SYNTHESIS AND CHARACTERIZATION OF STABLE IRON(IV), TIN(IV) AND RUTHENIUM(IV) THIATRANE COMPLEXES

by

Kerry A. Fusie-Clark

A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor T. Adrian George

Lincoln, Nebraska

July, 2001

Bell & Howell Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

DISSERTATION TITLE

Synthesis and Characterization of Stable Iron(IV), Tin(IV) and Ruthenium(IV) Thiatrane Complexes

BY

Ms. Kerry A. Fusie-Clark

SUPERVISORY COMMITTEE:

APPROVED	DATE
T. Adrian George Signature Dr. T. Adrian George Typed Name	July 12, 2001
Signature Dr. George Sturgeon Typed Name	7/12/01
Signature Dr. Victor Day Typed Name	7/12/01
Signature Dr. Peter Dowben Typed Name	7-12-01
Signature Dr. John Stezowski Typed Name	07/12/01
Signature Typed Name	

GRADUATE COLLEGE
UNIVERSITY OF NEBRASKA

SYNTHESIS AND CHARACTERIZATION OF STABLE IRON(IV), TIN(IV) AND RUTHENIUM(IV) THIATRANE COMPLEXES

Kerry A. Fusie-Clark, Ph.D.

University of Nebraska, 2001

Advisor: T. Adrian George

Iron(IV) is proposed to be a key oxidation state in many metalloenzymes that catalyze the selective oxidation of hydrocarbons and related compounds using oxygen. This work reports the designed synthesis of stable, diamagnetic, trigonal bipyramidal, iron(IV) thiatrane complexes starting from either iron(II) or iron(III). For example, the reaction of the tris-thiolate ligand, $P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3$, $(PS_3)^{TMS}$, (generated in situ from the $H_3PS_3^{TMS}$ proligand and Et_3N) with $FeCl_2$ under a nitrogen atmosphere produced an emerald green solution which contained $[Fe^{II}(PS_3)^{TMS}]^-$. Laboratory workup of this compound produced an intensely purpled-colored complex, $ClFe^{IV}(PS_3)^{TMS}$, which was the first diamagnetic iron(IV) complex and the first trigonal bipyramidal, iron(IV) thiatrane complex to be structurally characterized.

Utilizing this general procedure and a variety of tris-thiolate ligands, this dissertation focuses on the synthesis of complexes of the type $XM^{IV}(PS_3)$. Eight additional iron(IV) and the isostructural tin(IV) and ruthenium(IV) complexes with formulas $XFe(PS_3)^{TMS}$ where $(PS_3)^{TMS} = P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3$ and X= Br, I,

CN, $PhSn(PS_3)^{TMS}$, $PhSn(PS_3)^{Me}$ where $(PS_3)^{Me} = P(C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}S)_3$, $PhSn(PS_3)$ where $(PS_3) = P(C_6H_4\text{-}2\text{-}S)_3$, $ClRu(PS_3)^{TMS}$ and $ClRu(PS_3)$ have been synthesized. The mechanistic details for the formation of these stable complexes, the identification of metal and nonmetal-containing reaction coproducts and physical and chemical properties of these substances have been pursued.

Five of these complexes, $BrFe(PS_3)^{TMS}$, $IFe(PS_3)^{TMS}$, $PhSn(PS_3)^{TMS}$, $PhSn(PS_3)^{Me}$ and $PhSn(PS_3)$ have been studied crystallographically. $PhSn(PS_3)^{TMS}$ can be easily converted to either $ClFe(PS_3)^{TMS}$ or $ClRu(PS_3)^{TMS}$ via transmetalation reactions using $FeCl_3$, $FeCl_2$, $(Et_4N)_2[Fe_2OCl_6]$ and $RuCl_2(DMSO)_4$. These reactions gave insight into the lability of the fifth coordination site (halogen, cyanide or phenyl) in the trigonal bipyramidal complexs as well as the reactivity of the metal centers. The chemical reactivity of $ClFe(PS_3)^{TMS}$ has been explored by using this iron(IV) complex as a reagent in the attempted formation of six-coordinate $(Et_2NCS_2)Fe(PS_3)^{TMS}$.

Developing this chemistry and characterizing the resulting complexes provided the foundation needed to prepare a new group of functional and structural models for a wide range of metalloenzymes.

Table of Contents

List of Figures

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 6

List of Tables

Chapter 2

Chapter 3

List of Equations

Chapter 1

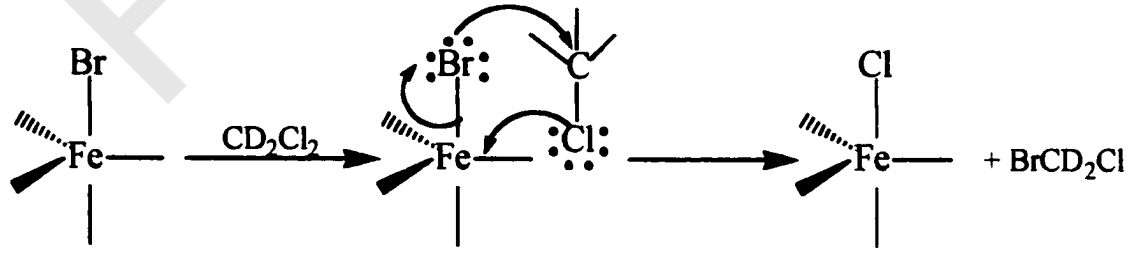
$$N_2 + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16Pi$$

Chapter 4

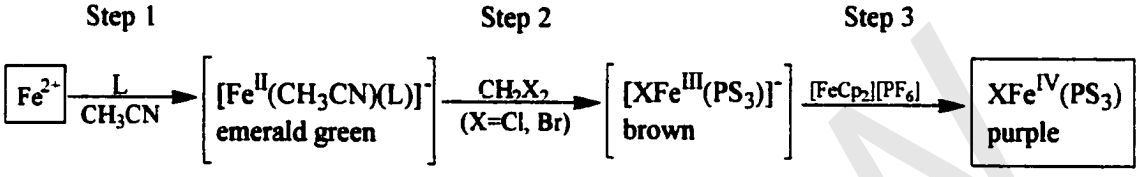
$$[ClFe^{III}(PS_3)]^- + I^- \rightarrow [IFe(PS_3)]^- + Cl^-$$

$$[Fe^{II}(CH_3CN)(PS_3)^{TMS}]^- + CN^- \xrightarrow[\text{Reaction}]{\text{No}} [CNFe(PS_3)^{TMS}]^{2-}$$

$$Fe(ClO_4)_2 \cdot 6H_2O + 3CN^- + H_3PS_3{}^{TMS} + 3Et_3N \xrightarrow[\text{or thf}]{CH_3CN} [CNFe^{II}(PS_3)^{TMS}]^{2-} + \text{others}$$



List of Charts



$$H_3PS_3 + Et_3N \rightleftharpoons H_2PS_3^- + Et_3NH^+$$

$$H_2PS_3^- + Et_3N \rightleftharpoons HPS_3^{2-} + Et_3NH^+$$

$$HPS_3^{2-} + Et_3N \rightleftharpoons PS_3^{3-} + Et_3NH^+$$

List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
3-NMA matrix	matrix used for FAB-MS
°C	degrees Celsius
δ	delta
η	eta
μ	mu
ν	nu
Å	angstrom
acac	acetylacetonate
ADP	adenosine diphosphate
ATP	adenosine triphosphate
Br	broad
n-Bu	n-butyl
ca.	about or approximately
calcd.	calculated
COSY	Correlated Spectroscopy
CV	cyclic voltammetry
CP/MAS	cross polarization magic angle spinning
Cys	cysteine
d (in parenthesis)	doublet

dd (in parenthesis)	doublet of doublets
ddd (in parenthesis)	doublet of doublet of doublets
dddd (in parenthesis)	doublet of doublet of doublet of doublets
dt (in parenthesis)	doublet of triplets
e^-	electron
ε $M^{-1}cm^{-1}$	epsilon, per molarity per centimeter
Et	ethyl
FAB-MS	fast atom bombardment ionization mass spectrometry
$[FeCp_2][PF_6]$	ferrocenium hexafluorophosphate
FTIR	fourier transform infrared spectroscopy
g	gram(s)
h	hour(s)
Heme	porphyrin-type ligand in biological systems
His	histidine
HMBC	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple Quantum Coherence
HOMO	highest occupied molecular orbital
Hz	Hertz
J	coupling constant
K	Kelvin
L	Liter

λmax	lambda maximum
LUMO	lowest occupied molecular orbital
m (in parenthesis)	multiplet
M	molarity
M^+	parent ion (mass spectrometry)
m/z	mass to charge ratio
Me	methyl
MHz	megahertz
mL	milliter
mm	millimeter
MMO	methane monooxygenase
mmol	millimole
nm	nanometer
NMR	nuclear magnetic resonance
O	ortho
P	para
P-450	used to name a specific cytochrome
Ph	phenyl
Pi	inorganic phosphate
ppm	parts per million
pr^i	isopropyl
s	second(s)