, 8H, β-H), 8.32 (d, 8H, $-C_6\mathit{H}_4CH_3$),

7.41 (d, 8H, $-\mathrm{C}_6H_4\mathrm{CH}_3$), 2.46 (s, 12H, $-\mathrm{C}_6\mathrm{H}_4\mathrm{C}H_3$), 0.30 (br, 8H, THF), -0.25 (br, 8H, THF); UV-vis (Toluene): 422 (soret), 574, 616.

12. Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

13. (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, *48*, 4251.

14. Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1990**, *28*, 38.

15. Schaefer, M. Ph.D. Dissertation, Iowa State University, 1971.

16. (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872. (c) Loliger, J.; Scheffold, R. *J. Chem. Ed.* **1972**, *49*, 646.

17. SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, USA.

18. (a) Poncet, J. L.; Barbe, J. M.; Guilard, R.; Oumous, H.; Lecomte, C.; Protas, J. *J. Chem. Soc. Chem. Comm.* **1982**, 1421. (b) Drew, M. G. B.; Mitchell, P. C. H.; Scott, C. E. *Inorg. Chim. Acta* **1984**, *82*, 63. (c) Poncet, J. L.; Barbe, J. M.; Guilard, R.; Oumous, H.; Lecomte, C.; Protas, J. *J. Chem. Soc. Dalton Trans.* **1984**, 2677. (d) Molinaro, F. S.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2278.

19. (a) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K; Lang, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302.

20. Schauer, C. K.; Anderson, O. P.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1985**, *24*, 4082.

21. Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96.

22. (a) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 4158. (b) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308. (c) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1992**, *31*, 141.

23. (a) Nakajima, M.; Latour, J. M.; Marchon, J. C. *J. Chem. Soc. Chem. Commun.* **1977**, 763. (b) Marchon, J. C.; Latour, J. M.; Grand, A.; Belakhovsky, M.; Loos, M.; Goulon, J. *Inorg. Chem.* **1990**, *29*, 57. (c) Latour. J. M.; Marchon, J. C.; Nakajima, M. *J. Am. Chem. Soc.* **1979**, *101*, 3974.

24. Boreham, C. J.; Buisson, G.; Duee, E.; Jordanov, J.; Latour, J. M.; Marchon, J. C. *Inorg. Chim. Acta* **1983**, *70*, 77.

25. Fournari, P.; Guilard, R.; Fontesse, M.; Latour, J. M.; Marchon, J. C. *J. Organomet. Chem.* **1976**, *110*, 205.

26. Malinski, T.; Chang, D; Latour, J. M.; Marchon, J. C.; Gross, M.; Giraudeau, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 3947.

APPENDIX A

Table I. Crystal Data for (TTP)VCl·THF· 2 C_6H_6

Formula	$VClN_4OC_{52}H_{44}\cdot 2(C_6H_6)$
Formula Weight	983.5
Space Group	$P2_1/m$
a, Å	11.968(2)
b, Å	17.072(3)
c, Å	12.649(2)
β, deg	98.62(2)
V, $Å^3$	2552.2(8)
Z	8
d_{calc}, g/cm^3	1.345
Crystal Size, mm	0.50 x 0.45 x 0.15
μ (Cu K_α), mm^{-1}	2.468
Data Collection Instrument	Siemens P4/RA
Radiation	CuK_α (λ = 1.54178 Å)
Temperature, K	213
Scan Type	2θ-θ
Scan Speed	Constant; 11.72°/min in x
Scan Range (x)	0.80° plus K_α-separation
Reflections Collected	7157
Independent Reflections	3580 (R_{int} = 2.86%)

Table I. (continued)

Observed Reflections	2747 ($F > 6.0r(F)$)
R[a]	0.0460
R_w[b]	0.0666
Quality of fit indicator[c]	1.56
Largest shift/esd. final cycle	0.017
Largest peak, e/Å^3	0.29

[a] $R = \Sigma| \, |F_o| - |F_c| / |F_o| \, |$

[b] $R = [\Sigma w(|F_o| - |F_c|^2 / \Sigma w |F_o|^2]^{1/2}$, $w = 1\text{-}\sigma^2 |F_o|$

[c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / N_{obs} - N_{parameters}]^{1/2}$

Table II. Atomic coordinates ($x10^5$) and equivalent isotropic displacement coefficients ($Å^2$ x 10^4)

	x	y	z	U(eq)
V	727(6)	25000	25973(6)	283(3)
Cl	10347(9)	25000	42883(10)	438(4)
C(3)	-30262(23)	21067(17)	38234(25)	318(10)
C(4)	-20533(22)	18526(16)	33715(22)	255(9)
N(1)	-14883(26)	25000	30790(mx)	265(11)
C(5)	-17096(22)	10638(16)	33103(22)	256(9)
C(6)	-7621(22)	8186(16)	28648(21)	272(9)
C(7)	-4824(24)	207(17)	26818(24)	348(11)
C(8)	4541(25)	249(18)	21968(25)	372(11)
N(2)	202(17)	13014(14)	25006(17)	290(8)
C(9)	7814(23)	8222(17)	20978(23)	325(10)
C(10)	17347(24)	10707(18)	16798(26)	375(11)
N(3)	14922(29)	25000	18835(31)	383(13)
C(11)	20754(27)	18540(19)	16176(31)	470(13)
C(12)	30642(34)	21043(21)	12061(43)	812(20)
C(51)	-23405(23)	4515(16)	38104(23)	278(10)
C(52)	-17820(24)	265(17)	46671(24)	340(10)
C(53)	-23219(26)	-5498(18)	51643(25)	392(11)
C(54)	-34520(27)	-7148(17)	48370(28)	402(11)

Table II. (continued)

	x	y	z	U(eq)
C(55)	-40172(25)	-2846(18)	39965(27)	401(11)
C(56)	-34773(24)	2828(17)	34789(25)	349(10)
C(57)	-40365(31)	-13520(20)	53752(32)	610(15)
C(101)	24223(26)	4614(18)	12186(28)	402(12)
C(102)	33145(30)	859(21)	18202(30)	540(14)
C(103)	39596(30)	-4527(22)	13647(32)	579(15)
C(104)	37322(30)	-6297(20)	2938(31)	509(14)
C(105)	28535(35)	-2454(24)	-3005(33)	723(17)
C(106)	22072(33)	2862(24)	1548(32)	667(16)
C(107)	44568(33)	-12083(23)	-2030(36)	769(18)
O(1)	-8096(26)	25000	9942(24)	424(11)
C(21)	-4984(73)	20059(48)	922(64)	716(34)
C(22)	-11678(120)	22481(55)	-8556(74)	1177(63)
C(23)	-18500(124)	29024(69)	-5260(75)	1354(67)
C(24)	-16930(66)	29874(48)	5780(60)	713(33)
C(1S)	-30250(47)	21001(29)	66964(36)	849(20)
C(2S)	-21343(61)	17095(29)	64231(37)	921(25)
C(3S)	-12434(46)	21014(33)	61555(38)	990(25)
C(4S)	17437(75)	28877(43)	79465(88)	1121(45)

Table II. (continued)

	x	y	z	U(eq)
C(5S)	26536(58)	32654(30)	77418(72)	1361(43)
C(6S)	36243(71)	28630(38)	75080(75)	1146(43)
C(7S)	25786(305)	28673(120)	87242(166)	1475(141)
C(8S)	24356(194)	28292(108)	69022(138)	1084(100)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table III. Selected Bond Distances (Å) and Angles (deg) for 2

V-Cl	2.272(1)	Cl-V-N(1)	94.4(1)
V-N(1)	2.050(3)	Cl-V-N(2)	93.6(1)
V-N(2)	2.050(2)	Cl-V-N(4)	94.5(1)
V-N(3)	2.040(4)	Cl-V-N(2A)	93.6(1)
V-N(2A)	2.050(2)	Cl-V-O(1)	179.1(1)
V-O	2.141(3)	N(1)-V-O(1)	86.5(1)
		N(2)-V-O(1)	86.4(1)
		N(3)-V-O(1)	84.6(1)
		N(2A)-V-O(1)	86.4(1)
		N(1)-V-N(2)	93.6(1)
		N(1)-V-N(3)	171.1(1)
		N(2)-V-N(3)	89.6(1)
		N(1)-V-N(2A)	89.8(1)
		N(2)-V-N(2A)	172.8(1)
		N(3)-V-N(2A)	89.6(1)

CHAPTER 3: RECENT ADVANCES IN THE SYNTHESIS OF TERMINAL CHALCOGENIDO COMPLEXES OF THE EARLY TRANSITION METALS AND MAIN GROUP ELEMENTS; SULFUR AND SELENIUM ATOM TRANSFER

While the chemistry of compounds containing terminal M=O bonds have been widely explored, related studies involving the heavier analogues, in particular terminal selenides and tellurides, have only recently appeared in the literature.[1,2] This chapter highlights recent developments in the synthesis and reactivity of early transition metal and main group complexes containing multiple bonds to the heavier chalcogenides. Examples of intermetal atom transfer reactions involving sulfur and selenium atom transfer will also be explored.

Synthesis of Group IV-VI terminal chalcogenido complexes

The chemistry of Group IV species containing multiple bonds to the Group 16 elements has been the focus of a number of recent studies, particularly emanating from the research labs of Bergman and Parkin. Bergman *et al.*, were the first to isolate a terminal chalcogenido species of zirconium.[3] Reported in 1990, $Cp^*_2Zr(S)(NC_5H_4R)$ (R = H, tBu), was prepared by dehydrohalogenation of $Cp^*_2Zr(SH)I$ and was subsequently trapped by pyridine to give the final product.

Parkin and Howard have reported the preparation of the first complete series of terminal Group 16 complexes of zirconium, all of the general formula $Cp'_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te; Cp' = Cp^* or η^5-C_5Me_4Et).[4] The complexes were prepared via the reaction of $Cp_2'Zr(CO)_2$ with either N_2O or the elemental chalcogen in the presence of pyridine. All species were characterized by single-crystal X-ray diffraction analysis.

The analogous terminal titanium oxo complex, $Cp^*_2Ti{=}O$(4-phenylpyridine), was reported by Andersen.[5] As with the synthesis of the above zirconium complexes, the terminal oxo species was prepared from a low-valent precursor. Treatment of Cp^*_2Ti with N_2O in pentane yielded a green insoluble material whose ^1H NMR spectrum indicated a mixture of compounds including $Cp^*_2Ti(CH_2C_5Me_4)(\mu\text{-}O)_2$ and $Cp^*_2Ti_4(\mu\text{-}O)_6$. If the reaction was carried out in the presence of pyridine:THF (1:10), an orange crystalline complex was isolated. The product, $Cp^*_2Ti(O)(py)$, was characterized using ^1H NMR, IR, mass spectrometry, and by single-crystal X-ray diffraction analysis (d_{Ti-O} = 1.665(3) Å). In contrast, synthesis of $Cp^*_2V{=}O$ did not require the presence of a two-electron donor ligand. Treatment of Cp^*_2V with nitrous oxide in hexane yielded the desired product in 45% isolated yield.

Interesting new terminal chalcogenide complexes of the Group 5 metals have been reported by Schrock and Arnold.[6] In each case, the complex is stabilized by a sterically demanding tetradentate substituted amine, $[(Me_3Si)HNCH_2CH_2]_3$, $H_3[N_3N]$.[7] Cummins and Schrock found that treatment of a low-valent vanadium precursor, $[N_3N]V$, with either elemental sulfur or ethylene sulfide gave $[N_3N]V{=}S$, while gray selenium reacts with $[N_3N]V$ to give $[N_3N]V{=}Se$. The terminal tellurido species is not formed from the reaction $[N_3N]V$ with elemental tellurium but may be generated and observed in solution upon treatment of $[N_3N]V$ with $Me_3P{=}Te$. The corresponding oxo derivative was synthesized via treatment of $[N_3N]V$ with propylene oxide, *cis*- or *trans*-2-butene oxide, pyridine-N-oxide, nitrous oxide, or dimethyl sulfoxide. The chalcogenide complexes $[N_3N]V{=}X$ (X = O, S, Se, Te) were characterized by ^{51}V NMR. Treatment of $[N_3N]V{=}Se$ with PMe_3 results in abstraction of the selenium from $[N_3N]V{=}Se$, forming $Me_3P{=}Se$ and regenerating $[N_3N]V$.

Terminal selenido and tellurido complexes of tantalum were prepared via treatment of the tantalum dihalide [$TaCl_2(N_3N)$] with $(THF)_2LiESi(SiMe_3)_3$ (E = Se[8], Te[9]). The new complexes were characterized using ^1H NMR, IR, mass spectrometry, Raman, ^{125}Te and ^{77}Se NMR spectroscopy, and X-ray crystallography.

Several recent studies have focused on the preparation and reactivity of new terminal sulfido, selenido, and tellurido complexes of the Group VI metals. Parkin, *et al.* have reported the synthesis of a new family of tungsten terminal chalcogenide complexes, all of the general formula trans-$W(PMe_3)_4(X)_2$ (X = S, Se, Te).[10] It should be noted that the tellurido analog was the first transition metal complex with a terminal tellurido ligand. The terminal sulfido and selenido complexes were prepared via the dehydrogenation of H_2S or H_2Se by $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. However, different intermediates were isolated in each case. In the preparation of the sulfido complex, a bis(hydrosulfido)complex, $W(PMe_3)_4(SH)_2H_2$, was isolated. In the preparation of the selenido species, a mono(selenido) complex, $W(PMe_3)_4(Se)H_2$ was isolated. The terminal tellurido complex was prepared via treatment of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with elemental tellurium. The terminal tellurido complex, *trans*-$W(PMe_3)_4(Te)_2$, has been found to undergo reductive coupling of the two terminal tellurido ligands to give an η^2-ditellurido derivative, $W(PMe_3)(CN^tBu)_4(\eta^2\text{-}Te_2)$ when treated with Bu^tNC.[11]

Group 14 complexes containing M=X (X = S, Se, Te)

Group 14 complexes containing multiple bonds to the heavier chalcogenides are rare.[12] Most such species have been observed simply as reactive intermediates. Parkin and Kuchta have recently reported the synthesis and structures of germanium terminal chalcogenido complexes of the formula (η^4-Me_8taa)GeE (E = S, Se, Te).[13] These complexes were prepared by treatment of $Li_2(Me_8taa)$[14] with $GeCl_2$(dioxane) in THF to give first the Ge(II) macrocyclic complexes. Addition of elemental sulfur or selenium to a benzene solution of (Me_8taa)Ge(II) produces the corresponding terminal sulfido and selenido species. The synthesis of the tellurido derivative requires the presence of PMe_3. The molecular structures have been determined for all three derivatives. The Ge=X bond lengths (Å) are: Ge=S, 2.110(2); Ge=Se, 2.247(1); and Ge=Te, 2.466(1). An interesting difference is associated with the configuration of the (η^4-Me_8taa) ligand. In the isostructural sulfido and selenido complexes, the ligand is saddle-shaped, whereas in the tellurido derivative, the ligand adopts an inverted umbrella configuration in which the benzo groups are now directed from the macrocyclic N_4 plane away from the Ge=Te bond.

The corresponding Sn terminal sulfido and selenido complexes were also reported by Parkin and Kuchta.[15] Again, treatment of the Sn(II) macrocyclic complex with the elemental chalcogen led to the formation of the Sn(IV) terminal complexes, [η^4-Me_8taa]SnX (X = S, Se). A terminal tellurido analog could not be isolated. The authors suggested that this may imply a Sn=Te interaction that is weaker than the corresponding Ge=Te interaction. This postulate was supported by the fact that when the tin(IV) terminal chalcogenides were treated with [η^4-Me_8taa]Ge(II), complete atom transfer occurred, indicating that Ge=X bonds are stronger than Sn=X bonds (X = S, Se).

Metalloporphyrin terminal sulfido and selenido complexes

Despite the large number of metalloporphyrin complexes known which contain terminal oxo ligands, very little is known about the corresponding terminal sulfido and selenido species.

In fact, the first metalloporphyrin containing a multiple bond to sulfur or selenium was not reported until 1983.[16] The following section discusses the synthesis and characterization of the known terminal sulfido and selenido metalloporphyrin complexes.

Titanium Porphyrins. Titanium porphyrins containing terminal sulfido and selenido ligands are readily available from Ti(II) acetylene starting materials.[17] When (TTP)Ti(η^2-PhC≡CPh) is treated with triphenylphosphine sulfide, $Ph_3P{=}S$, or triphenylphosphine selenide, $Ph_3P{=}Se$, in toluene at 50-60 °C, the corresponding titanium(IV) complex, (TTP)Ti=S or (TTP)Ti=Se, is formed in approximately 60-80% yield (eq 1). Treatment of

$$(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh) + X{=}PPh_3 \longrightarrow (TTP)Ti{=}X + PhC{\equiv}CPh + PPh_3 \qquad (1)$$

$$X = S \text{ or } Se$$

$$(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh) + [S] \longrightarrow (TTP)Ti(S_2) + PhC{\equiv}CPh \qquad (2)$$

$$[S] = S_8 \text{ or } Cp_2TiS_5$$

$$(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh) + Se \longrightarrow (TTP)Ti(Se_2) + PhC{\equiv}CPh \qquad (3)$$

(TTP)Ti(η^2-PhC≡CPh) with elemental sulfur or Cp_2TiS_5 (eq 2) does not result in the formation of a terminal sulfido complex, but instead produces a persulfido complex.[18] Utilizing Cp_2TiS_5 as the sulfur transfer reagent, the reaction is known to proceed via formation first of (TTP)Ti=S, followed by addition of a second sulfur atom to produce a persulfido ligand.[18] This is an example of an intermetal sulfur atom transfer process. A perselenido species, (TTP)$TiSe_2$, may be prepared by treating (TTP)Ti(η^2-PhC≡CPh) with elemental selenium.[18] The perchalcogenido species may also be prepared by treating the terminal chalcogenides with elemental sulfur or selenium (eqs 4,5). Guilard *et al.* were the first to report the synthesis of these perchalcogenido species from the treatment of (TTP)TiF or (TTP)TiF$_2$ with Cp$_2$TiS$_5$ or Cp$_2$TiSe$_5$.[20]

$$\text{(TTP)Ti=S} + 1/8\ \text{S}_8 \longrightarrow \text{(TTP)Ti(S}_2\text{)} \tag{4}$$

$$\text{(TTP)Ti=Se} + \text{Se} \longrightarrow \text{(TTP)Ti(Se}_2\text{)} \tag{5}$$

$$\text{(POR)V(THF)}_2 + \text{S}_8 \longrightarrow \text{(POR)V=S} \tag{6}$$

$$\text{(POR)V(THF)}_2 + \text{Cp}_2\text{TiSe}_5 \longrightarrow \text{(POR)V=Se} \tag{7}$$

Vanadium Porphyrins. Vanadium porphyrins containing terminal sulfido and selenido ligands may be prepared using very similar synthetic procedures. As illustrated in eq 6, treatment of a low-valent vanadium porphyrin, (POR)V(THF)$_2$, with elemental sulfur in THF results in the formation of (POR)V=S.[17,21] The corresponding selenido (eq 7) complex may be prepared from treatment of (POR)V(THF)$_2$ with Cp$_2$TiSe$_5$ in THF.[17,22] These complexes have been characterized on the basis of mass spectral, IR, UV-vis, and EPR data.

Tin Porphyrins. Again utilizing a low-valent metalloporphyrin precursor, tin porphyrins containing terminal sulfido and selenido ligands may be synthesized as illustrated in eq 8.[22,23] These terminal chalcogenides are the first example of a terminal oxo-type ligation for main group metalloporphyrins. (POR)Sn=X were characterized by mass spectrometry, IR, UV-vis, and ^{1}H NMR spectroscopies as well as by electrochemisty. A complete listing of the known metalloporphyrin terminal sulfido and selenido complexes is provided in Table 3.1. A metalloporphyrin complex containing a terminal sulfido or selenido ligand has not been structurally characterized.

$$\text{(POR)Sn(II)} + \text{Cp}_2\text{TiX}_5 \rightarrow \text{(POR)Sn=X} \qquad (8)$$

X = S or Se

Table 3.1. Known metalloporphyrins containing M=S or M=Se multiple bonds

Complex	POR	Reference
(POR)Ti=S	TTP	18
(POR)Ti=Se	TTP	18
(POR)V=S	TmTp, TpTP, TPP, OEP	17
(POR)V=Se	TmTP, TpTP, TPP, OEP	17
(POR)Sn=S	TPP, TmTP, TpTP, TMP, OEP	23
(POR)Sn=Se	TPP, TmTP, TpTP, TMP, OEP	23

Intermetal sulfur and selenium atom transfer

Atom transfer reactions continue to be an area of fundamental importance. Numerous studies have focused on oxygen atom transfer due to its relevance in both biological systems and industrial or laboratory oxidation processes.[24] The transfer of an oxygen atom between a transition metal complex and non-metal reagents has been recently reviewed.[25] The scope of intermetal oxygen atom transfer has also been recently reviewed.[26]

Despite the large number of characterized intermetal oxygen atom transfer reactions, little is known about transfer processes of the heavier chalcogenides. This has been suggested to be in part due to the lack of suitable terminal sulfido and selenido species.[26] Examples of intermetal sulfur or selenium atom transfer have largely involved the use of Cp_2TiS_5 and Cp_2TiSe_5 as transfer reagents. As shown in eqs 9-12, these reagents generally deliver S_2 or Se_2 fragments.[27] Exceptions are shown in eqs 13-15 in which a single sulfur or selenium atom is transferred to a vanadium(II) or tin(II) complex.[28]

A recently reported study involving oxygen, sulfur, and selenium atom transfer reactions of titanium porphyrins may allow for a systematic study of group 16 transfer reactions. Treatment of (TTP)Ti(PhC≡CPh)[29] with $(OEP)Ti(O_2)$[30] (eq 16) results in the quantitative

$$[Ir(dppe)_2]Cl + Cp_2TiS_5 \rightarrow [Ir(dppe)_2S_2]Cl \qquad (9)$$

$$[Ir(dppe)_2]Cl + Cp_2TiSe_5 \rightarrow [Ir(dppe)_2Se_2]Cl \qquad (10)$$

$$(TTP)TiF_2 + Cp_2TiS_5 \rightarrow (TTP)TiS_2 \qquad (11)$$

$$\text{(TTP)TiF}_2 + \text{Cp}_2\text{TiSe}_5 \rightarrow \text{(TTP)Ti(Se}_2\text{)} \tag{12}$$

$$\text{(OEP)V(THF)}_2 + \text{Cp}_2\text{TiSe}_5 \rightarrow \text{(OEP)V=Se} \tag{13}$$

$$\text{(POR)Sn(II)} + \text{Cp}_2\text{TiS}_5 \rightarrow \text{(POR)Sn=S} \tag{14}$$

$$\text{(POR)Sn(II)} + \text{Cp}_2\text{TiSe}_5 \rightarrow \text{(POR)Sn=Se} \tag{15}$$

$$\text{(OEP)Ti(O}_2\text{)} + \text{(TTP)Ti(PhC}\equiv\text{CPh)} \rightarrow \text{(OEP)Ti=O} + \text{(TTP)Ti=O} + \text{PhC}\equiv\text{CPh} \tag{16}$$

$$\text{(OEP)Ti(S}_2\text{)} + \text{(TTP)Ti(PhC}\equiv\text{CPh)} \rightarrow \text{(OEP)Ti=S} + \text{(TTP)Ti=S} + \text{PhC}\equiv\text{CPh} \tag{17}$$

$$\text{(OEP)Ti(Se}_2\text{)} + \text{(TTP)Ti(PhC}\equiv\text{CPh)} \rightarrow \text{(OEP)Ti=Se} + \text{(TTP)Ti=Se} + \text{PhC}\equiv\text{CPh} \tag{18}$$

formation of (TTP)Ti=O and (OEP)Ti=O. Formally, this reaction involves a two-electron reduction of peroxide (O_2^{2-}) to $2O^{2-}$ by Ti(II). Similarly, treatment of (TTP)Ti(PhC≡CPh) with (OEP)TiS_2 or (OEP)$TiSe_2$ results in formation of the corresponding terminal chalcogenido species (eqs 17-18).

The following two chapters will deal with the synthesis, characterization, and atom transfer reactions of molybdenum and tin metalloporphyrins containing terminal sulfido and selenido ligands.

References

1. (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, **1988**. (b) Muller, A.; Diemann, E. in *Comprehensive Coordination Chemistry*, Vol. 2 (Eds.: Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Pergamon, New York, **1987**. Sections 16.1 and 16.3
2. (a) Siemeling, U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 67. (b) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.
3. (a) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. (b) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761.
4. Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.
5. Smith, M. R., III; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.
6. (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (b) Christou, V.; Arnold, J. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1450.
7. Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.
8. The trianion of this amine has been designated as [N_3N] by Cummins and Schrock and as (TMStren) by Arnold and coworkers. Each abbreviation will be used within the text according to the author's designation.
9. Bonasia, P. J.; Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 6777.
10. Bonasia, P. J.; Gindleberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 5209.

11. (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904. (b) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 2313. (c) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421.
12. Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822.
13. Norman, N. C. *Polyhedron* **1993**, *12*, 2431.
14. Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351.
15. Me_8taa = octamethyldibenzotetraaza[14]annulene
16. Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 8372.
17. Poncet, J. L.; Guilard, R.; Friant, P.; Goulon, J. *Polyhedron* **1983**, *2*, 417.
18. Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.
19. Berreau, L. M.; Woo, L. K. Unpublished results.
20. Guilard, R.; Ratti, C.; Tabard, A.; Richard, P.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1990**, *29*, 2532.
21. POR = OEP, TPP, TmTP, TpTP
22. POR = TPP, TmTP, TpTP, TMP, OEP
23. Guilard, R.; Ratti, C.; Barbe, J. M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.
24. (a) Ostovic, D.; Bruice, T. *Acc. Chem. Res.* **1992**, *25*, 314 and references therein. (b) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *93*, 1125. (c) Jorgenson, K. A. *Chem. Rev.* **1989**, *89*, 431.
25. Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

26. Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125.

27. (a) Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223. (b) Guilard, R.; Ratti, C.; Tabard, A.; Richard, P.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1990**, *29*, 2532. (c) Ratti, C.; Richard, P.; Tabard, A.; Guilard R. *J. Chem. Soc,. Chem. Commun.* **1989**, 69.

28. (a) Poncet, J. L.; Guilard, R.; Friant, P.; Goulon-Ginet, C.; Goulon, J. *Nouv. J. Chim.* **1984**, *8*, 583. (b) Guilard, R.; Ratti, C.; Barbe, J. -M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.

29. Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

30. Guilard, R.; Latour, J. -M.; Lecomte, C.; Marchon, J. -C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1288.

CHAPTER 4: SULFUR AND SELENIUM ATOM TRANSFER REACTIONS OF TIN PORPHYRINS

A paper submitted to J. Am. Chem. Soc.[1]

Lisa M. Berreau and L. Keith Woo*[2]

Abstract

Treatment of (*meso*-tetraphenylporphyrinato)tin(IV) sulfide, (TPP)Sn=S, with (*meso*-tetra-*p*-tolylporphyrinato)tin(II), (TTP)Sn(II), in toluene results in the reversible exchange (K = 1.20 ± 0.03 at -10 °C) of a sulfur ligand to form (TPP)Sn(II) and (TTP)Sn=S. The net result is a formal two-electron redox process between Sn(II) and Sn(IV). This occurs with a second order rate constant at 30 °C of 0.40 ± 0.05 $M^{-1}s^{-1}$ ($\Delta H^{\ddagger}$ = 10.9 ± 0.9 kcal/mol, $\Delta S^{\ddagger}$ = -24.1 ± 2.8 cal(mol•K)$^{-1}$). Similarly, treatment of (*meso*-tetraphenylporphyrinato)tin(IV) selenide, (TPP)Sn=Se, with (*meso*-tetra-*p*-tolylporphyrinato)tin(II), (TTP)Sn(II), in toluene results in the reversible exchange (K = 1.45 ± 0.13 at -10 °C) of a selenium ligand to form (TPP)Sn(II) and (TTP)Sn=Se. This reaction occurs with a second order rate constant at 30 °C of 87.3 ±

---

[1] Reprinted with permission from *Journal of the American Chemical Society*, submitted for publication.

$8.06\ M^{-1}s^{-1}$ ($\Delta H^{\ddagger} = 9.3 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal(mol•K)$^{-1}$). Discussion of an inner sphere mechanism involving a μ-sulfido or a μ-selenido bridged intermediate is presented. The rate ratio of selenium to sulfur atom transfer is 218:1 at 30 °C. This rate behavior follows the "normal" trend as observed for the analogous halogen transfer reactions ($I^{-}>Br^{-}>Cl^{-}>F^{-}$).

Introduction

Atom transfer reactions continue to be an area of fundamental importance. Numerous studies have focused on oxygen atom transfer due to its relevance in both biological systems and industrial or laboratory oxidation processes.[3,4] While these have provided a large number of examples involving the transfer of an oxygen atom between a metal center and organic or nonmetal substrates, the related process of intermetal oxygen atom transfer reactions is still underdeveloped by comparison. The scope of intermetal oxygen atom transfer has recently been reviewed.[5]

Relatively few studies have been reported on sulfur or selenium atom transfer. Examples involving the transfer of a sulfur or selenium atom from a non-metal species (eg. phosphine chalcogenides or ethylene sulfide) to a low-valent metal center have recently been utilized to prepare novel terminal sulfido and selenido complexes of the early transition metals.[6] These reactions are unusual in that phosphines generally remove sulfur from metal complexes due to the strength of the phosphine sulfide bond (≅ 92 kcal/mol).[7] Intermetal atom transfer reactions utilizing Cp_2TiS_5 and Cp_2TiSe_5 as chalcogen transfer reagents have provided a synthetic route to new terminal and perchalcogenido species.[8,9,10,11] These reactions formally represent a secondary atom transfer process[4a] since reduction of the η^2-X_5 (X = S, Se) ligand has taken place.[5]

Metalloporphyrin complexes have been used to investigate a variety of inner-sphere redox processes involving intermetal halogen-,[12] oxygen-,[13] and nitrogen-atom transfer reactions.[14,15] We recently reported the discovery of intermetal oxygen, sulfur, and selenium atom transfer reactions involving titanium porphyrin complexes (eq 1).[16,17] Equation 1 also represents a secondary atom transfer process in which X_2^{2-} is reduced to 2 X^{2-}.[5]

We now wish to report the first comprehensive study of intermetal two-electron transfer mediated by sulfur or selenium atom transfer. The tin porphyrin complexes utilized for this work were recently described by Guilard, *et al.*[10,18]

$$\text{(OEP)Ti(X}_2\text{) + (TTP)Ti(PhC}\equiv\text{CPh)} \longrightarrow \text{(OEP)Ti=X + (TTP)Ti=X + PhC}\equiv\text{CPh} \qquad (1)$$

$$X = \text{O, S, Se}$$

Experimental

Instrumentation. All synthetic procedures were performed in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier. UV-visible spectroscopic measurements were obtained on a Hewlett-Packard HP 8452A diode array spectrophotometer. NMR spectra were recorded on a Nicolet NT300 spectrometer or on a Varian VXR 300-MHz spectrometer.

Chemicals. Toluene, tetrahydrofuran, toluene-d_8, benzene-d_6, and hexane for glovebox use were distilled from purple sodium/benzophenone ketyl solutions. Dry solvents were subsequently degassed on a vacuum line (10^{-5} torr) with three successive freeze-pump-thaw cycles. $(THF)_2Li_2(TTP)$ and $(THF)_2Li_2(TPP)$ were prepared according to the literature procedure for $(THF)_2Li_2(OEP)$.[19] (TTP)Sn=S and (TPP)Sn=S were prepared as described previously.[10] SnI_2, Cp_2TiS_5, and gray selenium were purchased from Aldrich and used without further purification. The following procedures are new synthetic routes for the preparation of previously reported tin porphyrins.[10,18]

(TTP)Sn(II). SnI_2 (153 mg, 0.410 mmol) and $(THF)_2Li_2(TTP)$ (144 mg, 0.174 mmol) were stirred in toluene (15 mL) at ambient temperature for 12 h, resulting in a color change from blue-green to dark green. The solution was then purified by column chromatography using a 1 x 10 cm neutral alumina column and toluene as the eluent. A green fraction containing (TTP)Sn(II) was collected from the column and was evaporated to dryness. The product was triturated in hexane (10 mL), collected by filtration, washed with hexane, and dried in vacuo (27 mg, 20%). (TPP)Sn(II) was prepared in an analogous manner. (TTP)Sn(II): ^1H NMR (C_6D_6, ppm): 9.19 (s, 8H, β-H), 8.04 (br, 8H, $-C_6H_4CH_3$), 7.27 (d, 8H, $-C_6H_4CH_3$), 2.40 (s, 12H, $-C_6H_5CH_3$). UV-vis (toluene, nm): 400, 490, 696. (TPP)Sn(II): ^1H NMR (C_6D_6, ppm): 9.08 (s, 8H, β-H), 8.11 (m, 8H, $-C_6H_5$), 7.45 (m, 12H, $-C_6H_5$). UV-vis (toluene, nm): 398, 490, 696.

(TTP)Sn=Se. SnI_2 (135 mg, 0.362 mmol) and $(THF)_2Li_2(TTP)$ (133 mg, 0.161 mmol) were stirred in toluene (15 mL) at ambient temperature for 12 h. The solution was then purified on a 1 x 10 cm neutral alumina column using toluene as the eluent. A green fraction containing (TTP)Sn(II) was collected from the column. Gray selenium (19 mg, 0.23 mmol) was added to this solution and the mixture was stirred for 12 h at 50-60 °C. After filtering the reaction mixture to remove excess selenium, the solvent was removed under reduced pressure. The product was triturated in hexane (10 mL), collected by filtration, washed with hexane, and dried in vacuo (46 mg, 33% based on $(THF)_2Li_2(TTP)$). (TPP)Sn=Se was prepared in an analogous manner. (TTP)Sn=Se: ^1H NMR (C_6D_6, ppm): 9.16 (s, 8H, β-*H*), 7.89 (d, 8H, -$C_6H_4CH_3$), 7.25 (br, 8H, -$C_6H_4CH_3$), 2.39 (s, 12H, -$C_6H_4CH_3$). UV-vis (toluene, nm): 346, 438(Soret), 532, 570, 612. (TPP)Sn=Se: ^1H NMR (C_6D_6, ppm): 9.02 (s, 8H, β-*H*), 7.91 (m, 8H, -C_6H_5), 7.42 (m, 12H, -C_6H_5). UV-vis (toluene, nm): 344, 438(Soret), 524, 568, 610.

Equilibrium Measurements. Samples for equilibrium determinations were prepared in a glovebox by adding specific volumes of known-concentration stock solutions of a sulfide or selenide complex, the appropriate tin(II) species, and an internal standard, triphenylmethane, into a 5-mm NMR tube attached to a ground glass joint. The solvent was removed under reduced pressure. The tube was then attached to a high-vacuum stopcock and connected to a high-vacuum line. After adding toluene-d_8 by vacuum distillation, the tube was flame sealed. The equilibrium constants were determined using a Lorentzian curve fitting to obtain an integrated intensity for each of the β-pyrrole signals associated with the species involved in the equilibrium. The samples were monitored in a temperature-controlled NMR probe until no further change in peak areas were observed.

Kinetic Measurements. The concentrations of stock solutions were determined spectrophotometrically prior to use. Rate data for the (TTP)Sn(II)/(TPP)Sn=X (X = S or Se) system were obtained on a UV-visible spectrophotometer equipped with a thermally regulated cell holder. Solutions of (TTP)Sn(II) and (TPP)Sn=S were loaded in a 1-mm cuvette in a glovebox. Typical initial concentrations ranged from 8.3×10^{-5} to 8.0×10^{-4} M for (TTP)Sn(II) and 3.0×10^{-4} to 7.4×10^{-4} M for (TPP)Sn=S. Initial Sn(IV) and Sn(II) concentrations were varied from a ratio of approximately 1:2 to 9:1. For the (TTP)Sn(II)/(TPP)Sn=Se system, solutions of

(TTP)Sn(II) and (TPP)Sn=Se were loaded in a 1-cm cuvette in a glovebox. Typical initial concentrations ranged from 5.61 x 10^{-5} to 1.70 x 10^{-4} M for (TTP)Sn(II) and 1.31 x 10^{-5} to 3.34 x 10^{-5} M for (TPP)Sn=Se. Initial Sn(II) and Sn(IV) concentrations were varied from a ratio of approximately 1.7:1 to 13:1. For both the sulfur and selenium transfer systems, the sealed cuvette was placed in the cell holder, and the run was monitored at 612 nm. Molar absorptivities of the metalloporphyrins at 612 nm are given in Table I. Rate constants were obtained using an integrated rate law for second-order equilibrium reactions as derived by King.[20] The rate constants reported were determined by averaging the values obtained from three or more individual kinetic runs. Equilibrium constants for the temperatures used in the kinetic study were extrapolated from the ^{1}H NMR equilibrium data.

Table I. Molar absorptivities for metalloporphyrins in toluene at 612 nm

compd.	molar absoptivity x 10^{-4} ($M^{-1}cm^{-1}$)	compd.	molar absorptivity x 10^{-4} ($M^{-1}cm^{-1}$)
(TTP)Sn(II)	0.232	(TTP)Sn=S	1.082
(TPP)Sn(II)	0.316	(TPP)Sn=S	0.816
(TTP)Sn=Se	0.767	(TPP)Sn=Se	0.646

Results

Reduction of Sulfidotin(IV) Porphyrin with Tin(II) Porphyrin. Treatment of (TPP)Sn=S with (TTP)Sn(II) in toluene-d_8 results in spectral changes which are consistent with the transfer of a terminally bound sulfur ligand between two metal complexes as shown in eq 2. The use of phenyl- and tolyl-labelled porphyrins (TPP and TTP) provides a convenient means of monitoring this reaction by ^{1}H NMR. For example, new β-pyrrolic proton resonances appear, signifying the formation of (TPP)Sn(II) (9.04 ppm) and (TTP)Sn=S (9.14 ppm). The β-pyrrolic proton signals for (TPP)Sn=S (8.99 ppm) and (TTP)Sn(II) (9.17 ppm) diminish but do not disappear, indicating that eq 2 is an equilibrium process. An equilibrium constant for eq 2 was measured by monitoring the ^{1}H NMR β-pyrrole signal of each metalloporphyrin species in

$$\text{(TTP)Sn(II)} + \text{(TPP)Sn=S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{(TTP)Sn=S} + \text{(TPP)Sn(II)} \qquad (2)$$

toluene-d_8 in flame-sealed NMR tubes. Due to the very similar nature of the porphyrins used in this study, an equilibrium constant of approximately unity was expected. As anticipated, the equilibrium constant for eq 2 in toluene-d_8 is 1.44 ± 0.12 at -40 °C and exhibited little change over a 30 °C temperature range (K = 1.21 ± 0.03 at -10 °C). Examination of the equilibrium at higher temperatures was not possible due to overlapping of the β-pyrrole resonances of the tetratolylporphyrinato species. A summary of the equilibrium constants for eq 2 is given in Table II. The thermodynamic parameters, $\Delta H° = -0.66 \pm 0.13$ kcal/mol and $\Delta S° = -2.1 \pm 0.4$ cal(mol·K)$^{-1}$, were determined from this temperature dependence.

It is also possible to follow this sulfur transfer reaction using UV-vis spectroscopy. Treatment of (TPP)Sn=S with (TTP)Sn(II) produces spectral changes consistent with the transfer of a terminally bound sulfur ligand. For example, bands at 570 and 612 nm, which are associated with both of the terminal sulfide species, increase in intensity over the

Table II. Equilibrium constants for eq 2 in toluene-d_8

temperature (°C)	K
-40	1.44 ± 0.12
-30	1.37 ± 0.14
-20	1.33 ± 0.03
-10	1.21 ± 0.03

course of the reaction. These changes are in agreement with the magnitudes of the extinction coefficients for the terminal sulfide complexes. Throughout the reaction, a well defined isosbestic point is observed at 630 nm.

The forward rates of eq 2 in toluene were examined spectrophotometrically by following the absorbance changes at 612 nm. A summary of rate constants for the forward direction are listed in Table III. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions (eq 3).[19] Plots of $\ln[\Delta/(\alpha + \Delta(1-1/K))]$ vs. time are linear for at least 3 half lives.

$$\ln\left[\frac{\Delta}{\alpha + \Delta(1 - 1/K)}\right] = -\alpha k_1 t + \text{constant} \qquad (3)$$

Table III. Forward rate constants for eq 2 in toluene

temperature (°C)	k_f ($M^{-1}s^{-1}$)
30	0.40 ± 0.05
40	0.83 ± 0.12
50	1.41 ± 0.05
60	2.39 ± 0.77

Reduction of Selenidotin(IV) Porphyrin with Tin(II) Porphyrin. Reversible intermetal selenium atom transfer occurs on treatment of (TPP)Sn=Se with (TTP)Sn(II) in toluene-d_8 (eq 4). This reaction parallels the analogous sulfur atom transfer process and can also be monitored by ^{1}H NMR. For example, as shown in Figure 1, new β-pyrrolic proton resonances appear for (TPP)Sn(II) (9.04 ppm) and (TTP)Sn=Se (9.14 ppm) while the signals associated with the β-pyrrolic protons of (TPP)Sn=Se (8.99 ppm) and (TTP)Sn(II) (9.17 ppm) diminish. An equilibrium constant for eq 4 was once again determined by ^{1}H NMR by monitoring the β-pyrrole signals of the each metalloporphyrin species versus the methine proton of triphenylmethane (5.38 ppm) in toluene-d_8. As expected, the equilibrium constant for eq 4 was found to be nearly unity (K = 1.54 ± 0.20 at -40 °C) and varied little over a 30 °C temperature range (K = 1.45 ± 0.13 at

$$\text{(TTP)Sn(II)} + \text{(TPP)Sn=Se} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{(TTP)Sn=Se} + \text{(TPP)Sn(II)} \qquad (4)$$

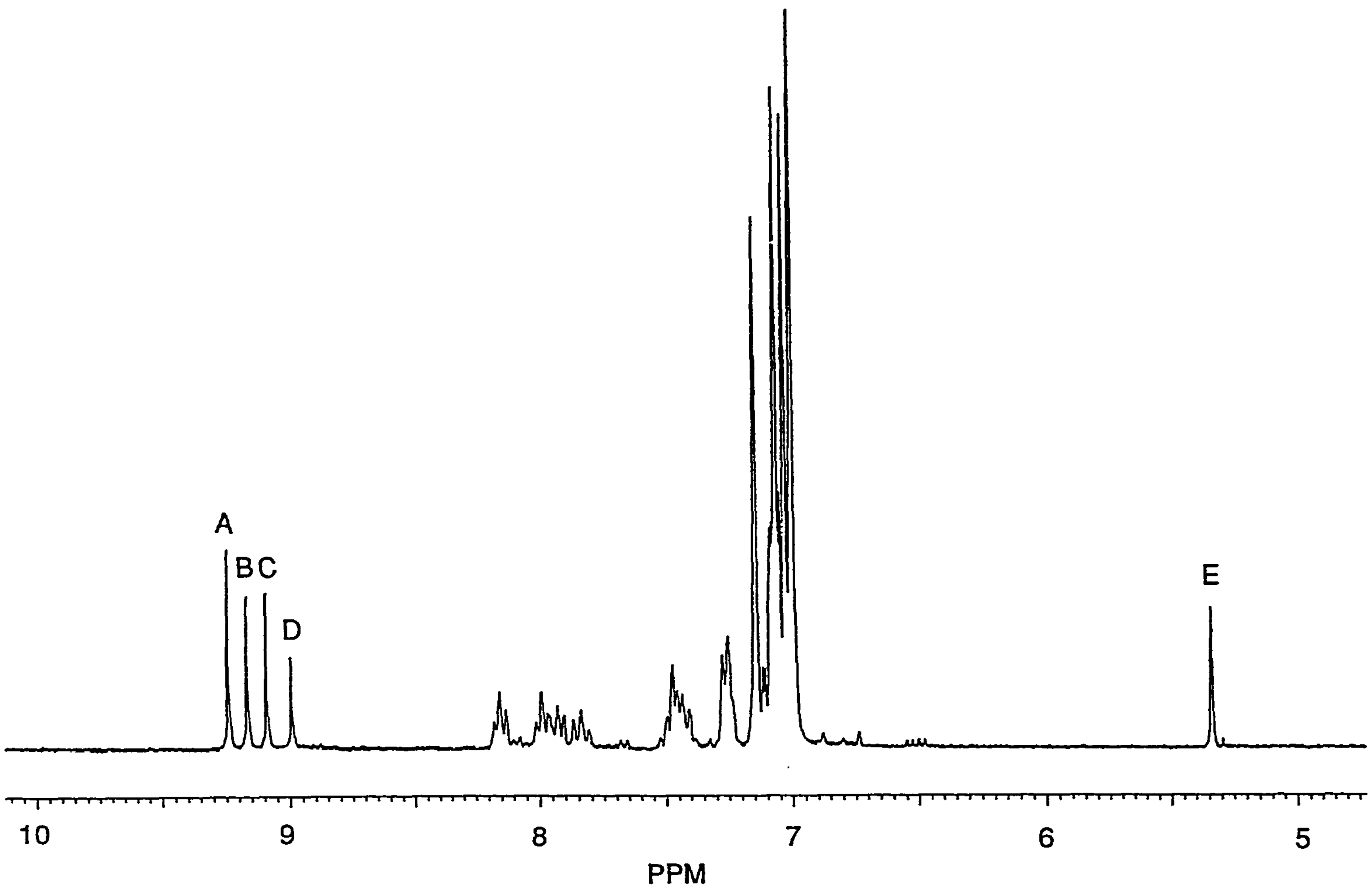


Figure 1. 300-MHz ^{1}H spectrum for eq 4. A is the β-pyrrole signal for (TTP)Sn(II), B is the β-pyrrole signal for (TTP)Sn=Se, C is the β-pyrrole signal for (TPP)Sn(II), D is the β-pyrrole signal for (TPP)Sn=Se, and E is the methine signal of Ph_3CH.

-10°C). Again, overlapping of the β-pyrrole resonances for the tetratolylporphyrinato species prevented studying this equilibrium at higher temperatures. A summary of the equilibrium constants for eq 4 is given in Table IV. The thermodynamic parameters, $\Delta H° = -0.25 \pm 0.02$ kcal/mol and $\Delta S° = -0.23 \pm 0.06$ cal(mol·K)$^{-1}$, were determined from this temperature dependence.

The selenium atom transfer reaction depicted in eq 4 was also examined using UV-vis spectroscopy. Treatment of (TPP)Sn=Se with (TTP)Sn(II) in toluene results in spectral changes very similar to those observed in the transfer of a terminal sulfide

Table IV. Equilibrium constants for eq 4 in toluene-d_8

temperature	K
-40	1.54 ± 0.20
-30	1.51 ± 0.17
-20	1.47 ± 0.14
-10	1.45 ± 0.13

Table V. Forward rate constants for eq 4 in toluene

temperature (°C)	k_f ($M^{-1}s^{-1}$)
0	14.4 ± 1.3
10	31.7 ± 5.1
20	59.2 ± 3.5
30	87.3 ± 8.1

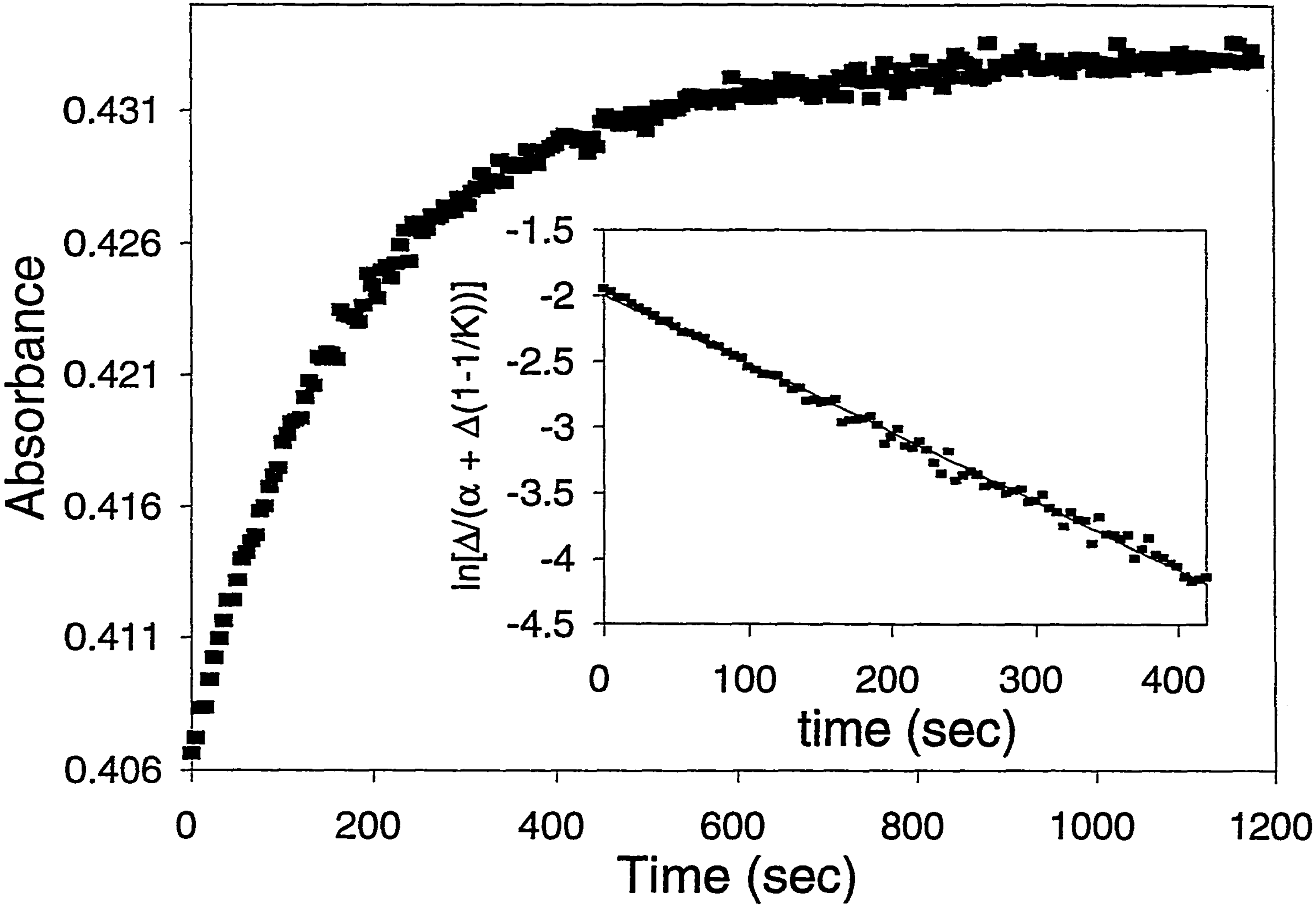


Figure 2. Representative absorption (612 nm) vs time plot for reaction 4 at 20 °C. $[(TPP)Sn{=}Se]_0 = 4.09 \times 10^{-5}$ M and $[(TTP)Sn(II)]_0 = 4.86 \times 10^{-5}$ M. Inset: plot of $\ln[\Delta/(\alpha + \Delta(1-1/K))]$ vs t.

ligand. Again, increases in absorbance at 570 and 612 nm were observed, consistent with the differences in extinction coefficients of the two terminal selenide complexes involved in the equilibrium. A well defined isosbestic point was observed at 630 nm.

The forward rates of eq 4 in toluene were examined spectrophotometrically by following the absorbance changes at 612 nm. A summary of the forward rate constants for eq 4 is given in Table V. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions as shown in eq 3. Plots of $\ln[\Delta/(\alpha + \Delta(1-1/K))]$ vs. time are linear for at least 3 half lives. A typical kinetic curve and the corresponding ln plot are illustrated in Figure 2.

Discussion

We have found that complete sulfur and selenium atom transfer between two metalloporphyrins can be achieved. This study represents the first comprehensive study of intermetal two-electron transfer mediated by sulfur or selenium atom transfer. It is possible to observe this process by using different porphyrin ligands as UV-vis and ^{1}H NMR spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction, eliminating complications due to ancillary ligand loss. Furthermore, stereochemical rearrangements found in other atom transfer systems are not possible here[21,22] Rate constants for sulfur atom transfer (eq 2) have been measured over a 30° temperature span. These rate constants range between 0.40 and 2.39 $M^{-1}s^{-1}$ for the forward direction. Varying the ratio of initial concentrations of Sn(IV) to Sn(II) from 1:2 to 9:1 resulted in comparable rate constants within the experimental error, indicating a reaction that is first order in each of the starting components. The temperature dependence of the forward rate yields activation parameters of $\Delta H^{\ddagger} = 10.9 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -24.1 \pm 2.8$ cal(mol•K)$^{-1}$. In an analogous manner, selenium atom transfer rate constants were measured over a 30° temperature range. The forward rate constants range between 14.4 and 87.3 $M^{-1}s^{-1}$. Varying the ratio of initial concentrations of Sn(II) to Sn(IV) from 1.7:1 to 13:1 resulted in comparable rate constants within the experimental error, indicating a reaction that is first order in each of the starting components. In this case, the temperature dependence of the forward rate yields activation parameters of $\Delta H^{\ddagger} = 9.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal(mol•K)$^{-1}$. Since $\Delta G^{\circ} \approx 0$, the activation parameters for equations 2 and 4 reflect the intrinsic tendency for sulfur or selenium atom transfer, respectively.

Electrochemical studies on tin porphyrins suggest that equations 2 and 4 do not involve an outer-sphere mechanism.[18,23] Kadish *et al.*, have demonstrated that the first and second electrochemical reductions of (TTP)Sn=S and (TTP)Sn=Se are ligand-based. Formation of the singly reduced complexes occurs at $E_{1/2} = -0.88$ V ((TTP)Sn=S) and $E_{1/2} = -0.87$ V ((TTP)Sn=Se) vs SCE. Since the $[(TTP^{-})Sn(II)]^{+}/[(TTP^{2-})Sn(II)]$ reduction potential is -0.60 V vs. SCE, Sn(II) porphyrins are not thermodynamically capable of reducing (POR)Sn=S or (POR)Sn=Se (POR = TTP, TPP) in an electron transfer pathway.[23]

The activation parameters for eqs 2 and 4 support an inner-sphere process. The low $\Delta H^{\ddagger}$ values suggest that significant bond formation occurs ($Sn^{IV}{=}X\cdot\cdot Sn$) to offset $Sn^{IV}{=}X$ bond dissociation. In addition, the negative entropies of activation ($\Delta S^{\ddagger} = -24.1 \pm 2.8$ cal(mol•K)$^{-1}$ for sulfur atom transfer; $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal(mol•K)$^{-1}$ for selenium atom transfer) are consistent with an associative type mechanism in which atom transfer occurs via a μ-sulfido or a μ-selenido intermediate. However, we have not detected this bridged species spectroscopically by UV-vis, ^{77}Se NMR, or EPR.

Finally, the increase in rate of selenium atom transfer versus sulfur atom transfer supports the results of a previous study of atom transfer reactions involving phosphines and phosphine chalcogenides (eq 5).[24] For these reactions, it was found that the atom transfer rate increased qualitatively with the size of the chalcogenide. However, absolute rates were not reported. The overall increase in rate in eq 5 upon descending the chalcogenide family was rationalized on the basis of diminishing covalent bond energies on progressing to the heavier elements of Group 16. This can be considered the "normal" trend as observed for halide transfer.[25] The relative rate of selenium versus sulfur atom transfer in the tin process

$$Ph_3P{=}X + Ph_2MeP \rightleftharpoons Ph_3P + Ph_2MeP{=}X \tag{5}$$

$$X = O, S, Se$$

(218:1 at 30 °C) is unexpectedly large compared to systems involving halogen transfer. In a study involving halogen exchange between cobalt porphyrins, the observed rates at 298 K (k_{Cl} = 27.1 x 10^3 M^{-1} s^{-1}; k_{Br} = 373 x 10^3 $M^{-1}s^{-1}$; k_I = 8170 x 10^3 M^{-1} s^{-1}) reflect only approximately a fourteen-fold and twenty-two-fold increase in rate in moving from chloride to bromide and bromide to iodide, respectively.[26] Based on the similar size increase when substituting chloride for bromide and sulfide for selenide, an approximate twenty-fold increase in relative rate was expected in the chalcogenide transfer reactions. The observed 218-fold increase in rate for selenium versus sulfur transfer may suggest a significant difference in Sn=S and Sn=Se covalent expected in the chalcogenide transfer reactions. The observed 218-fold increase in rate for selenium versus sulfur transfer may suggest a significant difference in Sn=S and Sn=Se covalent bond strengths. This supports the general premise that pπ-pπ bond strengths decrease on descending the main group elements.[27] A recent illustration of this trend involves the synthesis of the heavier chalcogenide tin complexes of the macrocyclic octamethyldibenzotetraaza[14]annulene ligand.[28] While the terminal sulfido and selenido complexes were readily isolated, the terminal tellurido species could not be isolated, suggesting a weak Sn=Te interaction.

References

1. Reprinted with permission from *Journal of the American Chemical Society*, submitted for publication. Unpuplished work copyright 1994 American Chemical Society.
2. Presidential Young Investigator, 1990-1995; Camille and Henry Dreyfus Teacher-Scholar 1993-1998.
3. For lead references, see: Ostovic, D.; Bruice, T. *Acc. Chem. Res.* **1992**, *25*, 314.
4. (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (c) Jorgenson, K. A. *Chem. Rev.* **1989**, *89*, 431.
5. Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125.
6. (a) Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. *Inorg. Chem.* **1993**, *32*, 4186. (b) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402 and references therein.
7. Chernick, C. L.; Pedley, J. B.; Skinner, H. A. *J. Chem. Soc.* **1957**, 1851.
8. Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223.

9. (a) Guilard, R.; Ratti, C.; Tabard, A.; Richard, P.; Dubois, D.; Kadish K. M. *Inorg. Chem.* **1990**, *29*, 2532. (b) Ratti, C.; Richard, P.; Tabard, A.; Guilard, R. *J. Chem. Soc., Chem. Commun.* **1989**, 69.

10. Guilard, R.; Ratti, C.; Barbe, J. -M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.

11. Poncet, J. L.; Guilard, R.; Friant, P.; Goulon-Ginet, C.; Goulon J. *Nouv. J. Chim.* **1984**, *8*, 583.

12. (a) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1582. (b) Cohen, I. A.; Jung, C.; Governo, T. *J. Am. Chem. Soc.* **1972**, *94*, 3003.

13. (a) Woo, L. K.; Goll, J. G.; Berreau, L. M.; Weaving, R. *J. Am. Chem. Soc.* **1992**, *114*, 7411. (b) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916.

14. (a) Woo, L. K.; Goll, J. G.; *J. Am. Chem. Soc.* **1989**, *111*, 3755. (b) Woo, L. K.; Czapla, D. J.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3915. (c) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478.

15. Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955.

16. Woo, L. K., Hays, J. A. *Inorg. Chem.* **1993**, *32*, 2228.

17. Abbreviations: TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion, OEP is the octaethylporphyrinato dianion, and TPP is the *meso*-tetraphenylporphyrinato dianion.

18. Barbe, J. -M.; Ratti, C.; Richard, P; Lecomte, C.; Gerardin, R.; Guilard, R. *Inorg. Chem.* **1990**, *29*, 4126.

19. Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976.

20. King, E. L. *Int. J. Chem. Kinet.* **1982**, *14*, 1285. For a second-order reversible

reaction, A + B $\rightleftharpoons$ C + D, Δ is the displacement of any species from its equilibrium value. $\Delta = [A] - [A]_\infty = [B] - [B]_\infty = [C]_\infty - [C] = [D]_\infty - [D]$ and $\alpha = [A]_\infty + [B]_\infty = ([C]_\infty + [D]_\infty)/K$.

21. Holm, R. H.; *Coord. Chem. Rev.* **1990**, *100*, 183.
22. Templeton, J. E.; Ward, B. C.; Chen, G. J. -J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.
23. Kadish, K. M.; Dubois, D.; Barbe, J. -M.; Guilard, R. *Inorg. Chem.* **1991**, *30*, 4498.
24. Baechler, R. D.; Stack, M.; Stevenson, K.; Vanvalkenburgh, V. *Phosphorus, Sulfur, and Silicon* **1990**, *48*, 49.
25. (a) Burdett, J. K. *Inorg. Chem.* **1978**, *17*, 2537. (b) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225. (c) Haim, A. *Inorg. Chem.* **1968**, *7*, 1475.
26. Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1582.
27. (a) Norman, N. C. *Polyhedron* **1993**, *12*, 2431. (b) Kutzelnigg, W. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272. (c) Jacobsen, H.; Zieglar, R. *J. Am. Chem. Soc.* **1994**, *116*, 3667.
28. Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 8372.

CHAPTER 5: SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF SULFIDO AND SELENIDO MOLYBDENUM(IV) PORPHYRIN COMPLEXES. X-RAY STRUCTURE OF SULFIDO(5,10,15,20-TETRATOLYLPORPHYRINATO)MOLYBDENUM(IV)

A paper to be submitted to Inorganic Chemistry

Lisa M. Berreau, Victor G. Young, Jr., and L. Keith Woo*[1]

Abstract

Treatment of (TTP)Mo(PhC≡CPh) (TTP = *meso*-tetra-*p*-tolylporphyrinato) with S_8 or Cp_2TiS_5 in toluene results in the formation of (TTP)Mo=S. The sulfide complex may also be prepared from the reaction of (TTP)$MoCl_2$ with Li_2S in THF. Similarly, a terminal selenide complex may be prepared from (TTP)$MoCl_2$ and Na_2Se. The structure of (TTP)Mo=S has been determined by single-crystal X-ray diffraction analysis (triclinic, $P\bar{1}$, a = 12.735(2) Å, b = 13.521(2)Å, c = 13.920(2) Å, α = 74.76(1)°, β = 78.95(1)°, γ = 80.85(1)°, V = 2254.7(5) $Å^3$, Z = 2, R = 3.1%, and R_w = 4.2%). Complete sulfur atom transfer occurs between (TTP)Mo(PhC≡CPh) and (TTP)Sn=S to give (TTP)Mo=S, (TTP)Sn(II), and PhC≡CPh. The net result is a formal two-electron redox process between Sn(IV) and Mo(II). Correspondingly, no reaction is observed between (TTP)Mo=S and (TTP)Sn(II) in the presence of excess PhC≡CPh. The analogous treatment of (TTP)Mo=Se with (TTP)Sn(II) in the presence of PhC≡CPh results in the reversible exchange (K = $4.6 \times 10^4 \pm 7.2 \times 10^3$ at 25 °C) of a selenium ligand to form (TTP)Mo(PhC≡CPh) and (TTP)Sn=Se. When treated with excess PPh_3, the sulfido or selenido

complex is reduced to (TTP)Mo(PPh_3)$_2$ with formation of either Ph_3P=S or Ph_3P=Se. However, when (TTP)Mo=S or (TTP)Mo=Se is reduced with PPh_3 in the presence of PhC≡CPh, (TTP)Mo(PhC≡CPh) is formed. The alkyne ligand of (TTP)Mo(PhC≡CPh) may be displaced by 4-picoline to give *trans*-(TTP)Mo(4-picoline)$_2$. Ligand preference for the porphyrin Mo(II) center is thus PPh_3 < PhC≡CPh < 4-picoline.

Introduction

The chemistry of molybdenum porphyrin complexes has been dominated by high oxidation state species containing terminal oxo ligands.[2] This stems in part from the lack of suitable starting materials for the synthesis of non-oxo containing derivatives. In general, insertion of molybdenum into a free base porphyrin results in the isolation of a very stable molybdenum(V) porphyrin complex of the formula (POR)Mo(O)X where X may be halide or alkoxide.[2] It is from these molybdenum(V) precursors that virtually all molybdenum porphyrins, from oxidation states +2 to +6, have been derived. Recently, we reported a new synthetic route for the preparation of (TTP)MoCl_2, a useful starting material for entry into the lower-valent chemistry of molybdenum porphyrins.[3] Most examples of molybdenum(IV) metalloporphyrins contain the very stable Mo=O unit and are therefore quite unreactive. The exception is (TTP)MoCl_2, which has been studied by Weiss as a precursor to the formally Mo(0) species (TTP)Mo(NO)$_2$, as well as to the Mo(II) species (TTP)Mo(PhC≡CPh), (TTP)Mo(CO)$_2$, (TTP)Mo(py)$_2$, and (TTP)Mo(NO)(CH_3OH).[4] (TTP)MoCl_2 has also been utilized as a precursor to a molybdenum(IV) porphyrin diazo compound, (TTP)Mo(-N=NPh)$_2$.[5]

As an extension of our work involving the synthesis and reactivity of early transition metal porphyrin complexes, we have initiated a study of the preparation of terminal sulfido and selenido molybdenum(IV) porphyrins. Prior to this work, only terminal sulfido and selenido complexes of titanium, vanadium, and tin porphyrins have been isolated.[6]

Experimental

General. Toluene, THF, benzene-d_6, and hexanes for glovebox use were distilled from purple sodium benzophenone ketyl solutions. CH_2Cl_2 was distilled from CaH_2. Dry solvents were subsequently degassed on a vacuum line (10^{-5} torr) with three successive freeze-pump-thaw cycles. Neutral alumina was purchased from Fisher and was heated at 150 °C for 24 h prior to use. Li_2S and Cp_2TiS_5 were purchased from Aldrich and used without further purification. Na_2Se was purchased from Alfa and used without further purification. Elemental sulfur was purchased from J.T. Baker and was sublimed prior to use. Elemental selenium was purchased from Alfa and was used without further purification. PPh_3 was purchased from Aldrich, recrystallized from hexanes, and dried under high vacuum at 50 °C for 12 h prior to use. (TTP)Mo(PhC≡CPh) and (TTP)$MoCl_2$ were prepared according to literature procedures.[3,4a] (TTP)Sn=S and (TTP)Sn=Se were prepared according to literature procedures.[7]

All manipulations were performed either in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV-visible data were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. ^1H NMR spectra were recorded on a Nicolet NT300 spectrometer or on a Varian VXR 300-MHz spectrometer. IR spectra were recorded from KBR pellets on a IBM\Bruker IR-98 or on a BIO-RAD Digilab FTS-7 spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Norcross, Georgia.

Sulfido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV), 1.

Method 1. From (TTP)Mo(PhC≡CPh) and S_8. (TTP)MoCl$_2$ (109 mg, 0.131 mmol), LiAlH$_4$ (26 mg, 0.65 mmol), and PhC≡CPh (133 mg, 0.747 mmol) were stirred in a toluene/THF (25 mL/0.3 mL) solution at 40-50 °C for 45 minutes. The reaction mixture was then checked by UV-vis to verify the formation of (TTP)Mo(PhC≡CPh) by the appearance of bands at 428 (Soret) and 544 nm. After allowing the solution to cool to room temperature, the solvent was removed *in vacuo*. The residue was dissolved in toluene (20 mL) and filtered. The filtrate was reduced in volume to ca. 15 mL. Elemental sulfur (55 mg, 0.22 mmol) was added to the solution in ca. 10 mL toluene. The reaction mixture was stirred at 50-60 °C for 30 minutes. After allowing the reaction mixture to cool to room temperature, the solvent was removed *in vacuo*. The residue was redissolved in CH$_2$Cl$_2$ (15 mL) and the solution filtered. The filtrate was evaporated to dryness. Recrystallization from CH$_2$Cl$_2$/hexanes (1:4) produced a red/purple solid (45 mg, 43% based on (TTP)MoCl$_2$). UV-vis (toluene, nm): 438 (Soret), 556. ^{1}H NMR (C$_6$D$_6$, 300 MHz, ppm): 9.27 (s, 8H, β-*H*), 8.06 (d, 4H, -C$_6$*H*$_4$CH$_3$), 7.99 (d, 4H, -C$_6$*H*$_4$CH$_3$), 7.28 (m, 8H, -C$_6$*H*$_4$CH$_3$), 2.41 (s, 12H, -C$_6$H$_4$C*H*$_3$). IR (KBr): $\nu_{Mo=S}$ = 542 cm^{-1}. MS {EI} Calcd. (found) m/e: 798 (798) [M]$^+$. Anal. Calcd. (found) for C$_{48}$H$_{36}$N$_4$MoS: C, 72.16 (71.60); H, 4.55 (4.74); N, 7.02 (6.87).

Method 2. From (TTP)Mo(PhC≡CPh) and Cp$_2$TiS$_5$. (TTP)MoCl$_2$ (91 mg, 0.11 mmol), LiAlH$_4$ (27 mg, 0.66 mmol), and PhC≡CPh (95 mg, 0.53 mmol) were stirred in a toluene (20 mL) solution at 50-60 °C for 24 hours. The reaction mixture was then checked by UV-vis to verify the formation of (TTP)Mo(PhC≡CPh). The reaction mixture was then filtered.

To the filtrate was added Cp_2TiS_5 (68 mg, 0.20 mmol) in ca. 10 mL toluene. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed *in vacuo*. The residue was redissolved in a minimal amount of toluene (4 mL) and was placed on a 1 cm x 12 cm basic alumina column. Using toluene as the eluent, an orange/red band was collected. The solvent was removed *in vacuo* and the product was recrystallized from toluene/hexanes (1:3). Filtration produced a purple microcrystalline solid (36 mg, 42% based on $(TTP)MoCl_2$). The ^1H NMR spectrum of the isolated product matched that obtained in Method 1.

Method 3. From $(TTP)MoCl_2$ and Li_2S. $(TTP)MoCl_2$ (83 mg, 0.10 mmol) was stirred with Li_2S (12 mg, 0.26 mmol) in THF (20 mL) at 40-50 °C for 10 h. During this time the color of the solution changed from green to orange/brown. The solution was then cooled to room temperature and was subsequently evaporated to dryness. The residue was redissolved in a minimal amount of toluene (ca. 3 mL) and was placed on a 1 cm x 10 cm neutral alumina column. Using toluene as the eluent, the first band off the column, an orange/red band was collected. Following removal of the solvent *in vacuo*, the product was redissolved in toluene (1.5 mL), layered with ca. 6 mL hexanes, and cooled to -20 °C for 36 h. Filtration produced a red/purple solid (15 mg, 19%). The ^1H NMR spectrum of the isolated product matched that obtained in Method 1.

Selenido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV), 2.

Method 1. From $(TTP)MoCl_2$ and Na_2Se. $(TTP)MoCl_2$ (81 mg, 0.10 mmol) was stirred with Na_2Se (20 mg, 0.16 mmol) in THF (20 mL) at 40-50 °C for 24 h. During this time the color of the solution changed from green to orange/brown. The solution was cooled to room temperature and was subsequently evaporated to dryness. The residue was redissolved in a minimal amount of toluene (ca. 5 mL) and was placed on a 1 cm x 10 cm neutral alumina column. Using toluene as the eluent, an orange/red band was collected. Following removal of the solvent in vacuo, the crude product was redissolved in ca. 1 mL toluene, layered with ca. 6 mL hexanes, and cooled to -20 °C for 2 h. Filtration produced a red/purple solid (14 mg, 17%). UV-vis (toluene, nm): 432 (Soret), 554. ^{1}H NMR (C_6D_6, 300 MHz, ppm): 9.25 (s, 8H, β-*H*), 8.03 (d, 4H, -$C_6\mathit{H}_4CH_3$), 7.96 (d, 4H, -$C_6\mathit{H}_4CH_3$), 7.27 (m, 8H, -$C_6\mathit{H}_4CH_3$), 2.41 (s, 12H, -$C_6H_4C\mathit{H}_3$). IR (KBr): $\nu_{Mo=Se}$ = 410 cm^{-1}. MS {EI} Calcd. (found) m/e: 844 (844) [M]$^+$. Anal. Calcd. (found) for $C_{48}H_{36}N_4MoSe$: C, 68.08 (68.09); H, 4.29 (4.53); N, 6.62 (6.30).

Method 2. From (TTP)Mo(PhC≡CPh) and elemental selenium. (TTP)$MoCl_2$ (111 mg, 0.130 mmol), $LiAlH_4$ (23 mg, 0.60 mmol), and PhC≡CPh (70.6 mg, 0.400 mmol) were stirred in a toluene/THF (15 mL/0.2 mL) solution at 40-50 °C for 45 minutes. The reaction mixture was then checked by UV-vis to verify the formation of (TTP)Mo(PhC≡CPh). After allowing the solution to cool to room temperature, the solvent was removed in vacuo. The residue was dissolved in toluene (20 mL) and filtered. Elemental selenium (42 mg, 0.54 mmol) was added to the solution in ca. 5 mL toluene. The reaction mixture was stirred at 50-60 °C for 48 h. After allowing the reaction mixture to cool to room temperature, the solvent was removed *in vacuo*. The reaction mixture was redissolved in a minimal amount of toluene (5 mL) and was placed on a 1 x 10 cm neutral alumina column. Using toluene as the eluent, an orange-red band was collected. The solvent was removed *in vacuo* and the product was redissolved in ca. 1 mL toluene. The solution was then layered with hexane (ca. 3 mL) and was stored at -20 °C for 1 h. Filtration produced a red solid (25 mg). ^{1}H NMR indicated that a mixture of (TTP)Mo(PhC≡CPh) and (TTP)Mo=Se (8:1) had been isolated.

Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=S. An NMR tube containing a C_6D_6 solution of (TTP)Sn=S and (TTP)Mo(PhC≡CPh) and sealed under nitrogen was monitored at ambient temperature over a 2 day period. ^1H NMR spectra indicated that complete sulfur atom transfer occurred, giving (TTP)Sn(II), (TTP)Mo=S, and PhC≡CPh.

Treatment of (TTP)Mo=S with (TTP)Sn(II) in the presence of PhC≡CPh. An NMR tube containing a C_6D_6 solution of (TTP)Mo=S, (TTP)Sn(II), and excess PhC≡CPh and sealed under nitrogen was monitored at ambient temperature over a 48 h period. ^1H NMR spectra indicated that no reaction occurred.

Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=Se. An NMR tube containing a C_6D_6 solution of (TTP)Sn=Se and (TTP)Mo(PhC≡CPh) and sealed under nitrogen was monitored at ambient temperature over a 2 day period. ^1H NMR spectra indicated the formation of an equilibrium mixture.

Equilibrium Measurements. Samples for equilibrium determinations were prepared in a glovebox by adding specific volumes of known-concentration stock solutions of (TTP)Mo=Se, (TTP)Sn(II), PhC≡CPh, and an internal standard, triphenylmethane, into a 5-mm NMR tube attached to a ground glass joint. The solvent was removed under reduced pressure. The tube was then attached to a high-vacuum stopcock and connected to a high-vacuum line. After adding benzene-d_6 by vacuum distillation, the tube was flame sealed. The equilibrium constants were determined using a Lorentzian curve fitting to obtain an integrated intensity for each of the β-pyrrole signals associated with the porphyrin species involved in the equilibrium. An integrated intensity was also obtained for the resonance associated with the *o*-protons of free PhC≡CPh. The samples were monitored in a temperature-controlled NMR probe until no further change in peak areas were observed.

Bis-triphenylphosphino(5,10,15,20-tetratolylporphyrinato)molybdenum(II), 3. (TTP)Mo=S (39 mg, 0.05 mmol) was stirred with PPh_3 (63 mg, 0.24 mmol) in toluene (15 mL) at 50-60 °C for 18 h. The solution was then cooled to room temperature and filtered, removing a green solid (14 mg). The filtrate was collected and the solvent was volume was reduced to ca. 8 mL. The solution was then stirred for an additional 24 h at room temperature. Filtration produced an additional crop of a green solid (22 mg, overall yield: 48%). UV-vis (toluene): 390 (Soret), 472, 490, 558, 582, 598. ^{1}H NMR (C_6D_6, 300 MHz, ppm): 30.67 (br, 12H, *o-H*, PPh_3), 12.08 (br, 6H, *p-H*, PPh_3), 11.50 (br, 12H, *m-H*, PPh_3), 4.09 (br, 8H, $-C_6H_4CH_3$), 2.63 (br, 8H, $-C_6H_4CH_3$), -1.63 (br, 12H, $-C_6H_4CH_3$), -11.60 (br, 8H, β-*H*). Anal. Calcd. (found) for $C_{84}H_{66}N_4MoP_2$: C, 78.25 (78.00); H, 5.16 (5.37); N, 4.35 (4.16).

Treatment of (TTP)Mo(PPh_3)$_2$ with PhC≡CPh. (TTP)Mo(PPh_3)$_2$ (37 mg, 0.03 mmol) and PhC≡CPh (11 mg, 0.06 mmol) were stirred in toluene at ambient temperature for 2 hours. The solvent was then removed in vacuo. Recrystallization of the product from toluene/hexane (1:4) produced a red solid (18 mg, 67%). ^{1}H NMR spectroscopy indicated formation of (TTP)Mo(PhC≡CPh). ^{1}H NMR (C_6D_6, 300 MHz, ppm): 8.99 (s, 8H, β-*H*), 8.04 (m, 8H, $-C_6H_4CH_3$), 7.30 (m, 8H, $-C_6H_4CH_3$), 6.54 (m, 6H, *m-*, *p-H*, PhC≡CPh), 4.90 (d, 4H, *o-H*, PhC≡CPh), 2.39 (s, 12H, $-C_6H_4CH_3$).

Treatment of (TTP)Mo(PhC≡CPh) with 4-picoline. (TTP)$MoCl_2$ (57 mg, 0.07 mmol), $LiAlH_4$ (13 mg, 0.35 mmol), and PhC≡CPh (37 mg, 0.21 mmol) were stirred in a toluene/THF mixture (15 mL/0.1 mL) for 1 h at ambient temperature. The reaction mixture was then checked by UV-vis to verify the formation of (TTP)Mo(PhC≡CPh). The solvent was then removed *in* *vacuo*. The residue was redissolved in toluene (15 mL) and filtered. 4-picoline (ca. 0.2 mL) was added to the filtrate. The reaction mixture was stirred at ambient temperature for 36 h. Over this time, the solution color gradually changed from the orange/red of the π-alkyne complex to the green/brown color of the bispicoline derivative. Filtration of the solution resulted in the isolation of a purple solid (21.0 mg, 33% based on (TTP)MoCl$_2$). UV-vis (toluene): 380 (Soret), 418, 470, 558, 652. ^{1}H NMR (C_6D_6, 300 MHz, ppm): 47.47 (br, 4H, *o-H*, picoline); 33.63 (br, 4H, *m-H*, picoline); 7.15 (br, 6H, *p-CH$_3$*, picoline); 5.52 (br, 8H, -$C_6H_4CH_3$); 2.76 (br, 8H, -$C_6H_4CH_3$); -0.15 (br, 8H, β-*H*); -1.59 (br, 12H, -$C_6H_4CH_3$). Anal. Calcd. (found) for $C_{60}H_{50}N_6Mo$: C, 75.61 (74.86); H, 5.29 (5.26); N, 8.82 (8.54).

X-Ray Crystal Structure Determination of (TTP)Mo=S. Crystals of (TTP)Mo=S•1.5(C_6H_6) suitable for single-crystal X-ray diffraction were grown by layering a benzene solution of (TTP)Mo=S with hexane. A purple crystal (0.40 x 0.25 x 0.25 mm) was attached to the tip of a glass fiber and mounted on a Siemens P4/RA diffractometer for data collection at 223 ± 1 K using Cu Kα radiation (λ = 1.54178 Å). High-angle cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° 2θ. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected. A semi-empirical absorption correction based on the azimuthal scans was applied to the data.

The space group $P\bar{1}$ was chosen based on the lack of systematic absences and intensity statistics. This assumption proved to be correct by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined as riding atoms with C-H distances of 0.96 Å with individual isotropic thermal parameters except in the case of the tolyl methyl groups and benzenes which were refined with common isotropic parameters. One of the benzene solvates is located on a general site while the other (half) molecule is centered at the origin.

Data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-PLUS programs.[8]

Results

Synthesis of sulfido and selenido Mo(IV) porphyrin complexes. A terminal sulfido Mo(IV) porphyrin complex, (TTP)Mo=S, may be prepared from either Mo(II) or Mo(IV) precursors. As illustrated in reactions 1 and 2, treatment of a Mo(II) η^2-diphenylacetylene complex with either elemental sulfur or Cp_2TiS_5 in toluene results in the formation of (TTP)Mo=S, **1**, in 40-45% yield. The sulfido complex exhibits a ^{1}H NMR spectrum typical of a diamagnetic porphyrin complex with a β-pyrrole proton singlet at 9.27 ppm and a tolyl-CH_3 singlet at 2.41 ppm in benzene-d_6. In the IR, the Mo=S stretch is observed as a medium intensity band at 542 cm^{-1}. The electronic absorption spectrum of **1** in toluene contains an intense Soret

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + 1/8\ S_8 \longrightarrow \text{(TTP)Mo=S} + \text{PhC}\equiv\text{CPh} \qquad (1)$$

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + Cp_2TiS_5 \longrightarrow \text{(TTP)Mo=S} + \text{PhC}\equiv\text{CPh} \qquad (2)$$

band at 438 nm with an additional band at 556 nm. Donor ligands such as THF do not appear to bind to the empty coordination site trans to the sulfido ligand; the complex exhibits the same UV-vis spectrum in pure toluene and in toluene/THF mixtures.

Treatment of (TTP)MoCl$_2$ with Li$_2$S in THF also results in formation of (TTP)Mo=S (eq 3). The yield from this reaction is low due to contamination with (TTP)Mo=O. The formation of the terminal oxo complex is probably the result of the reaction of either the starting material,

$$\text{(TTP)MoCl}_2 + \text{Li}_2\text{S} \longrightarrow \text{(TTP)Mo=S} + 2\ \text{LiCl} \qquad (3)$$

(TTP)MoCl$_2$, or (TTP)Mo=S with water which we have been unable to eliminate from the Li$_2$S. However, separation of the terminal oxo and sulfido complexes is quite simple using a neutral alumina column with toluene as the eluent. The sulfido complex moves quickly down the column whereas the terminal oxo species moves very slowly and requires a more polar solvent such as THF to be eluted.

Similar to the preparation of (TTP)Mo=S, a terminal selenido molybdenum(IV) porphyrin, (TTP)Mo=Se, **2**, may be prepared from (TTP)MoCl$_2$ and Na$_2$Se (eq 4). Again, contamination with (TTP)Mo=O requires purification of the product by column chromatography and results in a relatively low yield. The ^{1}H NMR spectrum of **2** is typical of a diamagnetic porphyrin complex

$$\text{(TTP)MoCl}_2 + \text{Na}_2\text{Se} \longrightarrow \text{(TTP)Mo=Se} + 2\ \text{NaCl} \qquad (4)$$

with a β-pyrrolic proton singlet at 9.25 ppm. The Mo=Se stretch is observed as a medium intensity band at 410 cm^{-1}. The electronic absorption spectrum in toluene of the terminal selenide complex has an intense Soret band at 432 nm with an additional band at 554 nm.

Attempts to prepare the terminal selenido complex from (TTP)Mo(PhC≡CPh) and elemental selenium (eq 5) resulted in the isolation of a mixture of (TTP)Mo(PhC≡CPh) and (TTP)Mo=Se (8:1) despite extended heating and reaction times.

$$\text{(TTP)Mo(PhC≡CPh)} + \text{Se} \longrightarrow \text{(TTP)Mo=Se} + \text{PhC≡CPh} \qquad (5)$$

X-ray structure of (TTP)Mo=S. The molecular structure of **1** was determined by single-crystal X-ray diffraction. The molecular structure and atom numbering scheme are shown in Figure 1. Crystallographic data for the structure determination, atomic positional parameters, and selected bond distances and angles are listed in Appendix A.

Complex **1** crystallizes in the space group $P\bar{1}$ with 2 molecules per unit cell. The Mo-N distances vary from 2.093(2) to 2.113(2) Å and are typical of those observed for other molybdenum porphyrins.[2,9] The Mo-S distance of 2.100(1) Å is similar to that reported for a number of complexes containing the Mo=S moiety.[10] The molybdenum ion is displaced from the mean porphyrin plane 0.65 Å toward the S ligand. A slight doming of the porphyrin ligand was observed. The structure of (TTP)Mo=S is very similar to the previously reported structure of (TTP)Mo=O [11]

Intermetal atom transfer reactions. Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=S in benzene-d_6 results in spectral changes consistent with the complete transfer of a terminally

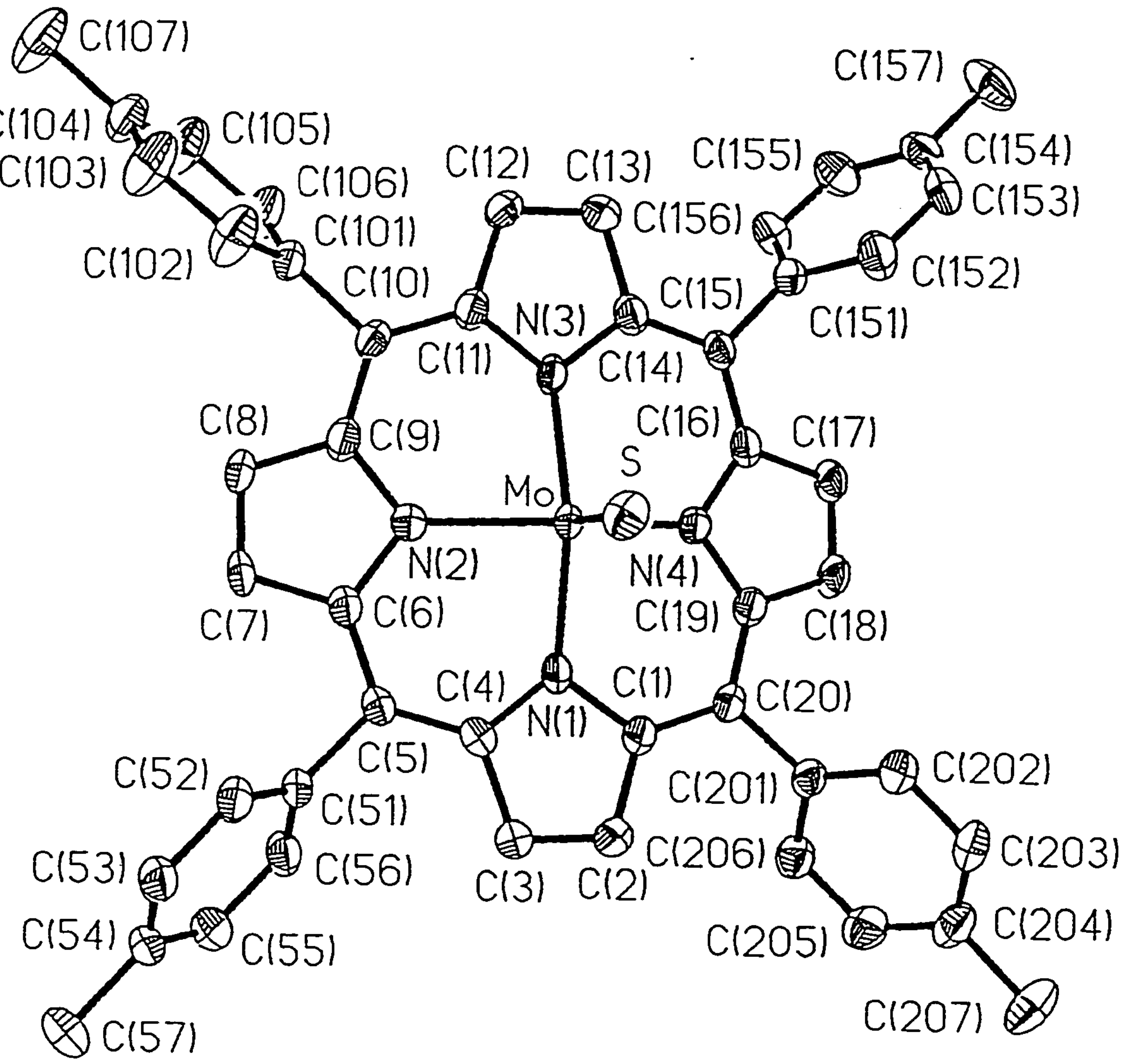


Figure 1. Molecular structure and atom numbering scheme for (TTP)Mo=S•1.5(C_6H_6).

bound sulfur ligand between two metal complexes as shown in eq 6. For example, new β-pyrrolic proton resonances appear, signifying the formation of (TTP)Mo=S (9.27 ppm) and (TTP)Sn(II) (9.19 ppm). The β-pyrrolic proton signals for (TTP)Mo(PhC≡CPh) (8.99 ppm) and (TTP)Sn=S (9.14 ppm) disappear, indicating that eq 6 is not an equilibrium process. Treatment

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{(TTP)Sn=S} \longrightarrow \text{(TTP)Mo=S} + \text{(TTP)Sn(II)} + \text{PhC}\equiv\text{CPh} \tag{6}$$

$$\text{(TTP)Mo=S} + \text{(TTP)Sn(II)} + \text{PhC}\equiv\text{CPh} \longrightarrow \text{NR} \tag{7}$$

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{(TTP)Sn=Se} \rightleftarrows \text{(TTP)Mo=Se} + \text{(TTP)Sn(II)} + \text{PhC}\equiv\text{CPh} \tag{8}$$

of (TTP)Mo=S with (TTP)Sn(II) in the presence of PhC≡CPh (eq 7) results in no reaction. However, reversible selenium atom transfer occurs on treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=Se in benzene-d_6 as shown in eq 8. For example, very small new β-pyrrolic proton resonances appear for (TTP)Mo=Se (9.25 ppm) and (TTP)Sn(II) (9.19 ppm) while signals associated with the β-pyrrolic protons of (TTP)Mo(PhC≡CPh) (8.99 ppm) and (TTP)Sn=Se (9.16 ppm) diminish only slightly, indicating an equilibrium that lies largely toward the reactants. The equilibrium constant for eq 8 was derived from the reverse reaction obtained by treatment of (TTP)Mo=Se with (TTP)Sn(II) in the presence of PhC≡CPh. At 25 °C, $K = 2.21 \times 10^{-5} \pm 3.75 \times 10^{-6}$ as determined by integration of the β-pyrrolic resonances for each of the porphyrin species involved in the equilibrium as well as the signal associated with the *o*-protons of free PhC≡CPh.

Atom transfer reactions involving PPh$_3$. Treatment of (TTP)Mo=S or (TTP)Mo=Se with an excess of PPh_3 (eq 9) in toluene results in the formation of $Ph_3P{=}S$ or $Ph_3P{=}Se$ and a new porphyrin complex, $(TTP)Mo(PPh_3)_2$. In the case of sulfur atom transfer, this reduction occurs over the course of hours with mild heating (50-60 °C) of the toluene solution. For selenium atom transfer from molybdenum to PPh_3, the transfer occurs over the course of minutes at ambient temperature. Once formed, the bis-phosphine complex precipitates from the toluene

$$(TTP)Mo{=}X\ +\ 3\ PPh_3\ \longrightarrow\ (TTP)Mo(PPh_3)_2\ +\ Ph_3P{=}X \qquad (9)$$

$$X = S \text{ or } Se$$

solution and is easily isolated by filtration. The ^1H NMR spectrum of $(TTP)Mo(PPh_3)_2$ indicates that the Mo(II) porphyrin complex is paramagnetic, with resonances distributed over a 40-ppm range from -11 ppm to 31 ppm. Despite the paramagnetism of the bis-phosphine species, sharp NMR signals are still observed and integration of the resonances indicates that two axial ligands are present. Furthermore, the *trans*-geometry of the complex is clearly evident from the AB multiplet pattern exhibited by the *o*- and *m*-protons of the tolyl substituents. Signals associated with the axially coordinated phosphine ligands are shifted dramatically downfield, with the *o*-protons of phenyl rings appearing at nearly 31 ppm. The *m*- and *p*-resonances are shifted to 12.08 and 11.50 ppm respectively. The porphyrin resonances are instead shifted dramatically upfield, with the β-pyrrole resonance being found at -11.60 ppm. A signal for the bound PPh_3 ligands was not observed in the ^{31}P spectrum over a window of ± 1000 ppm. The electronic absorption spectrum of $(TTP)Mo(PPh_3)_2$ is dramatically different than both the sulfido and selenido complexes with the Soret band shifted over 30 nm to 390 nm.

Ligand replacement reactions. Reduction of either the terminal sulfido or selenido complex by PPh_3 in the presence of diphenylacetylene, results in the formation of exclusively the Mo(II) π-alkyne complex (eq 10). In an independent experiment, treatment of $(TTP)Mo(PPh_3)_2$ with excess PhC≡CPh (eq 11) resulted in the rapid displacement of the phosphine ligands to produce (TTP)Mo(PhC≡CPh) and free PPh_3. For example, addition of diphenylacetylene to an NMR tube containing $(TTP)Mo(PPh_3)_2$ in benzene-d_6 results in a color change within seconds from the green of the bis-phosphine species to the orange/red of the π-alkyne complex which is easily distinguished by its ^{1}H NMR resonances. Displacement of the alkyne ligand from the molybdenum center results when (TTP)Mo(PhC≡CPh) is treated with 4-picoline (eq 12). In the ^{1}H NMR spectrum of this reaction mixture, signals associated with the alkyne complex disappear while signals for free diphenylacetylene and a new molybdenum porphyrin complex appear. This displacement reaction occurs over the course of hours at ambient temperature. The new

$$(TTP)Mo{=}X + PPh_3 + PhC{\equiv}CPh \longrightarrow (TTP)Mo(PhC{\equiv}CPh) + Ph_3P{=}X \qquad (10)$$

$$X = S \text{ or } Se$$

$$(TTP)Mo(PPh_3)_2 + PhC{\equiv}CPh \longrightarrow (TTP)Mo(PhC{\equiv}CPh) + 2\ PPh_3 \qquad (11)$$

$$(TTP)Mo(PhC{\equiv}CPh) + \text{4-picoline} \longrightarrow (TTP)Mo(\text{4-picoline})_2 + PhC{\equiv}CPh \qquad (12)$$

substitution product, a bis-picoline complex ((TTP)Mo($NC_6H_4CH_3)_2$), is paramagnetic as indicated by the broad chemical shift range in the ^1H NMR spectrum. For example, signals associated with the bound picoline ligands are shifted significantly downfield to 47.5 and 33.8 ppm in benzene-d_6. Similar to the bis-phosphine complex, the signals associated with the porphyrin ring are shifted significantly upfield, with the β-H signal appearing at -0.15 ppm.

Discussion

The first terminal sulfido and selenido molybdenum porphyrin complexes have been isolated and characterized. The terminal chalcogenides may be prepared by a number of synthetic routes involving either Mo(II) or Mo(IV) precursors. The terminal sulfido and selenido complexes are diamagnetic, similar to the terminal oxo complex.[10a] In the ^1H NMR spectrum, the β-*H* resonance for (TTP)Mo=S in benzene-d_6 is found at 9.27 ppm, shifted only slightly downfield of its position in (TTP)Mo=O (9.26 ppm). For the selenido derivative, the β-*H* resonance is shifted slightly upfield, appearing at 9.25 ppm. The remaining resonances in the ^1H NMR of all three chalcogenide complexes are at virtually the same chemical shift in benzene-d_6.

Although these molybdenum porphyrin chalcogenide complexes have very similar ^1H NMR properties, noticeable differences are exhibited for the Mo=X stretching frequencies. In the oxo complex, the Mo=O stretch appears near 980 cm^{-1}. However, for the sulfido analog, a new band of medium intensity is present at 542 cm^{-1}, which has been assigned as the Mo=S stretch. This assignment compares well with other complexes containing the Mo=S moiety. For example, in $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$ the Mo=S stretch is found at 512 cm^{-1} and in $[MoS(S_4)_2]^{2-}$ the same stretch is found at 525 cm^{-1}.[9,12] Similarly, for the selenido complex a new band of medium intensity at 410 cm^{-1} has been assigned as the Mo=Se stretch. This assignment falls between the values found for (TTP)V=Se (439 cm^{-1}) and (TTP)Ti=Se (465 cm^{-1}), and a value reported for $Cp^*Nb(=NAr)(Se)(PMe_3)$ (335 cm^{-1}).[6a,6b,13]

Electronic absorption spectra of the terminal chalcogenides differ only slightly, with the largest difference exhibited in the position of the Soret band in the oxo and selenido derivatives versus the sulfido complex. For the terminal oxo and selenido species, the Soret band appears at 432 nm in toluene while in (TTP)Mo=S, the Soret band is shifted to 438 nm. Addition of THF to a toluene solution of (TTP)Mo=X (X = S or Se) produces no change in position or intensity of the absorption maxima, indicating that THF does not appear to bind to the position trans to the chalcogenide.

(TTP)Mo=S is the first metalloporphyrin complex to be structurally characterized which contains a heavier Group 16 element as a terminal ligand. The Mo-S bond length is similar to those in other structurally characterized terminal sulfido molybdenum complexes.[9]

The molybdenum sulfido porphyrin complex may also be generated by an intermetal atom transfer reaction involving transfer of a terminally bound sulfur ligand from a tin porphyrin, (TTP)Sn=S, to a low-valent molybdenum porphyrin, (TTP)Mo(PhC≡CPh). In contrast to the irreversible transfer observed for sulfur, the analgous reaction between (TTP)Sn=Se and (TTP)Mo(PhC≡CPh) produces an equilibrium which largely favors the formation of (TTP)Sn=Se.

In contrast to the relative inertness of the Mo=O fragment, the heavier chalcogenide porphyrin complexes readily undergo reduction with PPh_3 to produce a paramagnetic bis-phosphine complex, $(TTP)Mo(PPh_3)_2$, and the corresponding phosphine chalcogenide. As shown in eq 13, (TTP)Mo=O cannot be reduced by PPh_3, presumably due to the very strong Mo=O

$$\text{(TTP)Mo=O} + \text{PPh}_3 \longrightarrow \text{No reaction} \qquad (13)$$

bond. The rate of atom transfer from molybdenum to phosphorus qualitatively increases on descending the chalcogenides. For example, treatment of (TTP)Mo=S with an excess of PPh_3 in C_6D_6 in an NMR tube at ambient temperature requires hours for the reduction to go to completion, whereas the same experiment utilizing (TTP)Mo=Se requires only minutes to reach completion. A similar trend has been observed in reactions involving intermetal sulfur and selenium atom transfer reactions between tin porphyrins.[7] In this case, the relative rate of selenium versus sulfur atom transfer at 30 °C was 218:1.

The molybdenum bis-phosphine complex is analogous to (OEP)Re$(PMe_3)_2$ and (OEP)W$(PEt_3)_2$ which were prepared as precursors to the corresponding metalloporphyrin dimers.[14] (TTP)Mo$(PPh_3)_2$ is paramagnetic as evidenced by its broad chemical shift range in the ^1H NMR. Despite is paramagnetic nature, sharp signals were observed in the ^1H NMR.

The phosphine ligands of (TTP)Mo$(PPh_3)_2$ are readily displaced upon addition of diphenylacetylene to give (TTP)Mo(PhC≡CPh) and free PPh_3. The alkyne may be displaced by addition of 4-picoline to give the bis-picoline derivative (TTP)Mo(4-picoline)$_2$. The analogous *trans*-(TTP)Mo(pyridine)$_2$ has been prepared and structurally characterized.[4c] Therefore, the order of ligand preference for Mo(II) porphyrins is: PPh_3 < PhC≡CPh < 4-picoline. The lability of the phosphine ligands in (TTP)Mo$(PPh_3)_2$ makes this an attractive complex for studying the reaction chemistry of the Mo(II) center.

Conclusions

Multiple bonding between the transition metals and the heavier main group elements has been the focus of a number of recent studies.[15] Interest in these derivatives stems from the limited number of known examples containing multiple bonds to N, P, S, Se, and Te.[16] As reported here, (TTP)Mo=S and (TTP)Mo=Se exhibit a rich chemistry unique to the metal-ligand multiple bonds of the heavier members of Group 16. In particular, reduction of the terminal chalcogenides represents a new synthetic route for the preparation of low-valent molybdenum porphyrins. Further studies of the synthesis and reactivity of low-valent early transition metal porphyrins are underway.

References

1. Presidential Young Investigator, 1990-1995; Camille and Henry Dreyfus Teacher-Scholar 1993-1998.
2. Matsuda, Y.; Murakami, Y. *Coord. Chem. Rev.* **1988**, *92*, 157.
3. Berreau, L.M.; Hays, J.A.; Young, V.G.; Woo, L.K. *Inorg. Chem.* **1994**, *33*, 105.
4. (a) De Cian, A.; Colin, J.; Schappacher, M.; Richard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1851. (b) Diebold, T.; Schappacher, M.; Richard, L.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1979**, 693. (c) Colin, J.; Strich, A.; Schappacher, M.; Chevrier, B.; Veillard, A.; Weiss, R. *Nouv. J. De Chim.* **1984**, *8*, 55.
5. Colin, J.; Butler, G.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 3828.
6. (a) Woo, L.K.; Hays, J.A.; Young, V.G.; Day, C.L.; Caron, C.; D'Souza, F.; Kadish, K.M. *Inorg. Chem.* **1993**, *32*, 4186. (b) Poncet, J.L.; Guilard, R.; Friant, P.; Goulon-

Ginet, C.; Goulon, J. *Nouv. J. Chim.* **1984**, *8*, 583. (c) Guilard, R.; Ratti, C.; Barbe, J. -M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.

7. (a) Berreau, L. M.; Woo, L. K. *J. Am. Chem. Soc.* Submitted. (b) Guilard, R.; Ratti, C.; Barbe, J. -M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.
8. SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI.
9. Kim, J. C.; Rees, W. S., Jr.; Goedken, V. L. *Inorg. Chem.* **1994**, *33*, 3191.
10. (a) Huneke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698. (b) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938.
11. (a) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.
12. (a) Simhon, E. D.; Baenziger, N. C.; Kanatizidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218. (b) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.
13. (a) Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1671. (b) Christou, V.; Arnold, J. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1450.
14. (a) Collman, J. P.; Garner, J. M.; Kim, K.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 4513. (b) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.
15. (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (b) Siemeling, U. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 67. (c) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181. (d) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. (e) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761. (f) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold,

A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453. (g) Rabinovich, D.; Parkin, F. *J. Am. Chem. Soc.* **1991**, *113*, 5904. (h) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421. (i) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240. (j) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 2313. (m) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

16. Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

APPENDIX A

Table I. Structure determination summary

Crystal Data

Empirical Formula	C_{57} H_{45} Mo N_4 S
Color; Habit	Purple, triclinic
Crystal Size (mm)	0.40 x 0.25 x 0.25
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	a = 12.735(2) Å
	b = 13.521(2) Å
	c = 13.920(2) Å
	α = 74.76(2)°
	β = 78.95(2)°
	γ = 80.85(2)°
Volume	2253.9(4) Å
Z	2
Formula Weight	914.0
Density (calc.)	1.347 Mg/m^3
Absorption Coefficient	3.143 mm^{-1}
F(000)	946

Table I. (continued)

Data Collection

Diffractometer Used	Siemens P4RA
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	223
Monochromator	Highly-oriented graphite crystal
2θ Range	4.0 to 115.0°
Scan Type	$2\theta - \theta$
Scan Speed	Variable; 8.0 to 24.0°/min. in ω
Scan Range (ω)	1.00° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-13 \leq h \leq 0$, $-14 \leq k \leq 14$ $-15 \leq l \leq 14$
Reflections Collected	6376
Independent Reflections	6047 (R_{int} = 1.13%)
Observed Reflections	5532 ($F \geq 6.0\ \sigma(F)$)
Absorption Correction	Semi-empirical
Min./Max. Transmission	0.6686 / 0.8504

Table I. (continued)

Solution and Refinement	
System Used	Siemens SHELXTL-Plus (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\Sigma\ w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.0016(2)$, where $F^* = F_c[1 + 0.002\ \chi\ F^2/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0003\ F^2$
Parameters Refined	599
Final R Indices (obs. data)	R = 2.86%, wR = 4.14%
R Indices (all data)	R = 3.10%, wR = 4.19%
Goodness-of-Fit	2.02
Largest and Mean Δ/σ	0.012, 0.001
Data-to-Parameter Ratio	9.2:1
Largest Difference Peak	0.36 e/Å^{-3}
Largest Difference Hole	-0.49 e/Å^{-3}

Table II. Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^2 x 10^3)

	x	y	z	U(eq)
Mo	4997(1)	3005(1)	4074(1)	22(1)
S	4046(1)	2469(1)	3284(1)	37(1)
N(1)	4027(2)	3087(2)	5460(2)	26(1)
N(2)	5883(2)	1734(2)	4929(2)	28(1)
N(3)	6479(2)	3227(2)	3115(2)	27(1)
N(4)	4654(2)	4613(2)	3678(2)	26(1)
C(1)	3134(2)	3817(2)	5559(2)	26(1)
C(2)	2384(2)	3405(2)	6423(2)	30(1)
C(3)	2832(2)	2464(2)	6878(2)	30(1)
C(4)	3861(2)	2262(2)	6287(2)	28(1)
C(5)	4572(2)	1376(2)	6507(2)	27(1)
C(6)	5530(2)	1148(2)	5886(2)	30(1)
C(7)	6293(2)	258(2)	6131(2)	39(1)
C(8)	7100(2)	294(2)	5335(2)	39(1)
C(9)	6855(2)	1214(2)	4585(2)	31(1)
C(10)	7519(2)	1531(2)	3666(2)	28(1)
C(11)	7337(2)	2471(2)	2976(2)	28(1)
C(12)	7990(2)	2814(2)	2027(2)	33(1)
C(13)	7559(2)	3776(2)	1593(2)	33(1)
C(14)	6634(2)	4050(2)	2273(2)	29(1)

Table II. (continued)

	x	y	z	U(eq)
C(15)	6015(2)	5012(2)	2149(2)	27(1)
C(16)	5133(2)	5286(2)	2832(2)	28(1)
C(17)	4559(2)	6299(2)	2758(2)	32(1)
C(18)	3728(2)	6238(2)	3528(2)	32(1)
C(19)	3768(2)	5188(2)	4097(2)	27(1)
C(20)	3005(2)	4801(2)	4925(2)	26(1)
C(51)	4303(2)	610(2)	7501(2)	28(1)
C(52)	4156(2)	-392(2)	7525(2)	32(1)
C(53)	3908(2)	-1091(2)	8447(2)	37(1)
C(54)	3797(2)	-803(2)	9346(2)	40(1)
C(55)	3949(3)	201(2)	9310(2)	41(1)
C(56)	4199(2)	895(2)	8394(2)	34(1)
C(57)	3509(3)	-1550(3)	10350(3)	65(2)
C(101)	8522(2)	820(2)	3450(2)	30(1)
C(102)	8471(3)	-132(3)	3294(3)	49(1)
C(103)	9405(3)	-803(3)	3141(3)	55(2)
C(104)	10404(3)	-533(2)	3133(3)	41(1)
C(105)	10448(3)	411(3)	3297(3)	51(1)
C(106)	9518(3)	1080(2)	3455(3)	48(1)
C(107)	11417(3)	-1255(3)	2955(4)	70(2)

Table II. (continued)

	x	y	z	U(eq)
C(151)	6341(2)	5836(2)	1224(2)	30(1)
C(152)	5724(3)	6141(3)	457(2)	42(1)
C(153)	5998(3)	6929(3)	-384(2)	44(1)
C(154)	6889(3)	7426(2)	-471(2)	38(1)
C(155)	7506(3)	7110(2)	289(2)	41(1)
C(156)	7242(3)	6318(2)	1125(2)	36(1)
C(157)	7182(3)	8288(3)	-1389(3)	59(2)
C(201)	1972(2)	5467(2)	5121(2)	27(1)
C(202)	1301(2)	5771(2)	4397(2)	35(1)
C(203)	303(2)	6335(2)	4583(3)	39(1)
C(204)	-51(2)	6597(2)	5494(3)	39(1)
C(205)	621(3)	6289(2)	6218(3)	41(1)
C(206)	1625(2)	5740(2)	6033(2)	34(1)
C(207)	-1157(3)	7179(3)	5703(3)	64(2)
C(31)	434(8)	5284(8)	1175(6)	141(5)
C(32)	1315(11)	4630(5)	1413(7)	167(5)
C(33)	2148(6)	5050(8)	1624(5)	146(4)
C(34)	2040(6)	6054(7)	1571(4)	116(4)
C(35)	1182(6)	6631(5)	1317(5)	114(3)

Table II. (continued)

	x	y	z	U(eq)
C(36)	371(6)	6264(7)	1137(6)	135(4)
C(41)	9026(3)	-340(4)	101(4)	80(2)
C(42)	9123(4)	398(4)	560(4)	84(2)
C(43)	10106(4)	735(4)	463(4)	89(2)

[*] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond lengths (Å)

Mo-S	2.100 (1)	C(6)-C(7)	1.430 (4)
Mo-N(1)	2.101 (2)	C(7)-C(8)	1.356 (4)
Mo-N(2)	2.113 (2)	C(8)-C(9)	1.433 (4)
Mo-N(3)	2.106 (2)	C(9)-C(10)	1.396 (4)
Mo-N(4)	2.093 (2)	C(10)-C(11)	1.394 (3)
N(1)-C(1)	1.393 (3)	C(10)-C(101)	1.503 (4)
N(1)-C(4)	1.386 (3)	C(11)-C(12)	1.425 (4)
N(2)-C(6)	1.391 (3)	C(12)-C(13)	1.358 (4)
N(2)-C(9)	1.388 (3)	C(13)-C(14)	1.428 (4)
N(3)-C(11)	1.394 (3)	C(14)-C(15)	1.397 (4)
N(3)-C(14)	1.395 (3)	C(15)-C(16)	1.395 (4)
N(4)-C(16)	1.388 (3)	C(15)-C(151)	1.503 (3)
N(4)-C(19)	1.388 (3)	C(20)-C(201)	1.494 (4)
C(1)-C(2)	1.431 (4)	C(16)-C(17)	1.434 (4)
C(1)-C(20)	1.395 (3)	C(17)-C(18)	1.350 (4)
C(2)-C(3)	1.352 (4)	C(18)-C(19)	1.431 (4)
C(3)-C(4)	1.435 (4)	C(19)-C(20)	1.400 (3)
C(4)-C(5)	1.385 (4)	C(51)-C(52)	1.387 (4)
C(5)-C(6)	1.396 (4)	C(51)-C(56)	1.372 (5)
C(5)-C(51)	1.510 (3)	C(52)-C(53)	1.393 (4)

Table III. (continued)

C(53)-C(54)	1.383 (5)	C(154)-C(155)	1.375 (5)
C(54)-C(55)	1.388 (5)	C(154)-C(157)	1.518 (4)
C(54)-C(57)	1.513 (4)	C(155)-C(156)	1.388 (4)
C(55)-C(56)	1.385 (4)	C(201)-C(202)	1.383 (4)
C(101)-C(102)	1.373 (5)	C(201)-C(206)	1.386 (4)
C(101)-C(106)	1.372 (5)	C(202)-C(203)	1.391 (4)
C(102)-C(103)	1.394 (5)	C(203)-C(204)	1.381 (5)
C(103)-C(104)	1.376 (5)	C(204)-C(205)	1.385 (5)
C(104)-C(105)	1.366 (5)	C(204)-C(207)	1.516 (5)
C(104)-C(107)	1.510 (5)	C(205)-C(206)	1.387 (4)
C(105)-C(106)	1.390 (4)	C(31)-C(32)	1.351 (15)
C(151)-C(152)	1.384 (5)	C(31)-C(36)	1.302 (15)
C(151)-C(156)	1.374 (5)	C(32)-C(33)	1.390 (16)
C(152)-C(153)	1.389 (4)	C(33)-C(34)	1.325 (14)
C(153)-C(154)	1.379 (5)	C(34)-C(35)	1.288 (10)
C(35)-C(36)	1.305 (12)	C(41)-C(42)	1.351 (8)
C(41)-C(43A)	1.351 (7)	C(42)-C(43)	1.369 (7)
C(43)-C(41A)	1.351 (7)		

Table IV. Bond angles (°)

S-Mo-N(1)	105.4(1)	Mo-N(1)-C(1)	123.5(2)
S-Mo-N(2)	109.4(1)	Mo-N(1)-C(4)	125.5(2)
N(1)-Mo-N(2)	85.3(1)	C(1)-N(1)-C(4)	106.0(2)
S-Mo-N(3)	106.2(1)	Mo-N(2)-C(6)	126.7(2)
N(1)-Mo-N(3)	148.5(1)	Mo-N(2)-C(9)	126.5(2)
N(2)-Mo-N(3)	84.8(1)	C(6)-N(2)-C(9)	106.0(2)
S-Mo-N(4)	104.6(1)	Mo-N(3)-C(11)	126.7(2)
N(1)-Mo-N(4)	85.6(1)	Mo-N(3)-C(14)	124.3(2)
N(2)-Mo-N(4)	146.0(1)	C(11)-N(3)-C(14)	105.8(2)
N(3)-Mo-N(4)	86.1(1)	Mo-N(4)-C(16)	126.8(2)
Mo-N(4)-C(19)	126.0(2)	C(4)-C(5)-C(6)	124.7(2)
C(16)-N(4)-C(19)	106.1(2)	C(4)-C(5)-C(51)	117.6(2)
N(1)-C(1)-C(2)	109.3(2)	C(6)-C(5)-C(51)	117.6(2)
N(1)-C(1)-C(20)	125.2(2)	N(2)-C(6)-C(5)	125.6(2)
C(2)-C(1)-C(20)	125.6(2)	N(2)-C(6)-C(7)	109.4(2)
C(1)-C(2)-C(3)	107.7(2)	C(5)-C(6)-C(7)	124.9(2)
C(2)-C(3)-C(4)	107.5(2)	C(6)-C(7)-C(8)	107.7(2)
N(1)-C(4)-C(3)	109.4(2)	C(7)-C(8)-C(9)	107.4(2)
N(1)-C(4)-C(5)	125.4(2)	N(2)-C(9)-C(8)	109.5(2)
C(3)-C(4)-C(5)	125.2(2)	N(2)-C(9)-C(10)	126.4(2)

Table IV. (continued)

C(8)-C(9)-C(10)	124.1(2)	C(18)-C(19)-C(20)	124.9(2)
C(9)-C(10)-C(11)	124.4(2)	C(1)-C(20)-C(19)	124.1(2)
C(9)-C(10)-C(101)	116.6(2)	C(1)-C(20)-C(201)	117.8(2)
C(11)-C(10)-C(101)	119.0(2)	C(19)-C(20)-C(201)	118.1(2)
N(3)-C(11)-C(10)	124.7(2)	C(5)-C(51)-C(52)	120.5(3)
N(3)-C(11)-C(12)	109.4(2)	C(5)-C(51)-C(56)	120.5(3)
C(10)-C(11)-C(12)	125.9(2)	C(52)-C(51)-C(56)	119.0(2)
C(11)-C(12)-C(13)	107.9(2)	C(51)-C(52)-C(53)	120.0(3)
C(12)-C(13)-C(14)	107.4(2)	C(52)-C(53)-C(54)	121.1(3)
N(3)-C(14)-C(13)	109.4(2)	C(53)-C(54)-C(55)	118.3(3)
N(3)-C(14)-C(15)	124.9(2)	C(53)-C(54)-C(57)	121.5(3)
C(13)-C(14)-C(15)	25.5(2)	C(55)-C(54)-C(57)	120.2(3)
C(14)-C(15)-C(16)	125.3(2)	C(54)-C(55)-C(56)	120.6(3)
C(14)-C(15)-C(151)	117.8(2)	C(51)-C(56)-C(55)	121.1(3)
C(16)-C(15)-C(151)	116.8(2)	C(10)-C(101)-C(102)	121.4(3)
N(4)-C(16)-C(15)	125.2(2)	C(10)-C(101)-C(106)	120.8(3)
N(4)-C(16)-C(17)	109.2(2)	C(102)-C(101)-C(106)	117.6(3)
C(15)-C(16)-C(17)	125.6(2)	C(101)-C(102)-C(103)	120.8(3)
C(16)-C(17)-C(18)	107.7(2)	C(102)-C(103)-C(104)	121.3(4)
C(17)-C(18)-C(19)	107.6(2)	C(103)-C(104)-C(105)	117.6(3)

Table IV. (continued)

N(4)-C(19)-C(18)	109.4(2)	C(103)-C(104)-C(107)	121.3(3)
N(4)-C(19)-C(20)	125.6(2)	C(105)-C(104)-C(107)	121.1(3)
C(104)-C(105)-C(106)	121.2(3)	C(204)-C(205)-C(206)	121.2(3)
C(101)-C(106)-C(105)	121.4(3)	C(201)-C(206)-C(205)	120.6(3)
C(15)-C(151)-C(152)	120.4(3)	C(32)-C(31)-C(36)	121.5(10)
C(15)-C(151)-C(156)	121.2(3)	C(31)-C(32)-C(33)	116.9(8)
C(152)-C(151)-C(156)	118.4(2)	C(32)-C(33)-C(34)	118.9(7)
C(151)-C(152)-C(153)	120.8(3)	C(33)-C(34)-C(35)	120.5(8)
C(152)-C(153)-C(154)	120.8(3)	C(34)-C(35)-C(36)	122.6(8)
C(153)-C(154)-C(155)	118.1(3)	C(31)-C(36)-C(35)	119.6(8)
C(153)-C(154)-C(157)	120.5(3)	C(42)-C(41)-C(43A)	120.0(5)
C(155)-C(154)-C(157)	121.3(3)	C(41)-C(42)-C(43)	119.9(5)
C(154)-C(155)-C(156)	121.4(3)	C(42)-C(43)-C(41A)	120.1(6)
C(151)-C(156)-C(155)	120.6(3)	C(201)-C(202)-C(203)	120.7(3)
C(20)-C(201)-C(202)	119.3(3)	C(202)-C(203)-C(204)	121.1(3)
C(20)-C(201)-C(206)	122.2(3)	C(203)-C(204)-C(205)	118.0(3)
C(202)-C(201)-C(206)	118.4(3)	C(203)-C(204)-C(207)	120.7(3)
C(205)-C(204)-C(207)	121.2(3)		

CHAPTER 6: EARLY TRANSITION METAL IMIDO COMPLEXES: A LITERATURE REVIEW

Group IV imido complexes and C-H bond activation

Group IV metal imido complexes have been the focus of recent research efforts due to their involvement in intriguing alkane and arene activations, 2 + 2 cycloadditions, and the catalytic amination of alkynes. This following section will highlight aspects of this chemistry.

Until 1988, there were no reports in the literature of Group IV metallocenes of the general formula $(\eta^5\text{-}C_5H_5)_2M{=}O$ or $(\eta^5\text{-}C_5R_5)_2M{=}NR'$ (M = Ti, Zr, Hf) suggesting that if generated, these could be highly reactive species. Bergman, *et al.* were the first to report generation of an imidozirconocene complex.[1] These researchers found that treatment of Cp_2ZrMe_2 with one equivalent of 4-*tert*-butylaniline in benzene at 85 °C resulted in the loss of one equivalent of methane with formation of the zirconocene amide, $Cp_2Zr(CH_3)(HNR)$ ($R = p\text{-}^tBu\text{-}C_6H_4$). The same complex could also be prepared from treatment of $Cp_2Zr(CH_3)(Cl)$ with $LiNH(4\text{-}^tBu\text{-}C_6H_4)$. Heating of the amido complex for 3 days in benzene led to elimination of a second equivalent of methane and formation of a bridging imido dimer, $(Cp_2Zr)_2(\mu\text{-}NR)_2$. It was postulated that the dimer was produced via generation of a transient zirconium imido complex, $Cp_2Zr{=}N\text{-}Ph$, which then dimerized to give the bridged product. When the more sterically hindered tertiary butyl amido complex, $Cp_2Zr(CH_3)(NHCMe_3)$, was heated in benzene for three days, a new amido zirconocene complex ($Cp_2Zr(NHCMe_3)(Ph)$) was isolated. This product was formed via reaction of the reactive Zr=N linkage with a C-H bond in benzene. The transient zirconium imido complex was trapped by treating the amido species with alkynes to give the azametallacyclobutene product $Cp^2Zr(\eta^2\text{-}1,3\text{-}N(^tBu)\text{-}CR'{=}CR\text{-})$. The imido complex could also be trapped by addition of THF, forming the adduct compound Cp$_2$Zr=NR•THF. Cp$_2$Zr=NCMe$_3$•THF is the first structurally characterized Group IV imido complex.

Similarly, Cummins and Wolczanski reported the transient formation of three-coordinate zirconium imido species via thermolysis of complexes of the formula (R$_3$SiNH)$_3$ZrR' (R = ^{t}Bu, R' = Me, Ph, Cy).[2] Once formed, these three coordinate species ((^{t}Bu$_3$SiNH)$_2$Zr=NSi^{t}Bu$_3$) will add a benzene C-H bond across the Zr=N linkage to give (^{t}Bu$_3$SiNH)$_3$Zr-Ph. Similar to Bergman's results, addition of THF allowed for isolation of the THF-adduct of the zirconium imido complex.

Terminal imido complexes of titanium may also be prepared via thermolyses that induce the abstraction of amide protons by neighboring HNSi^{t}Bu$_3$ groups.[3] Addition of MeLi in Et$_2$O to (^{t}BuSiNH)$_3$TiCl yielded the imido complex (^{t}BuSiNH)$_2$(Et$_2$O)Ti=NSi^{t}Bu$_3$ (55%) and methane. This reaction may be viewed as a dehydrochlorination and Et$_2$O-trapping of the transient imido complex. Thermolysis of the imido complex in benzene-d_6 at 97 °C for 2 hours resulted in complete deuteration of the amido protons. This H/D exchange probably occurs via a sequence of reactions, beginning with the dissociation of Et$_2$O from (^{t}BuSiNH)$_2$(Et$_2$O)Ti=NSitBu$_3$. The transient 3-coordinate imido complex may then add a C-D bond across the Ti=N functionality resulting in the formation of (^{t}Bu$_3$SiNH)$_2$(^{t}BuSiND)TiC$_6$D$_5$. An equivalent of C$_6$D$_5$H may then be released with reformation of a three coordinate imido complex which is subsequently trapped by Et$_2$O. A similar addition/elimination sequence may be observed using (^{t}Bu$_3$SiNH)$_3$TiX (X = Cl, Br, ^{t}Bu$_3$SiNH) as the imido precursor. In each of these cases, the imido complex is generated after loss of ^{t}Bu$_3$SiNH$_2$. Thermolysis of (^{t}Bu$_3$SiNH)$_3$TiCl in THF led to the formation of (^{t}Bu$_3$SiNH)(THF)ClTi=NSi^{t}Bu$_3$.

Isolated titanium imido complexes

Compounds containing metal-nitrogen multiple bonds are common for the elements of groups 5 to 8.[4] In contrast, for the Group IV metals, only imidozirconocenes had been isolated and characterized prior to 1990.[1] The first reported examples of structurally characterized imido titanium complexes were provided by Roesky and Rothwell.[5] As illustrated in eq 1, Roesky demonstrated that treatment of N,N-bis(trimethylsilyl)diphenylthiophosphinamide with $TiCl_4$ in the presence of pyridine results in the formation of an imidotitanium complex. The Ti-N bond length (1.702(2) Å) and the Ti-N-P bond angle of 172.5(2)° indicate an almost linear imido ligand which acts as a four electron donor to the metal center. Rothwell reported three routes by which titanium imido species may be obtained. As shown in Scheme 1, treatment of an η^2-imine complex with azobenzene in the presence of 4-pyrrolidinopyridine (py') leads to the formation of an η^2-azobenzene complex. When the azobenzene species is heated to 100 °C, over the course of several days, a titanium phenylimido complex is formed along with free azobenzene. The Ti-N distance of 1.719(3) Å is very similar to the distance observed in $(py)_3Cl_2Ti{=}NP(S)Ph_2$. An alternative method for the preparation of Rothwell's titanium imido

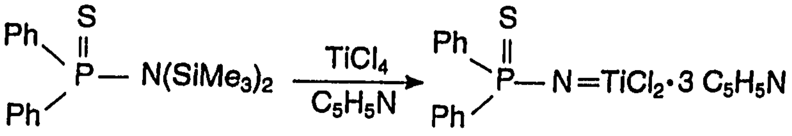
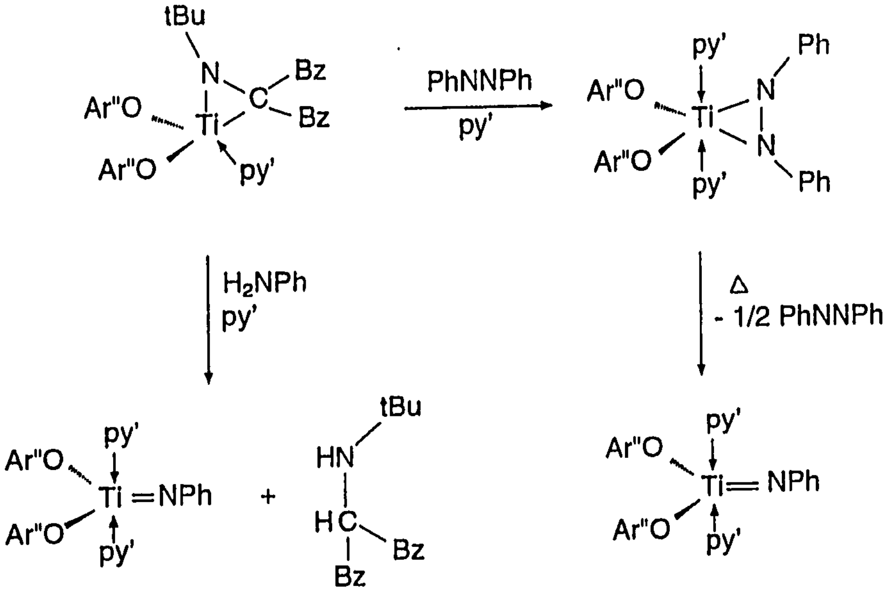


Figure 1. Roesky's preparation of a titanium imido complex.



Scheme 1. Synthetic routes for the preparation of titanium phenylimido complexes as reported by Rothwell.

complex involves the direct reaction of the η^2-imine complex with aniline in the presence of 4-pyrrolidinopyridine. An additional synthetic route involving treatment of a dialkyl titanium complex with two equivalents of aniline in benzene results in the formation of a bis(phenylamido) complex in high yield. Treatment of the bis(phenylamido) complex with 2 equivalents of 4-pyrrolidinopyridine (py') leads to the elimination of one equivalent of aniline and formation of the phenylimido complex.

Low-valent titanium complexes may also be used as precursors to titanium imido complexes. Gambarotta *et al.*, have reported a novel reaction in which treatment of (TMEDA)$TiCl_2$ with acetonitrile at -30 °C results in the formation of a dimetallic product

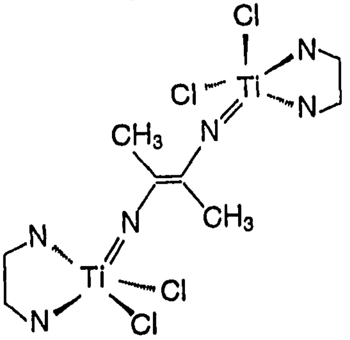


Figure 2. Gambarotta's titanium imido complex.

containing two Ti=N moeties (Figure 2).[6] An additional synthetic route involves treatment of (TMEDA)$TiCl_2$ with azobenzene in THF at -30 °C to form the corresponding (TMEDA)Ti(=NPh)Cl_2. The ease of this reaction is in sharp contrast to the hard pyrolitic conditions employed for the preparation of $(Ar''O)_2(py)_2Ti{=}NPh$.

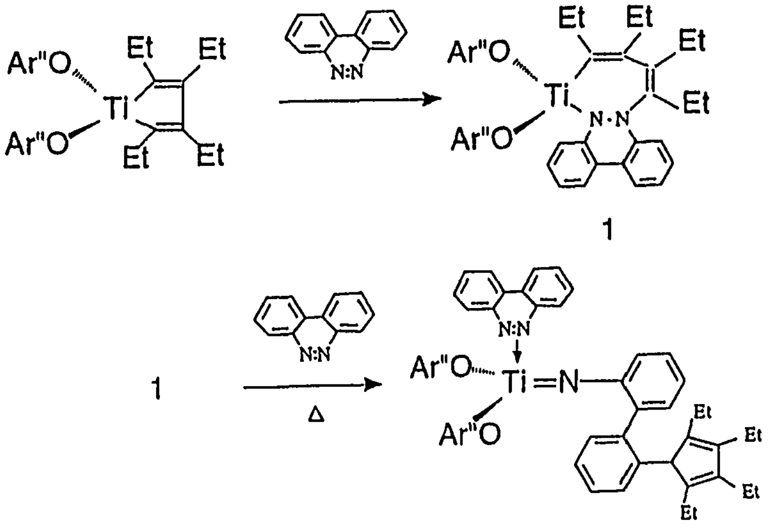


Figure 3. Formation of a titanium imido complex by cleavage of the N=N double bond of benzo[*c*]cinnoline.

Rothwell has also demonstrated that an imidotitanium complex may be prepared by cleavage of the N=N double bond in benzo[*c*]cinnoline results in the formation of a complex containing a 2,3-diazametallacyclohepta-4,6-diene ring (Figure 3). However, in the presence of an extra equivalent of benzo[*c*]cinnoline, the 7-membered metallacycle is converted at 100 °C to an aryl imidotitanium complex. The Ti=N distance of 1.708(5) Å is similar to those found in other structurally characterized imidotitanium complexes as described previously.

Mountford and coworkers have found a general route for the preparation of sandwich and half-sandwich titanium imido complexes.[7] Utilizing the 4-^{t}Bupy (4-^{t}Bupy = 4-*tert*-butylpyridine) titanium *tert*-butylimido complex, $[Ti(N^tBu)Cl_2(Bu^tPy)_2]$, **1**, several new titanium imido species have been obtained. For example, treatment of **1** with one equivalent of NaC_5H_5 or LiC_5Me_5 results in the formation of a monomeric half-sandwich Cp complex $[Ti(\eta^5\text{-}C_5R_5)(N^tBu)Cl(^tBupy)]$ (R = H, Me). Addition of two equivalents produced the bis (η^5-Cp) derivatives. Similarly, an η^5-trimethylindenyl π-complex may be formed from treatment of **1** with $Li(C_9H_4Me_3)$.

Titanium imido complexes containing chelating ligands were also prepared. A pyrazolylborate-imido complex was produced by a simple metathesis reaction between **1** and K(dmpbz).[8] The first example of a Group 4 macrocyclic imido derivative was also reported. This complex, $[Ti(Me_8taa)(N^tBu)]$, obtained from the reaction of **1** and $Li_2[Me_8taa]$[9], was structurally characterized by single crystal X-ray diffraction analysis. The Ti=N distance of 1.724(4) Å is quite long when compared to Ti=N linkages in general (typical range: 1.672(7) - 1.723(4) Å).

Group IV imido complexes and imine metathesis

While alkylidene complexes and their role in olefin metathesis have been studied immensely, the related chemistry of imine metathesis mediated by imido complexes has been the subject of few reports.[10] Bergman and coworkers have recently found that $Cp_2Zr(=N^tBu)(THF)$ undergoes a [2+2] cycloaddition reaction with one equivalent of benzaldehyde-N-phenylimine to produce the 2,4-diazametallacyclobutane, $Cp_2\overline{Zr(-N(Ph)CH(Ph)-N}{}^tBu$.[11] Addition of a second equivalent of imine produced $Cp_2\overline{Zr(-N(Ph)CH(Ph)-N}(Ph)$ and one equivalent of benzaldehyde-N-*tert*-butylimine. The initial reaction was found to proceed via an initial dissociative process that generates a three-coordinate transient imido complex intermediate, which may be trapped by an imine to the give the cyclic product.

Group IV and V imido complexes in organic synthesis

Novel reactions involving titanium imido complexes have led to new synthetic routes for the preparation of dihydropyrrole and tetrahydropyridine derivatives.[12] It was found that treatment of 5-phenylpent-4yn-1-ylamine with $CpTi(Me)_2Cl$ and $(i\text{-}Pr)_2NEt$ in THF at 25 °C led to the formation of the Δ^1-pyrroline in 74% yield. The reaction was found to proceed via the formation of the proposed titanacycle 3 (Figure 4) following loss of CH_4. Protonation of the metallacyclic complex results in the formation of the Δ^1-pyrroline. Direct trapping with isobutylnitrile followed by protonation gave the vinylogous amidine in 63% yield (7).

Group V imido complexes and C-H bond activation

Similar activation of C-H bonds has been observed utilizing vanadium imido

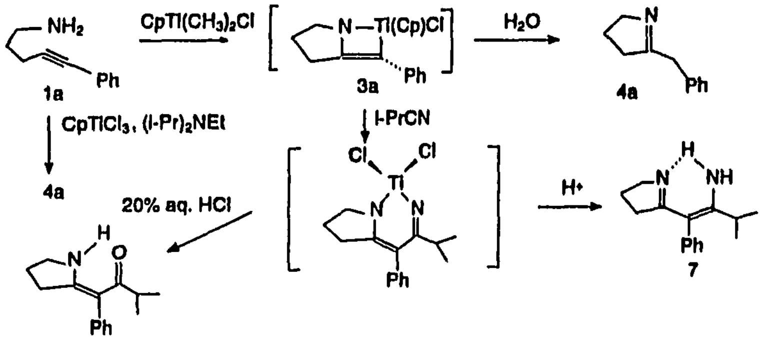


Figure 4. Preparation of dihydropyrrole an tetrahydropyridine derivatives.

complexes.[13] Horton and coworkers have studied the generation and chemistry of bisimido complexes of the formula [(RN=)$_2$V-NHR] (R = ^{t}Bu$_3$Si). Treatment of [(RN=)V(HNR)$_2$Cl] with LiR' (R' = Me, n-Bu, CH$_2$CMe$_3$, CH$_2$SiMe$_3$) gave the 4-coordinate vanadium amido imido species (RN=)V(NHR)$_2$(R'). These σ-bonded complexes readily activate C-H bonds. For example, treatment of the methyl derivative with benzene for 5 hours at 80 °C gave the phenyl species (RN=)V(NHR)$_2$(C_6H_5). A number of substrates cleanly afforded the activation products (n-C_6H_{14}, CH_4, etc.). The intermediate bisimido complex may trapped with Et$_2$O, THF, or pyridine. Using 1-alkenes as the substrates, trans-alkenyl complexes of the formula (RN=)V(HNR)$_2$(CH=CHR') (R' = ^{t}Bu, Me, Ph) are isolated. Formation of an enolatovanadium complex occurs upon treatment of (RN=)V(NHR)$_2$(R') (R' = Me) with acetone, reflecting the greater affinity of the electrophilic V^V center for oxygen rather than carbon atoms. It is evident that use of bulky ligands on the small vanadium(V) center to create a sterically and electronically unsaturated three coordinate intermediate leads to its remarkable C-H bond activation chemistry.

Horton and coworkers have reported an extension of the chemistry of these vanadium imido complexes involving their reactions with alkynes and ethene.[14] Themolysis of $(RN)_2V(HNR)(Et_2O)$ with either 2-butyne or 3-hexyne at 80 °C for 16 h in the inert cyclohexane afforded quantitative yields of a chelating ligand containing a unique η^3-azaallyl coordination to the metal center (Figure 5). ^1H NMR studies of the reaction using 2-butyne at 25 °C revealed an initial formation of a 2+2 cycloaddition product to afford the 2-azametallacyclobutene complex. This metallacycle was subsequently converted to the chelate species. In an attempt to prepare 2-azametalloacyclobutane complexes, the bisimido vanadium complex was treated with propene or ethene. Instead of isolating the metallacycle, alkenyl complexes of the formula $(RN{=})V(NHR)_2(\text{-}CH{=}CHR')(R' = H, Me)$ were isolated. Monitoring the reaction with ethene by ^1H NMR, the authors were able to view the rapid formation of a proposed metallacyclobutane complex. The metallacycle then slowly rearranges to give the alkenyl product.

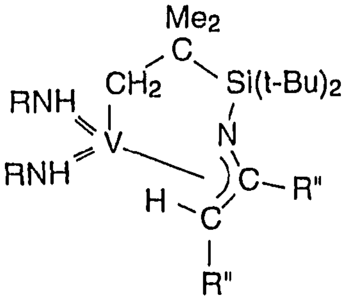


Figure 5. Vanadium complex formed upon reaction of $(RN)_2V(HNR)(Et_2O)$ with alkynes.

Metalloporphryin imido complexes

Despite the large number of metallopophryins containing M=O multiple bonds, the chemistry of the analogous imido complexes remains largely undeveloped. Cytochrome P-450[15] as well as Fe-[16] and Mn-porphyrins[17] catalyze the transfer of the oxygen atom of iodosylbenzene, hypochlorite, hydrogen peroxide, etc. to alkanes and alkenes. High-valent metal-oxo complexes, Fe^V=O[18] and Mn^V=O[17], are presumed to be the active intermediates in these reactions. Interest in metalloporphyrin complexes containing M=N multiple bonds as analogues to these high-valent oxo species began with studies involving the formation of porphyrin-iron-nitrene complexes, Fe^{IV}=N-NR_2[19], and a porphyrin-manganese-nitrene complex, Mn^V=N-$COCF_3$.[20] Mansuy *et al.*, have demonstrated that treatment of iron(II) porphyrins with 1-amino-2,2,6,6-tetramethlypiperidine in the presence of either dioxygen or one equivalent of iodosobenzene results in the formation of a pentacoordinate nitrene complex, (POR)Fe(=NNC_9H_{18}).[19,21] These complexes may also be formed by treatment of the iron(II) porphyrins with the free nitrene NNC_9H_{18} at -80 °C in CH_2Cl_2. Magnetic susceptibility measurements suggest a well-defined high spin ferrous ($S = 2$) state for these complexes.

Groves and Takahashi provided the first example of metal nitride activation to give aziridines in the presence of double bonds, formally, the aza analog of epoxidation.[20] Treatment of (TMP)Mn≡N with trifluoracetic acid in CH_2Cl_2 leads to the formation of a manganese(V) complex, (TMP)Mn(=N-C(O)CF_3)(O_2CCF_3). Addition of cycoloctene to solutions of (TMP)Mn(=N-C(O)CF_3)(O_2CCF_3) gave (TMP)Mn^{III}(TFA) and the (trifluoroacetyl)aziridine of cyclooctene in 82-94% yield. Mansuy, *et al.*, reported another example of metalloporphyrin catalyzed aziridation.[22] Treatment of either (TPP)FeCl or (TPP)MnCl with PhI=NTs[23] in the presence of an olefin[24] resulting in the generation of two major products, toluene-*p*-sulphonamide ($TsNH_2$) and the N-tosylaziridine derived from the addition of the N-Ts moiety to the double bond of the alkene. The amine is presumably formed due to reaction with advantitious water. The N-tosylaziridation reaction catalyzed by (TPP)FeCl is stereoselective in that it gives exclusively the more stable *trans*-N-tosyl-2,3-diphenylaziridine from either *cis*- or *trans*-stilbene. This is in contrast to the epoxidation reactions catalyzed by (TPP)FeCl using PhI=O in which the olefin stereochemistry for both *cis*- and *trans*-stilbene is retained in the product.[18]

Additional examples of NR transfer from PhI=NR have been reported by Breslow.[25] Catalytic amounts of (TPP)Fe(II) or (TPP)MnCl will catalyze the tolsylamination of cyclohexane. This reaction is analogous to the hydroxylations by iodosobenzene with metal porphyrin catalysts extensively studied as models for oxidations by the cytochrome P-450 class of enzymes.[26] (TPP)FeCl and (TPP)MnCl have also been found to catalyze intramolecular insertion of NR into a C-H bond.[26b] As shown in Figure 6, treatment of the (imidoiodo)benzene derivative with a catalytic amount of (TPP)FeCl resulted in insertion of the nitrene into the C-H bond of the isopropyl group in 85% yield.

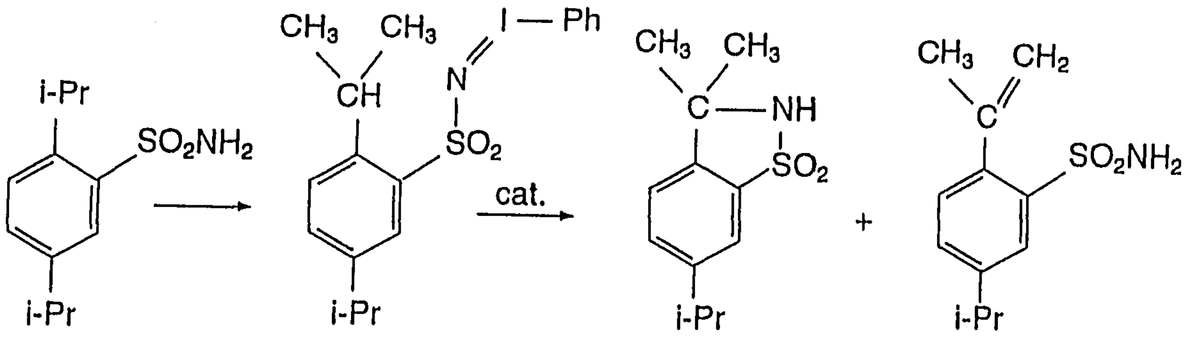


Figure 6. Intramolecular nitrene C-H insertion mediated by (TPP)FeCl

Mansuy has gone on to report that, upon aziridation of alkenes by PhI=NTs catalyzed by Fe(III) tetraarylporphyrins, the starting porphyrin is totally converted to an Fe(III) complex where the N-Ts nitrene moiety is inserted between the iron and a porphyrin nitrogen atom.[27]

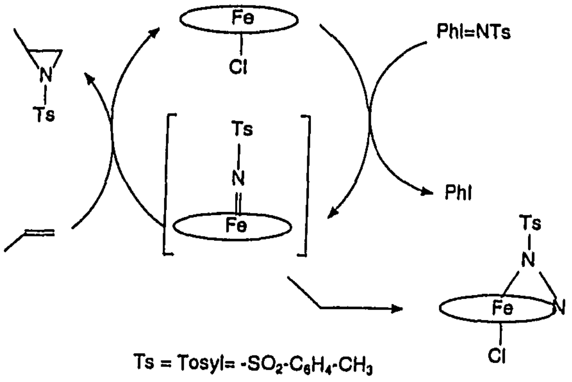


Figure 7. Formation of an iron(III) porphyrin complex with a nitrene group inserted into a Fe-N bond.

As shown in Figure 7, treatment of PhI=NTs with cytclooctene in the presence of (TPP)FeCl leads to the formation of the N-tosylaziridine of cyclooctene (17%) and tosyl-NH$_2$ (80%). When the reaction is run in the absence of alkene, a new porphyrin complex is formed in which the N-tosyl group has been inserted into (TPP)FeCl. (TPP)Fe(NTs)(Cl) (Figure 7) will not transfer its bridging NTs moiety to an alkene. However, in the presence of excess PhI=NTs, the corresponding aziridine is produced in 17% yield.

The first examples of early transition metal porphyrin imido complexes were reported by Buchler *et al.*[28] Treatment of (TTP)V=O with oxalyl chloride gave the reactive intermediate, (TTP)VCl$_2$. This dichloride complex may then undergo aminolysis when treated with a variety of primary amines, RNH$_2$, (R = ^{t}Bu, Ph, *p*-Tol, *p*-ClPh, *p*-Anis, *p*-Biph, *p*-^{t}BuPh) to give the imido complexes, (TTP)V=NR. These paramagnetic complexes were characterized by elemental analysis, mass spectrometry, and UV-vis and ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra, no resonances were observed for the organoimido ligands, presumably due to their proximity to the paramagnetic metal center. An unsuccessful attempt to prepare a titanium porphyrin imido complex was also reported.

West *et al.*, have reported the formation of a chromium imido complex.[29] In this case, the imido complex was prepared by treatment of a low-valent chromium porphyrin, (TPP)Cr(II), with *p*-tolyl azide. This high spin Cr(IV) imido complex was characterized by mass spectroscopy, elemental analysis, UV-vis, and magnetic susceptibility. The UV-visible spectrum of (TTP)Cr=NTolyl displayed a Soret band at 423 nm. Addition of THF or N-methylimidazole resulted in shifts in the position of the Soret band and the appearance of several new bands at higher wavelengths, indicating coordination of these donor molecules to the Cr atom of (TPP)Cr=NTolyl to give a six-coordinate complex. Treatment of (TPP)Cr=NTolyl with PPh_3 yielded the phosphine-imide, TolylN=PPh_3, and (TPP)Cr(II). Oxygen atom transfer from (TTP)Cr=O to PPh_3 is also known.[30]

The most recent work involving imido metalloporphyrin complexes has utilized the heavier elements of the iron triad. Che *et al.*, reported the first stable *t*-butylimido complexes of ruthenium(VI) and osmium(VI) porphyrins.[31] Treatment of (TPP)M(N_2)(THF) (M = Ru or Os) with an excess of *t*-butylamine at room temperature gave (TPP)M($NH_2{}^tBu$)$_2$. When a solution of (TPP)Os($NH_2{}^tBu$)$_2$ was stirred in the air for 24 h, three products were produced, (TPP)Os(=N-^{t}Bu)$_2$, (TPP)Os(=N-^{t}Bu)(O), and (TPP)Os(O)$_2$. (TPP)Ru(=N-^{t}Bu)(O) was prepared by bromine oxidation in the presence of excess amine. The bis(*t*-butylimido) ruthenium porphyrin was not isolated. These new imido complexes were characterized by ^1H NMR and IR spectroscopies. Limited reactivity studies reveal that (TPP)Ru(=N-^{t}Bu)(O) reacts rapidly with PPh_3 to give bis(triphenylphosphine)-ruthenium(II)porphyrin, $Ph_3P=O$, and $Ph_3P=N$-^{t}Bu within minutes at room temperature.

Utilizing a similar synthetic method, Che reported the synthesis of 4-fluorphenylimido osmium(VI) porphyrins.[32] Again starting with dinitrogen osmium(II) porphyrins, treatment with 4-fluoroaniline in THF resulted in the formation of (POR)Os(=N(*p*-C_6H_4F)(O).

Smeija *et al.* have recently reported the first structurally characterized metalloporphyrin imido complex, (TTP)Os(=N-C_6H_4-NO_2)$_2$.[33] This species was prepared by treatment of the osmium porphyrin dimer, $[Os(TTP)]_2$, with *p*-nitrophenylazide. The Os=N distances of 1.822(4) Å and 1.820(4) Å are longer than other structurally characterized osmium organoimido bonds.[34] The organoimido ligands are strongly bent with Os-N-C = 144.8(3)° and Os-N-C = 142.0(4)°. Combined with the long Os=N bond lengths, these small bond angles may indicate metal-organoimido bonds that have largely double bond character.

The following two chapters present our research involving the synthesis, characterization, and reactivity of early transition metal porphyrin imido complexes.

References

1. Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.
2. Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

3. Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

4. Mayer, J. M.; Nugent, W. A. *Metal-Ligand Multiple Bonds*; Wiley and Sons: New York, 1988.

5. Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 669.

6. (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 664. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

7. Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2007.

8. dmbpz = tris(3,5-dimethylpyrazolyl)borate

9. Me_8taa^{2-} = octamethyldibenzotetraza[14]annulene

10. (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Dragutan, V.; Balban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclic Olefins*; Wiley-Interscience: Chichester, 1985.

11. Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669.

12. McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459.

13. de With, J.; Horton, A. D. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 903.

14. de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493.

15. Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 68.

16. (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786. (c) Lindsay-Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans.* **1982**, *2*, 1009.

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

18. Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

19. Mahy, J. P.; Battioni, P.; Mansuy, D.; Fisher, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699.

20. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

21. POR = TPP, TTP, TpClPP

22. Mansuy, D.; Mahy, J. P.; Dureault, A.; Bedi, G.; Battioni P. *J. Chem. Soc., Chem Commun.* **1984**, 1161.

23. Ts = $-SO_2-C_6H_4-CH_3$

24. Olefins examined: styrene, *cis*-stilbene, *trans*-stilbene, 1,1-diphenylethylene.

25. (a) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. (b) Breslow, R.; Gellman, S.H. *J. Am. Chem. Soc.* **1983**, *105*, 6728.

26. (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (c) Chang, C. K.; Kuo, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3413. (d) Chang, C. K.; Ebina, F. *J. Chem. Soc., Chem. Commun.* **1981**, 778. (e) Smegal, J. A.; Schardt, B. C.; Hill, C.

L. *J. Am. Chem. Soc.* **1983**, *105*, 3510. (f) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515. (g) Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781.

27. Mahy, J. P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079.
28. Buchler, J. W.; Dreher, C.; Lay, K. L. *Z. Natuforsch., Teil B* **1982**, *37*, 1155.
29. Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191.
30. Groves, J. T.; Kruper, W. J.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.
31. Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1992**, 161.
32. Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K. *Inorg. Chim. Acta* **1991**, *190*, 161.
33. Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614.
34. (a) Danopoulus, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J.* Chem. Soc., Dalton Trans. **1991**, 1855. (b) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H. Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595.

CHAPTER 7: SYNTHESIS AND CHARACTERIZATION OF IMIDO TITANIUM(IV) PORPHYRIN COMPLEXES. X-RAY STRUCTURE OF PHENYLIMIDO(TETRATOLYLPORPHYRINATO)TITANIUM(IV).

A paper accepted by Inorganic Chemistry[1]

Lisa M. Berreau, Victor G. Young, Jr., and L. Keith Woo*[2]

Abstract

Treatment of dichloro(*meso*-tetra-*p*-tolylporphyrinato)titanium(IV), (TTP)TiCl$_2$, with LiNHR (R = -C$_6$H$_5$, -C$_6$H$_4$-*p*-CH$_3$, -C$_6$H$_{11}$) in toluene produces the imido complexes (TTP)Ti=N-C$_6$H$_5$, **1**, (TTP)Ti=N-C$_6$H$_4$-*p*-CH$_3$, **2**, and (TTP)Ti=N-C$_6$H$_{11}$, **3**. The structure of the phenylimido complex, **1**, has been determined by single-crystal X-ray diffraction analysis. Complex **1**, C$_{54}$H$_{41}$N$_5$Ti, crystallizes in the centrosymmetric space group $P\bar{1}$ with a = 13.338(4) Å, b = 13.740(2) Å, c = 13.861(3) Å, α = 91.86(2) °, β = 100.20(2) °, γ = 112.09(2) °, V = 2302.9(9) Å^3, Z = 2, R = 0.0552, R$_\omega$ = 0.1502. The Ti-N bond distance is 1.703(2) Å and the Ti-N-C$_{ipso}$ bond angle is 170.6(2)°.

---

[1] Reprinted with permission from *Inorganic Chemistry*, accepted for publication. Unpublished work copyright 1994 American Chemical Society.

Introduction

Group 4 metal complexes containing terminal imido ligands have received considerable attention over the past few years.[3,4,5,6,7,8] However, metalloporphyrin species containing imido ligands are quite rare and only a small number have been characterized.[9,10,11,12] Smieja *et al.* recently reported the first X-ray crystallographic study of an organoimido metalloporphyrin complex, $(TTP)Os(=NC_6H_4\text{-}p\text{-}NO_2)_2$.[13,14] We now wish to report a general method for the preparation of the first organoimido titanium porphyrin complexes from the reaction of $(TTP)TiCl_2$ with lithium amides.[15]

Results and discussion

As illustrated in eq 1, treatment of $(TTP)TiCl_2$ with LiNHR results in the formation of Ti(IV) organoimido complexes. In a typical reaction, 88 mg of $(TTP)TiCl_2$[15] (0.11 mmol)

$$(TTP)TiCl_2 + LiNHR \longrightarrow (TTP)Ti{=}NR \qquad (1)$$

$$\begin{array}{l} \mathbf{1},\ R = \text{-}C_6H_5 \\ \mathbf{2},\ R = \text{-}C_6H_4\text{-}p\text{-}CH_3 \\ \mathbf{3},\ R = \text{-}C_6H_{11} \end{array}$$

and 35 mg $LiNHC_6H_5$[16] (0.36 mmol) were stirred in toluene (15 mL) under N_2 at 22 °C. Within minutes after the addition of solvent to the solid starting materials, the green solution turned into the orange-red color of the phenylimido complex, **1**. After allowing the reaction mixture to stir for 4 hours, the solution was filtered, and the filtrate was concentrated to ca. 2 mL. Hexane (4 mL) was added and the solution was cooled to -20 °C for 1 h. Filtration yielded an orange-red solid (58 mg, 64%) after washing with hexane and drying in vacuo.[17] The tolyl and cyclohexyl analogs, **2** and **3**, can be prepared in a similar manner.[18]

The new porphyrin complexes were characterized by ^{1}H NMR, UV-vis, and IR spectroscopy. The ^{1}H NMR spectra confirm the expected diamagnetism of these d^0 Ti(IV) complexes. For the phenyl- and tolyl-imido complexes, the β-pyrrole resonance appears as a sharp singlet at 9.21 ppm. This signal is shifted downfield slightly for the cyclohexyl derivative, appearing as a singlet at 9.24 ppm. These chemical shifts are very similar to that observed for (TTP)Ti=O (9.24 ppm), suggesting that the oxo and imido ligands exhibit similar π-donating ability to the titanium atom. The porphyrin tolyl protons appear as two doublets, each integrating to four protons, and a multiplet, integrating to eight protons. The magnetic equivalence of the four tolyl groups is consistent with a time-averaged C_{4v} symmetry of the metalloporphyrin complexes. The protons associated with the axial imido ligand are shifted upfield relative to those of the corresponding free amine. This phenomenon is consistent with the position of the imido substituent above the porphyrin ring current.

The electronic absorption spectra of **1-3** are characteristic of porphyrin complexes with an intense Soret peak at 426 nm (R = $-C_6H_5$, $-C_6H_5$-*p*-CH_3) or 424 nm (R = $-C_6H_{11}$) and an additional Q-band at 548 nm. These absorption spectra are similar to those of other titanium porphyrins.[19] Addition of THF to a toluene solution of (TTP)Ti=N-C_6H_5 produces no change in position or intensity of the absorption maxima, indicating that THF does not appear to bind to the position trans to the imido group.

Infrared spectra of complexes **1-3** exhibit intense porphyrinato stretching modes in the region of 1500 cm^{-1} to 500 cm^{-1}.[17,18] These bands are similar to those observed in the spectrum of (TTP)Ti=O. Although the Ti=O stretch in (TTP)Ti=O is readily observed as an intense band at

983 cm^{-1},[19,20,21] unambiguous assignment of a metal nitrogen double bond stretch has not been possible. However, two additional bands are present in the spectrum of (TTP)Ti=N-C_6H_5 (753 cm^{-1} and 687 cm^{-1}) and may be assigned as the out-of-plane bending and puckering modes associated with the phenyl ring of the imido ligand.

Crystals of (TTP)Ti=N-C_6H_5, **1**, suitable for single-crystal X-ray diffraction were grown by layering a benzene solution of **1** with hexane. Complex **1** crystallized in the centrosymmetric space group $P\bar{1}$ with 2 molecules per unit cell.[22] The porphyrin framework of (TTP)Ti=N-C_6H_5 is saddle-shaped. The geometry about the Ti is square-pyramidal with the four pyrrole nitrogens forming the basal plane and the imido group at the apical site. The titanium atom is displaced from the mean plane of the pyrrole nitrogens towards the imido ligand by 0.52 Å. The Ti-N(5) distance is 1.703(2) Å. This value compares well with that reported for $(OAr')_2Ti=N-C_6H_4-C_6H_4NC_4Et_4$ (Ti-N: 1.708(5) Å, Ti-N-C: 170.4(4); OAr' = 2,6-diisopropylphenoxide),[6b] but is noticeably shorter than the distance reported for $(Ar'O)_2Ti=N-C_6H_5(py')_2$ (Ti-N: 1.719(3) Å, Ti-N-C: 173.1(3); py' = 4-pyrrolidinopyridine).[6b] The imido ligand is nearly linear with a Ti-N(5)-C(21) angle of 170.6(2). The slight deviation from 180° is possibly due to close intermolecular contacts with adjacent methyl groups. For example, C(107) of one molecule is 3.693 Å from C(24) of the imido phenyl of a neighboring molecule. Consequently, the nearly linear Ti-N-C angle is suggestive of substantial $Ti-N_{imido}$ triple bond character.

As illustrated in eq 2, the imido complexes are readily hydrolyzed to the corresponding free amine and (TTP)Ti=O.[23] Treatment of (TTP)Ti=N-C_6H_5 with PPh_3 in the presence of an alkyne results in no reaction (eq 3).[24] In contrast, chromium porphyrin organoimido complexes have been reported to yield the corresponding phosphineimine and Cr(II)(POR) when treated with

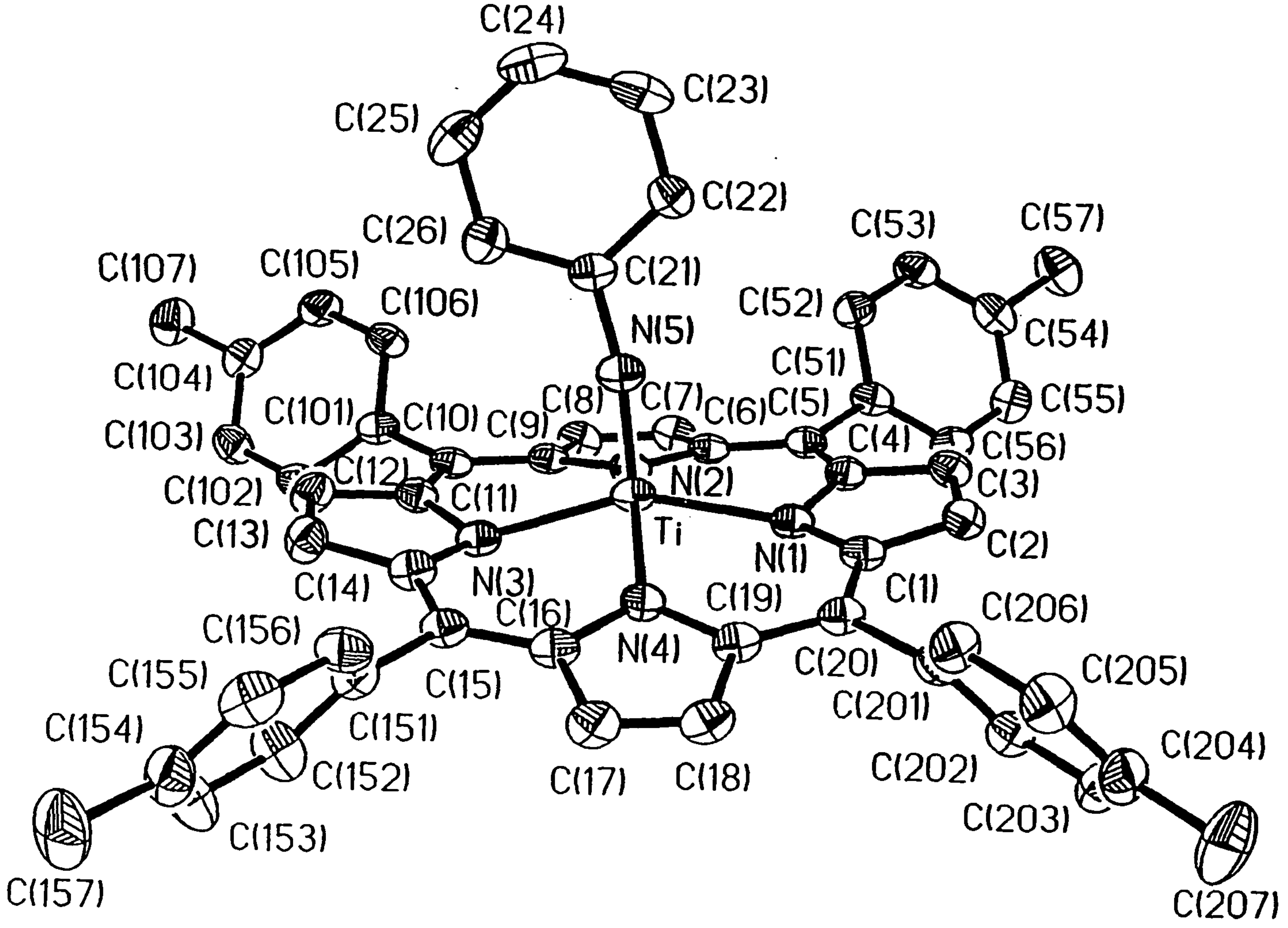


Figure 1. Molecular structure and atom-numbering scheme for (TTP)Ti=N-C$_6$H$_5$•C$_6$H$_6$ (1). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Ti-N$_5$, 1.703(2); Ti-N$_1$, 2.101(3); Ti-N$_2$, 2.100(2); Ti-N$_3$, 2.098(2); Ti-N$_4$, 2.104(2); N$_5$-C$_{21}$, 1.386(4). Selected bond angles (deg): Ti-N$_5$-C$_{21}$, 170.6(2); N$_1$-Ti-N$_4$, 86.29(9); N$_2$-Ti-N$_4$, 150.64(9); N$_2$-Ti-N$_3$, 86.45(9); N$_3$-Ti-N$_1$, 151.68(9); N$_2$-Ti-N$_1$, 86.35(9); N$_3$-Ti-N$_4$, 86.69(9).

$$(TTP)Ti{=}NPh + H_2O \longrightarrow (TTP)Ti{=}O + H_2NPh \qquad (2)$$

$$(TTP)Ti{=}NPh + PPh_3 + PhC{\equiv}CPh \longrightarrow \text{No reaction} \qquad (3)$$

$$(TTP)Ti{=}S + S_8 \longrightarrow (TTP)TiS_2 \qquad (4)$$

$$(TTP)Ti{=}NPh + S_8 \longrightarrow \text{No reaction} \qquad (5)$$

PPh_3.[9] Finally, it has been shown that treatment of terminal sulfido and selenido titanium porphyrin complexes with the elemental chalcogenide results in the formation of a perchalcogenido species (eq 4).[25] In an attempt to prepare a mixed (Ti-N-S) 3-membered metallacycle, (TTP)Ti=NPh was treated with elemental sulfur (eq 5). After stirring with mild heating for 12 h in toluene/THF, no reaction was detected by ^1H NMR.[26] Further studies involving the synthesis and reactivity of early transition metal porphyrinato organoimido complexes are underway.

References

1. Reprinted with permission from *Inorganic Chemistry*, accepted for publication. Unpublished work copyright 1994 American Chemical Society.
2. Presidential Young Investigator, 1990-1995; Camille and Henry Dreyfus Teacher-Scholar, 1993-1998.
3. Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

4. (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

5. Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 669.

6. (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 664. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

7. Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.

8. Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, *7*, 2007.

9. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

10. (a) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K. *Inorg. Chim. Acta.* **1991**, *190*, 161. (b) Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1992**, 161.

11. Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191.

12. Buchler, J. W.; Pfeifer, S. Z. *Naturforsch, B: Inorg. Chem., Org. Chem.* **1985**, *40B*, 1362.

13. Abbreviations: TTP = dianion of 5,10,15,20-tetra-(p-tolylporphyrin).

14. Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614.

15. (a) Berreau, L. M.; Hays, J. A.; Young, V. G., Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105.

(b) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

16. The lithium amide salts $LiNHC_6H_5$, $LiNHC_6H_4$-*p*-CH_3, and $LiNHC_6H_{11}$ were prepared by adding equimolar n-butyllithium to a diethylether solution of the appropriate amine at -78 °C. The reaction mixture was then allowed to warm to room temperature and stir for 2-4 hours. The solvent was then removed in vacuo. The lithium salt was triturated with hexane and collected by filtration. A near quantitative yield was obtained after washing the lithium amide with hexane and drying the product in vacuo.

17. Analytical Data for (TTP)Ti=N-C_6H_5. ^1H NMR (C_6D_6, 300 MHz, ppm): 9.21 (s, 8H, β-H), 8.14 (d, 4H, -$C_6H_4CH_3$), 8.03 (d, 4H, -$C_6H_4CH_3$), 7.30 (d, 8H, -$C_6H_4CH_3$), 5.72 (m, 3H, *m-,p-H*), 3.85 (d, 2H, *o-H*), 2.41 (s, 12H, -$C_6H_4CH_3$). UV-vis (toluene): 426 (Soret), 548. MS(EI) calcd (found) (m/e): 806 (807), $[M]^+$. IR (KBr, cm^{-1}): Bands associated with porphyrin ligand: 1473, 1327, 1201, 1181, 1109, 1071, 1007, 889, 846, 802, 727, 516. Bands associated with =N-C_6H_5 (cm^{-1}): 753, 687.

18. Analytical Data. (TTP)Ti=N-C_6H_4-*p*-CH_3: ^1H NMR (C_6D_6, 300 MHz, ppm): 9.21 (s, 8H, β-*H*), 8.15 (d, 4H, -$C_6H_4CH_3$), 8.04 (d, 4H, -$C_6H_4CH_3$), 7.30 (d, 8H, -$C_6H_4CH_3$), 5.53 (d, 2H, *m-H*), 3.81 (d, 2H, *o-H*), 2.41 (s, 12H, -$C_6H_4CH_3$), 1.29 (s, 3H, -CH_3). UV-vis (toluene): 426 (Soret), 548. IR (KBr, cm^{-1}): Bands associated with porphyrin ligand: 1491, 1333, 1324, 1202, 1181, 1109, 1070, 1006, 847, 798. 724, 525. MS(EI) calcd (found) (m/e): 821 (821), $[M]^+$. Anal. calcd. (found) for $C_{55}H_{43}N_5Ti$: C, 80.36 (80.29); H, 5.28 (5.47); N, 8.52 (8.20). (TTP)Ti=N-C_6H_{11}: ^1H NMR (C_6D_6, 300 MHz, ppm): 9.24 (s, 8H, β-*H*), 8.31 (d, 4H, -$C_6H_4CH_3$), 8.05 (d, 4H, -$C_6H_4CH_3$), 7.34 (d,

8H, $-C_6H_4CH_3$), 2.42 (s, 12H, $-C_6H_4CH_3$), 0.31 (br, 1H, -Cy), 0.19 (br, 1H, -Cy), -0.25 (br, 2H, -Cy), -0.42 (br, 1H, -Cy), -0.65 (br, 2H, -Cy), -0.97 (br, 2H, -Cy), -1.59 (br, 2H, -Cy). UV-vis (toluene): 424 (Soret), 548. IR (KBr, cm^{-1}): Major bands associated with porphyrin ligand: 1445, 1335, 1202, 1181, 1107, 1070, 1006, 886, 846, 798, 723, 524. MS(EI) calcd (found) (m/e): 813 (813), $[M]^+$.

19. Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87.

20. (TTP)Ti=O: IR (KBr, cm^{-1}): Major bands associated with porphyrin ligand: 1488, 1335, 1203, 1182, 1109, 1071, 1008, 847, 800, 727, 522. Ti=O (cm^{-1}): 983.

21. (a) Richard, P.; Poncet, J. L.; Barbe, J. M.; Guilard, R.; Goulon, J.; Rinaldi, D.; Cartier, A.; Tola, J. *J. Chem. Soc. Dalton Trans.* **1982**, 1451. (b) Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782.

22. (TTP)Ti=N-C_6H_5 crystallizes in the centrosymmetric space group $P\bar{1}$ with a = 13.338(4) Å, b = 13.740(2) Å, c = 13.861(3) Å, α = 91.86(2)°, β = 100.20(2)°, γ = 112.09(2)°, V = 2302.9(9) $Å^3$, Z = 2, R = 0.0552 and R_w = 0.1502. The calculated density ($C_{54}H_{41}N_5Ti$, M = 807) per unit cell is 1.278 g/cm^3. Data were collected at -60 °C on a Siemens P4RA diffractometer with Cu Kα radiation using an ω scan technique over the range $3.26 < 2\theta < 56.74°$. Unique reflections (5334) with $I > 2\sigma(I)$ were used after correction for absorption. All non-hydrogen atoms except for those in the solvent were refined with anisotropically.

23. An NMR tube containing a C_6D_6-solution of (TTP)Ti=N-C_6H_5 and sealed under N_2 with a rubber septum was injected with 1 µL of degassed water. The ^1H NMR spectrum clearly showed the complete conversion of the imido complex to

(TTP)Ti=O and the free amine. Signals for (TTP)Ti=O (C_6D_6, 300 MHz, ppm): 9.24 (s, 8H, β-*H*), 7.99 (d, 8H, $-C_6H_4CH_3$), 7.28 (d, 8H, $-C_6H_4CH_3$), 2.42 (s, 12H, -$C_6H_4CH_3$). Signals for $C_6H_5NH_2$: 7.05 (t, $-C_6H_5NH_2$), 6.7 (t, 1H, $-C_6H_5NH_2$), 6.3 (d, 2H, $-C_6H_5NH_2$), 5.4 (br, 2H, $C_6H_5NH_2$).

24. An NMR tube containing a C_6D_6-solution of (TTP)Ti=N-C_6H_5 (1.6 mg, 1.98 x 10^{-3} mmol), PPh_3 (3.7 mg, 1.41 x 10^{-2} mmol), and PhC≡CPh (7.0 mg, 3.93 x 10^{-2} mmol) and sealed under nitrogen was monitored at ambient temperature over a 15 day period. ^1H NMR spectra indicated that no reaction occurred.

25. Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186.

26. (TTP)Ti=N-C_6H_5 (7.0 mg, 8.66 x 10^{-3} mmol) was treated with S_8 (2.4 mg, 9.38 x 10^{-3} mmol) in a solution of 10 mL toluene and 5 drops THF for 12 h with mild heating under a N_2 atmosphere. After the heat was removed and the reaction mixture had cooled to room temperature, the solvent was removed in vacuo. A ^1H NMR in C_6D_6 of the reaction mixture indicated that no reaction had taken place.

APPENDIX A

Table I. Structure determination summary

<u>Crystal Data</u>	
Empirical Formula	$C_{60}H_{47}N_5Ti$
Color, Habit	Purple, triclinic
Crystal Size (mm)	0.38 x 0.35 x 0.30
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	a = 13.338(4) Å
	b = 13.740(2) Å
	c = 13.861(3) Å
	α = 91.86(2)°
	β = 100.20(2)°
	γ = 112.09(2)°
Volume	2302.9(9) $Å^3$
Z	2
Formula Weight	885.93
Density(calc.)	1.278 Mg/m^3
Absorption Coefficient	1.927 mm^{-1}
F(000)	928

Table I. (continued)

Data Collection	
Diffractometer Used	Siemens P4RA
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	213(1)
Monochromator	Graphite
θ Range	3.26 to 56.74°
Scan Type	$\omega - 2\theta$
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$ $0 \leq l \leq 15$
Reflections Collected	6447
Independent Reflections	6140 (R_{int} = 0.0272)
Observed Reflections	5334 ($I \geq 2\sigma(I)$)
Min./Max. Transmission	0.933 / 0.674
Absorption Correction	Semi-empirical
Solution and Refinement	
System Used	SHELXL-93 (Sheldrick, 1993)
Solution	Direct methods
Refinement Method	Full-matrix least-squares on F^2
Extinction Correction	0.0014(3)

Table I. (continued)

Extinction Expression	$Fc^{*} = kFc[1 + 0.001 \text{ x } Fc^{2}l^{3}/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Riding
Weighting Scheme	$w = 1/[\sigma^{2}(Fo^{2}) + (0.0992P)^{2} + 0.9343P]$
	where $P = (Fo^{2} + 2Fc^{2})/3$
Parameters Refined	619
Final R Indices $[I \geq 2\sigma(I)]$	R1 = 0.0503, wR2 = 0.1467
R Indices (all data)	R1 = 0.0552, wR2 = 0.1502
GooF, Observed and All Data	1.175, 1.113
Largest and Mean Δ/σ	-0.030, 0.000
Largest Difference Peak	$0.871 e/Å^{-3}$
Largest Difference Hole	$-0.520 e/Å^{-3}$

Table II. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 1

Atom	x	y	z	U_{eq}
Ti	-522(1)	7699(1)	275(1)	23(1)
N(1)	897(2)	8581(2)	1346(2)	24(1)
N(2)	-1054(2)	8929(2)	503(2)	24(1)
N(3)	-1482(2)	7417(2)	-1156(2)	25(1)
N(4)	492(2)	7089(2)	-324(2)	24(1)
N(5)	-1353(2)	6722(2)	839(2)	28(1)
C(1)	1792(2)	8308(2)	1631(2)	25(1)
C(2)	2329(2)	8762(2)	2619(2)	28(1)
C(3)	1774(2)	9314(2)	2932(2)	28(1)
C(4)	897(2)	9232(2)	2129(2)	24(1)
C(5)	189(2)	9776(2)	2107(2)	24(1)
C(51)	319(2)	10468(2)	3013(2)	26(1)
C(52)	-560(2)	10299(2)	3490(2)	30(1)
C(53)	-425(3)	10883(2)	4364(2)	34(1)
C(54)	585(3)	11663(2)	4804(2)	34(1)
C(55)	1455(3)	11857(2)	4320(2)	33(1)
C(56)	1325(2)	11275(2)	3438(2)	31(1)
C(57)	742(3)	12286(3)	5778(2)	46(1)

Table II. (continued)

Atom	x	y	z	U_{eq}
C(6)	-654(2)	9689(2)	1306(2)	24(1)
C(7)	-1261(2)	10361(2)	1199(2)	28(1)
C(8)	-2047(2)	9981(2)	368(2)	28(1)
C(9)	-1948(2)	9065(2)	-66(2)	25(1)
C(10)	-2661(2)	8391(2)	-896(2)	24(1)
C(101)	-3726(2)	8502(2)	-1264(2)	26(1)
C(102)	-4082(2)	8599(2)	-2251(2)	30(1)
C(103)	-5101(3)	8631(2)	-2586(2)	32(1)
C(104)	-5822(2)	8582(2)	-1958(2)	31(1)
C(105)	-5457(2)	8516(2)	-967(2)	33(1)
C(106)	-4441(2)	8467(2)	-632(2)	30(1)
C(107)	-6950(3)	8578(3)	-2330(3)	44(1)
C(11)	-2462(2)	7581(2)	-1376(2)	26(1)
C(12)	-3203(2)	6823(2)	-2172(2)	31(1)
C(13)	-2677(2)	6231(2)	-2461(2)	33(1)
C(14)	-1599(2)	6598(2)	-1832(2)	28(1)
C(15)	-783(2)	6204(2)	-1900(2)	27(1)
C(151)	-979(2)	5442(2)	-2777(2)	29(1)
C(152)	-1151(3)	5727(3)	-3726(2)	42(1)

Table II. (continued)

Atom	x	y	z	U_{eq}
C(153)	-1336(3)	5028(3)	-4539(3)	49(1)
C(154)	-1367(3)	4023(3)	-4450(3)	41(1)
C(155)	-1177(3)	3746(2)	-3507(3)	40(1)
C(156)	-984(3)	4440(2)	-2676(2)	34(1)
C(157)	-1606(4)	3261(3)	-5346(3)	63(1)
C(16)	213(2)	6490(2)	-1221(2)	26(1)
C(17)	1111(3)	6204(2)	-1354(2)	34(1)
C(18)	1918(3)	6608(2)	-546(2)	32(1)
C(19)	1536(2)	7161(2)	113(2)	26(1)
C(20)	2132(2)	7684(2)	1042(2)	26(1)
C(201)	3226(2)	7616(2)	1410(2)	28(1)
C(202)	4187(2)	8528(2)	1620(2)	30(1)
C(203)	5207(3)	8474(3)	1902(2)	37(1)
C(204)	5319(3)	7514(3)	1983(2)	38(1)
C(205)	4356(3)	6607(3)	1787(2)	38(1)
C(206)	3330(3)	6654(2)	1508(2)	32(1)
C(207)	6438(3)	7462(3)	2255(4)	66(1)
C(21)	-2171(2)	5927(2)	1176(2)	24(1)
C(22)	-1995(3)	5668(2)	2139(2)	29(1)

Table II. (continued)

Atom	x	y	z	U_{eq}
C(23)	-2809(3)	4854(3)	2451(3)	41(1)
C(24)	-3805(3)	4287(3)	1818(3)	46(1)
C(25)	-3996(3)	4551(3)	883(3)	43(1)
C(26)	-3197(2)	5357(2)	550(2)	33(1)
C(30)	5000	5000	5000	50
C(31)	5541(6)	4406(7)	4702(7)	240(9)
C(32)	5490(6)	5238(8)	4200(4)	227(7)
C(33)	4948(8)	5831(5)	4500(7)	242(7)
C(41A)	5359(16)	12045(10)	5467(17)	144(9)
C(42A)	5851(11)	11347(13)	5270(17)	114(7)
C(43A)	5224(12)	10262(12)	5110(15)	82(4)
C(44A)	4105(12)	9875(11)	5147(17)	106(6)
C(45A)	3613(12)	10574(16)	5345(17)	160(10)
C(46A)	4240(16)	11659(14)	5505(14)	109(6)
C(41B)	5622(20)	11294(11)	5400(17)	144(9)
C(42B)	6130(15)	10662(14)	5071(17)	114(7)
C(43B)	5513(16)	9592(13)	4761(15)	82(4)
C(44B)	4389(16)	9155(12)	4779(17)	106(6)
C(45B)	3882(15)	9787(17)	5107(18)	160(10)

Table II. (continued)

Atom	x	y	z	U_{eq}
C(46B)	4498(20)	10857(16)	5418(17)	109(6)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond lengths (Å)

Ti-N(5)	1.703(2)	C(5)-C(51)	1.494(4)
Ti-N(3)	2.098(2)	C(51)-C(56)	1.391(4)
Ti-N(2)	2.100(2)	C(51)-C(52)	1.396(4)
Ti-N(1)	2.101(3)	C(52)-C(53)	1.376(4)
Ti-N(4)	2.104(2)	C(53)-C(54)	1.385(5)
N(1)-C(1)	1.379(4)	C(54)-C(55)	1.386(4)
N(1)-C(4)	1.384(4)	C(54)-C(57)	1.513(4)
N(2)-C(6)	1.383(4)	C(55)-C(56)	1.387(4)
N(2)-C(9)	1.386(4)	C(6)-C(7)	1.434(4)
N(3)-C(14)	1.384(4)	C(7)-C(8)	1.349(4)
N(3)-C(11)	1.392(4)	C(8)-C(9)	1.438(4)
N(4)-C(16)	1.378(4)	C(9)-C(10)	1.402(4)
N(4)-C(19)	1.382(4)	C(10)-C(11)	1.410(4)
N(5)-C(21)	1.386(4)	C(10)-C(101)	1.488(4)
C(1)-C(20)	1.409(4)	C(101)-C(102)	1.394(4)
C(1)-C(2)	1.429(4)	C(101)-C(106)	1.394(4)
C(2)-C(3)	1.352(4)	C(102)-C(103)	1.375(4)
C(3)-C(4)	1.432(4)	C(103)-C(104)	1.391(4)
C(4)-C(5)	1.405(4)	C(104)-C(105)	1.392(5)
C(5)-C(6)	1.399(4)	C(104)-C(107)	1.500(4)

Table III. (continued)

C(105)-C(106)	1.380(4)	C(201)-C(202)	1.391(4)
C(11)-C(12)	1.430(4)	C(202)-C(203)	1.378(4)
C(12)-C(13)	1.351(4)	C(203)-C(204)	1.388(5)
C(13)-C(14)	1.436(4)	C(204)-C(205)	1.388(5)
C(14)-C(15)	1.400(4)	C(204)-C(207)	1.502(5)
C(15)-C(16)	1.395(4)	C(205)-C(206)	1.380(4)
C(15)-C(151)	1.497(4)	C(21)-C(22)	1.394(4)
C(151)-C(156)	1.386(4)	C(21)-C(26)	1.403(4)
C(151)-C(152)	1.389(5)	C(22)-C(23)	1.379(5)
C(152)-C(153)	1.381(5)	C(23)-C(24)	1.380(5)
C(153)-C(154)	1.377(5)	C(24)-C(25)	1.364(5)
C(154)-C(155)	1.379(5)	C(25)-C(26)	1.377(5)
C(154)-C(157)	1.505(5)	C(30)-C(32)	1.37
C(155)-C(156)	1.393(4)	C(30)-C(33)#1	1.37
C(16)-C(17)	1.432(4)	C(30)-C(33)	1.37
C(17)-C(18)	1.344(5)	C(30)-C(31)#1	1.37
C(18)-C(19)	1.442(4)	C(30)-C(31)	1.37
C(19)-C(20)	1.397(4)	C(31)-C(33)#1	1.37(2)
C(20)-C(201)	1.496(4)	C(31)-C(32)	1.37
C(201)-C(206)	1.389(4)	C(32)-C(33)	1.37

Table III. (continued)

C(33)-C(31)#1	1.37(2)	C(43B)-C(41B)#2	1.52(3)
C(41A)-C(46A)	1.39	C(43B)-C(44B)#2	1.77(3)
C(41A)-C(42A)	1.40	C(44B)-C(41B)#2	0.65(2)
C(42A)-C(43A)	1.40	C(44B)-C(42B)#2	0.87(4)
C(42A)-C(44A)#2	1.78(4)	C(44B)-C(45B)	1.40
C(43A)-C(43A)#2	0.75(3)	C(44B)-C(46B)#2	1.56(4)
C(43A)-C(44A)#2	1.10(3)	C(44B)-C(43B)#2	1.77(3)
C(43A)-C(44A)	1.39	C(43B)-C(44B)	1.39
C(45B)-C(42B)#2	0.65(4)	C(45B)-C(43B)#2	0.91(4)
C(44A)-C(43A)#2	1.10(3)	C(45B)-C(46B)	1.40
C(44A)-C(45A)	1.40	C(45B)-C(41B)#2	1.99(3)
C(44A)-C(42A)#2	1.78(3)	C(46B)-C(43B)#2	0.65(3)
C(45A)-C(46A)	1.40	C(46B)-C(44B)#2	1.56(4)
C(41B)-C(44B)#2	0.65(3)	C(46B)-C(42B)#2	1.98(4)
C(41B)-C(42B)	1.39	C(41B)-C(46B)	1.40
C(41B)-C(43B)#2	1.52(4)	C(41B)-C(45B)#2	1.99(4)
C(42B)-C(45B)#2	0.65(4)	C(42B)-C(44B)#2	0.87(4)
C(42B)-C(43B)	1.40	C(42B)-C(46B)#2	1.98(4)
C(43B)-C(46B)#2	0.65(3)	C(43B)-C(45B)#2	0.91(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1;
#2 -x+1,-y+2,-z+1.

Table IV. Bond angles (°)

N(5)-Ti-N(3)	101.39(11)	N(1)-C(1)-C(20)	125.6(3)
N(5)-Ti-N(2)	102.20(10)	N(1)-C(1)-C(2)	109.3(2)
N(3)-Ti-N(2)	86.45(9)	C(20)-C(1)-C(2)	125.1(3)
N(5)-Ti-N(1)	106.90(11)	C(3)-C(2)-C(1)	107.8(3)
N(3)-Ti-N(1)	151.68(9)	C(2)-C(3)-C(4)	107.2(3)
N(2)-Ti-N(1)	86.35(9)	N(1)-C(4)-C(5)	124.7(3)
N(5)-Ti-N(4)	107.13(10)	N(1)-C(4)-C(3)	109.3(2)
N(3)-Ti-N(4)	86.69(9)	C(5)-C(4)-C(3)	125.8(3)
N(2)-Ti-N(4)	150.64(9)	C(6)-C(5)-C(4)	124.6(3)
N(1)-Ti-N(4)	86.29(9)	C(6)-C(5)-C(51)	117.6(2)
C(1)-N(1)-C(4)	106.3(2)	C(4)-C(5)-C(51)	117.8(3)
C(1)-N(1)-Ti	125.2(2)	C(56)-C(51)-C(52)	117.3(3)
C(4)-N(1)-Ti	123.6(2)	C(56)-C(51)-C(5)	121.8(3)
C(6)-N(2)-C(9)	107.0(2)	C(52)-C(51)-C(5)	120.9(3)
C(6)-N(2)-Ti	126.2(2)	C(53)-C(52)-C(51)	121.2(3)
C(9)-N(2)-Ti	126.5(2)	C(52)-C(53)-C(54)	121.5(3)
C(14)-N(3)-C(11)	106.1(2)	C(53)-C(54)-C(55)	117.6(3)
C(14)-N(3)-Ti	122.9(2)	C(53)-C(54)-C(57)	121.5(3)
C(11)-N(3)-Ti	123.0(2)	C(55)-C(54)-C(57)	120.8(3)
C(16)-N(4)-C(19)	106.5(2)	C(54)-C(55)-C(56)	121.2(3)

Table IV. (continued)

C(16)-N(4)-Ti	126.1(2)	C(55)-C(56)-C(51)	121.1(3)
C(19)-N(4)-Ti	127.4(2)	N(2)-C(6)-C(5)	125.6(2)
C(21)-N(5)-Ti	170.6(2)	N(2)-C(6)-C(7)	109.0(2)
C(5)-C(6)-C(7)	125.4(3)	N(3)-C(11)-C(10)	124.5(3)
C(8)-C(7)-C(6)	107.5(3)	N(3)-C(11)-C(12)	109.2(2)
C(7)-C(8)-C(9)	108.0(3)	C(10)-C(11)-C(12)	126.3(3)
N(2)-C(9)-C(10)	125.4(2)	C(13)-C(12)-C(11)	107.9(3)
N(2)-C(9)-C(8)	108.4(2)	C(12)-C(13)-C(14)	107.4(3)
C(10)-C(9)-C(8)	126.1(3)	N(3)-C(14)-C(15)	125.1(3)
C(9)-C(10)-C(11)	124.4(3)	N(3)-C(14)-C(13)	109.4(2)
C(9)-C(10)-C(101)	117.7(2)	C(105)-C(106)-C(101)	121.7(3)
C(15)-C(14)-C(13)	125.5(3)	C(16)-C(15)-C(14)	124.8(3)
C(11)-C(10)-C(101)	117.8(3)	C(16)-C(15)-C(151)	117.5(2)
C(102)-C(101)-C(106)	116.8(3)	C(14)-C(15)-C(151)	117.8(3)
C(102)-C(101)-C(10)	122.4(2)	C(156)-C(151)-C(152)	117.7(3)
C(106)-C(101)-C(10)	120.7(3)	C(156)-C(151)-C(15)	121.7(3)
C(103)-C(102)-C(101)	121.4(3)	C(152)-C(151)-C(15)	120.5(3)
C(102)-C(103)-C(104)	121.9(3)	C(106)-C(105)-C(104)	121.2(3)
C(153)-C(152)-C(151)	121.0(3)	C(154)-C(153)-C(152)	121.9(3)
C(103)-C(104)-C(105)	117.0(3)	C(153)-C(154)-C(155)	117.1(3)

Table IV. (continued)

C(103)-C(104)-C(107)	121.8(3)	C(153)-C(154)-C(157)	121.1(3)
C(105)-C(104)-C(107)	121.2(3)	C(155)-C(154)-C(157)	121.8(3)
C(154)-C(155)-C(156)	121.9(3)	C(205)-C(204)-C(207)	121.6(3)
C(151)-C(156)-C(155)	120.3(3)	C(206)-C(205)-C(204)	121.6(3)
N(4)-C(16)-C(15)	125.8(2)	C(205)-C(206)-C(201)	121.0(3)
N(4)-C(16)-C(17)	109.3(3)	N(5)-C(21)-C(22)	121.1(3)
C(15)-C(16)-C(17)	124.8(3)	N(5)-C(21)-C(26)	120.4(3)
C(18)-C(17)-C(16)	107.8(3)	C(22)-C(21)-C(26)	118.4(3)
C(17)-C(18)-C(19)	107.4(3)	C(23)-C(22)-C(21)	120.2(3)
N(4)-C(19)-C(20)	125.8(3)	C(22)-C(23)-C(24)	120.6(3)
N(4)-C(19)-C(18)	109.0(3)	C(25)-C(24)-C(23)	119.7(3)
C(20)-C(19)-C(18)	125.2(3)	C(24)-C(25)-C(26)	120.9(3)
C(19)-C(20)-C(1)	124.3(3)	C(25)-C(26)-C(21)	120.1(3)
C(19)-C(20)-C(201)	117.6(2)	C(32)-C(30)-C(33)#1	119.9(9)
C(1)-C(20)-C(201)	118.0(3)	C(32)-C(30)-C(33)	60.1
C(206)-C(201)-C(202)	117.7(3)	C(33)#1-C(30)-C(33)	180.0(14)
C(206)-C(201)-C(20)	122.0(3)	C(32)-C(30)-C(31)#1	119.9(9)
C(202)-C(201)-C(20)	120.3(3)	C(33)#1-C(30)-C(31)#1	120.2
C(203)-C(202)-C(201)	120.9(3)	C(33)-C(30)-C(31)#1	59.8(9)
C(202)-C(203)-C(204)	121.7(3)	C(32)-C(30)-C(31)	60.1

Table IV. (continued)

C(203)-C(204)-C(205)	117.1(3)	C(33)#1-C(30)-C(31)	59.8(9)
C(203)-C(204)-C(207)	121.2(3)	C(33)-C(30)-C(31)	120.2
C(31)#1-C(30)-C(31)	180.0(11)	C(43A)#2-C(44A)-C(43A)	32.0(2)
C(33)#1-C(31)-C(30)	60.1(5)	C(43A)#2-C(44A)-C(45A)	149.0(2)
C(33)#1-C(31)-C(32)	120.0(5)	C(43A)-C(44A)-C(45A)	120.0
C(30)-C(31)-C(32)	60.0	C(43A)#2-C(44A)-C(42A)2	51.4(13)
C(30)-C(32)-C(31)	60.0	C(43A)-C(44A)-C(42A)#2	83.0(2)
C(30)-C(32)-C(33)	60.0	C(45A)-C(44A)-C(42A)#2	156.0(2)
C(31)-C(32)-C(33)	119.9	C(46A)-C(45A)-C(44A)	120.0
C(31)#1-C(33)-C(30)	60.1(5)	C(41A)-C(46A)-C(45A)	120.0
C(31)#1-C(33)-C(32)	120.0(5)	C(44B)#2-C(41B)-C(42B)	28.0(4)
C(30)-C(33)-C(32)	60.0	C(44B)#2-C(41B)-C(46B)	92.0(4)
C(46A)-C(41A)-C(42A)	120.0	C(42B)-C(41B)-C(46B)	120.0
C(43A)-C(42A)-C(41A)	120.0	C(44B)#2-C(41B)-C(43B)#2	67.0(3)
C(43A)-C(42A)-C(44A)#2	37.9(12)	C(42B)-C(41B)-C(43B)#2	94.6(10)
C(41A)-C(42A)-C(44A)#2	156.4(13)	C(46B)-C(41B)-C(43B)#2	25.4(10)
C(43A)#2-C(43A)-C(44A)2	96.0(3)	C(44B)#2-C(41B)-C(45B)#2	19.0(3)
C(43A)#2-C(43A)-C(44A)	51.0(2)	C(42B)-C(41B)-C(45B)#2	8.8(11)
C(44A)#2-C(43A)-C(44A)	148.0(2)	C(46B)-C(41B)-C(45B)#2	111.2(11)
C(43A)#2-C(43A)-C(42A)	161.0(4)	C(43B)#2-C(41B)-C(45B)#2	85.8(12)

Table IV. (continued)

C(44A)#2-C(43A)-C(42A)	91.0(2)
C(44A)-C(43A)-C(42A)	120.0
C(44B)#2-C(42B)-C(41B)	20.0(2)
C(45B)#2-C(42B)-C(43B)	32.0(3)
C(42B)-C(43B)-C(44B)#2	29.2(13)
C(44B)#2-C(42B)-C(43B)	100.0(2)
C(41B)-C(42B)-C(43B)	120.0
C(45B)#2-C(42B)-C(46B)#2	22.0(2)
C(44B)#2-C(42B)-C(46B)#2	110.0(3)
C(41B)-C(42B)-C(46B)#2	130.1(12)
C(43B)-C(42B)-C(46B)#2	10.1(12)
C(46B)#2-C(43B)-C(45B)#2	126.0(5)
C(46B)#2-C(43B)-C(44B)	92.0(4)
C(45B)#2-C(43B)-C(44B)	142.0(2)
C(46B)#2-C(43B)-C(42B)	148.0(4)
C(45B)#2-C(43B)-C(42B)	22.0(2)
C(44B)-C(43B)-C(42B)	120.0
C(46B)#2-C(43B)-C(41B)#2	67.0(4)
C(45B)#2-C(43B)-C(41B)#2	168.0(3)
C(44B)-C(43B)-C(41B)#2	25.4(10)
C(45B)#2-C(42B)-C(44B)#2	132.0(5)
C(45B)#2-C(42B)-C(41B)	152.0(3)
C(44B)-C(43B)-C(44B)#2	90.8(13)
C(45B)#2-C(43B)-C(44B)#2	51.5(13)
C(41B)#2-C(43B)-C(44B)#2	116.0(2)
C(41B)#2-C(44B)-C(42B)#2	132.0(5)
C(41B)#2-C(44B)-C(43B)	88.0(3)
C(42B)#2-C(44B)-C(43B)	140.0(2)
C(41B)#2-C(44B)-C(45B)	152.0(3)
C(42B)#2-C(44B)-C(45B)	20.0(2)
C(43B)-C(44B)-C(45B)	120.0
C(41B)#2-C(44B)-C(46B)#2	63.0(3)
C(42B)#2-C(44B)-C(46B)#2	165.0(3)
C(43B)-C(44B)-C(46B)#2	24.6(14)
C(45B)-C(44B)-C(46B)#2	144.6(14)
C(41B)#2-C(44B)-C(43B)#2	177.0(4)
C(42B)#2-C(44B)-C(43B)#2	51.0(2)
C(43B)-C(44B)-C(43B)#2	89.2(13)
C(45B)-C(44B)-C(43B)#2	30.8(13)
C(46B)#2-C(44B)-C(43B)#2	114.0(2)

Table IV. (continued)

C(42B)-C(43B)-C(41B)#2	145.4(10)	C(42B)#2-C(45B)-C(43B)#2	126.0(5)
C(46B)#2-C(43B)-C(44B)#2	177.0(5)	C(42B)#2-C(45B)-C(46B)	148.0(3)
C(43B)#2-C(45B)-C(46B)	22.0(2)	C(44B)#2-C(46B)-C(42B)#2	85.3(12)
C(42B)#2-C(45B)-C(44B)	28.0(3)	C(45B)-C(46B)-C(42B)#2	10.1(11)
C(43B)#2-C(45B)-C(44B)	98.0(2)	C(41B)-C(46B)-C(42B)#2	109.9(11)
C(46B)-C(45B)-C(44B)	120.0	C(43B)#2-C(46B)-C(42B)#2	22.0(3)
C(42B)#2-C(45B)-C(41B)#2	19.0(2)	C(45B)-C(46B)-C(44B)#2	95.4(10)
C(43B)#2-C(45B)-C(41B)#2	106.0(2)	C(41B)-C(46B)-C(44B)#2	24.6(10)
C(46B)-C(45B)-C(41B)#2	128.8(10)	C(43B)#2-C(46B)-C(44B)#2	63.0(3)
C(44B)-C(45B)-C(41B)#2	8.8(10)	C(41B)-C(46B)-C(45B)	120.0
C(43B)#2-C(46B)-C(41B)	88.0(4)	C(43B)#2-C(46B)-C(45B)	32.0(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1;
#2 -x+1,-y+2,-z+1.

CHAPTER 8: SYNTHESIS, CHARACTERIZATION, AND INTERMETAL IMIDO GROUP TRANSFER REACTIONS OF IMIDO MOLYBDENUM(IV) PORPHYRIN COMPLEXES

A paper to be submitted to Inorganic Chemistry

Lisa M. Berreau and L. Keith Woo*[1]

Abstract

Treatment of dichloro(*meso*-tetra-*p*-tolylpophyrinato)molybdenum(IV), (TTP)MoCl$_2$, with LiNHR (R = -C$_6$H$_5$, -C$_6$H$_4$-*p*-CH$_3$) in toluene produces the imido complexes (TTP)Mo=N-C$_6$H$_5$•(H$_2$N-C$_6$H$_5$)$_n$, **1**, and (TTP)Mo=N-C$_6$H$_4$-*p*-CH$_3$•(H$_2$N-C$_6$H$_4$-*p*-CH$_3$)$_n$, **2**, where $n \leq 1$. When treated with pyridine derivatives, NC$_5$H$_4$-*p*-X (X = -CH$_3$, -CH(CH$_3$)$_2$, -C≡N), the coordinated amine is displaced to form a new six coordinate complex, (TTP)Mo=NR•NC$_6$H$_5$-*p*-X. When the six coordinate molybdenum imido complexes, (TTP)Mo=N-C$_6$H$_5$•(H$_2$N-C$_6$H$_5$) or (TTP)Mo=N-C$_6$H$_5$•(H$_2$N-C$_6$H$_4$-*p*-CH$_3$) are treated with (TTP)Ti(PhC≡CPh), complete imido group transfer occurs to give (TTP)Mo(PhC≡CPh), (TTP)Ti=N-C$_6$H$_5$ or (TTP)Ti=N-C$_6$H$_4$-CH$_3$, and free amine.

Introduction

The transfer of an oxygen atom from transition-metal oxo complexes to organic or nonmetal substrates is a well documented process.[2] The related process of intermetal oxygen atom transfer continues to be an area of intense research and has recently been reviewed.[3] However, few examples have been reported involving imido group transfer from transition-metal complexes.[4,5,6,7,8,9] Furthermore, the imido group transfer processes reported to date have largely involved transfer to nonmetal substrates, eg phosphines, alkanes, and alkenes. Gibson, *et al.*, have recently reported a series of intermetal pairwise exchange reactions involving oxo, imido, and alkylidene ligands which do not involve a net redox process.[10]

Metalloporphyrin complexes have been used to investigate a variety of inner sphere redox processes involving intermetal halogen-,[11] oxygen-,[12] nitrogen-,[13] sulfur-,[14] and selenium-atom transfer reactions.[14] We now wish to report an example of a two-electron intermetal redox process mediated by imido group transfer. We have recently discovered that (TTP)TiCl$_2$, when treated with various lithium amides, results in the formation of Ti(IV) organoimido complexes.[15] Metalloporphyrin complexes containing organoimido ligands are rare,[16,17,18,19,20] with only two such species having been characterized by single crystal X-ray diffraction analysis.[15,16] Having extended this synthetic methodology to molybdenum porphyrins, we have been able to prepare organoimido molybdenum(IV) porphyrin complexes. Treatment of(TTP)Mo=NR•(H$_2$NR)$_n$ (R = -C$_6$H$_5$, -C$_6$H$_4$-*p*-CH$_3$; n $\leq$ 1) with a low-valent titanium porphyrin, (TTP)Ti(PhC≡CPh), results in complete intermetal imido group transfer, a formal two-electron redox process, to yield (TTP)Ti=NR and (TTP)Mo(PhC≡CPh).

Results and discussion

As illustrated in eq 1, treatment of (TTP)MoCl$_2$ with LiNHR results in the formation of Mo(IV) organoimido complexes. In a typical reaction, 50.4 mg of (TTP)MoCl$_2$[14] (0.060 mmol) and 19.2 mg LiNHPh (0.19 mmol) were stirred in toluene (15 mL) under N$_2$ with mild heating for 1.5 h. The solution was then stirred an additional 18 h at 22 °C. Within minutes after the

$$(TTP)MoCl_2 + LiNHR \longrightarrow (TTP)Mo(=NR)(L)_x \qquad (1)$$

$$\mathbf{1}, R = -C_6H_5$$
$$\mathbf{2}, R = -C_6H_4\text{-}p\text{-}CH_3$$

$$L = H_2NR,\ x = \leq 1$$

addition of solvent to the solid starting materials, the green solution became the orange-red color of the phenylimido complex, **1**. After cooling the reaction mixture to room temperature, and removing the solvent in vacuo, the remaining solid was redissolved in toluene (10 mL) and filtered. The filtrate was evaporated to dryness and the product redissolved in a minimal amount of toluene and layered with hexane (ratio ca. 1:3). The solution was cooled to -20 for 1 h. Filtration yielded an orange-red solid (30 mg, 58%) after washing with hexane and drying in vacuo.[21] The tolyl analog can be prepared in a similar manner.[22]

The new porphyrin complexes were characterized by ^{1}H NMR, UV-Vis, and IR spectroscopy. The ^{1}H NMR spectra are characteristic of diamagnetic porphyrin complexes. Molybdenum(IV) porphyrins have been shown to exhibit both paramagnetic ((TTP)MoCl$_2$)[23] and diamagnetic ((TTP)Mo=O) behavior.[23] ^{1}H NMR spectra of the isolated imido complexes indicate the presence of ≤ 1 equivalent of the corresponding amine, bound as a sixth ligand in the position trans to the imido group. The position of the β-pyrrole resonance is dependent upon the amount of amine present, with the signal shifting upfield with increasing amount of coordinated amine. A range of 8.4-8.7 ppm has been observed for the β-pyrrole resonance. The porphyrin tolyl protons appear as two multiplets, each integrating to eight protons. The protons associated with the imido ligand are shifted upfield relative to those of the corresponding free amine, appearing in the region of 5-6.5 ppm. This observation is consistent with the position of the imido substituent about the porphyrin ring current. Signals for the coordinated amine are shifted upfield as well appearing at 6.81(d, 2H), 6.09(d, 2H) and 2.12 (s, 3H) in complex **2**.

Treatment of the imido complexes with pyridine derivatives results in the displacement of the coordinated amine and formation of a new six-coordinate complex, (TTP)Mo=NR•L',

$$\text{(TTP)Mo(=NR)(H}_2\text{NR)}_x + \text{L} \longrightarrow \text{(TTP)Mo(=NR)(L')} \qquad (2)$$

3a, R = Tolyl, L' = 4-methylpyridine
3b, R = Phenyl, L' = 4-methylpyridine
4, R = Phenyl, L' = 4-isopropylpyridine

with the pyridine derivative now occupying the position trans to the imido ligand.[24] The ^{1}H NMR spectrum of **3a** clearly exhibited a new methyl signal at 1.63 (s, 3H) corresponding to the new picoline fragment. Significant shifts are observed for all resonances associated with the porphyrin ligand for the picoline complexes. For example, the β-pyrrole resonance has been shifted upfield and is observed as a sharp singlet at 6.92 ppm. Resonances corresponding to the tolyl groups of the porphyrin ligand are also shifted upfield, with the methyl resonance now appearing at 2.24 ppm. The signals associated with the tolyl group of the imido ligand are instead shifted downfield slightly appearing in the region of 6.2-6.4 ppm. Similar shifts are observed for the picoline derivative of the phenylimido complex, **3b**.

Other pyridine derivatives also react with **1** and **2** to give new six-coordinate imido complexes. Addition of 4-isopropylpyridine to **1** affords the molybdenum imido complex *trans*-

(4-*i*-Pr-py)(TTP)Mo(=N-Ph), **4**, which is isolated in 61% yield after recrystallization from toluene/hexane (1:3).[25]

We have found that a net two-electron redox process, mediated by imido group transfer, is possible utilizing metalloporphyrin complexes. As shown in eq 3, treatment of (TTP)Mo=N-$C_6H_5\bullet(H_2N\text{-}C_6H_5)_n$ with a (*meso*-tetra-*p*-tolylporphyrinato)-titanium(II) η^2-acetylene complex, (TTP)Ti(PhC≡CPh),[26] results in complete intermetal imido group transfer, yielding a titanium porphyrin organoimido complex, (TTP)Ti=NR,[15] and a molybdenum(II) η^2-alkyne complex, (TTP)Mo(PhC≡CPh).[27] In a typical reaction, an NMR tube containing a C_6D_6-solution of

$$\text{(TTP)Mo=NR}(H_2NR)_n + \text{(TTP)Ti(PhC}\equiv\text{CPh)} \longrightarrow$$

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{(TTP)Ti=NR} + H_2NR \qquad (3)$$

$$R = \text{-}C_6H_5 \text{ or -}C_6H_4\text{-p-}CH_3,\ n \leq 1$$

(TTP)Mo=NPh was treated with a slight excess of (TTP)Ti(PhC≡CPh). The reaction was monitored over a period of 3 days. After 14 h, new β-pyrrole resonances corresponding to (TTP)Ti=NPh (9.21 ppm) and (TTP)Mo(PhC≡CPh) (8.99 ppm) began to appear. Over the course of the reaction, the resonances of the starting materials diminish, while those of the products intensify, yielding a final spectrum composed of the resonances of (TTP)Mo(PhC≡CPh) and (TTP)Ti=NPh. The overall time required for the reaction to go to completion is approximately 2 weeks. The reaction is slow presumably due to steric problems associated with a putative μ-imido intermediate. Further studies involving the synthesis and reactivity of early transition metal porphyrinato imido complexes are underway.

References

1. Presidential Young Investigator, 1990-1995; Camille and Henry Dreyfus Teacher-Scholar, 1993-1998.
2. (a) Ostovic, D.; Bruice, R. *Acc. Chem. Res.* **1992**, *25*, 314. (b) Holm, R.H. *Chem. Rev.* **1987**, *87*, 1401. (c) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571. (d) Jorgenson, K. A. *Chem. Rev.* **1989**, *89*, 314.
3. Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125.
4. Holm, R. H.; Harlan, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 186.
5. Dobbs, D. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 3836.
6. Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744.
7. Mahy, J.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079.
8. Mansuy, D.; Mahy, J.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.
9. Svastis, E. W.; Dawson, J. H. ; Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 6427.
10. Jolly, M; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc. Dalton Trans.* **1992**, 1331.
11. (a) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1582. (b) Cohen, I. A.; Jung, C.; Governo, T. *J. Am. Chem. Soc.* **1972**, *94*, 3003. (c) Reed, C. A.; Kouba, J. K.; Brimes, C. J.; Cheung, S. K. *Inorg. Chem.* **1978**, *17*, 2666.
12. (a) Woo, L. K.; Goll, J. G.; Berreau, L. M.; Weaving, R. *J. Am. Chem. Soc.* **1992**, *114*, 7411. (b) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916.

13. (a) Woo, L. K.; Goll, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3755. (b) Woo, L. K.; Czapla, D. J.; Goll, J. *Inorg. Chem.* **1990**, *29*, 3915. (c) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. (d) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955.

14. (a) Woo, L. K.; Hays, J. A. *Inorg. Chem.* **1993**, *32*, 2228. (b) Berreau, L. M.; Woo, L. K. *J. Am. Chem. Soc.* Submitted.

15. Berreau, L. M.; Young, V. G.; Woo, L. K. *Inorg. Chem.* Submitted.

16. Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614.

17. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

18. (a) Che, C. M. Huang, J. S.; Li, Z. Y.; Poon, C. K. *Inorg. Chim. Acta.* **1991**, *190*, 161. (b) Huang, J. S.; Che, C. M.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1992**, 161.

19. Elliot, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *12*, 2191.

20. Buchler, J. W.; Pfeifer, S. Z. *Natuforsch, B: Inorg. Chem., Org. Chem.* **1985**, *40B*, 1362.

21. Analytical Data for (TTP)Mo=NPh: ^{1}H NMR (C_6D_6, 300 MHz, ppm): 8.73 (s, 8H, β-*H*), 7.96 (d, 8H, $-C_6H_4CH_3$), 7.24 (m, 8H, $-C_6H_4CH_3$), 6.0 (t, 1H, *p-H*), 5.88 (t, 2H, *m-H*), 4.77 (d, 2H, *o-H*), 2.36 (s, 12H, $-C_6H_4CH_3$). UV-Vis (toluene): 430 (Soret), 550. MS(FAB,CH_3CN)(+): 857 (857). IR (KBr, cm^{-1}): Bands associated with porphyrin ligand: 1475, 1332, 1208, 1182, 1109, 1069, 1005, 844, 800, 724, 523. Bands associated with =NPh (cm^{-1}): 753, 686.

22. Analytical Data for (TTP)Mo=N($-C_6H_4CH_3$)$\bullet H_2NC_6H_4-CH_3$: ^{1}H NMR (C_6D_6, 300 MHz,

ppm): 8.39 (s, 8H, β-*H*), 7.88 (d, 8H, $-C_6H_4CH_3$), 7.27 (m, 8H, $-C_6H_4CH_3$), 6.81 (d, 2H, $H_2NC_6H_4$-CH_3), 6.09 (d, 2H, $H_2NC_6H_4$-CH_3), 5.81 (d, 2H, $=N$-C_6H_4-CH_3), 5.01 (d, 2H, $=N$-C_6H_4-CH_3), 2.34 (s, 12H, $-C_6H_4CH_3$), 2.12 (s, 3H, $H_2NC_6H_4$-CH_3), 1.42 (s, 3H, $=N$-C_6H_4-CH_3). UV-vis (toluene, nm): 302, 430 (Soret), 452 (sh), 550, 570 (sh).

23. Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.

24. (TTP)Mo(=N-Tolyl)(4-methylpyridine): ^1H NMR (C_6D_6, 300 MHz, ppm): 8.32 (d, 2H, *pic*), 7.51 (m, 8H, $-C_6H_4CH_3$), 7.09 (m, 8H, $-C_6H_4CH_3$), 6.92 (s, 8H, β-*H*), 6.2-6.4 (m, 6H, =N-*Tolyl, pic*), 2.24 (s, 12H, $-C_6H_4CH_3$), 1.86 (s, 3H, $=N$-$C_6H_4CH_3$), 1.63 (s, 3H, *pic*).

    (TTP)Mo(=N-Ph)(4-methylpyridine): ^1H NMR (C_6D_6, 300 MHz, ppm): 7.94 (m, 2H, *pic*), 7.51 (m, 8H, $-C_6H_4CH_3$), 7.10 (m, 8H, $-C_6H_4CH_3$), 6.95 (s, 8H, β-*H*), 6.2-6.6 (m, 6H, =N-*Ph, pic*), 2.23 (s, 12H, $-C_6H_4CH_3$), 1.58 (s, 3H, *pic*).

25. (TTP)Mo(=N-Ph)(4-*i*-Pr-py): ^1H NMR (C_6D_6, 300 MHz, ppm): 8.12 (br, 2H, *py*), 7.67 (d, 8H, $-C_6H_4CH_3$), 7.54 (s, 8H, β-*H*), 7.15 (m, 8H, $-C_6H_4CH_3$), 6.5 (br, 2H, *py*), 6.34 (m, 2H, =N-*Ph*), 6.09 (t, 1H, =N-*Ph*), 5.74 (m, 2H, =N-*Ph*), 2.28 (s, 12H, $-C_6H_5CH_3$), 0.780 (m, 7H, *py*).

26. Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

27. (TTP)Mo(PhC≡CPh): ^1H NMR (C_6D_6, 300 MHz, ppm): 8.99 (s, 8H, β-*H*), 8.04 (m, 8H, $-C_6H_4CH_3$), 7.30 (m, 8H, $-C_6H_4CH_3$), 6.54 (m, 6H, *m-,p-H,PhC≡CPh*), 4.90 (d, 4H, *o-H, PhC≡CPh*), 2.39 (s, 12H, $-C_6H_4CH_3$). De Cian, A.; Colin, J.; Schappacher, L.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850.

GENERAL CONCLUSIONS

This dissertation focuses on the preparation of metalloporphyrin complexes containing multiply bonded axial ligands. A fundamental breakthrough in this research involved first the development of new synthetic routes for the preparation of metalloporphyrin halide complexes of the early transition metals. Because traditional synthetic routes for metallation of free base porphyrins often resulted in the formation of very stable oxo complexes, little chemistry was known of early transition metal porphyrins. As we have demonstrated, treating a porphyrin dianion with metal halides of vanadium, titanium, molybdenum, and tungsten results in the formation of the corresponding porphyrin halide complex. This reaction is quite general and can be used for the synthesis of most early transition metal as well as main group metalloporphyrin halide complexes.

Utilizing these halide species as starting materials, we have been able to prepare the first molybdenum terminal sulfido and selenido metalloporphyrin complexes. The heavier chalcogenides, unlike the terminal oxo complex, are easily reduced with PPh_3, to give $(TTP)Mo(PPh_3)_2$ and the corresponding phosphine chalcogenide. The phosphine ligands of $(TTP)Mo(PPh_3)_2$ are very labile and may be replaced by alkynes or pyridine derivatives. The lability of the phosphine ligands makes $(TTP)Mo(PPh_3)_2$ an attractive complex for studying reactions of low-valent molybdenum porphyrins.

Atom transfer reactions involving transfer of the heavier chalcogenides are rare. The sulfur and selenium atom transfer reactions involving tin porphyrins reported here represent the first comprehensive study of a two-electron redox process mediated by sulfur or selenium atom transfer. As with halide transfer, the rate of transfer increases on descending the chalcogenides.

Metalloporphyrin halide complexes may also be used as precursors to early transition metal porphyrin imido complexes. Utilizing simple synthetic routes, we have been able to prepare imido complexes of titanium and molybdenum porphyrins. Upon treatment with a low-valent titanium porphyrin, molybdenum imido porphyrins are reduced with transfer of the imido group from molybdenum to titanium, formally a two-electron transfer. This reaction is the imido group analog of intermetal oxygen atom transfer.

ACKNOWLEDGEMENTS

I would like to thank my family for their support and encouragement throughout my years of education. The visits, telephone calls, and letters kept me going when sometimes I wanted to give it all up.

Secondly, I would like to thank Keith Woo. I am grateful for your encouragement, guidance, and most of all, for your energy and enthusiasm for research. You have taught me many things, the most important of which is probably that hard work does lead to success.

I am also grateful to my fellow Woo group members. Along with teaching me most of the techniques needed for my research, Jim Goll, Alan Hays, and Dan Smith were a tremendous help with preparation for my seminars and oral exam. Hongping Yuan and his sayings (YOU ARE IN BIG TROUBLE!, WANNA MAKE A BET?, WHAT A LOSER!) made me laugh through our many hours in the lab. I will probably always owe Hongping at least one dinner. The endless discussions about sports with Hongping and Chris Hamaker were a way to pass the time as well as make money. I would also like to acknowledge Jean-Pierre Djukic. I consider the year Jean-Pierre spent in the group to be the most productive year of my graduate school career.

Many friends have helped me through my years in Ames. Becky Rich and Karen Nordell were always there for me when I needed to talk or just get away from everything having to do with chemistry. The Foley family (Brooks, Polly, Maureen, and Alex) fed me many times and brought me up to date on the most recent children's literature. Maureen and Alex often gave me a reason to smile when my chemistry was driving me crazy.

I would also like to thank Harold Hall, Trond Forre, Eldon Ness, and the other members of the machine shop for making research just a little bit easier to endure. I would like to acknowledge Victor G. Young for his work involving the crystal structures reported here. I also acknowledge the help of Dave Scott, Karen Ann Smith, Kamel Herrata, Jan Beane, and Charles Baker in obtaining NMR and mass spectral data.