Production of Transition Metal Oxidants Through Design and Synthesis of Polyanionic Chelating Ligands

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PREFACE

This thesis is divided into four parts: organic chemistry, osmium, copper, and cobalt. Each is a story in itself which should make sense on its own. Those reading this document for the inorganic chemistry may wish to skip over the organic section. However, this section describes some of our greatest frustrations and hurdles and is a crucial part of the story for that reason alone. From this document, the reader should learn a lot more about the design of ligands and their interactions with high-valent metals, and maybe a little about me.

ABSTRACT

Ligand design criteria for stabilization of high valent metals have been developed and applied to osmium, copper, and cobalt. Ligands have been designed to have favorable coordination properities, be noninnocent, and be resistant to oxidative degradation.

A new subset of ligands has been synthesized, these being called Class II polyanionic chelating (PAC) ligands. These ligands possess two N-amido donors and two alkoxy donors. Both units have pKa's of approximately 18 and so would be expected to be very powerful donors. A number of ligands of this type have been developed with 5,5,5; 5,6,5; 6,5,6; and 6,6,6 coordination geometries. The key steps in all of the syntheses are coupling of highly hindered carboxylic acids with highly hindered diamines.

It is found that the 5,5,5; 5,6,5; and 6,5,6 coordinating ligands all stabilize Os(VI) monooxo compounds. The 5,6,5 and 6,5,6 coordinating ligands also stabilize Os(IV) complexes of octahedral geometry. The 6,6,6 ligands of this type do not coordinate to osmium. Of the 5,6,5 ligands, the most interesting results have been obtained with H_4-HMPA-DMP, or 2,4-bis-hydroxymethylpropamido-2,4-dimethyl-3-pentanone. Reaction of this with potassium osmate produces Os(VI)(η^4-HMPA-DMP)O. This molecule has been structurally characterized. It assumes a distorted square pyramidal geometry with the metal atom 0.8 Å above the plane formed by the four donor atoms of the PAC ligand. The distortion appears to occur by pyramidalization at the amide nitrogen atoms, as is shown by the χ_N values (17.0° and 9.1°). Os(HMPA-DMP)O undergoes a number of interesting reactions. It is cleanly converted to the *trans*-K_2Os(η^4-HMPA-DMP)O_2 species with base; it can be electrochemically reduced to a stable (although highly air-sensitive) Os(V) species; and it can be chemically reduced to produce *trans*-Os(IV)(η^4-HMPA-DMP)L_2 complexes where L can be a wide variety of pyridines. These Os(IV) compounds may be oxidized chemically or electrochemically to produce Os(V) compounds. The

Os(V)/(IV) potential may be precisely controlled by appropriate choices of L allowing production of tunable oxidants. It is also observed that these Os(IV) compounds react with molecular oxygen to regenerate the Os(VI) monooxo species. The compounds catalytically reduce molecular oxygen and oxidize triphenylphosphine to triphenylphosphine oxide. Kinetic studies are consistent with a rate-determining step involving dissociation of a pyridine ligand from the *trans*-Os(IV)(η^4-HMPA-DMP)L_2 species to generate a vacant coordination site to which oxygen may bind. The reaction has been examined with a variety of pyridine ligands. The rate of air oxidation decreases with increased electron donor ability of substituents on the pyridine ring, k_{obs} being 1.9(1) X 10^{-6} min^{-1} for the compound synthesized from 4-bromopyridine and k_{obs} for compounds synthesized with dialkylaminopyridines being virtually too small to measure. Similar Os(VI) monooxo and octahedral Os(IV) compounds have been synthesized with a number of other Class II PAC ligands. The Os(IV) and Os(VI) compounds produced in this work have been compared to similar species produced with Class I PAC ligands.

The Class II PAC ligands have also been used to stabilize trivalent copper. A number of such compounds have been synthesized (one of which, [TPP][Cu(η^4-HMPA-B)]) has been structurally characterized) and compared with the corresponding Class I compounds. While no Cu(III)-Class I PAC complexes were stable (although reversible Cu(III)/(II) were observed in these cases), the Class II PAC ligands led to stable Cu(III) complexes, exhibiting Cu(III)/(II) potentials as low as -1.06 V vs Fc^+/Fc. Such potentials are much lower than have been seen for any complexes synthesized to date with first-row donor atoms. The [TMA][Cu(III)(HMPA-DMP)] complex is an example of a Cu(III) compound with a completely innocent ligand complement. In this case, resonance structures from lower oxidation states are not possible thus enabling the oxidation state in this complex to be unambiguously assigned as +III.

The Class II PAC ligands stabilize cobalt in the rare trivalent, square planar form. These compounds, while paramagnetic with two unpaired spins, may be

characterized by proton NMR. One such complex, Na[Co(III)(HMPA-B)] has been characterized by X-ray crystallography. These compounds catalyze the epoxidation of styrene using iodosoarenes as the stoichiometric oxidants.

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ABBREVIATIONS

Ac	acetyl
B.M.	Bohr magnetons
BPG	basal planar graphite
br	broad
^{tert}bu	*tertiary*-butyl
CO	carbon monooxide (or carbonyl)
CV	cyclic voltammogram
d	doublet
DMSO-d_6	deuterated dimethylsulfoxide
E°	redox potential
et	ethyl
Fc^+/Fc	ferrocinium/ferrocene
H_4-CHBA-Et	1,2-bis(3,5-dichloro-2-hydroxybenzamido)-ethane
H_4-CHBA-DCB	1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene
H_4-CHBA-Pr	1,3-bis(3,5-dichloro-2-hydroxybenzamido)-propane
H_4-HBA-B	1,2-bis(2-hydroxybenzamido)benzene
H_4-HMBuA-B	1,2-bis(3-hydroxy-3-methylbutamido)benzene
H_4-HMBuA-DCB	1,2-bis(3-hydroxy-3-methylbutamido)-4,5-dichlorobenzene
H_4-HMBuA-Et	1,2-bis(3-hydroxy-3-methylbutamido)ethane
H_4-HMBuA-DMP	1,2-bis(3-hydroxy-3-methylbutamido) 2,4-dimethyl-3-pentanone
H_4-HMPA-Bu	1,4-bis(3-hydroxy-3-methylbutamido)butane
H_4-HMPA-Et	1,2-bis(2-hydroxy-methylpropamido)ethane

H_4-HMPA-Pr	1,3-bis(2-hydroxy-methylpropamido)propane
H_4-HMPA-B	1,2-bis(2-hydroxy-methylpropamido)benzene
H_4-HMPA-DCB	1,2-bis(2-hydroxy-methylpropamido)-4,5-dichlorobenzene
H_4-HMPA-DMP	2,4-bis(2-hydroxy-methylpropamido)-2,4-dimethyl-3-pentanone
hr	hour
IR	infrared
J	coupling constant
L	any monodentate neutral ligand
m	meta
Me	methyl
MeO	methoxy
mult	multiplet
NMR	Nuclear Magnetic Resonance
o	ortho
"oxo"	an apical oxygen atom bound to a metal
p	para
PAC	polyanionic chelating ligand
PPh_3	triphenylphosphine
pr	propyl
py	pyridine
q	quartet
R	alkyl
RT	room temperature
s	singlet
SCE	saturated calomel electrode
t	triplet
TBA	tetrabutylammonium

TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIP	temperature independent paramagnetism
TLC	thin layer chromatography
TMA	tetramethylammonium
TPP	tetraphenylphosphonium
Ts	tosyl (p-toluenesulfonyl)
UV-vis	ultraviolet-visible (spectroscopy)

Unless otherwise stated, all PAC ligands when coordinated to transition metals may be assumed to be bound at all four donor atoms.

INTRODUCTION

As the title of this report states, this project has focused on the design and synthesis of ligand environments which will stabilize highly oxidized and highly oxidizing transition metals.

Most oxidations are carried out under heterogeneous conditions.[1] To design a homogeneous transition metal oxidant, it is crucial to design an environment in which the oxidizing agent will be stable. To a large extent, this occurs naturally. While the scope is limited, simple ligands such as nitrido, oxo, and halides are capable of stabilizing transition metals in high valencies;[2] there are many useful oxidants of this type. Another important class of naturally occurring ligands are the porphyrins and related systems, which are highly complex molecules. The porphyrins are also able to stabilize metals in high oxidation states.[3] Many important biological (and biomimetic) oxidations are carried out by such systems.[4] High valent metals have long been used as powerful chemical oxidants; through the use of such metals in high oxidation states, great contributions to chemical synthesis have been made.[5] A simple demonstration of this is a monograph which has recently appeared and cites over two thousand pieces of research devoted to metal mediated oxidations of organic compounds.[6] Besides the organic synthetic applications, energy technologies (as energy generation so often involves combustion) and material science (as many paths of material degradation and causes for failure are oxidative) are also directly connected with oxidations.[7] Advances made in the understanding of oxidation chemistry will accelerate progress in these related fields as well.

Such studies of metals in high valencies, while clearly advancing and making great contributions (see reference 6) to both knowledge and practice, are hampered by a number of problems. One of the most severe is the lack of specificity of most oxidations. It is often the case that rather than one particular functional group being transformed, either the entire molecule will be overoxidized or the reaction at the individual functional group cannot be terminated at the desired stage.[7] In metal mediated oxidations, usually more than one active oxi-

dizing agent is present. This is clearly the case in many of the oxidative systems involving manganese, iron and chromium. A second problem is that the true nature of the oxidizing species is often unknown, due to the multiplicity of oxidants and the inherent difficulty in characterizing them; many are paramagnetic and can not be studied by NMR.[7,8] It becomes clear that an increased understanding of oxidation processes is dependent on a better understanding of the nature of such species.[9,10] Through the approach described below and in the rest of this report, I, along with the other researchers in the Collins group have attempted to gain this understanding and therefore address the problems facing contemporary oxidation chemistry.

The work described here is part of a larger project, the general goal of which has been to produce stable oxidizing agents by concentrating on the ligating groups and to developing correct and applicable ligand design criteria. What we have observed through this approach is a new area of unusual coordination chemistry. It is useful at this point to see how our understanding of the ligand requirements has evolved in the last few years and to describe some of what we have achieved in the process of developing these ligand design criteria.

From the start, it was clear that there were several important ligand design criteria which had to be met.[8,11,12] First, to stabilize the electron deficient metal centers, anionic nitrogen and oxygen donors were chosen. To precisely define coordination environments and to enhance the stability of the coordination complexes, tetradentate ligands were chosen, incorporating only five and six membered rings (as these rings are most easily formed). It was also realized that the ligand would have to be resistant to oxidation. This is not only important from the standpoint of the ligands being stable under the conditions which would be used to oxidize the metal center, but also, to prevent a highly oxidized metal center from simply oxidizing the ligand itself, thus destroying the capability of synthesizing and storing a powerful oxidant. It was also put forth that the ligands should be easily synthesized, through short, economical methods. While most of the early

ligands satisfied this criteria,[11] the work which follows involves combining tactical organic synthesis with coordination chemistry, and so ligands have been designed and synthesized where the syntheses are neither short nor simple.

An early ligand used by our research group, 1,2-bis-(3,5-dichloro-2-hydroxy-benzamido)-ethane, H_4-CHBA-Et, (0-1), is shown in Figure (0-1).

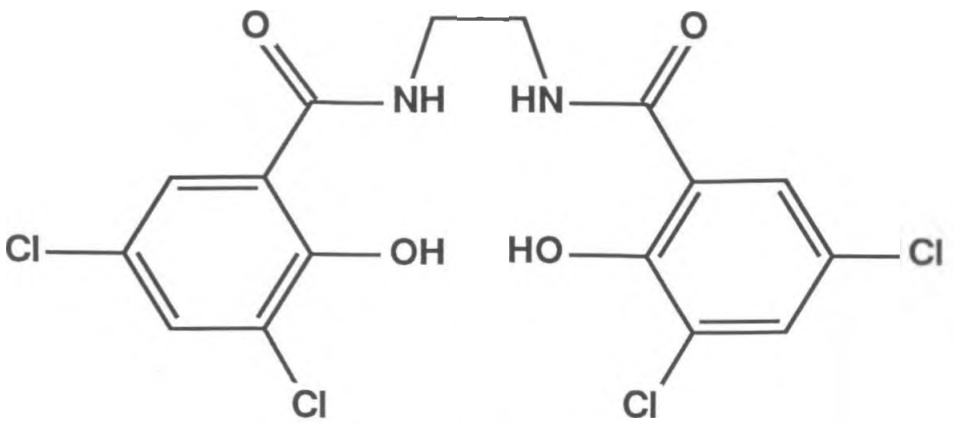


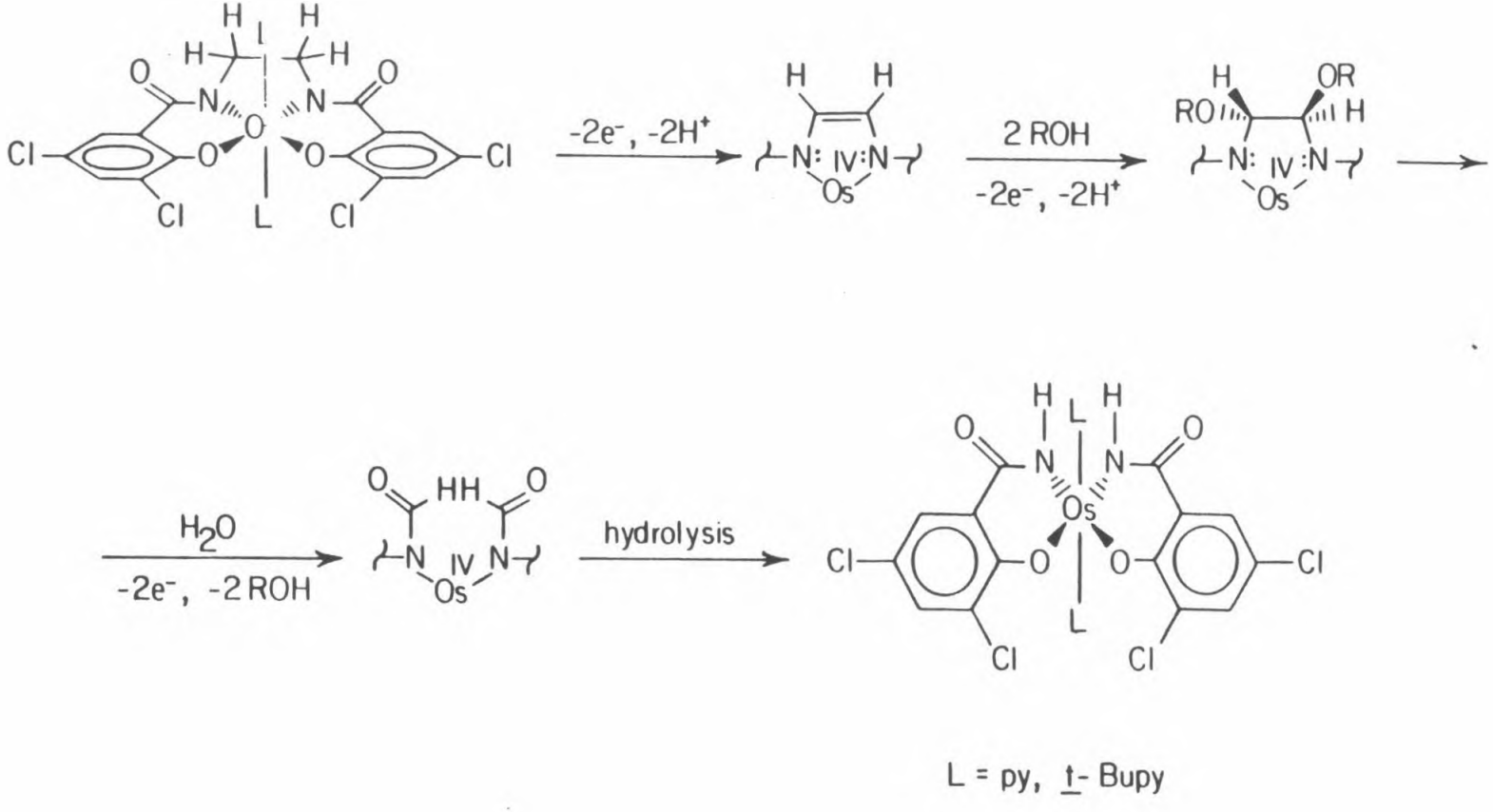
Figure 0-1: H_4-CHBA-Et

Note the salient features of the ligand: It is tetradentate, and will form two six membered rings and one five membered ring on coordination; it is potentially tetraanionic; the donor atoms are both hard and have high Bronsted basicities.[2,13] This ligand may be synthesized in high yield in three steps from commercially available starting materials.[14] While the ligand proves to coordinate to metals very well and the complexes may be easily isolated in good yields, the ligand is not resistant to oxidation. Terry Krafft and Steve Gipson demonstrated that the ethylene bridge is quite sensitive to oxidizing environments.[15] The lig-

and is coordinated to osmium in the (VI) oxidation state and reduced to form an octahedral Os(IV) species. However, attempts to oxidize this species to the rare[16] Os(V) oxidation state brought about a very complex ligand decomposition cascade, eventually resulting in complete bridge destruction. The decomposition process is illustrated in Scheme (0-I). Fifteen intermediates were observed, and six of them were characterized by X-ray crystallography. The final decomposition product serendipitously catalyzes the electrochemical conversion of alcohols to aldehydes and ketones.[12,17,18]

While such results are interesting and useful, the fact remains that the ethylene bridge unit precludes formation of powerful oxidants. As this is the goal of the research, the problem must be dealt with. The ethylene bridge was replaced by *o*-phenylene and 4,5-dichloro-*o*-phenylene units, neither of which have C-H bonds adjacent to nitrogen donors and so would be expected to be more stable under oxidizing conditions.[11] This led to two novel ligands (1,2-bis-(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene, H_4-CHBA-DCB, 0-2, and 1,2-bis-(2-hydroxybenzamido)-benzene, H_4-HBA-B, 0-3) whose coordination chemistry was explored. These ligands are shown in Figure (0-2). From Os(IV) studies similar to those described above, a novel isomerization was observed as shown in Scheme (0-II).[11]

The isomerization occurs by rotation around the carbon-nitrogen bond of the amide unit. This leads to what are referred to as non-planar amides, so called because the lone pair on the nitrogen atom is no longer co-planar with the carbonyl π system. Three types of non-planar amides have been produced. The first involves non-planarity induced by changes in electron demand at the metal center.[11,18,19] The second type is caused by demands of the metal coordination sphere.[11,19] The third is brought about by steric repulsions. That coordination complexes should isomerize in such a manner is a very interesting discovery and suggests that the integrity of the amide unit must be considered in cases where such groups are coordinated to transition metals.[20]



Scheme 0-1: Oxidative degradation of a polyanionic chelating ligand

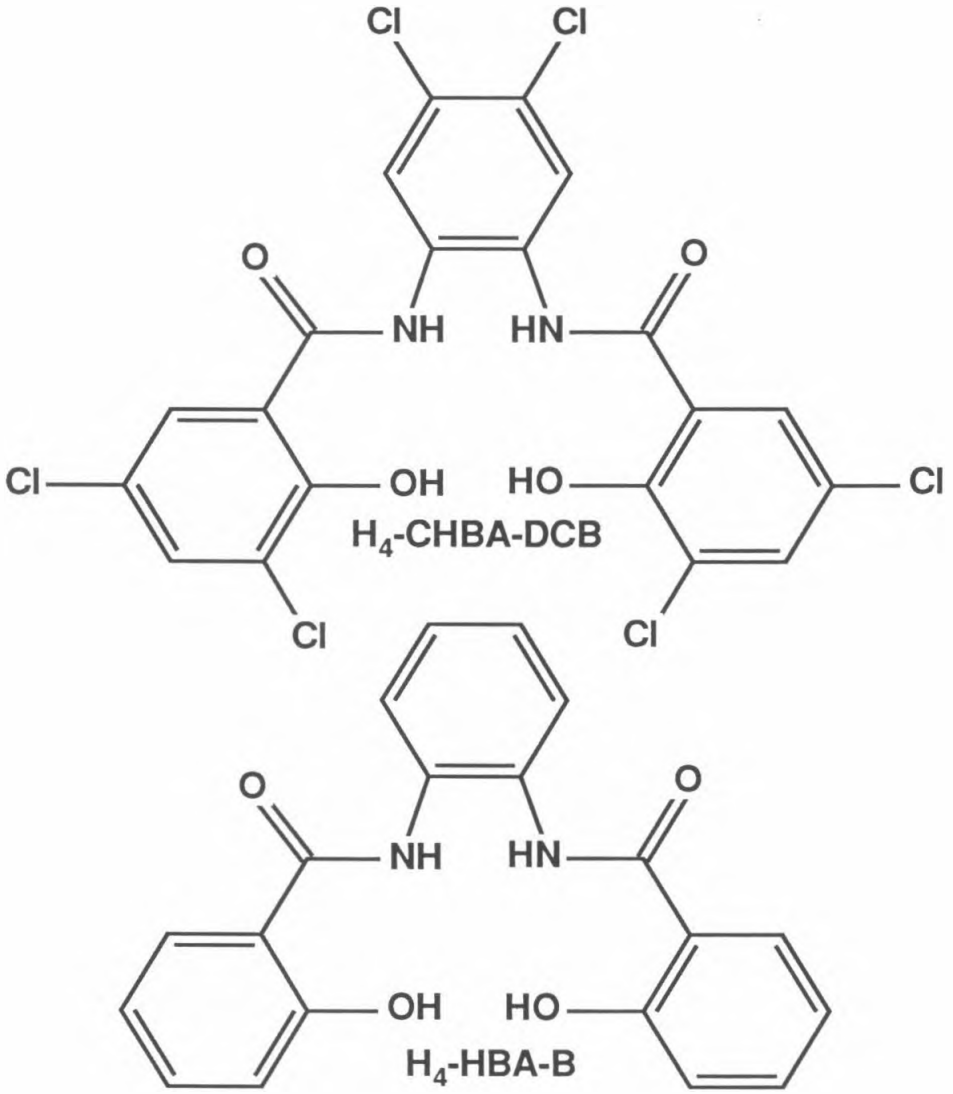
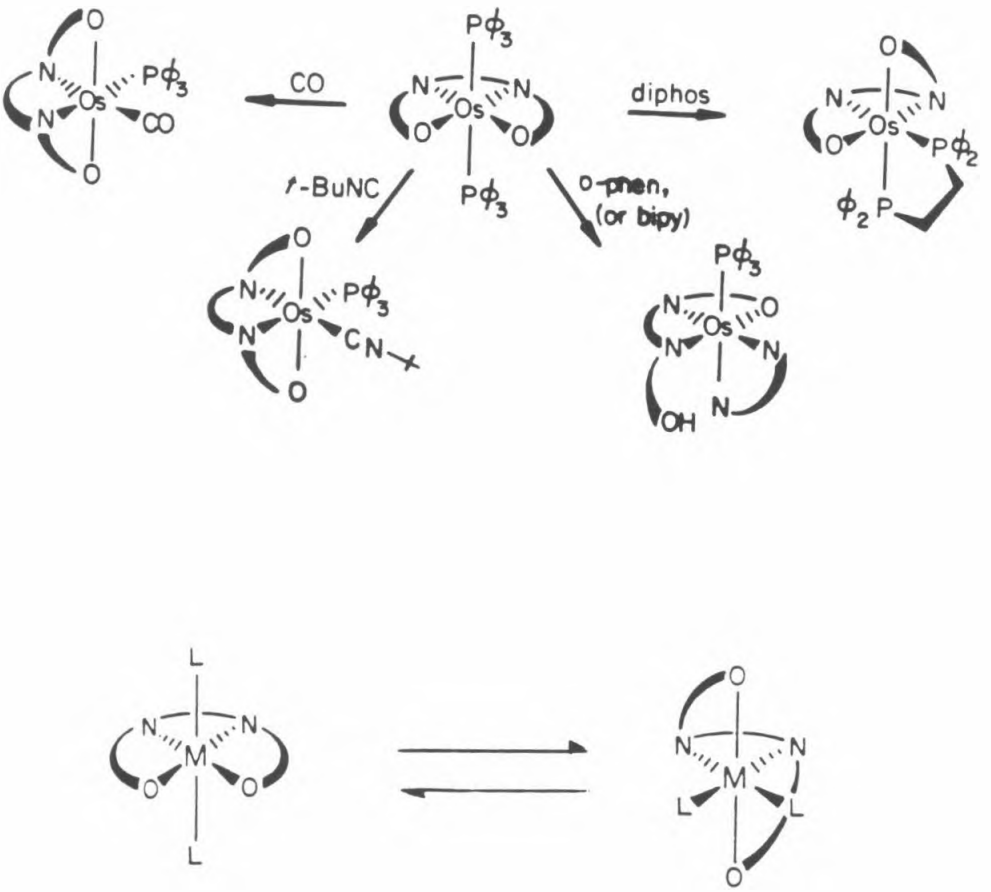


Figure 0-2: Two new and oxidatively resistant ligands useful for stabilizing high valent metals



Scheme 0-II: Isomerization of PAC ligands leading to the formation of non-planar amides

Other osmium complexes incorporating these ligands exhibit very high reversible redox couples, 1.8 v. SCE, close to the highest reversible potentials ever observed. This attests to the robust nature of the polyanionic chelating ligands.[14,15]

While the oxidation state formalism is often not the best indication of the reactivity of the metal center, it is a good tool for generally assessing the properties of a metal center. In addition, it is often useful as a guide in the development of a catalytic system.[16] The significance of the coordination chemistry and high potentials discussed above does not rest on assignment of oxidation states. However, if new oxidation states are claimed, the ability to unambiguously assign the oxidation state takes on greater importance. The ligands used in the research up to this point contain two phenoxy donors and two amido donors. The amido donors are linked via a phenylene unit. Such *o*-phenylenediamine (and related catechol and *o*-benzenedithiol) units are known to be *noninnocent*, that is, they may exist in a number of resonance structures.[21] These resonance structures affect the oxidation state of the metal as shown in Figure (0-3).

There are hundreds of cases where a coordinated catechol or catechol-like ligand is found to be best described as a coordinated semiquinone radical.[21] In cases where a phenylenediamine unit is coordinated to a metal center, assignment of oxidation states becomes very difficult. There is another possibly more serious problem. If a metal is surrounded by a noninnocent ligand environment, and an electron is removed from the metal, the metal may in turn oxidize the ligand. What *was* a potentially strong oxidizing agent has now oxidized the ligand fragment instead. What remains is a stabilized system which will not serve as an oxidant. It is very similar to dissolving a superacid in water. No matter how strong the superacid is, once it is dissolved in water, the acidity of the solution can be no greater than that of the hydronium ion.

These problems are particularly apparent for cases where we have synthesized metals in unusually high oxidation states, for example, Co(IV)[22] or Os(V)[23]. The

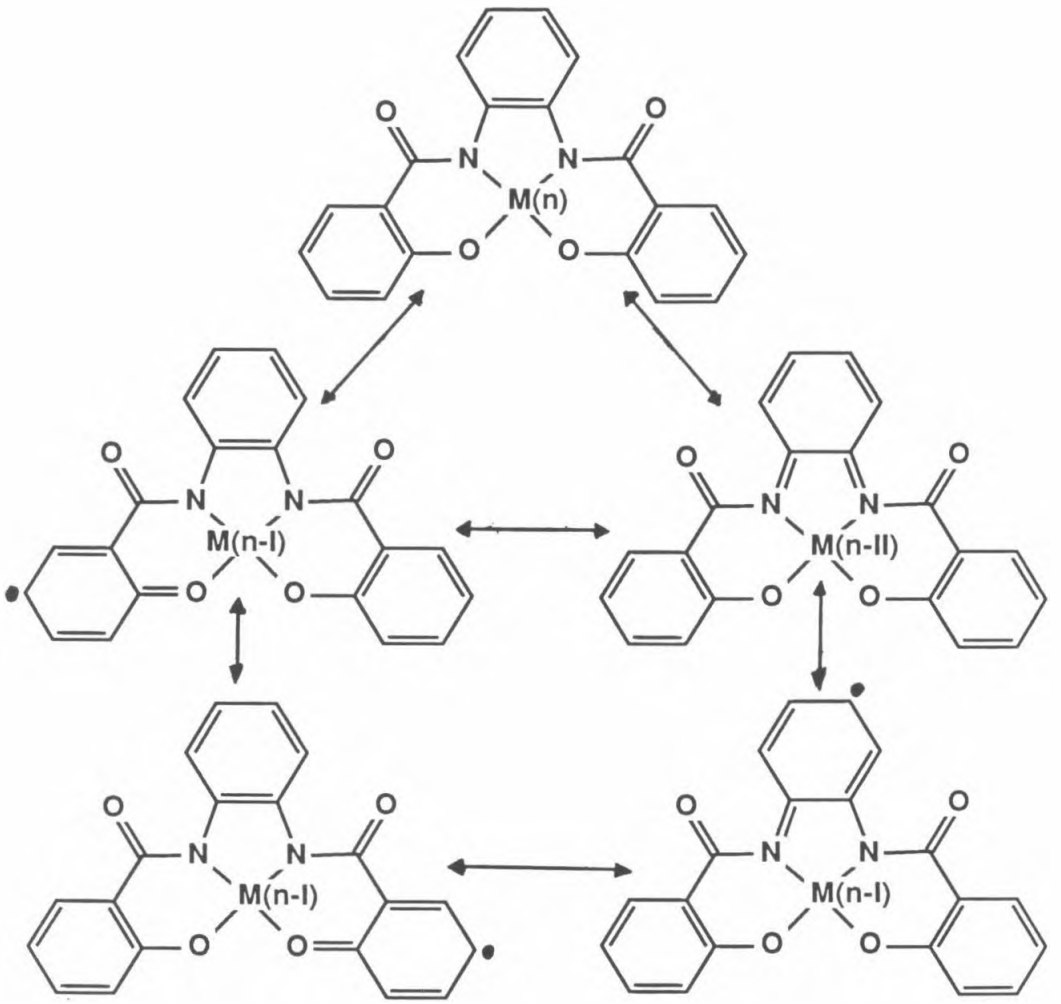


Figure 0-3: Resonance structures of a non-innocent PAC ligand, with corresponding changes in the oxidation state of the coordinated metal.

ligands involved in these species are noninnocent, and while there may not be any contributions from resonance structures where the metal is in lower oxidation states, merely the possibility of such contributions makes it difficult to prove that the metal center is in the proposed oxidation state. In the case of Co(IV), there are a number of resonance structures which can be written which put the metal in a lower oxidation state. Even the best physical data often are not sufficient to prove or disprove such contributions.[22] For these reasons, it was necessary to re-examine the ligands again, to eliminate oxidative sensitivity and noninnocence.

It is here, at the point where new and fascinating coordination chemistry has been observed and studied in great detail and where very high and reversible electrochemical potentials have been observed that this project begins. The goal has been to produce potent transition metal oxidants by designing ligands which will coordinate to metals, be stable to oxidizing conditions and be innocent. It is through such ligand complexes that a direct contribution to modern oxidation chemistry may be made.

It should be mentioned at this point that our ligands are not the only ligands which have been designed to deal with the problems of oxidation chemistry, nor is this approach the only way to attack oxidation chemistry. Other strategies in oxidation chemistry are to use biological systems, and work on generalizing their reactivity. A good example of this approach is that presently being carried out with horse liver alcohol dehydrogenase.[25] Another approach to the problem is to examine oxidizing agents which are known to be useful and to broaden their utility by modifying reaction conditions to improve selectivity, catalyst lifetime, reaction rates and/or stereoselectivity. Sharpless' work on selenium and ruthenium oxidations, along with his contribution of the asymmetric epoxidation catalyst, are excellent examples of this approach.[24]

Our particular approach, that of ligand modification, also receives attention. There are a number of bidentate, tridentate, tetradentate and even higher chelat-

ing ligands. Typically, the number of anionic donors has been limited to two. Some representative ligands which have been used by other groups to stabilize high valent metal centers are illustrated in Figure (0-4).[26] The ligand modifications designed in the following chapters are aimed at addressing the problems of oxidation chemistry described above. It will become clear that not only has more interesting coordination chemistry been discovered, but we also have uncovered interesting and new forms of oxidative reactivity. Osmium, copper and cobalt have been produced high and unusual oxidation states. Several families of oxidation catalysts have been produced, some using molecular oxygen as the stoichiometric oxidant.

This report begins with an explanation of the organic chemistry involved in ligand design and synthesis. The conception and synthesis of these ligands are explained. Next there is a description of the very rich coordination and oxidation chemistry of osmium systems studied. The progress in the chemistry of copper in higher oxidation states follows. Finally, the synthesis of unusual valencies of cobalt and their catalytic activities are described. It will be obvious that our design criteria have been well chosen.

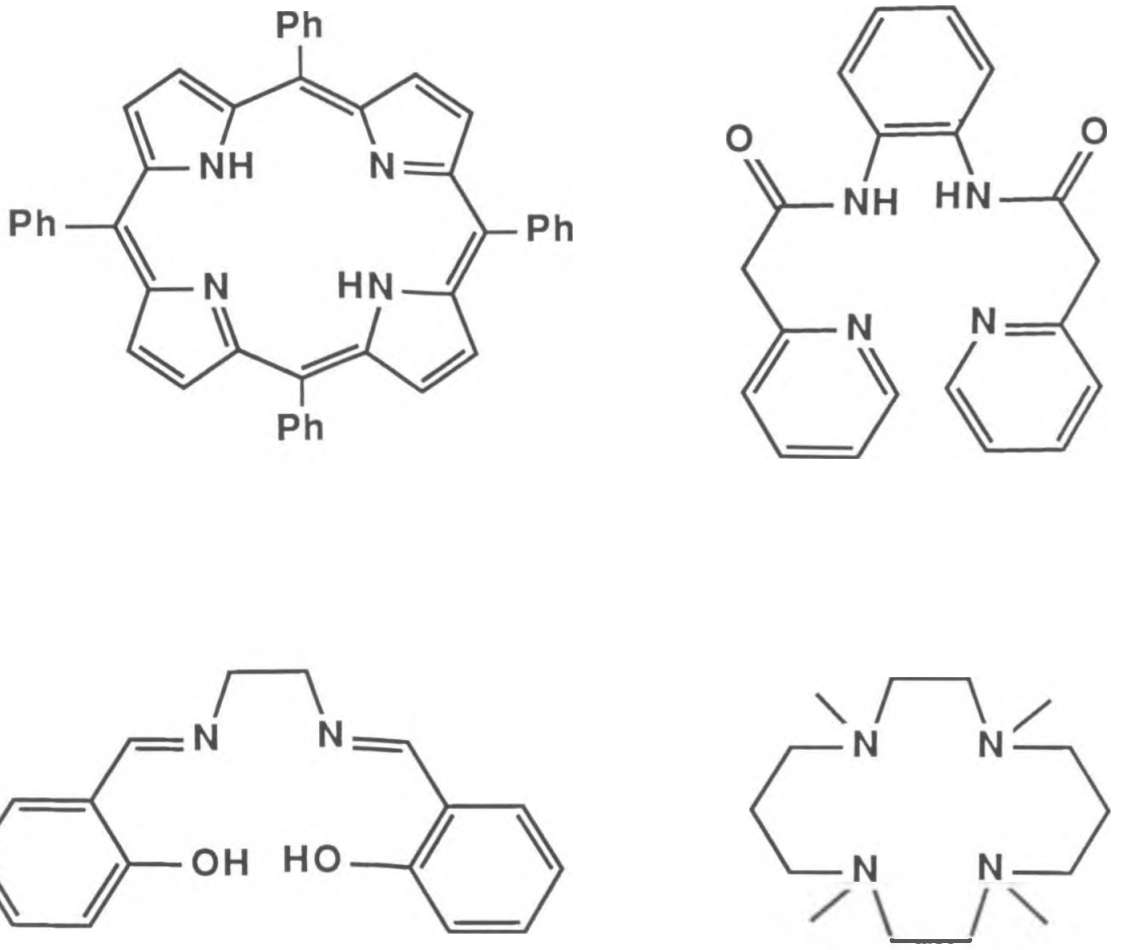


Figure 0-4: Ligands which have been successfully utilized to stabilize high-valent metals. Upper left, tetraphenyl-porphyrin; upper right, the Vagg ligand; lower left, SALEN; lower right, 1,4,8,11-tetramethyl-1,4,8,11-tetraaza-cyclotetra-decane. See text for references.

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CHAPTER ONE:
THE ORGANIC CHEMISTRY OF LIGAND DESIGN

In this section the design criteria and synthetic strategy of polyanionic chelating (PAC) ligands will be explained.

With few exceptions, the ligands utilized in the Collins research effort have been tetradentate, potentially tetraanionic ligands.[1] The first ligand of this type which was used to coordinate to transition metals was 1,2-bis-(2-hydroxybenzamido)-ethane, H_4-HBA-B, (1-1). Later chlorine substituents were introduced at the 3 and 5 substituents of the phenolic rings to protect these rings from oxidation.[1] This ligand (H_4-CHBA-Et, 0-1) as shown in the Introduction, has the great advantage of excellent coordination properties (metal complexes have been successfully made with cobalt,[2] copper,[3] nickel,[4] osmium,[5] ruthenium,[6] and titanium[7]) but the significant disadvantage of oxidative sensitivity. The ethylene unit in particular is readily decomposed under electrooxidative conditions (see above). To modify the ligand such that it will be more robust to oxidizing environments, the ethylene bridge was replaced with (1) a 1,2-phenylene bridge and (2) a 4,5-dichloro-1,2-phenylene bridge.[1] These ligands, while significantly more oxidatively resistant, are noninnocent. A general discussion of noninnocence may be found in the Introduction.

We decided to redesign the ligand system completely, with the goal of eliminating both the oxidative sensitivity and noninnocence dilemmas. Our strategy is organized as is shown in Figure (1-1), where the goals and problems of ligand design are described in terms of three problems which must be addressed simultaneously. Any ligand must be evaluated as to the ligand's potential stability under oxidizing conditions, noninnocence, and its ability to coordinate to the transition metal(s) of interest. Almost all ligands will decompose under *some* conditions, and not all ligands will coordinate to *every* metal in *all* available oxidation states. We must decide what we can accept in terms of these problems and ensure that no one problem becomes so severe that it would lead to failure of the experiments. Or, referring to the figure, we must see that we are not pulled to close to any one vertex. We must choose the appropriate ligand for the task at hand. If we

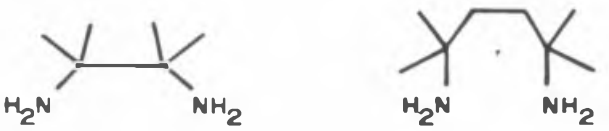
do not plan on suscepting the ligand to extreme conditions, perhaps we will be able to accept a certain degree of oxidative sensitivity. If we are not as concerned with oxidation state assignment, we may be willing to accept noninnocence. But if the ligand is unable to coordinate to a particular transition metal, it *must* be redesigned, even if this redesign introduces potential oxidative sensitivity or non-innocence. It is essential that we understand that there is a trade-off of one advantage for another at times. The perfect ligand may not exist. This notion of a trade-off will become a recurrent theme in our chemistry.

It is common practice in the Collins research effort to refer to the organic units which contain the oxygen donors as "arms" of the ligand and the unit which connects the amide donors as the "bridge." We chose to modify the arms first, while utilizing the bridges which have already proven useful. This strategy is illustrated in Figure (1-2).

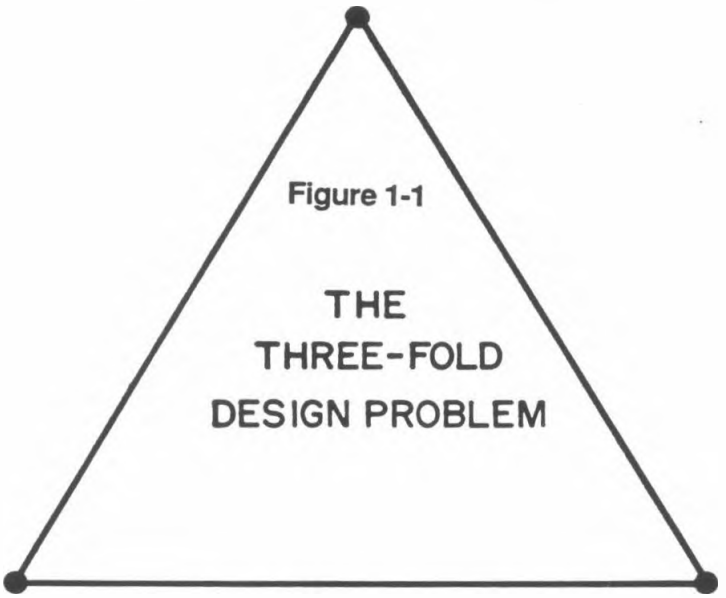
The first modification was replacement of the phenoxy or dichlorophenoxy donors with more strongly donating, aliphatic tertiary butoxy donors. Introduction of these strongly basic donor groups confers enormous differences in coordination and oxidation chemistry of the derived metal complexes. Therefore, we make a distinction between the two types of ligands. Class I refers to the ligands with phenoxy or dichlorophenoxy arms. Class II refers to ligands with tertiary butoxy donors.

The first and simplest Class II ligand, bis-1,2-hydroxymethylpropamido ethane, H_4-HMPA-Et, (1-2) was synthesized.

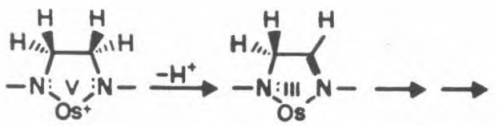
After several other methods failed, 1-2 was synthesized in 60 percent yield by heating two equivalents of methyl α-methyllactate and one equivalent of ethylenediamine in toluene at ca. 100° C. The reaction is shown in scheme (1-I). After one week of heating, the product began to precipitate from the reaction mixture. By an analogous procedure, a similar ligand, bis-1,2-hydroxymethylpropamido propane, H_4-HMPA-Pr, (1-3), was also synthesized. Isolation and characteriza-



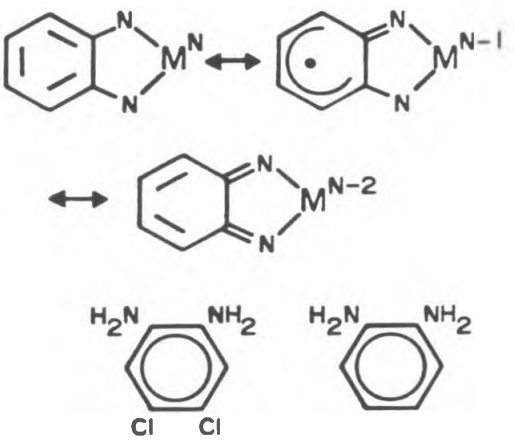
POOR COORDINATION PROPERTIES



OXIDATIVE SENSITIVITY



NON-INNOCENCE



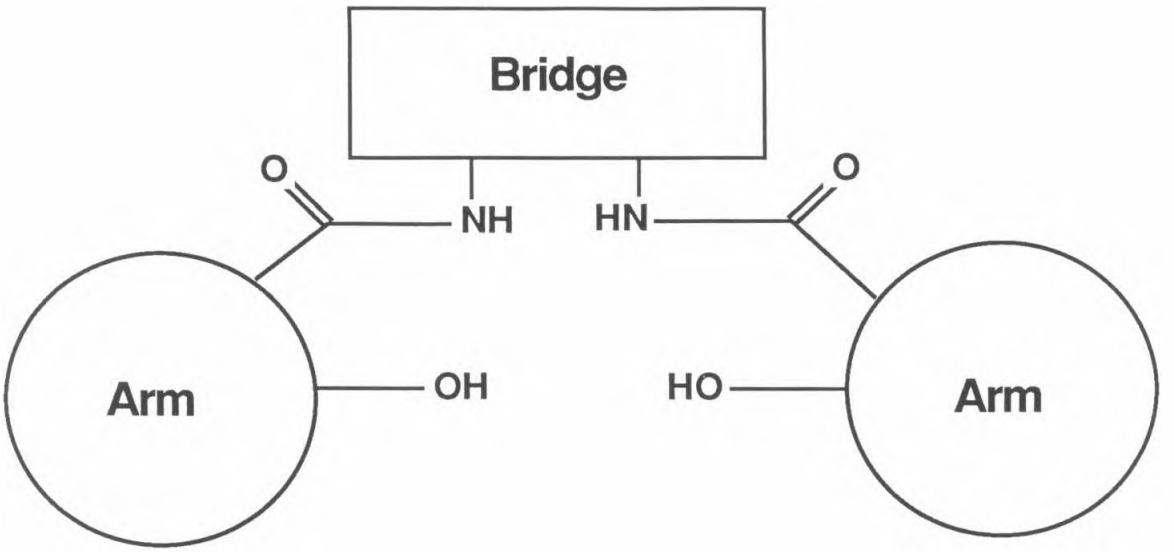
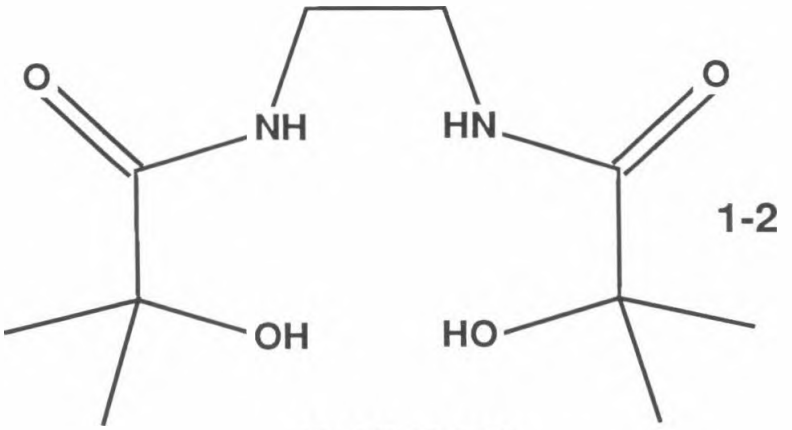
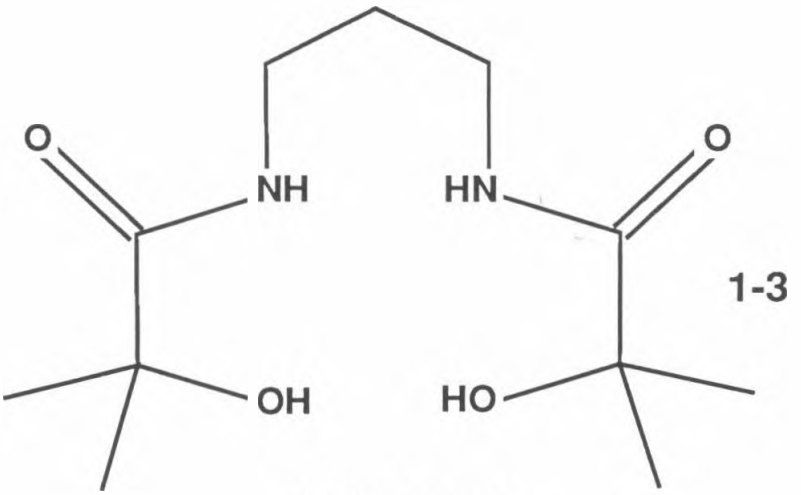


Figure 1-2: Ligand redesign strategy. Look at "Arms" and "Bridge" as general organic units which may be changed to modify the reactivity of the metal center. Change the "Arms" first, while utilizing present "bridges."



H_4-HMPA-Et

1,2-bis(2-hydroxy-2-methylpropamido)ethane



H_4-HMPA-Pr

1,3-bis(2-hydroxy-2-methylpropamido)propane

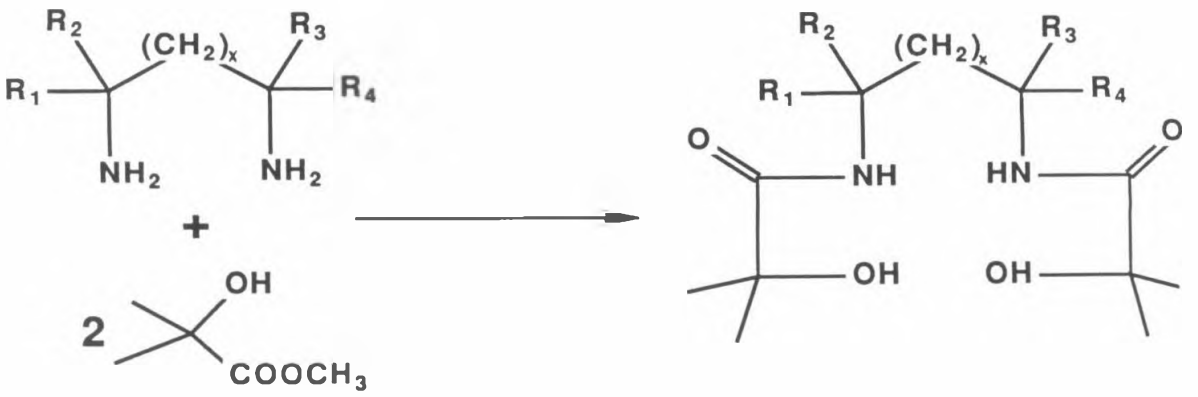
Figure 1-3: Class II Ligands.
Two new ligands incorporating tertiarybutoxy donors.

tion of the ligand were considerably more difficult. While the H_4-HMPA-Et ligand precipitated as a solid, H_4-HMPA-Pr was formed as an oil which required purification by chromatography. The ligand was characterized by NMR with spin-spin decoupling.[7]

Several other ligands could be synthesized similarly (see Scheme 1-I), but two limitations of this method soon became evident. *iso*-propyl and ethyl amine functionalities may be acylated by this method,[8] but we found *tert*-butyl amine functional groups to be completely unreactive under the conditions described above.[9] The method is also totally unsuitable for aromatic diamines, which yield benzimidazoles instead of the desired diamide ligands via the reaction illustrated in Scheme (1-II). This ring closure is commonly observed in reactions of *o*-phenylenediamines with acylating agents, and has been observed as a side reaction in the synthesis of several Class I ligands.[10]

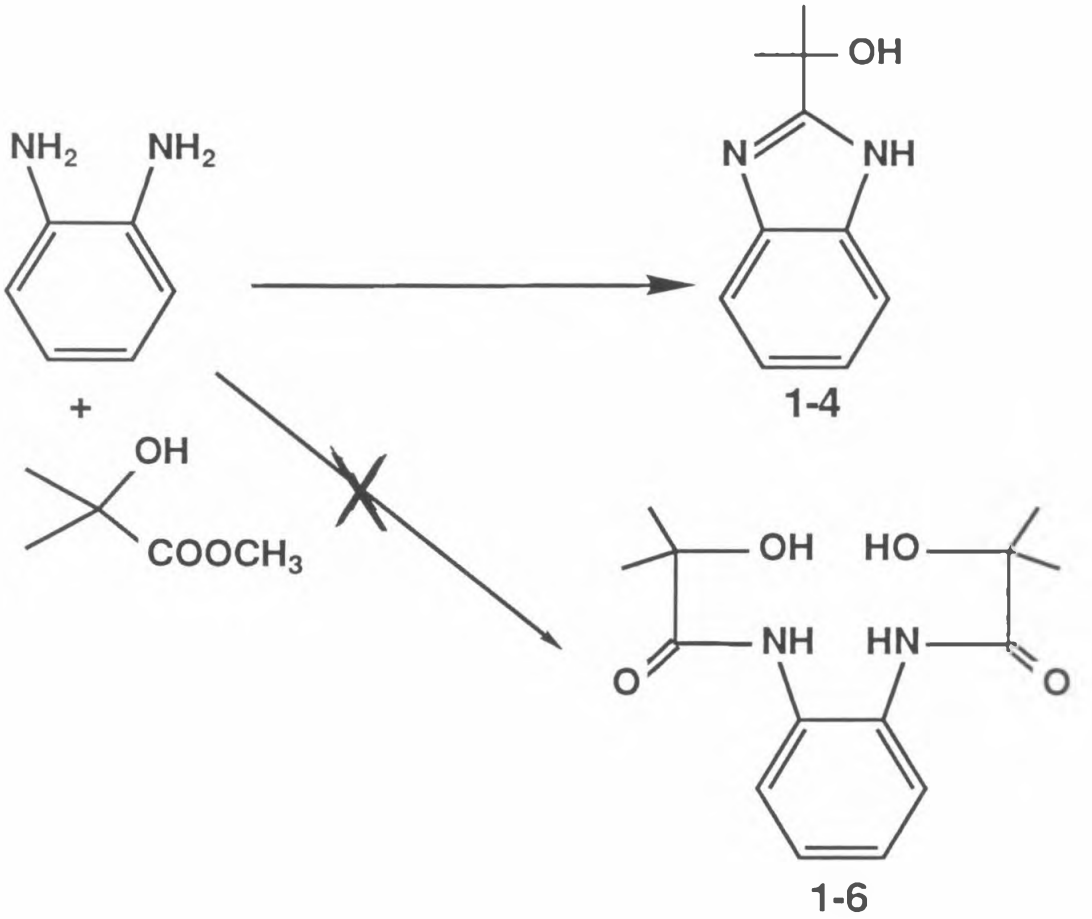
A general synthetic method clearly required a more active acylating agent. A protected acid chloride was the logical choice. While the acetyl group has been the standard protecting group for this type of reaction in the syntheses of the Class I ligands, we feared that such a choice would not have been a good one in this case. The acid chloride is highly hindered. An incoming nucleophile has two choices in such a case. It may react with the acid chloride functionality, or it may react with the ester of the protecting group.[11] When 2-acetoxy isobutyryl chloride reacts with nucleophiles, the latter reactivity pathway is usually observed. We chose to discourage this pathway through the use of a more hindered protecting group, pivolate (trimethyl acetoxy).[12] In this case, the ester group is substantially more hindered than the acid chloride unit, and so reactivity with the acid chloride is favored. A potential disadvantage of this approach is that the pivolate group is considerably more difficult to cleave than the acetate group, and more vigorous deprotecting conditions are necessary.[12] This has not proven to be a major problem.

The desired protected acid chloride (2-trimethylacetoxy-2-methyl-*iso*--



R_1	R_2	R_3	R_4	X
H	H	H	H	0
H	H	H	H	1
H	H	H	H	2
H	H	H	H	3
CH_3	H	H	H	0

Scheme 1-I: Synthesis of a variety of PAC ligands by direct condensation of amines with methyl -2-hydroxy-iso-butyrate



Scheme 1-II: Attempted synthesis of H_4-HMPA-B, leading to benzimidazole formation

butyryl chloride, 1-5) was synthesized in ca. 65 percent yield from the commercially available α-methyl lactic acid. Reaction with both aromatic diamines and diamines having *tert*-butyl amine-like functionalities, followed by basic deprotection yielded the desired ligands incorporating aromatic bridges, 1,2-bis-(hydroxymethylpropamido)-benzene, H_4-HMPA-B, (1-6), and 1,2-bis-(hydroxymethylpropamido)-4,5-dichlorbenzene, H_4-HMPA-DCB, (1-6a). The general reaction scheme is shown as Scheme (1-III).[13]

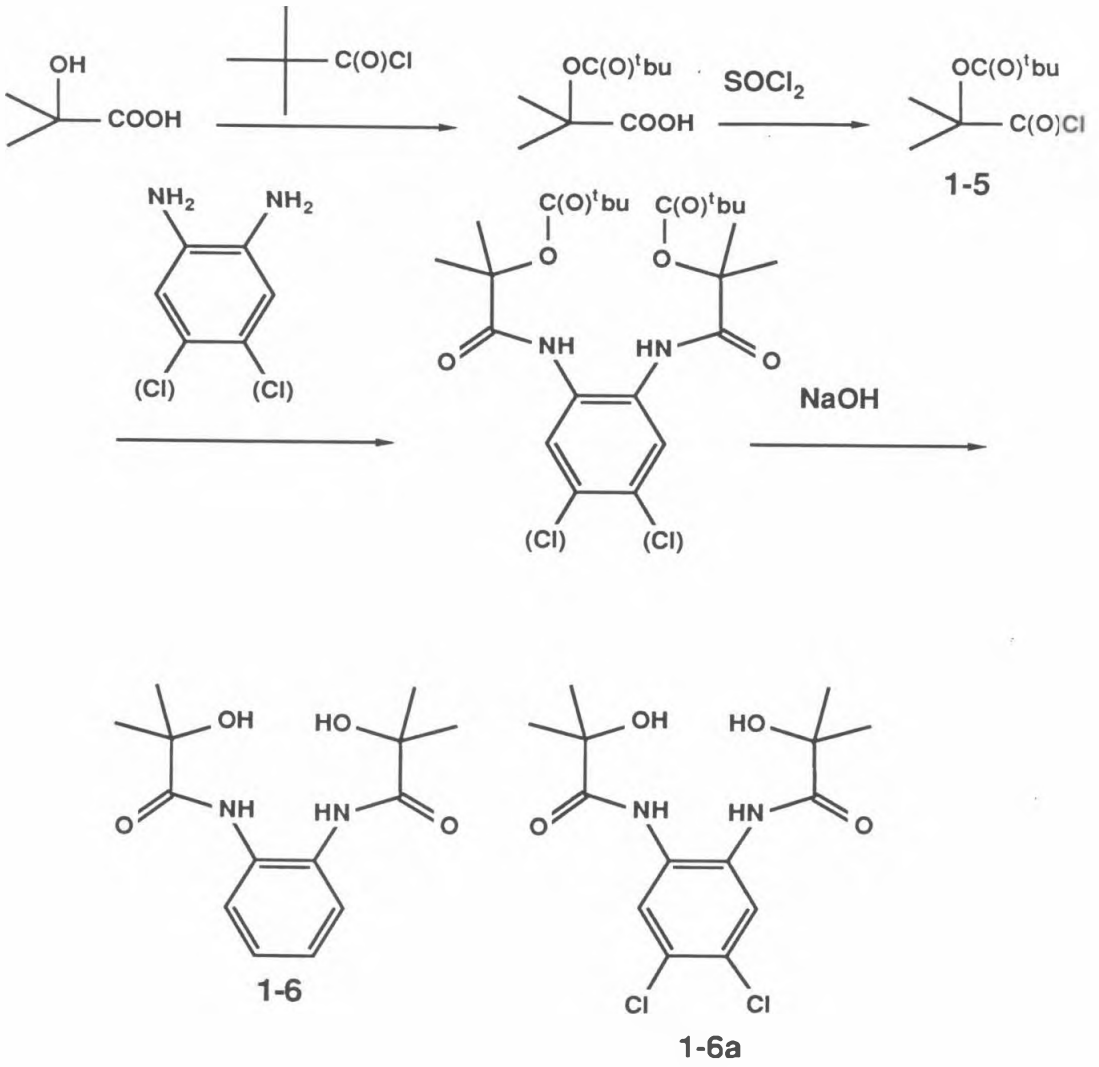
A critical examination of all of the ligands which we have synthesized based on the concepts outlined in Figure (1-1) will show that all of the Class II ligands synthesized suffer from one or more serious weaknesses. The flaws lie primarily with the choice of bridge. We stated that we would change the arms first, using the present bridges. At this point, the bridge problem had to be addressed.

In no case were we able to synthesize a metal complex from a ligand incorporating the 2,3-diamino, 2,3-dimethylbutane bridge. We believe that coordination of a ligand containing this unit would bring about severe gauche 1,2 methyl interactions. Such interactions would be highly unfavorable to coordination. It appeared necessary to remove these interactions by separating the methyl groups with a methylene unit. The logical candidate for the ideal bridge would be 2,4-diamino-2,4-dimethylpentane, (1-7).

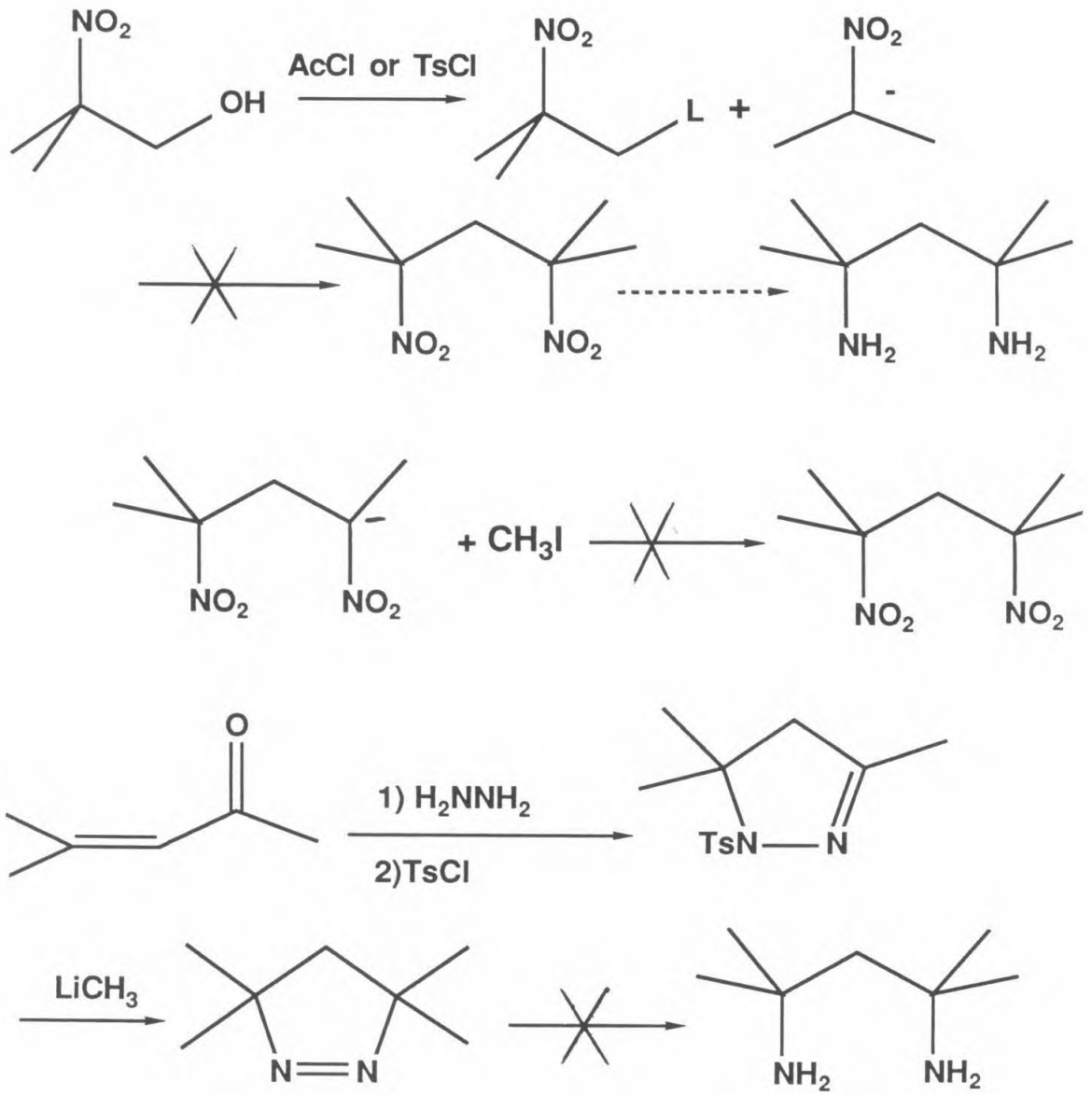
This compound had not been synthesized, nor had the corresponding dinitro compound (2,4-dimethyl-2,4-dinitropentane, 1-7a) which would be the logical precursor. Numerous attempts to synthesize (1-7) and (1-7a) were invariably unsuccessful.[14-18] Our attempts are shown in Scheme (1-IV).

It became obvious that making this compound would be exceedingly difficult. However, in our search for new synthetic routes to (1-7), we discovered 2,4-diamino-2,4-dimethyl-3-pentanone, (1-8). (1-8) is an excellent candidate for the desired bridge; it has several advantages over (1-7):

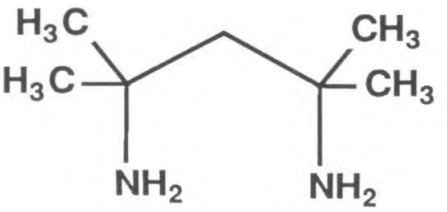
(1:) It is a known compound;



Scheme 1-III: Syntheses of H_4-HMPA-B and H_4-HMPA-DCB

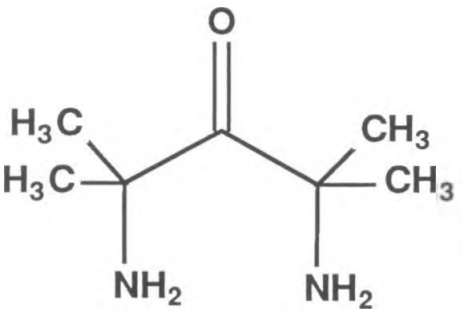


Scheme 1-IV: Attempts to synthesize 2,4-diamino-2,4-dimethylpentane



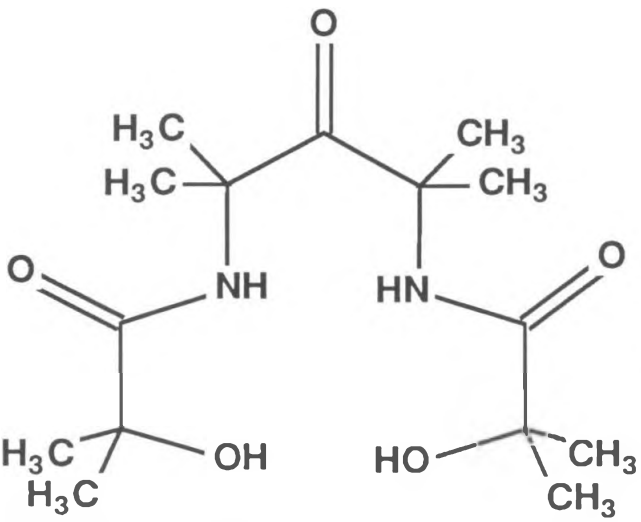
1-7

2,4-diamino-2,4-dimethylpentane



1-8

2,4-diamino-2,4-dimethyl-3-pentanone



1-9

2,4-bis(2-hydroxy-2-methylpropamido)-
2,4-dimethyl-3-pentanone (H_4-HMPA-DMP)

Figure 1-4: A desired bridge (top), the bridge utilized (middle) and the ligand synthesized incorporating this bridge (bottom).

(2:) Replacing the hydrogens with an oxo group will eliminate CH_3-H interactions which could discourage planar coordination;

(3:) The ketone group is a good IR marker;

(4:) The ketone functionality allows for future derivatization of the ligand.

Bromination of 2,4-dimethyl-3-pentanone, followed by reaction with sodium azide and subsequent reduction with ammonium sulfide gave the desired diamine in high yield.[19] Reaction with the protected acid chloride (1-5), followed by basic deprotection gave the desired ligand, 2,4-bis-hydroxymethylpropamido-2,4-dimethyl-3-pentanone, H_4-HMPA-DMP, (1-9) in ca. 35 percent yield from the starting diamine.

There remained one final modification of the ligand. This was to expand the ring sizes. The H_4-HMPA-DMP ligand is a 5,6,5 coordinator; that is, on coordination to a transition metal, it will form one six- and two five-membered rings. We wished to examine the effect of different ring sizes with the same donor environments. It is also known that the α-methyl lactate unit, when coordinated to high-valent metals, can decompose via acetone elimination.[20] This will be discussed further in Chapters Two and Four. We wished to avoid such a decomposition.

The proposed solution was to insert methylene groups into the ligand. This would produce a 6,x,6 (x = 5,6) ligand structure, that is, a ligand which, on coordination would form two six membered rings (through the arms) and one x membered ring (through the bridge) where x is five or six, depending on the choice of the bridge.

The key intermediate appeared to be 3-hydroxy-3-methylbutyric acid, (1-10). 3-hydroxy-3-methylbutyric acid[21] was prepared by a Reformatskii[22] reaction from acetone and α-bromo-*tert*-butyl acetate, followed by removal of the tertiary butyl group with trifluoracetic acid. Unfortunately, attempts to acylate the hydroxy acid with acid chlorides was unsuccessful. An alternative route to these com-

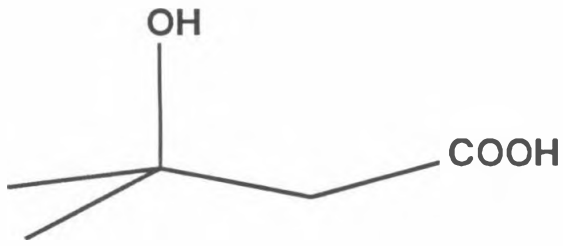
pounds was found.[23]

The hydroxy olefin, 2-hydroxy-2-methyl-4-pentene, (1-11) was benzoylated with benzoic anhydride in triethylamine with a dimethylaminopyridine catalyst.[24] The olefinic ester (1-12) was cleaved to form the acid (1-13) by a "purple benzene" oxidation ($KMnO_4$/water/benzene/tetrabutylammonium bromide).[25] The protected acid was converted to the acid chloride (1-14) with oxalyl chloride ($Cl(CO)_2Cl$).

Attempts to purify this material led to decomposition. (1-14) was used as isolated. Reaction of two equivalents of (1-14) with one equivalent of (1-8) yielded a mixture of two products from which the desired ligand precursor was isolated. Basic deprotection led to the desired ligand, 2,4-bis-(3-hydroxy-3-methylbutamido)-2,4-dimethyl-3-pentanone, (1-15).

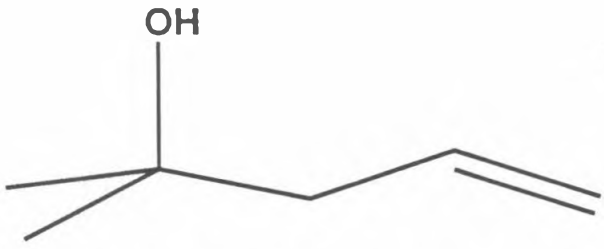
Similar procedures, substituting *o*-phenylenediamine and 4,5-dichloro-*o*-phenylenediamine for (1-8) led to analogous 6,5,6 ligands with aromatic bridges (1,2-bis-(3-hydroxy-3-methylbutamido)-benzene, (1-16) and 1,2-bis-(3-hydroxy-3-methylbutamido)-4,5-dichlorobenzene, 1-16a) The synthetic scheme is shown in Scheme (1-V).

The design and synthesis of the ligands used in this work have been described. The following chapters describe the interactions of these ligands with various metals.



1-10

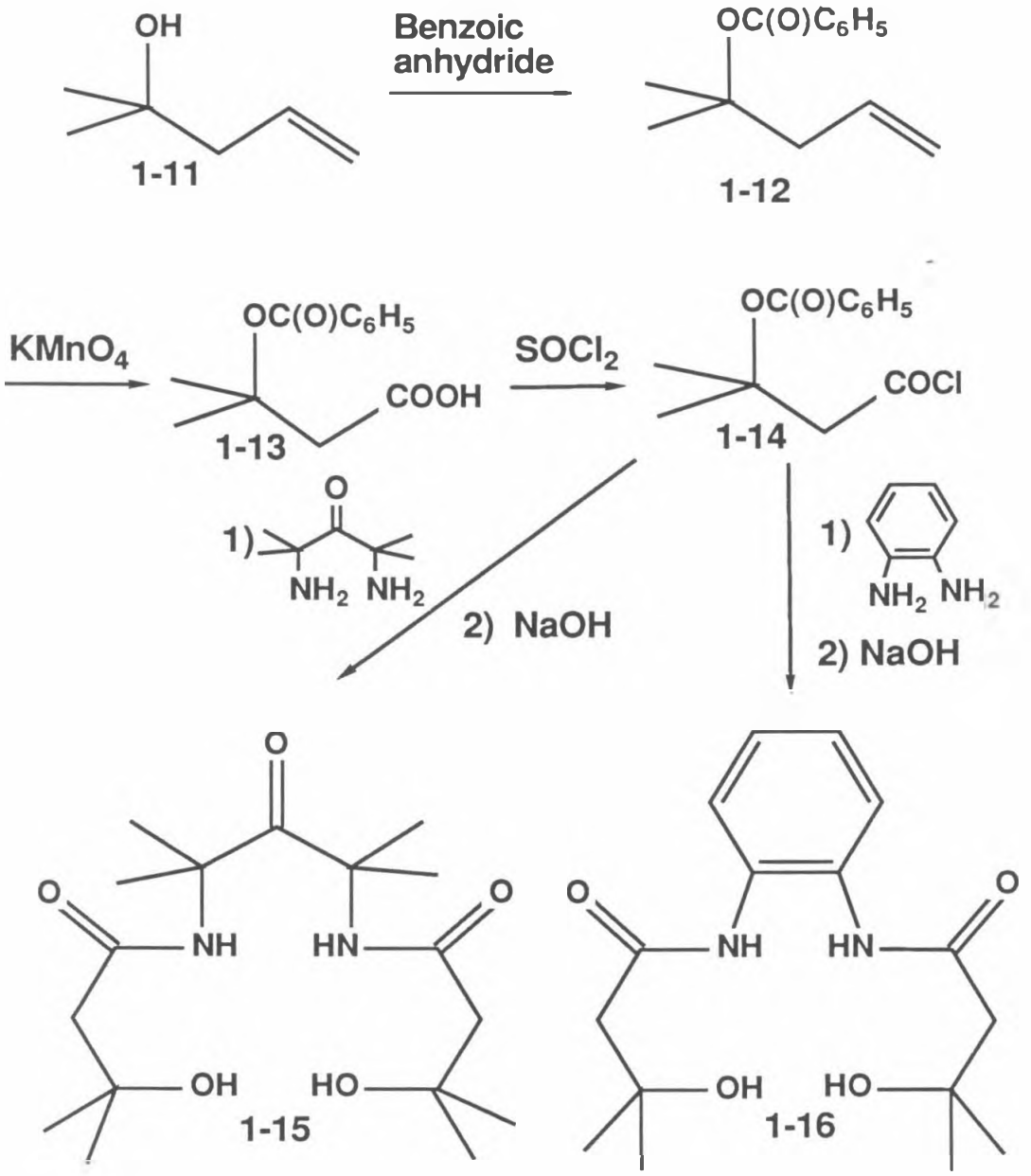
3-hydroxy-3-methylbutyric acid



1-11

2-hydroxy-2-methyl-4-pentene

Figure 1-5: Two starting materials in the synthesis of 6,x,6 ligands



Scheme 1-V: Syntheses of H_4-HMBuA-B and H_4-HMBuA-DMP

EXPERIMENTAL

Materials: All solvents were reagent grade (Aldrich, Baker, Malinckrodt, M.C.B., or U.S.I.) and were used as received. α-Methyl lactic acid (Aldrich), methyl-α-methyl lactate (Aldrich), trimethylacetyl chloride (Aldrich), ethylenediamine (Aldrich), 1.3-diaminopropane (Aldrich), thionyl chloride (Baker), oxalyl chloride (Aldrich), benzoic anhydride (Aldrich), o-phenylenediamine (Aldrich), 4,5-dichloro-1,2-phenylenediamine (Aldrich), 1,4-diaminobutane (Aldrich), dimethylaminopyridine (Aldrich), N-bromosuccinimide (Aldrich), tosyl chloride (Aldrich), sodium azide (Baker), 4-hydroxy-4-methyl-2-pentene (Malinckrodt), potassium permanganate (Baker), tetrabutylammonium bromide (Baker), pyridine (Baker), triethylamine (Baker), sodium hydroxide (Baker), 2-methyl-2-nitro-1-propanol (Lancaster) were all used as received. Analytical and preparative thin layer chromatography plates, 250 and 1000 μm, respectively, were silica gel GF (Analtech). Flash and gravity column chromatography were performed using Silica Gel Woelm, 30-80 mesh.

Physical Measurements: ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM 390 or on a JEOL FX90-Q spectrometer. Unless otherwise noted ^{1}H shifts are reported in δ ppm versus TMS as internal standard. IR spectra were recorded on a Beckman IR 4240 spectrophotometer. Elemental analyses were obtained by Larry Henling at the Caltech analytical facility.

1,2-bis-hydroxymethylpropamido ethane (H_4-HMPA-Et) methyl α-methyl lactate (9.1g, 0.77 mol) and ethylenediamine (2.3g, 0.38 mol) were heated in 100 ml toluene (100° C, three weeks). The brownish precipitate which formed was filtered off. This material was washed with 100 ml of CH_2Cl_2 and 20 ml of THF. 5.7g (65 percent) of a white solid were isolated. ^{1}H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 7.8-8.0 (br s, 2H, N-H), 5.3-5.5 (br s, 2H, O-H), 3.2-3.4 (d, 4H, -CH_2-CH_2-), 1.4 (s, 12H, CH_3) IR (cm^{-1}, nujol): 1650 ν(amide carbonyl); Anal. Calcd for $C_{10}H_{20}N_2O_4$; C, 51.70; H, 8.62; N, 12.06. Found: C, 51,59; H, 8.23; N, 12.02.

1,3-bis-hydroxymethylpropamido propane (H_4-HMPA-Pr) methyl α-methyl lactate (10.0g, 0.085 mol) and 1,3-diaminopropane (3.15g, 0.040 mol) were heated in 100 ml toluene (100° C, 3 days). A dark red oil formed which was reduced dryness under reduced pressure (0.005 torr). A small fraction was washed through a two inch plug of silica gel with methylene chloride followed by THF. The THF fraction was reduced to dryness on a rotary evaporator leaving 0.5g of H_4-HMPA-Pr as a white powder. ^{1}H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 7.7-7.9 (t, 2H, N-H), 5.3 (br s, 2H, O-H), 1.4-1.6 (t, 2H, -C-CH_2-C-) 2.9-3.2 (q, 4H, -N-CH_2-), 1.3 (s, 12H, CH_3) IR (cm^{-1}, nujol): 1645 ν(amide carbonyl); Anal. Calcd for $C_{11}H_{22}N_2O_4$: C, 53.64; H, 9.00; N, 11.37. Found: C, 53.72; H, 8.86; N, 11.43.

1,4-bis-hydroxymethylpropamido butane (H_4-HMPA-Bu) H_4-HMPA-Bu was synthesized in 32 percent yield using the same procedure as for H_4-HMPA-Et) substituting 1,4-diaminobutane for ethylenediamine.^{1}H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 7.6-7.8 (t, 2H, N-H), 5.2-5.4 (br s, 2H,O-H), 3.0-3.3 (q, 4H, -C-CH_2-CH_2-C-). IR (cm^{-1}, nujol): 1650 ν(amide carbonyl); Anal. Calcd for $C_{12}H_{24}N_2O_4$: C, 55.36; H, 9.29; N, 10.76. Found: C, 55.50; H, 9.18; N, 10.47.

1-(1-hydroxy isopropyl) benzimidazole Methyl α-methyl lactate (10.0 g, 0.098 mol) and o-phenylenediamine (4.6g, 0.043 mol) were refluxed in toluene under nitrogen (3 days). The reaction mixture was reduced to dryness on a rotary evaporator. A gummy solid remained which was washed with CH_2Cl_2 to yield 2.7 g of the product (20 percent yield). ^{1}H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 7.1-7.6 (mult, 4H, aromatics), 1.7 (s, 6H, CH_3). IR shows no stretch in the carbonyl region; Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.14; H, 6.82; N, 15.91. Found: C, 67.92; H, 6.89; N, 15.78.

1-tosyl-2-nitro-2-methylpropane 2-methyl-2-nitropropanol (12.5 g, 0.12 mol), tosyl chloride (21.9 g, 0.12 mol) and pyridine (10 ml) were refluxed in toluene (3 days). The reaction mixture was cooled, filtered, and reduced to dryness on a

rotary evaporator. The material was purified by flash chromatography on silica gel (80 CH_2Cl_2 / 20 THF). 11.6 g (40 percent) of product were isolated as a clear oil. ^1H NMR (δ, $CDCl_3$) 7.3-7.8 (mult, 4H, aromatics), 4.3 (s, 2H, -CH_2-), 1.6 (s, 6H, CH_3).

2-Methyl-2-(trimethylacetoxy)propanoic acid 2-Methyl lactic acid (30 g) and pivaloyl chloride (35.5 mL) were mixed in tetrahydrofuran (100 mL). Pyridine (36 mL, 1 equiv.) was added in aliquots (3 mL). The mixture was stirred (18 h) and the precipitate was removed by filtration. The solvent was removed on a rotary evaporator, and the residue was dissolved in dichloromethane, filtered, and crystallization was effected by slow removal of dichloromethane on a rotary evaporator to afford a white crystalline product which was dried at 60 ^{0}C under vacuum: yield 48 g (88.5%). ^1H NMR (δ, $CDCl_3$) 1.2 (s, 9H, $(CH_3)_3C$-), 1.6 (s, 6H, -$(CH_3)_2C$-).

2-Methyl-2-trimethylacetoxypropanoyl chloride. 2-Methyl-2-(trimethyl-acetoxy) propanoic acid (10 g) was stirred in thionyl chloride (10 mL, 18h). The excess SO_2Cl_2 was removed by distillation at room pressure under N_2. The acid chloride was distilled from the remaining oil (50-55 ^{0}C, 0.005 torr): yield 6.25 g (57%). ^1H NMR (δ, $CDCl_3$) 1.2 (s, 9H, $(CH_3)_3C$-), 1.6 (s, 6H, -$(CH_3)_2C$-); IR (cm^{-1}) 1800 ν_{CO} (acid chloride carbonyl).

1,2-bis(2-trimethylacetoxy-2-methyl)propamidobenzene. 2-Methyl-2-trimethylacetoxypropanoyl chloride (6.25 g, 29.1 mmol) was dissolved in dichloromethane (25 mL) and tetrahydrofuran (50 mL). 1,2-Phenylenediamine (1.5 g, 13.9 mmol) in THF (10 mL) was added followed by triethylamine (10 mL) and the mixture was stirred (18 h). The white precipitate was separated by filtration and the solvents were removed on a rotary evaporator to give a white solid: yield 6.0 g (91%). ^1H NMR data (δ, $CDCl_3$) 8.2 (broad s, 2H, N-H), 7.1-7.5 (m, 4H, C_6H_4), 1.7 (s, 12H, -$(CH_3)_2CO$-), 1.3 (s, 18H, $(CH_3)_3CC(O)O$-).

1,2-bis(2-hydroxy-2-methyl-propamido)-benzene

1,2-bis(2-trimethylacetoxy-2-methyl) propamidobenzene (11.3 g, 21 mmol) and sodium hydroxide (4 g, 100 mmol) were added to a mixture of methanol (100 mL) and ethanol (20 mL) and were heated under reflux (3 h). Analytical TLC (CH_2Cl_2/THF, 9:1) showed no starting material remained. The solvents were removed on a rotary evaporator and the residue was dissolved in acetone (200 mL). The solvent volume was reduced to 100 mL, the mixture was filtered, and the filtrate was passed through silica gel (2" in 60 mL scintered glass crucible). The solvent volume was reduced to 25 mL and dichloromethane was added to give a white solid product (4.05 g). A second crop was obtained by addition of diethyl ether to the mother liquor (1.4 g): Total yield 5.45 g (88%, 80% from starting diamine). ^{1}H NMR (δ, DMSO-d_6) 9.4 (s, 2H, N-H) 7.0-7.5 (m, 4H, C_6H_4) 1.3 (s, 12H, -$(CH_3)_2$CO-). IR (cm^{-1} nujol) 1660 ν_{CO} (amide). Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 60.02; H, 7.14; N, 9.99. Found: C, 59.65; H, 7.03; N, 9.92.

1,2-bis(2-hydroxy-2-methyl-propamido)-3,4-dichlorobenzene This material was prepared in 48% yield in an analogous manner to the compound described above with the exception that 4,5-dichloro-1,2-phenylenediamine was used in place of 1,2-phenylene. ^{1}H NMR (δ DMSO-d_6) 9.3-9.8 (s, 2H, N-H), 7.8 (s, 2H, C_6H_4), 3.3-3.7 (s, 2H, O-H), 1.3 (s, 12H, -$(CH_3)_2$CO-). IR (cm^{-1}, nujol) 1665 ν_{CO} (amide). Anal. Calcd for $C_{14}H_{18}Cl_2N_2O_4$: C, 48.17; H, 5.16; N, 8.02. Found: C, 47.85; H, 5.15; N, 7.97.

2,4-bis(2-hydroxy-2-methylpropamido)-2,4-dimethyl-3-oxopentane 2,4-Diamino-2,4-dimethyl-3-pentanone[19] (4.69 g, 27 mmol) and trimethylacetoxyisobutyryl chloride (10.83 g, 53.9 mmol) were mixed in THF (100 mL). Triethylamine (10.83 g, 53.9 mmol) was added leading to an exothermic reaction with formation of a white precipitate. The reaction mixture was stirred (18 h) and filtered. The solvent volume was reduced on a rotary evaporator to give a pale oil which was heated under reflux (12 h) in methanol (100 mL) with NaOH (0.320 g, 80 mmol). The reaction mixture was cooled, the solvents were removed on a rotary evaporator and the residue was stirred in acetone (100 mL, 12 h). The

white insoluble material (primarily sodium pivolate) was removed by filtration. The filtrate was again reduced in volume on a rotary evaporator. The oil was stirred in dichloromethane (200 mL, 1 h). An oily solid remained undissolved which was removed by filtration and an equal volume of hexane was added to the filtrate. The solvent volume was slowly reduced on a rotary evaporator giving the product as a white powder: yield 2.92 g (35% based on starting diamine). ^{1}H NMR (δ, $CDCl_3$) 7.5 (s, 2H, N–H), 2.82 (s, 2.5H, O–H plus residual H_2O), 1.7, (s, 12H, -CH_3), 1.2 (s, 12H, -CH_3). IR (cm^{-1}, nujol): 1710 ν_{CO} (ketone); 1650 ν_{CO} (amide). Anal. Calcd for $C_{15}H_{28}N_2O_5 \cdot 0.25(H_2O)$: C, 56.18; H, 8.88; N, 8.73. Found: C, 56.18; H, 8.53; N, 8.67. Water solvate quantified by ^{1}H NMR.

3-benzoyloxy-3-methyl butyryl chloride 3-benzoyloxy-3-methyl butyric acid was stirred (3 hr, 21° C) in oxalyl chloride. The oxalyl chloride was removed under vacuum (0.005 torr, 21° C), leaving a pale orange oil. Attempts to purify this oil led to decomposition and it was used without further purification. IR (cm^{-1}, nujol): 1802 ν(acid chloride); 1712 ν(ester).

H_2-P_2-HMBuA-DMP (P = benzoyloxy) 3-Benzoyloxy-3-methyl butyryl chloride (9.4 g, 0.0391 mol) and 2,4-diamino-2,4-dimethyl-3-pentanone were stirred in THF (50 ml). Triethylamine (5 g) was added, whereupon a white solid began to form, and the reaction mixture began to spontaneously rise in temperature. The reaction mixture was stirred (18 hr, 20° C) and the white solid (triethylamine hydrochloride) was removed by filtration. The filtrate was reduced to dryness on a rotary evaporator and chromatographed (85 CH_2Cl_2:15 THF) three times. The material was recrystallized from a mixture of CH_2Cl_2 and hexane to yield 7.3 g (65 percent from diamine) of pure product.IR (cm^{-1}, nujol): ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.5 (s, 12H, methyls), 1.8 (s, 12H, methyls),2.8 (s, 4H, methylenes), 6.6 (broad s, 2H, amide), 7.6-8.1 (mult., 10H, arom). 1650 ν(amide carbonyl); 1705 ν(ester carbonyl); 1730 ν(ketone); 3280 ν (NH).

H_4-HMBuA-DMP H_2-P_2-HMBuA-DMP(0.50g, 0.00091 mol) was dissolved in absolute ethanol (100 ml). Excess (0.30 g, .0075 mol) NaOH was added and the mixture was heated to reflux (3 hr). At this time, no starting material remained, as evidenced by TLC). The reaction mixture was cooled, filtered, and reduced to dryness on a rotary evaporator CH_2Cl_2. To the residue was added CH_2Cl_2 (200 ml) and the mixture was stirred (2 hr). Insoluble material was removed by filtration. The filtrate was reduced to dryness on a rotary evaporator and stirred with pentane (50 ml). Between 1 and 5 ml portions of CH_2Cl_2 were added to induce crystallization. After several minutes of further stirring, the deprotected ligand was collected by filtration (0.10 g, 32 percent yield). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.3 (s, 12H, methyls), 1.6 (s, 12H, methyls), 2.4 (s, 4H, methylenes), 6.6 (broad s, 2H, amide), 7.6-8.1 (mult., 10H, arom.). 1650 ν(amide carbonyl);IR (cm^{-1}, nujol): 1640 ν(amide carbonyl); 1710 ν(ketone); 3200-3400 ν(NH, OH). Anal. Calcd for $C_{17}H_{32}N_2O_5$: C, 59.32; H, 9.30; N, 8.14. Found: C, 59.09; H, 8.93; N, 8.38.

H_2-P_2-HMBuA-DCB 3-Benzoyloxy-3-methylbutyrylchloride (8.16 g, 0.0339 mol) and 3,4-dichloro-o-1,2-phenylenediamine (2.00g, 0.113 mol) were added to dry THF (80ml). Triethylamine (3.5 g) was added, initiating refluxing of the solvent and formation of a white precipitate (triethylamine hydrochloride). The reaction mixture was stirred (18 hr, 20° C), after which time the precipitate removed by filtration. The filtrate was reduced to dryness on a rotary evaporator and the residue was pumped (0.005 torr, 20° C, 3 hr) The residue was stirred in hexane (150 ml) and insoluble materials were removed by filtration. Addition of an equal amount of hexane to the filtrate induced slow crystallization of product. This was removed by filtration and set aside. The mother liquor, containing approximately equal quantities of the desired product and an unidentified impurity, was reduced to dryness on a rotary evaporator and chromatographed (3 times, 98 CH_2Cl_2:2 THF) to obtain additional product. This was combined with the original material removed by filtration to yield 3.2 g of pure produce (48 percent

based on diamine)^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.7 (s, 12H, methyls), 2.9 (s, 4H, methylene), 7.2-8.0 (mult, 12H, aromatic). IR (cm^{-1}, nujol): 1650 ν(amide carbonyl);1710 ν(ester carbonyl); 3230 ν(N-H).

H_4-HMBuA-DCB H_2-P_2-HMBuA-DCB (0.23 g, 0.000394 mol) was dissolved in methanol (100 ml). NaOH (0.25 g) was added to the solution and the resulting mixture was capped and stirred (10 days, 21° C). The reaction mixture was then reduced to dryness on a rotary evaporator and THF (100 ml) was added to the resulting oil. After stirring (1 hr, 21° C) insoluble impurities were removed by filtration. The filtrate was reduced to dryness on a rotary evaporator and the resulting oily solid was treated with CH_2Cl_2. The deprotected H_4-HMBuA-DCB ligand became a solid which was collected by filtration (0.090 g, 65 percent) ^{1}H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 1.2 (s, 12H, methyls), 2.4 (s, 4H, methylenes), 8.1 (s, 2H, arom.). IR (cm^{-1}, nujol): 1650 ν(amide carbonyl); 3200-3450 (broad) ν(OH, NH).

H_2-P_2-HMBuA-B 3-Benzoyloxy-3-methyl butyryl chloride (2.21 g, 0.0092 mol), *o*-phenylenediamine (0.33 g, 0.0031 mol) and triethylamine (1 ml) were stirred (18 hr, 21° C) in CH_2Cl_2 (10 ml) and THF (2 ml). A white precipitate (triethylamine hydrochloride) formed which was removed by filtration and the filtrate was reduced to dryness on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (100 ml), filtered, and an equal volume of hexane was added. Slow removal of CH_2Cl_2 on a rotary evaporator caused precipitation of the desired bis-protected ligand as a white solid. The filtrate was reduced to dryness on a rotary evaporator and chromatographed (2X, 96 CH_2Cl_2: 4 THF) to give additional pure product. Combined yield, 0.88 g (56 percent) ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.8 (s, 12H, methyls), 3.0 (s, 4H, methylene), 7.0-8.2 (mult., 14H, arom). IR (cm^{-1}, nujol): 1671 ν(amide carbonyl); 1715 ν(ester carbonyl); 3260 ν(NH).

H_4-HMBuA-B H_2-P_2-HMBuA-B (1.3 g, 0.00252 mol) was dissolved in

methanol (150 ml). To the solution was added NaOH (1.3 g). The reaction mixture was capped and stirred (10 days, 21° C). Following this the reaction mixture was reduced to dryness on a rotary evaporator, and the oil was treated with THF (100 ml). Insoluble impurities were removed by filtration, and the filtrate was reduced to dryness on a rotary evaporator. The oil was purified via preparative TLC eluting with 50 CH_2Cl_2:50 THF, giving the desired ligand as a white solid (0.80 g, 82 percent). ^1H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 1.2 (s, 12H, methyls), 2.4 (s, 4H, methylene), 4.8 (broad s, 2H, OH), 7.0-7.2 (mult., 2H, arom), 7.5-7.7 (mult., 2H, arom.), 9.4 (broad s., 2H, NH). IR (cm^{-1}, nujol): 1655 ν(amide carbonyl); 3180-3340 ν(OH, NH). Anal. Calcd for $C_{16}H_{24}N_2O_4$: C, 62.36; H, 7.89; N, 9.09. Found: C, 61.51; H, 7.44; N, 8.86.

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CHAPTER TWO:
OSMIUM

Osmium has been a metal of great interest; it posseses a rich variety of oxidation states and coordination environments.[1,2a]. Though relatively rare, osmium is a metal of great utility. In its lower oxidation states, osmium cluster compounds are useful as catalysts for carbon monooxide hydrogenation[3,4] and reduction of α,β-unsaturated aldehydes.[5] In its high oxidation states, osmium is involved in the selective *cis*-hydroxylation of olefins and amine transfer.[6] Despite the many oxidation states available, several are considerably less well understood than others, particularly in the range of higher oxidation states, these being Os(V), Os(VI), Os(VII), and Os(VIII).[1,2a]

Osmium(V) chemistry is extremely poorly understood. Prior to the contribution of the Collins research effort, there were only a small number of such compounds. These compounds were restricted to simple halo and oxo complexes. Both OsF_5[7] and OsF_6^{1-}[2,8] have been synthesized. These are obtained from reduction of OsF_6 in bromine or anhydrous HF. The analogous chloride complexes have also been synthesized by action of SCl_2 on OsO_4.[9] Recently, the $OsBr_6^-$ ion has been synthesized. Aside from these complexes, few other compounds have been shown to contain Os(V). Os(V) has been suggested to exist in both Os_2O_{10},[10] obtained by high temperature oxidation of osmium metal, and $[NH_3OsCl_4(N)OsCl_3NH_3NOsCl_4NH_3]^{3-}$.[2] Attempts to extend Os(V) chemistry to include a wider range of ligands have largely been unsuccessful. In several cases, complexes reported to contain Os(V) have been later shown to be impure mixtures.[11] When so little is known of this oxidation state, it is difficult to say much of its general reactivity.

While few Os(V) species have been isolated, Os(V) has been at times implicated as a reactive intermediate. An example is Meyer's $Os(trpy)(bipy)O^{3+}$.[12] Particularly interesting are two complexes which serve as catalysts for the epoxidation of olefins using iodosobenzene as the stoichiometric oxidant. Both complexes are isolated in the Os(III) oxidation state, and in both cases the researchers propose that these are oxidized (by oxygen atom transfer) to highly reactive Os(V)

oxo species.[13] It is this species which is believed to transfer oxygen to the olefin. Neither reactive intermediate has been characterized.

Comparatively more is known of Os(VI), particularly when in complexes of octahedral geometry. The five-coordinate species are not as well understood. Examples of five-coordinate Os(VI) are $OsCl_4O$[14] and $OsCl_4N^{-1}$.[15] Most other Os(VI) species are analogs of these compounds, where the halides are replaced with hydroxy or alkoxy groups. The range of donors is fairly restricted.[2a]

Os(VII) is extremely rare,[2] being well-characterized only in the case of $OsOF_5$[2a,c] and OsF_7.[2b] A one electron reduction of osmium tetroxide has also been observed.[16]

Os(VIII), the basis for a number of extremely useful oxidizing processes, is also quite rare. In general, Os(VIII) is better known and understood than Os(VII). The most common example is OsO_4 which may be obtained by combustion of osmium metal in air.[2a] Several pyridine and tertiary amine adducts of OsO_4 are also known.[2a] There is also a family of Os(VIII) species where one or more of the oxo groups are replaced by nitrido (or amido) groups.[17] The range of geometries is quite limited in these cases, as the vast majority of Os(VIII) species possess tetrahedral geometry. Several years ago, the syntheses of a number of octahedral Os(VIII) species were described.[18] The complexes contain oxo and nitrido groups *trans-* to each other, with biuret-related ligands in the plane in various stages of deprotonation. The compounds have not been fully characterized, however.

It is clear that the coordination chemistry of osmium in oxidation states higher than (V) is poorly understood. If indeed Os(V) is an intermediate in olefin epoxidation, more information concerning such species will aid in the design and optimization of such systems. In addition, as it is known that Os(VIII) species are quite reactive in atom transfer, production of such complexes with a wider range of ligands would likely lead to new forms of reactivity. With these goals in mind, we have attempted to use the new class of highly electron donating ligands

to stabilize osmium in its higher oxidation states. The Collins research program has been involved in this for several years now, as alluded to in the introduction, where a summary of the progress to date may be found; more detailed information may be found in the references.[19]

Novel Osmium(VI) Monooxo complexes

This represents one of the rarer classes of osmium complexes. The known compounds are generally intermediates in the OsO_4 catalyzed oxidation of alkenes to *cis*-diols.[2,20] One such complex has been structurally characterized (see below). Prior to this work, no such complexes with amide donors[21] or with six-membered chelating rings were seen.

In previous work in our group, $K_2Os(OH)_4O_2$ was observed to react with polyanionic chelating ligands to produce *trans*-$K_2Os(\eta^4\text{-PAC})O_2$ species (often referred to as *trans*-dioxo species). In such compounds, the ligand assumes a fully planar geometry on coordination. Note, however, that such ligands are 6,5,6 coordinators (see chapter one) incorporating phenoxy donors. The first ligand examined in this study was H_4-HMPA-Et, a 5,5,5 coordinating ligand incorporating tertiary alkoxy (much more strongly σ-donating), and, as might be expected, this ligand brought about a different reactivity altogether. Instead of observing instantaneous production of the *trans*-dioxo dianionic species, a neutral brick-red microcrystalline solid was obtained after 18 hours of reaction time. NMR, IR, Mass spectrometry, and elemental analysis led to the assignment of the structure shown in Figure (2-1).

In this compound, the osmium is in the +VI oxidation state, in the form of a five-coordinate monooxo species. The amide donors represent an important extension of the range of ligands which are available in such systems.

The infrared spectrum showed a very strong peak at 970 cm^{-1}.[20] Such a band is characteristic of an Os(VI)O unit. However, the stretch corresponding to the

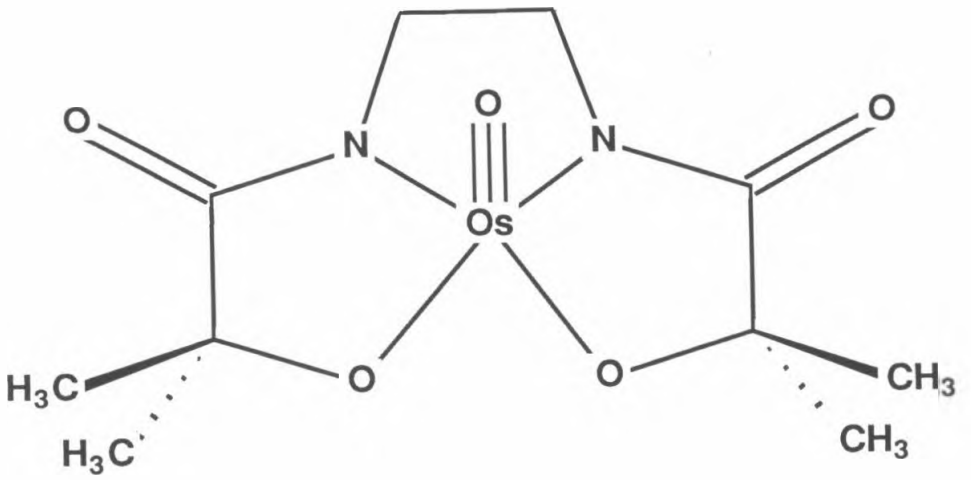


Figure 2-1: Os(HMPA-Et)O

amide carbonyl occurred at 1700 cm^{-1}. This is significantly higher than what is normally seen for an amide (approximately 1650 cm^{-1}).[22] We have usually observed the amide stretch to shift to a lower frequency on coordination of a metal.[19c] The shift to a higher frequency in this case was confusing. Where non-planar amide coordination[19a,b,f] is seen, the amide stretch is observed to shift to a higher frequency. We concluded, then, that some type of distortion of the ligand causing amide non-planarity was occurring as the ligand coordinated to the metal center. Building molecular models showed *cis*-α and *cis*-β[19a] coordination geometries to be unfavorable. However, a *trans*, purely planar conformation also appeared to be strained. In purely organic systems, small, simple rings (including 5-membered rings) usually pucker to some degree to relieve strain. We concluded that what is most likely is a slight puckering of the ligand, with the osmium atom sitting slightly above the plane of the four coordinating atoms. This was consistent with the structurally characterized Os(-O-CH_2-CH_2-O-)$_2$O which shows similar puckering.[20]

Similar reactivity was observed with a number of the other ligands. In reactions with $K_2Os(OH)_4O_2$, H_4–HMPA-Pr, H_4–HMPA-DMP, H_4–HMBuA-Et, H_4–HMBuA-B, and H_4-HMBuA-DCB all yielded Os(VI) monooxo species. In one case, that of H_4-HMPA-DMP, X-ray quality crystals were grown and a structure determination was performed. The Os(η^4-HMPA-DMP)O molecule crystallizes in space group $P2_1/c$. An ortep of the structure is shown as Figure (2-2). The osmium-apical oxygen atom ("oxo") bond length is 1.670(3) Å. This is identical (within experimental error) to that which is measured in the complex $OsCl_4O$,[14] which has very recently been characterized by gas phase electron diffraction. The lengths of the bonds between the osmium and the "equatorial" donor atoms are 1.930 Å and 1.899 Å for the Os-N(amido) and the Os-O(alkoxy) units, respectively. As predicted by IR spectroscopy and comparisons with structural data of similar molecules, the entire complex is distorted from perfectly square pyramidal geometry. The bond angles for the N-Os-oxo and O-Os-oxo units (both of

which would be 90° were the complex perfectly square pyramidal) are 111.8° and 108.1° respectively. This corresponds to the osmium atom being positioned 0.802 Å above the plane formed by the four "equatorial" donor atoms. This data can be compared to that obtained for the $OsCl_4O$ species. In the latter molecule, the osmium is positioned 0.709 Å above the plane of the four chlorine atoms. The explanation which these researchers give for the distortion is electron pair repulsion between the four chlorines and the filled, nonbonding d_{xy} orbital. Note that more distortion is observed in Os(η^4-HMPA-DMP)O than for in $OsCl_4O$. This can be explained by examining the relative "equatorial bond lengths." The Os-O and Os-N distances in Os(η^4-HMPA-DMP)O are significantly shorter than the Os-Cl distances in $OsCl_4O$. As the bonding groups are moved closer to the central atom, repulsion between these groups and the d_{xy} electrons should increase. This would bring about further distortion from planarity.[14]

The torsion angles and Dunitz parameters for Os(η^4-HMPA-DMP)O have been calculated and are included in Appendix A. The infrared evidence suggests that there is some distortion of the amide unit. Dunitz parameters are excellent tools for assessing the character of the amide. The values of $\bar{\tau}$, a useful measure of the relative twisting of the p-orbitals (or rotation of the C-N bond) making up the amide unit, are 4.1° and 6.2° for the two amides in Os(η^4-HMPA-DMP)O. These are within normal limits; there is little twisting in this compound. χ_C values for the two amides, which indicate the relative pyramidalization of the amide carbon atom, have been determined to be -0.6° and 0.3°. The values are both close to zero, indicating essentially no pyramidalization of this sort. The χ_N values, indicators of the pyramidalization at the amide nitrogen atom, are relatively large. χ_N equals 17.0° and 9.1° for the two amides. These values, which would be zero for a perfectly sp^2 hybridized nitrogen, demonstrate that there is significant pyramidalization of the amide nitrogen atoms. This accounts for the observed puckering of the molecule. Relatively large values for χ_N are significantly more common than for $\bar{\tau}$ and χ_C as pyramidalization at the nitrogen atom is

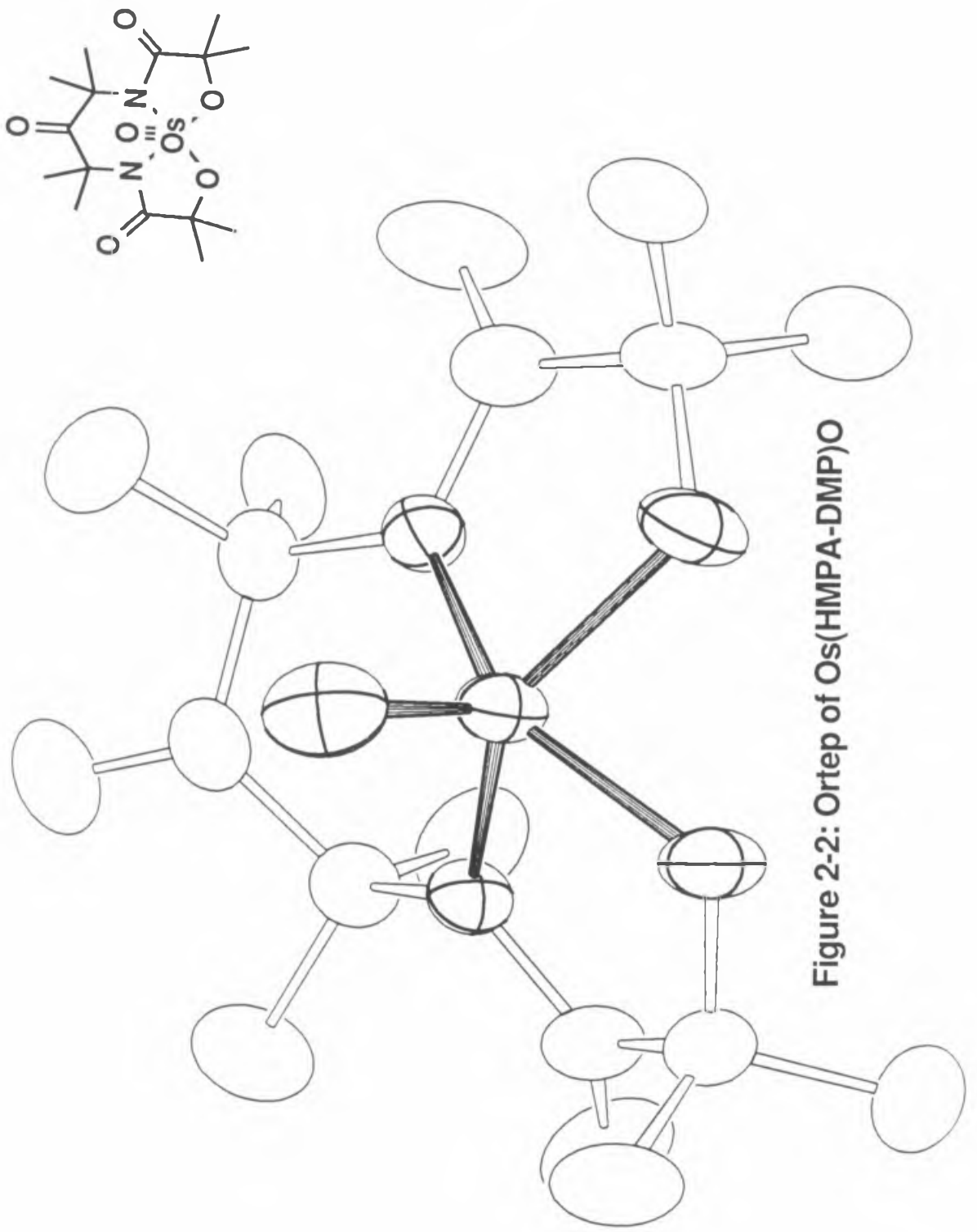


Figure 2-2: Ortep of Os(HMPA-DMP)O

energetically less demanding than pyramidalization at carbon or rotation about the C-N bond.[46] There is certainly some non-planar character to these amides, although it is not nearly as pronounced as in the cis-α and cis-β compounds synthesized by other workers in the Collins group.[19,32,33]

It was originally surmised that the Os(η^4-HMPA-Et)O complex assumed a puckered configuration because of the steric demands of the ligand. However, the crystal structure shows that even a ligand which can assume a planar conformation will pucker in a five-coordinate monooxo complex. This is similar to the structure which had been previously reported for the Os(-O-CH_2-CH_2-O-)$_2$O structure referred to earlier. Even in this case, while there are certainly fewer demands due to ring strain, it is known that cyclopentane rings prefer puckered conformations. Note that even in the $OsCl_4O$ case, where there are no rings involved in the "equatorial" ligands, the complex still assumes a geometry distorted from perfect square pyramidal.[20] It is reasonable to suppose that in the Os(η^4-HMPA-Et)O species, the preferred conformation of the ligand and the preferred geometry of the metal complex are coincidentally the same. To some extent this explains the inertness of Os(η^4-HMPA-Et)O, which will be described later.

All of the monooxo species belong to the C_s point group, possessing a single mirror plane passing through the osmium-oxo unit and bisecting the bridge.[23]

The complexes are easily characterized by their NMR spectra, which are usually quite simple. Exceptions are the complexes with unsubstituted aliphatic bridges. In the case of ethylene bridges, the C_s symmetry leads to there being a set of chemically inequivalent protons and a set of chemically equivalent, magnetically inequivalent protons. This leads to an AA'BB' pattern. A similar case is observed for the propane bridged compound.[22]

A particular advantage of these species is that they may be studied by mass spectrometry. A typical mass spectrum, that of Os(η^4-HMPA-DMP)O, is shown in Figure (2-3). In all cases, the parent ion and the expected fragment weight

distribution due to osmium isotopes are observed. In this mass spectrum, there are two important fragmentation processes leading to high molecular weight products. The first involves a loss of 28 amu. It is likely that this is a loss of carbon monoxide, possibly from the carbonyl group of the bridge. The second involves a loss of 58 amu which probably involves elimination of acetone, in varying degrees, for most of the Os(VI) monooxo species described in this work. The loss of acetone may be a common decomposition pathway under extreme conditions.

It is interesting to ask why monooxo species are observed in the case of Class II ligands, while *trans*-dioxo species are observed for Class I ligands.[19] There are a number of rationalizations; one would be that the increased electron density at the metal center induced by the Class II ligands causes the metal to behave as if in a lower oxidation state. Lower oxidation states are less likely to form oxo species. Another possibility is the that the difference in ring sizes of the ligands causes 5-coordinate distorted square pyramidal species to be favored in some cases and 6-coordinate octahedral species in others. Also, it is possible that in the Class I ligands, the monooxo species would polymerize and so not be observed as such, while the increased steric bulk of methyl substitution of Class II ligands prevents this from occurring.

No one of these factors accounts for all that is observed. It is likely that all these factors contribute to the observed reactivity. Some light is shed by the observation that the Os(VI) complex of the H_4-HMPA-DMP ligand can be isolated as either the *trans*-dioxo species or as the monooxo. In the preparation of the Os(VI) monooxo species, a mixture of the *trans*-dioxo and the monooxo species is produced. Addition of several drops of trifluoroacetic acid converts the mixture entirely to the monooxo species. Since it is easiest to purify the Os(VI) species in the neutral form, this procedure is usually followed in the preparation. An equilibrium exists between the monooxo and *trans*-dioxo forms; this can be observed by NMR. The NMR spectrum of the monooxo species shows four sharp singlets (as expected for a molecule with eight methyl groups and C_s symmetry).

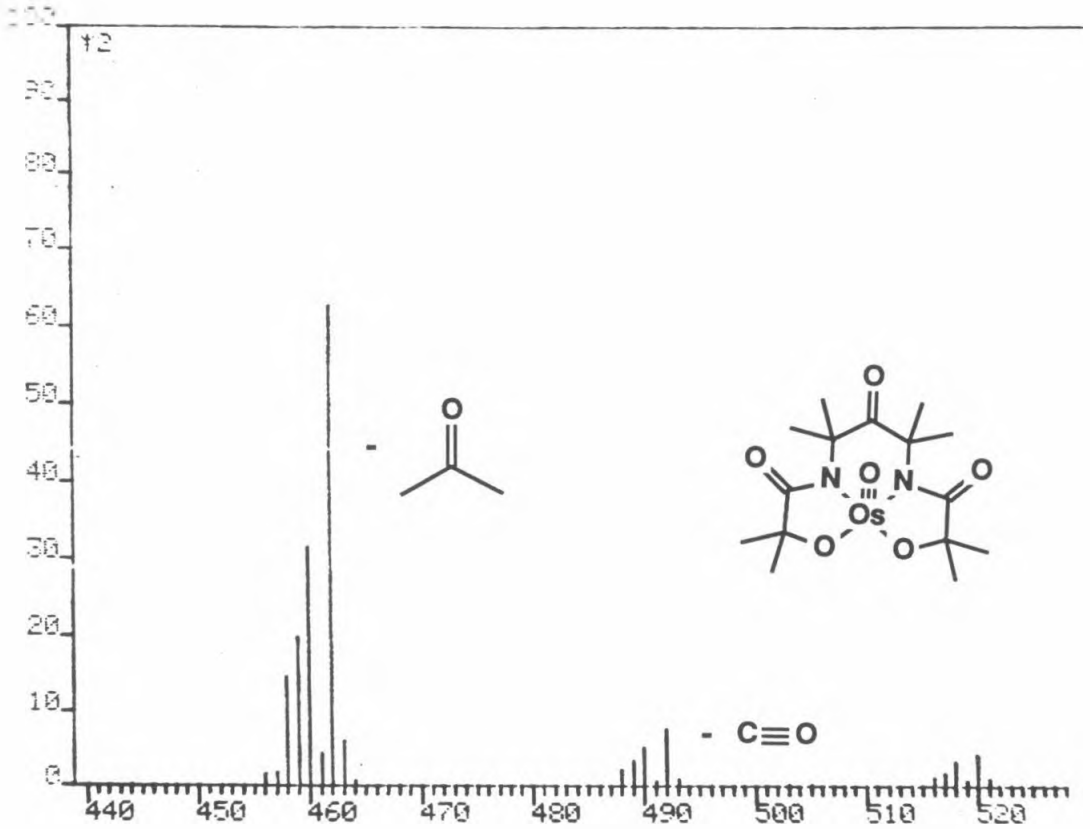


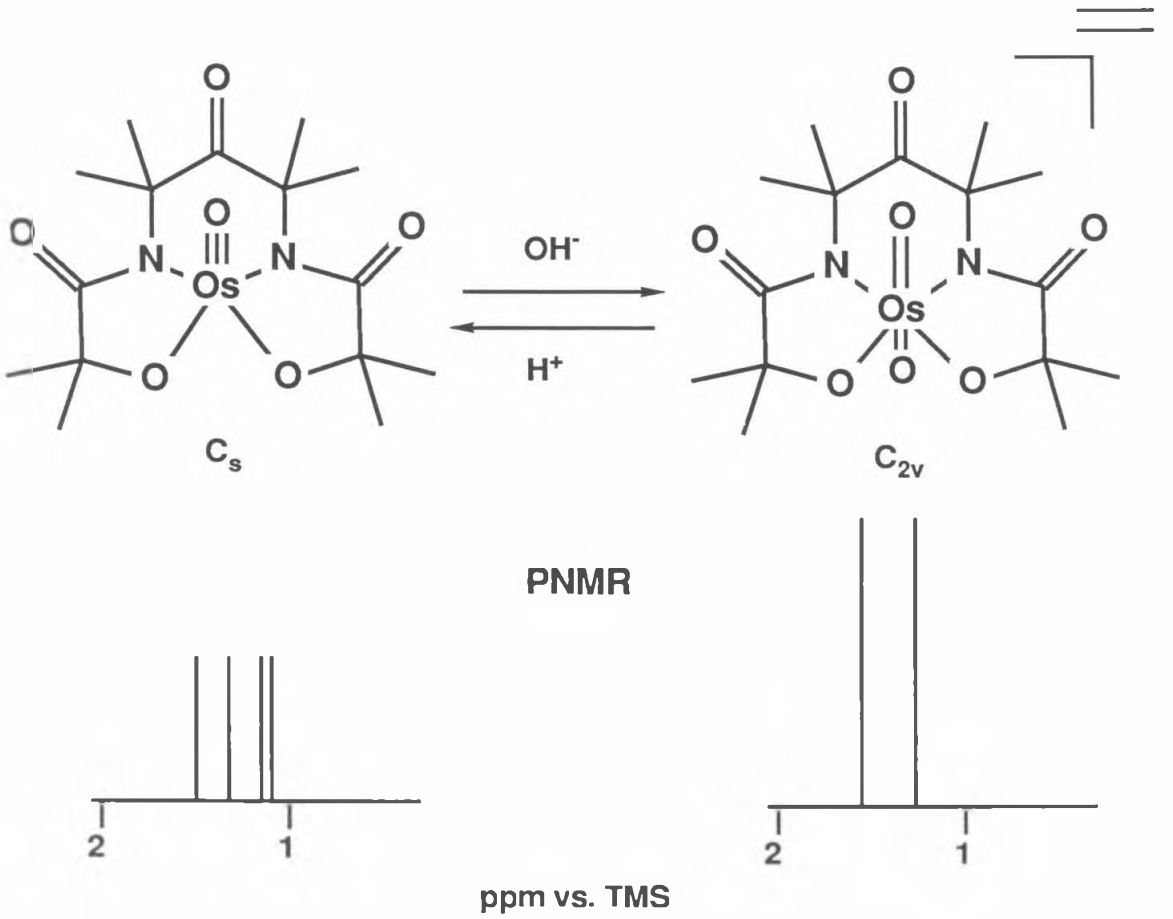
Figure 2-3: Mass spectrum of Os(HMPA-DMP)O

Addition of sodium hydroxide causes the singlets to broaden. Further addition of sodium hydroxide brings about the appearance of two sharp singlets (indicative of the *trans*-dioxo species, C_{2v} symmetry).[23] Addition of trifluoracetic acid regenerates the four peak NMR spectrum of the Os(η^4-HMPA-DMP)O molecule. The reaction is freely reversible, and the conversion can be repeated several times (although dilution makes the species more difficult to observe). In no case could both species be observed at once, however. It is likely that the interconversion occurs rapidly on the NMR time scale. Similar behavior is observed for the Os(η^4-HMPA-Pr)O complex. The interconversion is illustrated in Scheme (2-I). Note that in these cases the equilibrium is an acid-base equilibrium, not a redox equilibrium. The oxidation state of the metal remains unchanged at +VI.

For a particular ligand, monooxo and *trans*-dioxo species are not mutually exclusive. The experiments described above suggest that observation of one species may also be due to reaction conditions favoring one species relative to another. It is difficult to dissect out the factors favoring one form over another. If the ligand cannot assume a planar conformation, the *trans*-dioxo species will not be observed. If the monooxo polymerizes, it will not be observed (at least not as a monomer). If *trans*-dioxo complexes of class I ligands are treated with acid, insoluble black materials result (possibly polymers, although they have not been characterized). In addition, there is no doubt that the electronic nature of the ligand is also a factor, at least affecting the position of the monooxo/*trans*-dioxo equilibrium. (A related phenomenon is seen for cobalt systems.[24] This will be discussed later.) It is clear that even within our framework of two anionic nitrogen and two anionic oxygen donors, relatively minor changes in the ligand can lead to substantial differences in reactivity at the metal center.

Electrochemistry

For many of the Os(VI) monooxo species synthesized here, reversible, one electron reductions to form the Os(V) species were observed. The potentials of the



Scheme 2-I: Illustration of the interconversion of Os(VI) monooxo and transdioxo species

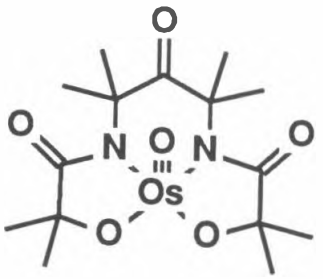
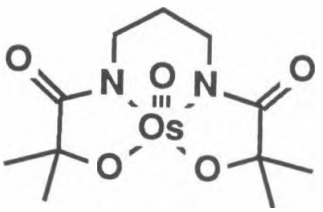
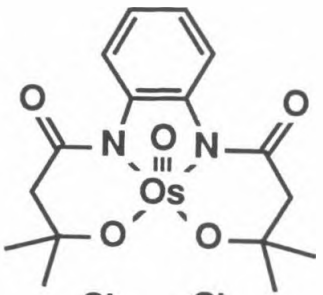
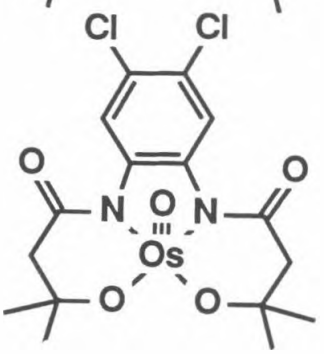
Os(VI)/Os(V) reduction are listed in Table (2-I). In the cases where the ligands are completely devoid of aromatic groups, the potential can be ascribed to a Os(VI)/Os(V) couple with confidence. If aromatic groups are involved, oxidation state assignment may be clouded. However, the aromatic groups of Os(VI) these monooxo compounds, as written, are fully reduced. A valid objection to this argument is that the Os(VI) monooxo species may indeed involve oxidation of the aromatic moiety and so not be pure Os(VI) species. Such prior ring oxidation would allow the reducing electron to enter a molecular orbital primarily centered in the aromatic ring. However, research with Os(VI) catecholate systems suggests that these are probably best described as Os(VI) and that there is little ligand oxidation. Such oxidation is even less likely in the better-donating Os(VI)-Class II PAC systems.[25]

The potentials shown in Table (2-I) are in general agreement with what we would expect based on our knowledge of Bronsted basicity. Aliphatic amides are more strongly basic than are aromatic amides, and so the complexes of the former should be more electron rich, and, therefore, harder to reduce. This is observed. Chlorine substituents on the aromatic ring raise the observed potential by approximately 55 mV each. This is consistent with what has been previously observed in the Collins research group. One observation which is confusing is that the Os(η^4-HMPA-Pr)O complex is reduced at a potential 290 mV more negative than the Os(η^4-HMPA-DMP)O complex. It is difficult to rationalize this solely on the basis of different electron donating or withdrawing substituents on the substituted bridge. It is conceivable that there is a structural difference between the two complexes. A crystal structure of Os(η^4-HMPA-Pr)O would be very informative; unfortunately we have been unable to grow suitable crystals.

We were able to isolate the reduction product of Os(VI)(η^4-HMPA-DMP)O. Electrochemical reduction by passage of 1 Faraday per mole of Os(VI) starting material successfully produced the reduced product which was dark green in solution. Attempts to separate the product from the large excess of supporting

FORMAL POTENTIALS FOR MONOOXO COMPOUNDS

V vs. Fc^+ /Fc

	E° (VI/V)
	-0.81
	-1.10
	-0.68
	-0.57

electrolyte failed. To circumvent this problem, the compound was reduced with a sodium amalgam. The product was highly air sensitive and appeared to rapidly revert to the Os(VI) species on standing in air. Isolation was effected by cannulating the Os(V) solution directly into a flask containing degassed pentane. The product precipitated as a pale green solid.

We were interested in the effect of a one electron reduction on the bonding in the Os(η^4-HMPA-DMP)O compound. One possibility is that the electron would enter a π^* orbital of the Os=O unit. If this were the case, the IR stretching frequency (970 cm^{-1} for the neutral compound) would shift to a significantly lower value. The Os=O stretching frequency does not change significantly on reduction, decreasing only 5 cm^{-1} to appear at 965 cm^{-1}. It seems that the osmium-oxo bond is not greatly perturbed. The amide stretching frequency, however, shifts from 1700 cm^{-1} to 1600 cm^{-1}. This suggests that there is a gross change in the geometry of the complex. The ligand seems to assume a planar geometry on reduction of the complex. The relatively small shift in the Os=O stretching frequency also suggests that the LUMO of the Os(η^4-HMPA-DMP)O species into which the reducing electron goes has relatively little Os=O π-antibonding character.

This Os(V)-oxo species is very interesting as it is one of a very small number of Group VIII metal oxo species where the metal is in the (+V) oxidation state. Such a system may be looked at as a model compound for the Fe(V)O intermediate of cytochrome P-450. However, it is a model only in that it would be isoelectronic. While the Fe(V)O species is a powerful oxidant, the Os(V)O species is strongly reducing.[26]

It seems that the ability of the coordinating ligand to assume several conformations has an enormous effect on the reactivity of the corresponding osmium complex. The ethylene bridged ligand is only reduced quasi-reversibly, while utilizing ligands with slightly larger ring size allows both puckered and planar

conformations. Great care must be taken in choosing appropriate ring sizes. In no case were we able to coordinate a ligand containing a seven-membered ring to osmium (or to any metal). This is not greatly surprising, as few 7-membered ring metallocycles are known. In addition, the H_4-(2,4-bishydroxymethylbutamido)-2,4-dimethyl-3-pentanone (H_4-HMBuA-DMP) ligand did not coordinate to osmium. Attempts with other metals were unsuccessful also. In high valent coordination chemistry of osmium with polyanionic chelating ligands, there seems to be a general rule: 5,5,5 coordination allows only puckered geometries; 6,5,6 and 5,6,5 coordination permits both puckered and planar conformations; x,7,x and 6,6,6 ring forming ligands will not coordinate.[27] We have not examined systems which would be 6,5,5 or 5,6,6 coordinators; these systems might be instructive but the syntheses of the ligands would be difficult. Such rules are helpful in designing new systems.

Chemical Reactivity of Osmium Complexes

The Os(VI) monooxo species of the polyanionic chelating ligands were found to be resistant to a number of chemical oxidants including peroxides, hydroperoxides, osmium tetroxide, bromine and Ce(IV). Nor were electrochemical oxidations, reversible or otherwise, observed even sweeping to the limiting potential of the solvent (CH_2Cl_2 or acetonitrile). The electrochemistry of Os(η^4-HMPA-DMP)O was examined using liquid sulfur dioxide as the medium. Much higher potentials can be observed in liquid sulfur dioxide than typical organic solvents. If the supporting electrolyte employed is tetrabutylammonium perchlorate, potentials of up to 3.1 V vs. Fc^+/Fc can be observed.[28] If the tetrafluoroborate salt is used as the supporting electrolyte, the window of oxidation can be extended to approximately 3.7 V vs Fc^+/Fc.[29] A number of factors contribute to the wider range of potentials which is possible using liquid sulfur dioxide. One is that the solvent itself is very difficult to oxidize. Another important factor is that while oxidized species may react with the solvent, at the low temperatures employed when using

sulfur dioxide (below -40° C, the boiling point of sulfur dioxide) such reactions are much slower. Therefore reversible couples may still be observed.[30] Even at such higher potentials, no oxidations were observed. These observations attest to both the stability of the Os(VI)=O unit and to the overall resistance to oxidation of the Class II polyanionic chelating ligands, particularly HMPA-DMP. While it is encouraging that the HMPA-DMP ligand, when coordinated to a metal center, is stable under extremely oxidizing conditions, it would be premature to conclude that the ligand will be conducive to stabilizing metals in high oxidation states. The goal has been to synthesize ligand environments compatible with high valent metal centers. Such high valent metal centers would be expected to (and have often been observed to) irreversibly oxidize the ligand.[31] Since no oxidation state higher than +VI, that of the starting material, was produced by these experiments, we cannot conclude that the ligand would not be degraded by a metal center in an unusually high valency.

Previous workers in the Collins research effort have had more success in oxidizing osmium compounds with polyanionic ligands in the +IV oxidation state, where the complexes are devoid of oxo ligands. It is from these Os(IV) species that we have extracted much of the information concerning the relationship between the nature of the PAC ligands and the reactivity of the corresponding coordination complexes.[19,31-33]

We were unable to cleanly reduce Os(η^4-HMPA-Et)O chemically. However, Os(η^4-HMPA-DMP)O, Os(η^4-HMPA-Pr)O, Os(η^4-HMBuA-B)O, and Os(η^4-HMBuA-DCB)O are all cleanly reduced to octahedral *trans*-Os(IV)-bispyridine complexes.

When the *trans*-K_2Os(η^4-Class I PAC)O_2 complexes were reacted with triphenylphosphine (in the presence acid), complexes of the type *trans*-Os(IV)(η^4-Class I PAC)(ϕ_3P)$_2$ were obtained. These compounds could undergo substitution reactions with pyridine to produce either *trans*-Os(IV)(η^4-Class I PAC)(pyridine)(triphenylphosphine) complexes, or in some cases and under more

forcing conditions, *trans*-Os(IV)(Class I PAC)(pyridine)$_2$ compounds.[32,33] When the Os(η^4-Class II PAC)O compounds were reacted with triphenylphosphine and pyridine, the *trans*-Os(IV)(η^4-Class II PAC)(pyridine)$_2$ compounds were obtained directly. In no case were we able to isolate a complex with a coordinated triphenylphosphine ligands. In addition, while only triphenylphosphine and pyridine are needed to effect reduction of the Os(VI) monooxo compounds, the *trans*-dioxo complexes are unreactive unless trifluoroacetic acid is added to the reaction medium. In the last section it was demonstrated that addition of trifluoroacetic acid to the *trans*-K_2Os(η^4-HMPA-DMP)O_2 complex brought about a clean conversion to Os(η^4-HMPA-DMP)O. These observations suggest that the true reactive intermediate in the reduction of the Os(VI) species is the Os(VI) monooxo.[19c] Trifluoracetic acid causes this conversion *in situ*. Such a conversion would allow coordination of a ligand *trans* to the oxo ligand, which may be necessary before reduction can occur.

We believe that we do not observe triphenylphosphine complexes because the phenyl groups of the triphenylphosphine ligands would undergo severe interactions with the methyl groups of the Class II ligands. Such steric interactions govern much of the reactivity of such complexes (see below).

Not only is Os(η^4-HMPA-Pr)O much more difficult to reduce electrochemically than Os(η^4-HMPA-DMP)O, but it is also more difficult to reduce the former compound chemically. The Os(η^4-HMPA-DMP)O reduction proceeds cleanly at room temperature. Os(η^4-HMPA-Pr)O must be heated to ca. 100° C in the presence of triphenylphosphine and a 4-substituted pyridine to effect reduction to the analogous Os(IV) bispyridine complexes. Although the potentials for both complexes are higher, i.e. they are easier to reduce electrochemically, both Os(η^4-HMBuA-B)O and Os(η^4-HMBuA-DCB) also require heating for reduction to occur. The PAC ligands differ greatly in these complexes (6,5,6 coordination vs. 5,6,5 coordination; aromatic bridge vs. aliphatic bridge); it is risky to draw conclusions from these observations.

The compounds are very easily characterized from their IR and NMR spectra. Planar coordination of polyanionic chelating ligands typically reduces the IR stretching frequencies of the carbonyl groups by 50 cm^{-1} relative to the free amides.[19c,31-33] Non-planar coordination typically raises the stretching frequency by a similar amount. In all the cases described here, we observe the IR stretching frequency to appear at approximately 1600 cm^{-1}, indicative of planar PAC ligand coordination. The NMR is also useful in characterizing the complexes. Depending on the coordination geometry, i.e. *trans*, *cis*-alpha, or *cis*-beta, the complex will posses C_{2v}, C_2, or C_1 symmetry respectively.[19a] In the HMPA-DMP fragment, there are eight methyl groups. If the symmetry is C_{2v}, there will be only two sets of inequivalent methyl groups, and two peaks will be observed in the NMR. If the symmetry is reduced to C_2, four peaks will be observed. If there is no symmetry, all eight methyl groups will be chemically inequivalent, and there will be eight signals observed in the NMR spectrum. For the compounds discussed here, we see only two methyl resonances in the proton NMR spectrum, indicating *trans* geometry. This reasoning is illustrated in Figure (2-4). We can use identical arguments to determine the ligand geometry for Os(IV) complexes containing the HMPA-DMP, HMBuA-B, and HMBuA-DCB units. In these complexes also, the ligands are observed to be in the *trans* geometry.

The Os(IV) species so produced are indefinitely stable in the solid state. Stability in solution varies according to the nature of both the PAC and axial ligands (see below). The complexes have been characterized by NMR, IR, cyclic voltammetry, and elemental analysis.

The Os(IV) octahedral species possess temperature independent paramagnetism (TIP), as has been demonstrated for a variety of Os(IV) octahedral complexes previously synthesized in the Collins research effort.[31-33] This property is evidenced by a large shift in the proton NMR resonances. The compounds are observed to be paramagnetic, but the magnetic moments are relatively small. For example, *trans*-Os(η^4-HMPA-Pr)(4-^{tert}butylpyridine)$_2$ has an effective magnetic

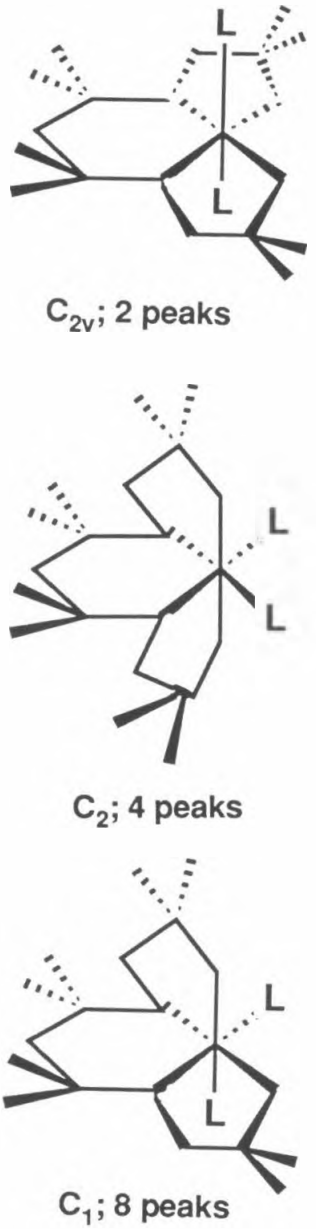


Figure 2-4: Schematic illustration of the number of peaks expected in the NMR spectrum of an Os(HMPA-DMP)L_2 complex, based on the symmetry of the metal complex

moment of 1.2 B.M; *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ has an effective magnetic moment of 1.3 B.M. Such moments are significantly less than would be expected for a low spin d^4 octahedral complex, but are close to what is typically seen for complexes of this type.[32,33] (As would be expected, the Os(VI) monooxo species, exhibiting unshifted NMR spectra, are diamagnetic.) In one respect TIP makes characterization more difficult, as the chemical shift values become meaningless. However, the TIP causes the shifts to appear over a much wider range than is seen in normal, diamagnetic compounds. Shifts which might ordinarily be superimposed are separated by as much as thirty ppm. In studies with the Class I ligands, characterization would be almost impossible without the TIP. For these reasons, the assistance in characterization by TIP has caused the metal centers to be termed "internal shift reagents."[32] It is difficult to rationalize the shift values for individual resonances in these Os(IV) complexes, but if Os(IV) complexes with the same PAC ligand but differing pyridine ligands are compared, the resonances are relatively similar. The shifts for most of the Os(IV) complexes appear between +12 and -25 ppm vs. TMS. In the complexes incorporating the HMPA-pr unit, some resonances appear as far downfield as +63 ppm vs. TMS. In Figure (2-5) is shown a proton NMR spectrum of *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ to illustrate both the sharp spectrum and the unusual chemical shifts. Inset is the aliphatic region of the NMR spectrum of the free ligand, H_4-HMPA-DMP.

A wide variety of Os(IV) bispyridine complexes have been synthesized. The reduction is quite facile when the pyridine ligand possesses an electron donating substituent at the 4-position. Os(IV) species with 4-substituted pyridine axial ligands where the substituent may be methyl, ethyl, tertiarybutyl, methoxy, dimethylamino, and pyrrolidino have been synthesized. Synthesis of Os(IV) species where X is an electron withdrawing group has been much more difficult. Of such species, We have had no success with 4-nitro or 4-cyano substituents, although we have been able to synthesize *trans*-Os(η^4-HMPA-DMP)(4-

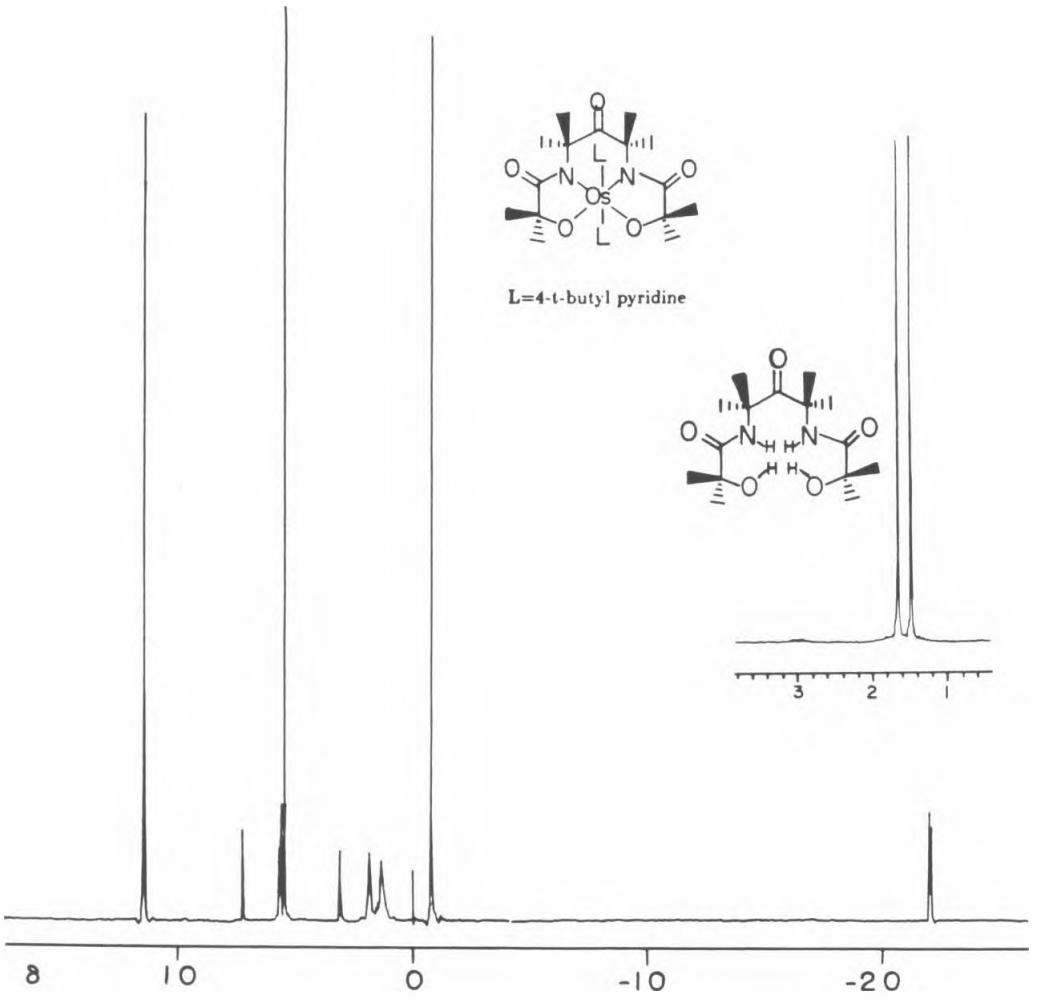


Figure 2-5: PMR spectrum of trans-Os(HMPA-DMP)(4-^{t}butylpyridine)$_2$. Inset is spectrum of H_4-HMPA-DMP.

bromopyridine)$_2$.

An interesting case occurs when 4-acetylpyridine is employed to serve as the axial ligands. A compound is isolated in fair yield with elemental analysis data consistent with the formulation Os(HMPA-DMP)(4-Ac-pyridine)$_2$. What is in doubt is the geometry. The NMR spectrum shows no isotropic shifting. Four resonances are observed between 1.5 and 2.0 ppm. In addition, a single resonance occurs at 2.1 ppm, which is probably due to the methyl protons of the 4-acetyl substituent. This would suggest that the ligand is in the *cis*-alpha conformation. One would expect that the IR data would be helpful, but as their are five different carbonyl groups in this molecule, it is difficult to assign any individual stretches. The redox potentials go against trends which were observed with other pyridines (see below). Such observations in previous work have indicated ligand isomerization. It is possible that this compound is a *cis*-alpha isomer. An X-ray structure determination would be necessary to make such absolute conclusions. Attempts to grow crystals have been unsuccessful.

It is difficult to explain the curious behavior of this complex, or, more precisely, the anomalous behavior of the 4-acetylpyridine ligand. We and other researchers have previously observed such inconsistencies with 4-formyl and 4-acetyl pyridines. Two explanations have been offered. The first, which Collins has proposed based on electrochemical data, is that there are significant π-backbonding effects in 4-acetylpyridine which do not operate (or operate to a much lesser degree) in other pyridines.[19a,d,f] The second explanation, proposed by Del Bene based on molecular orbital calculations, is that the non-bonding orbital of 4-acetylpyridine is significantly delocalized onto the acetyl oxygen, and so there is decreased electron density at the donor nitrogen atom.[34] Both explanations concur in that 4-formyl and 4-acetyl pyridines are anomalously poor donors. For these reasons, data for acetyl and formyl pyridines must be looked at with great care, particularly when comparing such data with that for other pyridines. When the π effects of the acetyl group are removed by ketalization, the resulting *trans*-

Os(IV)(η^4-HMPA-DMP)(4-X-pyridine)$_2$ where X is the ketal of the acetyl group is observed to be in the trans geometry; the anomalous π-effect seems to disappear.

The Os(IV) complexes of the type *trans*-Os(η^4-HMPA-DMP)(4-X-pyridine)$_2$ described here are good candidates for the production of stable electron transfer oxidants. While the Os(IV) species themselves are not oxidizing, they may be chemically (using Br_2 or Ce(IV)) or electrochemically (employing platinum or basal planar graphite electrodes) oxidized to stable Os(V) species of the type *trans*-Os(η^4-HMPA-DMP)(4-X-pyridine)$_2^+$. Coulometric experiments demonstrate that these oxidations are one electron processes. As separation of a charged product from a large excess of supporting electrolyte is in general very difficult, it is simplest to produce the Os(V) compounds chemically. Using either bromine or Ce(IV), removal of by-products was facile, and the Os(V) species could be isolated as red solids. The stability of the compounds in the solid state varied depending on the choice of the pyridine axial ligands. Os(V) compounds with highly electron donating pyridine axial ligands were indefinitely stable, while analogous compounds with electron withdrawing pyridines were stable only for a matter of hours.

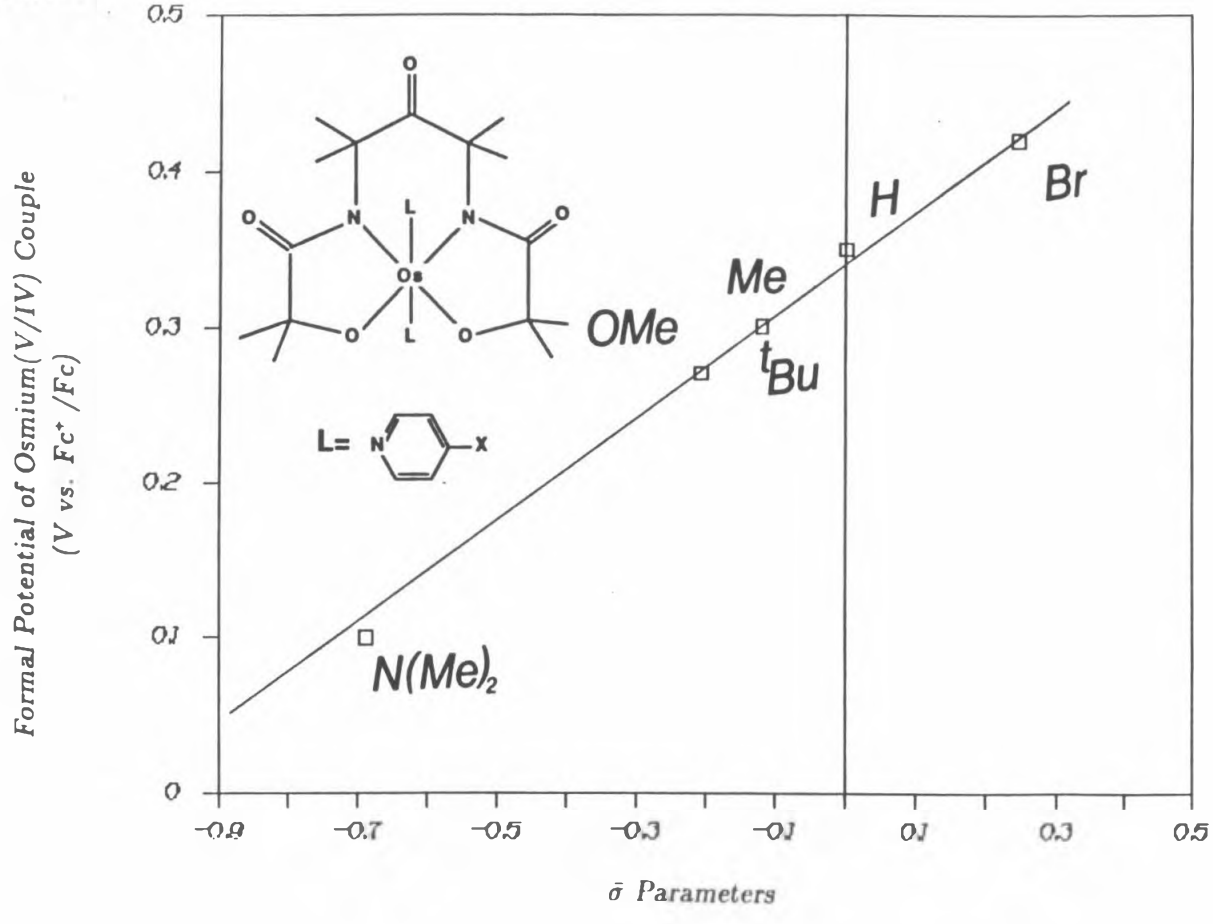
As is shown in Figure (2-6), the value of the Os(V/IV) couple varies linearly with the $\bar{\sigma}$ parameter.[35] This substituent parameter was derived from the Bronsted basicities of substituted pyridines. (The slope of this plot is 0.338(9), R = .999; ρ is calculated to be 5.71(15). For the Os(IV/III) couples, slope = 0.316(58), R = .938; ρ is calculated to be 5.4(9). The ρ values are equal within the error limits and demonstrate significant sensitivity of the couples to the pyridine substituents.) The Os(V/IV) couples have rather low values; in several cases, the Os(V/IV) couple only exceeds the Fc^+/Fc couple by 70 mV. It is encouraging that not only can a large family of Os(V) species be readily produced, but the potential can be precisely controlled by choosing the appropriate substituted pyridine to serve as axial ligands. Over a 360 mV range, an Os(V) compound

TABLE 2-II

Redox potentials for Os(HMPA-DMP)(4-X-pyridine)$_2$ Complexes
Volts vs. Fc^+/Fc (CH_2Cl_2)

X	E° (IV/III)	E° (V/IV)
Br	-1.03	0.42
H	-1.31	0.35
^{t}Bu	-1.36	0.31
OMe	-1.35	0.27
NMe_2	-1.58	0.11
N-$(CH_2)_{-4}$	-1.54	0.07
Me	-1.34	0.30
-C(O)CH_3	-1.28	0.33

Figure 2-6


Formal Potential of Osmium(V/IV) Couple
(V vs. Fc+/Fc)
0.5
0.4
0.3
0.2
0.1
0
-0.9
-0.7
-0.5
-0.3
-0.1
0.1
0.3
0.5
σ Parameters
O
N
L
Os
OMe
L=
X
N(Me)2
Me
tBu
H
Br

may be produced with virtually any desired potential. Such an accomplishment contributes significantly to the field of electrochemistry, as the search for tunable oxidants has historically received a great deal of attention. Previous to our work, Os(V) was such a rare oxidation state that designing selective oxidants based on Os(V) did not seem to be a realistic goal. When the only Os(V) species available are simple halides and oxides which are produced under extremely forcing conditions, there is little hope for designing an Os(V) species for a specific purpose. With the polyanionic chelating ligands described in this work, not only can the potentials be fine-tuned, but the Os(V) species so produced can be unambiguously assigned as such, as the aromatic rings have been removed from the polyanionic chelating ligand, eliminating non-innocence. The availability of such Os(V) compounds and data concerning them is crucial to the further understanding of this rare oxidation state.

Higher reversible redox couples, which we assign as Os(VI)/(V) couples, may also be observed for these complexes if liquid sulfur dioxide is used as the electrochemical solvent. A typical cyclic voltammogram showing both the (V/IV) and (VI/V) couples Of *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ is shown in Figure (2-7). The Os(V/IV) couple occurs at 0.49 V vs Fc^+/Fc; the Os(VI/V) couple occurs at 1.35 V vs Fc^+/Fc. While these potentials approach the highest yet observed electrochemically, the compounds so produced are not stable in solution which precludes their use as oxidants. It is not immediately obvious why the oxidized species would decompose. Complexes similar to those we have synthesized have previously been studied where the metal center is chromium in the +V oxidation state. These complexes also possess tertiarybutoxy donors. In such systems, decomposition occurs via acetone elimination. Osmium compounds with the HMPA-DMP ligand show fragment losses in the mass spectrum which can be assigned to elimination of acetone (see above). These observations suggest that under very highly oxidizing conditions, the tertiarybutoxy unit may be fragile and unstable. We were led to synthesize the H_4-HMBuA-DMP ligand for

L=4-t-butyl pyridine

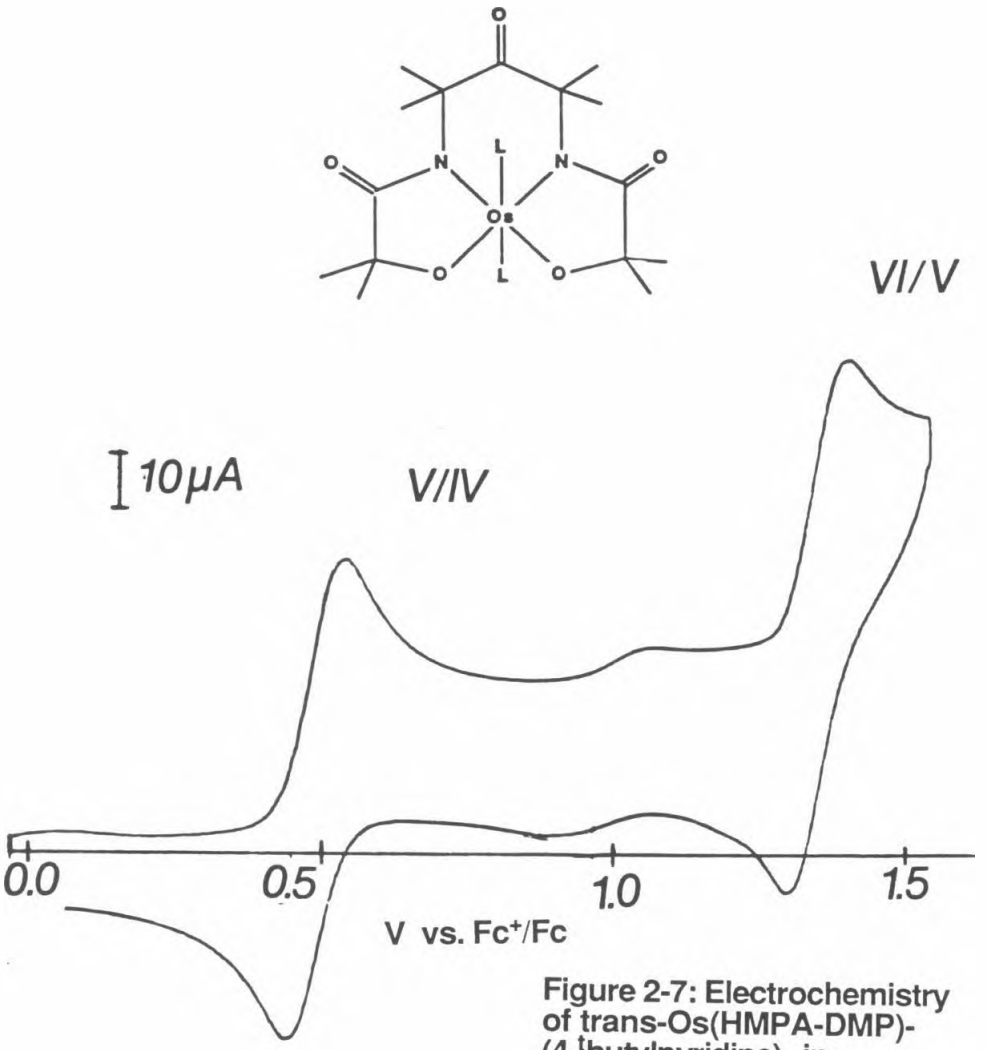


Figure 2-7: Electrochemistry of trans-Os(HMPA-DMP)-(4-^{t}butylpyridine)$_2$ in liquid SO_2.

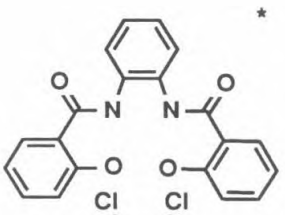
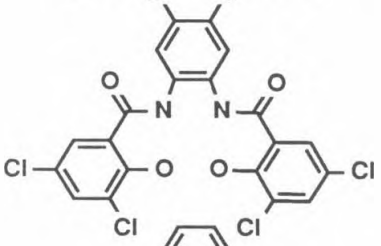
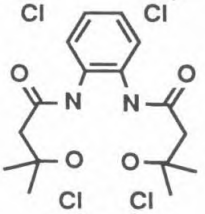
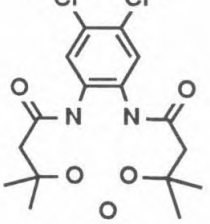
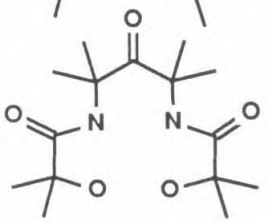
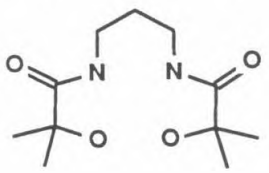
these reasons, as insertion of the methylene unit would circumvent this decomposition pathway; the ligand would also be an innocent ligand. Unfortunately, we were unable to prepare osmium complexes with this ligand. Replacing the dimethylpentanone bridge with a phenylene or dichlorophenylene bridge leads to ligands with better coordination properties. Results with these ligands are included in Tables 2-I and 2-III.

The Os(IV/III) couple (see Table (2-II)) is also interesting, as it is an excellent indication of relative donor abilities of the ligand. While noninnocent PAC ligands may display behavior indicative of ligand oxidation at higher oxidation states (+V, +VI), such considerations are unlikely to be important for the Os(IV) and Os(III) oxidation states. Consequently, a comparison of the Os(IV/III) potentials for ligands with the same axial ligands but different PAC ligands will demonstrate the greater donor abilities of the Class II ligands relative to the Class I ligands. A table comparing data for six complexes of different polyanionic chelating ligands is shown as Table (2-III).

It is immediately evident that the Os(IV/III) couple may vary considerably in the systems examined. Changing the PAC ligand from HBA-B (1,2-bis(2-hydroxybenzamido)benzene) to HMPA-DMP brings about a 600 mV lowering of the (IV/III) potential.[32] This is almost certainly due to the increased σ-donation of HMPA-DMP and the corresponding increased electron density at the metal center. This may easily be understood by comparing the pKa's of the donor groups of the ligands. While the amide pKa's are relatively similar, the pKa of a phenol is approximately 10 (and decreases significantly on incorporation of chloro substituents on the ring), as compared with 19 for tertiarybutanol.[36] While making such comparisons implies a number of gross simplifications, not least of which is equating a metal with a proton, the numbers are good indications of the relative σ donor abilities of the ligands. With such a large increase in electron donation to the metal, is is easy to see why both potentials and reactivity change drastically.

Table 2-III

Redox potentials for trans-Os(PAC)(t-butylpyridine)$_2$ for various PAC ligands in CH_2Cl_2 vs Fc^+/Fc.

PAC	(IV)/(III)	(V)/(IV)
	-0.76	+0.35
	-0.51	+0.70
	-1.22	+0.08
	-1.03	+0.34
	-1.36	+0.30
	-1.34	+0.22

* calculated

This is somewhat in contrast to the case for what is observed for the Os(V/IV) potentials. The Os(V/IV) couples of *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ and *trans*-Os(η^4-HBA-B)(4-^{tert}butylpyridine)$_2$[32] are virtually identical. Simple σ-donation arguments suggest that the *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ complex should exhibit a significantly lower potential. It is conceivable that the lack of a large difference between the two couples is due to partial ligand oxidation in the case of *trans*-Os(η^4-HBA-B)(4-^{tert}butylpyridine)$_2$. Such partial ring oxidation would introduce resonance structures corresponding to Os(IV) and Os(III) which would contribute to the overall nature of the oxidized product. Such contributions would be expected to stabilize the oxidized product considerably and would lead to a lowering of the oxidation potential. Partial ligand oxidation could originate from the phenoxy groups and/or the phenylenediamine bridge. In cases of ligand noninnocence, it is difficult to assign formal oxidation states. See the Introduction for the possible sources of noninnocence in these compounds and the changes in the nature of the ligand and the oxidation state of the metal. Consequently, rather than referring to such a couple as a (V/IV) couple, often such a couple is referred to using noncommittal "(+/IV)" or even "(+/0)" notation. Where the formal oxidation state is not given, all that this terminology signifies is the charge of the species. The improvement of replacing the phenoxy donors with tertiarybutoxy donors lies not only in the ligand being more electron-donating, but also in the simplicity of oxidation state assignment.

It is also interesting to examine the Os(IV/III) and Os(V/IV) potentials for compounds synthesized with the HMPA-DMP and analogous HMPA-Pr ligand units which are not significantly different. The electron donating effects of the methyl substituents on the bridge may be counterbalanced by the electron withdrawing effects of the ketone group in the HMPA-DMP ligand, or, there simply may not be a great contribution from the bridge substituents. As it is unlikely that there are significant geometric changes in oxidizing or reducing the Os(IV)

octahedral species, the arguments concerning ring planarity and steric repulsions (which were invoked to rationalize the difference between the Os(VI/V) potentials of Os(η^4-HMPA-DMP)O and Os(η^4-HMPA-Pr)O) do not apply in these cases.

A comparison of the redox potentials for *trans*-Os(η^4-HMBuA-B)(4-^{tert}butylpyridine)$_2$ and *trans*-Os(η^4-HMBuA-DCB)(4-^{tert}butylpyridine)$_2$ is also informative. From previous work, it has been determined that chlorine substitution on one of the rings in the PAC ligand will raise the redox couple approximately 60 mV per chlorine substituent.[33] This holds for the Os(IV/III) couples (-1.03 V vs. Fc^+/Fc for *trans*-Os(η^4-HMBuA-DCB)(4-^{tert}butylpyridine)$_2$; -1.22 V vs. Fc^+/Fc for *trans*-Os(η^4-HMBuA-B)(4-^{tert}butylpyridine)$_2$). However, the Os(V/IV) couple is elevated significantly more than expected (+0.34 V vs. Fc^+/Fc for *trans*-Os(η^4-HMBuA-DCB)(4-^{tert}butylpyridine)$_2$; +0.08 V vs. Fc^+/Fc for *trans*-Os(η^4-HMBuA-B)(4-^{tert}butylpyridine)$_2$). This may be due to the chlorine substituents on the ring protecting the aromatic ligand from oxidation. This was the original rationale for incorporating such chlorine substituents. If the ligand were significantly more difficult to oxidize, the resonance structures involving metal centers with lower oxidation states would contribute less, leading to higher potentials, as observed.

A particularly fascinating feature of the *trans*-Os(IV)(η^4-HMPA-DMP)(4-X-pyridine)$_2$ complexes is their reactivity in solution in the presence of air. It is observed that at room temperature, in organic solvents, these *trans*-Os(IV)(η^4-HMPA-DMP)(4-X-pyridine)$_2$ complexes are spontaneously oxidized to the Os(VI)(η^4-HMPA-DMP)O species (also the starting material used to synthesize the octahedral complexes). The reaction does not occur when air is excluded from the medium. The conversion has been observed by NMR, UV-vis spectroscopy, thin layer chromatography, cyclic voltammetry, and unambiguous isolation of the product.

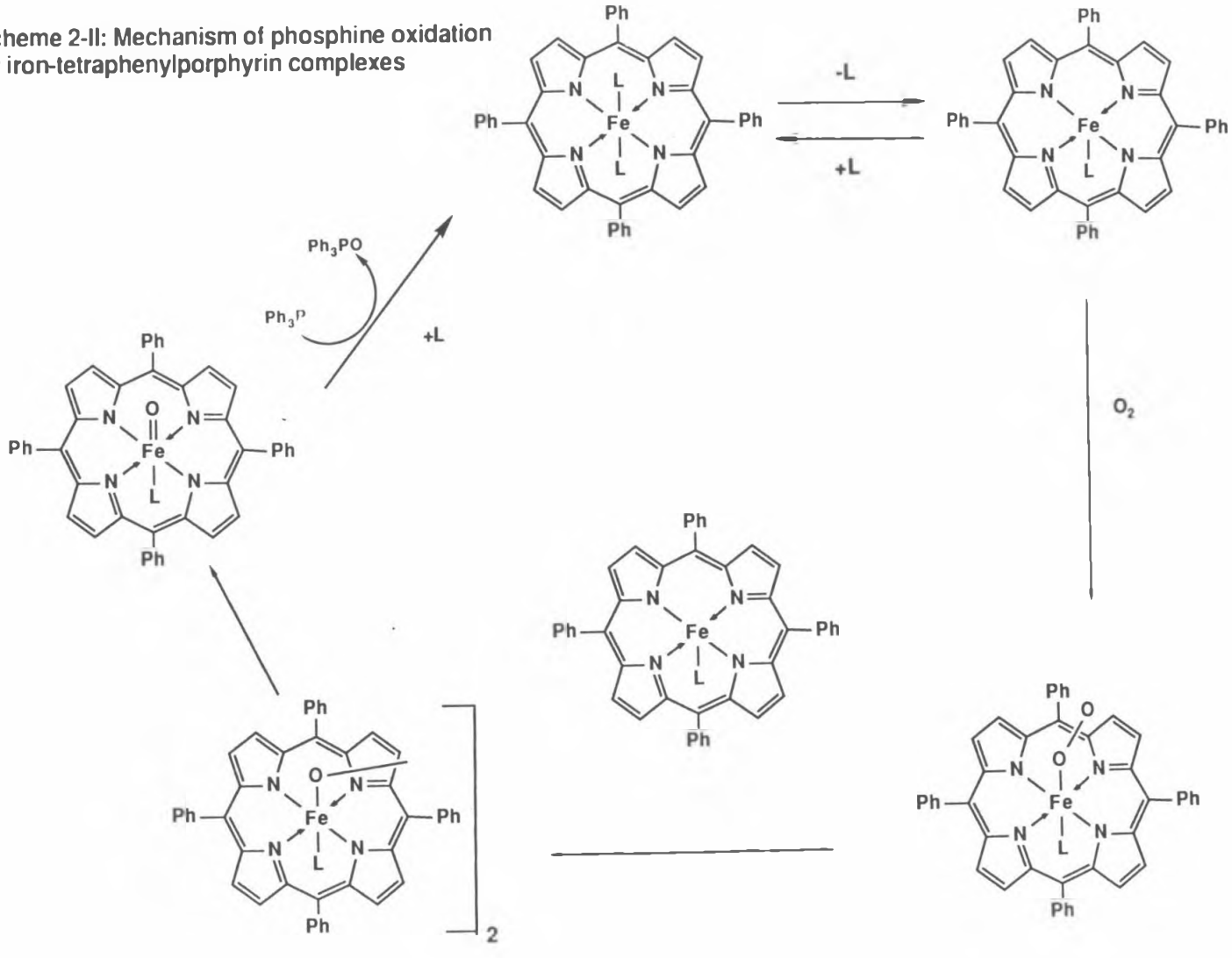
The mechanism of the conversion is complicated. There are a number of systems which undergo similar air oxidations. Mechanistic studies have been per-

formed on some of these. In particular, Fe(II)Tetraphenylporphyrin(pyridine)$_2$ undergoes a very similar air oxidation to produce a reactive Fe(IV)(Tetraphenylporphyrin)O intermediate. This is reduced with triphenylphosphine in pyridine to regenerate Fe(II)Tetraphenylporphyrin(pyridine)$_2$. The Fe(IV) species may also react with a molecule of the five-coordinate Fe(II) intermediate leading to a μ-oxo Fe(III) dimer. This dimer is catalytically inactive and represents the primary mode of catalyst deactivation.[37] It has been demonstrated that both atoms of molecular oxygen are utilized. The proposed mechanism of the process is shown in Scheme (2-II). There are some other interesting transition metal systems in which molecular oxygen is the stoichiometric oxidant. Examples are Pt(phosphine)$_3$,[38] which catalytically oxidizes phosphines to phosphine oxides (in this system, both atoms of the molecular oxygen molecule are incorporated into product), silver catalysts for oxirane production, rhodium catalysts for alkene oxidations and iridium catalysts for butane autoxidation.[39] A potentially very useful catalyst based on ruthenium for the epoxidation of alkenes has been recently produced.[40]

In light of the excellent work which has been carried out with systems such as these, and given the fact that the we have been unable to use a reducing agent besides phosphines (and dimethylaminopyridines with heating) to generate the Os(IV) species, a highly detailed mechanistic study on this system does not seem to be warranted. It is likely that the mechanism is very similar to that of the Fe(II)-tetraphenylporphyrin system shown in Scheme (2-II). There are certainly additional factors which contribute to the reactivity of the osmium system. We were curious as to why Os(IV) bispyridine complexes with most other PAC ligands do not undergo similar reactions. With these thoughts in mind, we have examined some of the steps of the conversion process.

While the conversions of Fe(II) tetraphenylporphyrin systems and Os(IV) PAC ligand systems appear similar, it is interesting to compare the ligands and oxidation states. The tetraphenylporphyrin ligand is a strongly donating, dianion

Scheme 2-II: Mechanism of phosphine oxidation by iron-tetraphenylporphyrin complexes



when coordinated to a transition metal. Fe(II) is known to react with molecular oxygen in many systems, a ubiquitous example of which is hemoglobin.[39] Fe(II) can be called a low to intermediate oxidation state. A potentially tetraanionic ligand, such as H_4-HMPA-DMP, causes an oxidation state ordinarily considered to be intermediate to high (Os(IV)) to have reactivity more characteristic of a low valent system.

The kinetics of the Os(IV) to Os(VI) conversion were studied by UV-vis spectroscopy in $CHCl_3$. As molecular oxygen possesses a solubility in $CHCl_3$ which is approximately three orders of magnitude greater than the concentrations of the Os(IV) species employed, oxygen could be considered to be in large excess at all times; therefore the oxygen concentration was assumed to be constant.

The conversion was found to be pseudo-first order in the *trans*-Os(η^4-HMPA-DMP)(4-X-pyridine)$_2$ complex (to greater than three half-lives, where the half-lives made measurements to greater than three half-lives feasible). This is consistent with a rate determining dissociation of a pyridine ligand (bond breaking) followed by rapid and irreversible combination with molecular oxygen.

The reaction has been examined with three complexes synthesized with different pyridine axial ligands: 4-tertiarybutylpyridine was used as a representative electron-donating pyridine. 4-bromopyridine was used as a representative electron-withdrawing pyridine. These systems were compared with the complex synthesized from unsubstituted pyridine. Intuitively, one might expect that the more electron rich the system, the more rapid should be the reaction with molecular oxygen. The opposite is observed. The compounds with electron-donating pyridines as axial ligands react far more slowly that do those with electron withdrawing pyridines. In fact, the compounds *trans*-Os(IV)(η^4-HMPA-DMP)(4-dimethylaminopyridine)$_2$ and *trans*-Os(IV)(η^4-HMPA-DMP)(4-pyrrolidinopyridine)$_2$ are almost entirely unreactive. Only after days of exposure to pure oxygen could any conversion be observed.

The half-lives of the compounds were easily measured (at 22° C in chloroform). *trans*-Os(η^4-HMPA-DMP)(4-bromopyridine)$_2$ has a $t_{1/2}$ of 36 minutes; *trans*-Os(η^4-HMPA-DMP)(pyridine)$_2$ has a half life of 94 minutes; and *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ has a $t_{1/2}$ of approximately 636 minutes; The half-lives for compounds incorporating more electron donating pyridines (e.g. methoxy, dimethylamino, pyrollidino) were too large too measure. The time-dependent UV-vis spectrum of the conversion of *trans*-Os(η^4-HMPA-DMP)(pyridine)$_2$ to Os(η^4-HMPA-DMP)O is shown as Figure (2-8). The first 20 scans are five minutes apart; the remaining are each separated by one hour.

Four isosbestic points are observed in the UV-vis spectrum. This is consistent with there being only two species present in significant concentrations,[45] the Os(IV)bispyridine and the Os(VI)monooxo. This supports the assertion that steps following pyridine dissociation are rapid, as is seen for the analogous air oxidation of Fe(II)TPP(pyridine)$_2$. If this is the case, it will be very difficult to observe the intermediates. It is possible, however, to trap the five-cooordinate intermediate with carbon monoxide. If *trans*-Os(η^4-HMPA-DMP)(pyridine)$_2$ is dissolved in THF, a yellow solution results. If the solution is saturated with carbon monoxide and sealed, a slow color change from yellow to red is observed. Os(η^4-HMPA-DMP)(CO)(pyridine) is isolated from this solution. The intermediate appears to react more quickly with carbon monoxide than with molecular oxygen. This reactivity is also similar to that observed for Fe(II)-TPP systems.[39]

The relative reactivity of pyridines is yet to be explained. It may simply be that the more strongly donating pyridines form stronger bonds with the osmium metal center leading to decreased tendency to dissociate.

The Fe(II) tetraphenylporphyrin systems catalytically convert phosphine to phosphine oxide. Synthesizing the Os(IV) from the Os(VI) species by reduction with triphenylphosphine (with concurrent production of triphenylphosphine oxide), followed by air oxidation of the Os(IV) species to the Os(VI) starting material constitute the elements of a catalytic cycle. While the actual chemical

conversion itself is trivial, if our mechanism is correct, and both atoms of molecular oxygen are being incorporated into product, this represents an important new form of reactivity for Os(IV). One of the most important goals of oxidation chemistry is the activation of molecular oxygen, particularly sought after are systems which utilize both atoms of molecular oxygen. We have found that this reaction can indeed proceed under catalytic conditions. Os(η^4-HMPA-DMP)O in pyridine solution can catalytically oxidize triphenylphosphine to triphenylphosphine oxide in the presence of air. Over a three day period, approximately 100 equivalents of triphenylphosphine were oxidized, with significant catalytic activity remaining.

An interesting question is whether other Os(IV) complexes of PAC ligands will perform similar catalysis. Obvious candidates are the *trans*-Os(IV)(η^4-HMPA-Pr)(4-X-pyridine)$_2$ complexes. The Os(IV/III) and Os(V/IV) redox couples for these complexes are very similar. One might expect similar reactivity. However, we find that in air at room temperature, *trans*-Os(η^4-HMPA-Pr)(pyridine)$_2$ undergoes no conversion to the corresponding Os(VI) monooxo species. Only in refluxing benzene does the material show any signs of air oxidation. We have verified the production of Os(η^4-HMPA-Pr)O, but the oxidation process is not clean. Numerous other products appear.

We sought to explain this difference in reactivity. As the (V/IV) oxidation potentials for *trans*-Os(η^4-HMPA-DMP)(4-^{tert}butylpyridine)$_2$ and *trans*-Os(η^4-HMPA-Pr)(4-^{tert}butylpyridine)$_2$ are so similar, it is unlikely that there is a large difference in electron richness of the complexes in question; this makes it difficult to invoke electronic effects to explain the large differences in reactivity.

There are significant steric differences between the compounds with HMPA-DMP and HMPA-Pr ligands. CPK models show that there is significant interaction between the protons at the 2-position of the pyridine ligands and the methyl groups of the polyanionic chelating ligand. Such interactions would be expected to be destabilizing, and so could lead to weakened metal-pyridine bonding and increased lability for the pyridine ligands. In the *trans*-Os(η^4-HMPA-Pr)(pyridine)$_2$

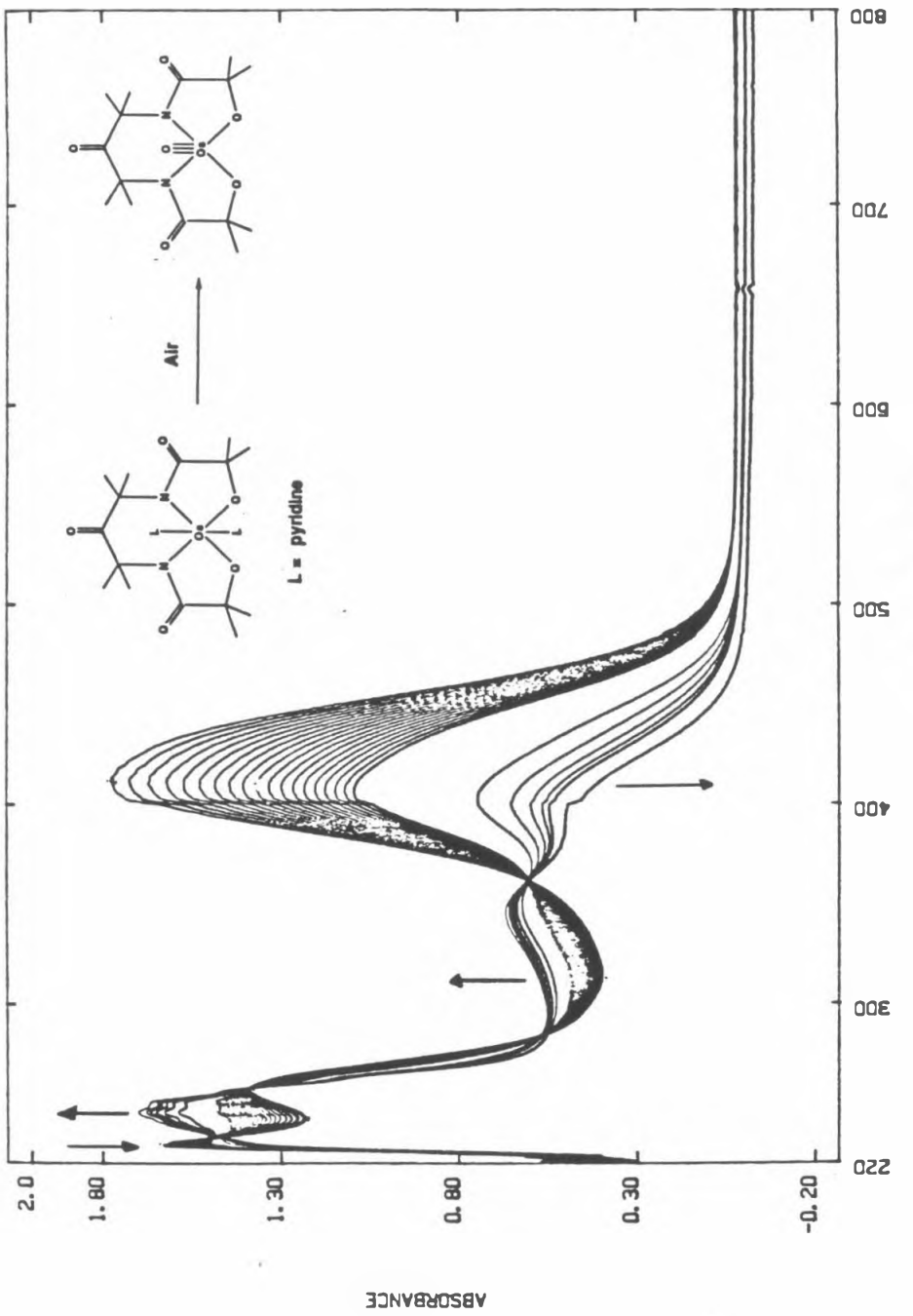
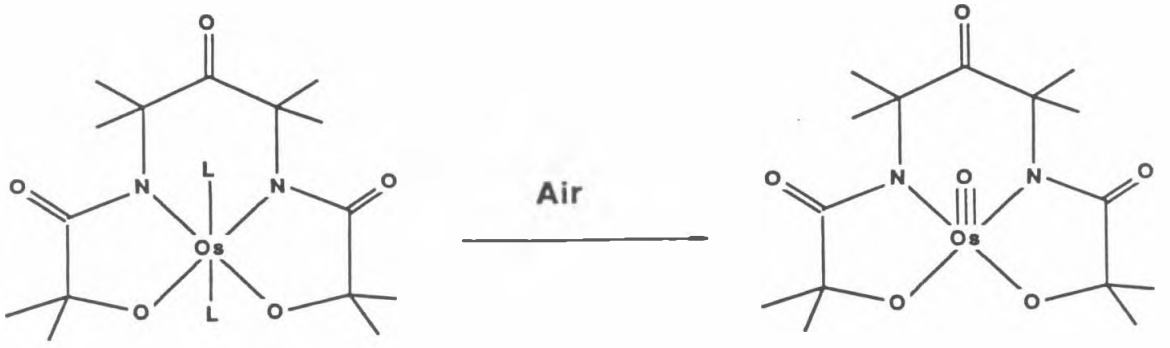


Figure 2-8: UV-vis spectra demonstrating conversion of trans-Os(HMPA-DMP)py_2 to Os(HMPA-DMP)O

complex, the absence of methyl groups on the propylene bridge will decrease such steric interactions (although the interactions with the tertiarybutyl methyl groups remain), and so the pyridine ligands would not be labilized to the same degree. If the rate determining step is a dissociation of a pyridine ligand, decreased steric repulsions would explain the stability of *trans*-Os(η^4-HMPA-Pr)(pyridine)$_2$. A schematic illustration of the steric interactions between the ligand methyl groups and the *ortho*-protons of the ancillary pyridine ligands is included as Figure (2-9).

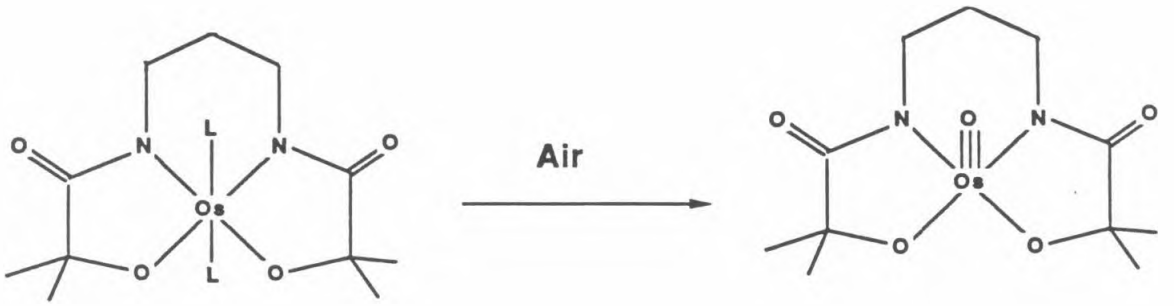
The multitude of products observed in the higher temperature air oxidation of *trans*-Os(η^4-HMPA-Pr)(pyridine)$_2$ is most likely due to the instability of the simple propane bridge relative to the dimethylpentanone bridge. It has been previously observed that C-H bonds α- to a nitrogen are highly oxidatively sensitive (see the Introduction). It is such sensitivity which leads to the ultimate bridge destruction of *trans*-Os(η^4-CHBA-Et)(pyridine)$_2^+$. In the electrochemical oxidation of *trans*-Os(η^4-HMPA-Pr)(pyridine)$_2$ to the Os(V) compound, we see formation of another species which could be a product of bridge decomposition.

We believe that the conversion proceeds by way of the steps discussed below and illustrated in Scheme (2-IV). After the initial pyridine dissociation, the five-coordinate species can undergo a number of reactions. It can recombine with pyridine (we have verified this by NMR), react with molecular oxygen, or react with an external added ligand (e.g. CO). The product derived from reaction with molecular oxygen, most likely a superoxide complex, would be expected to be very unstable. Few complexes of dioxygen with osmium are known, and no superoxide complexes have been seen. Combination with a mole of the reactive five-coordinate species would be expected to be rapid. This would be followed by rapid oxygen-oxygen bond scission leading to two moles of *trans*-Os(η^4-HMPA-DMP)O(pyridine). We have been unable to detect this product. We know that there is a weak interaction between pyridines and Os(η^4-HMPA-DMP)O as we see a change in color from orange-brown to dark green on addition of a pyridine to an Os(η^4-HMPA-DMP)O solution. We have been unable to observe this in-



L = pyridine

Fast, clean



L = pyridine

Slow, complex

Scheme 2-III: Comparison of air oxidation of trans-Os(HMPA-DMP)py_2 and trans-Os(HMPA-Pr)py_2.

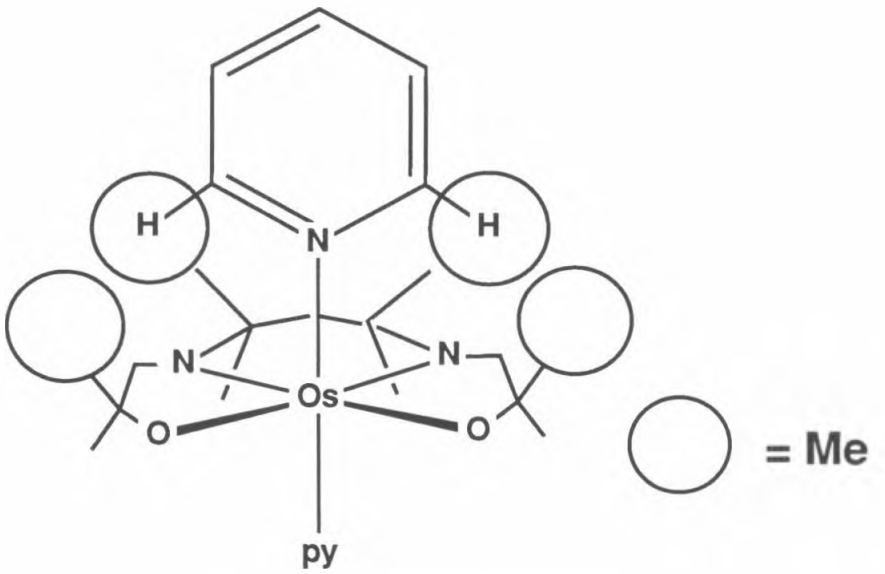


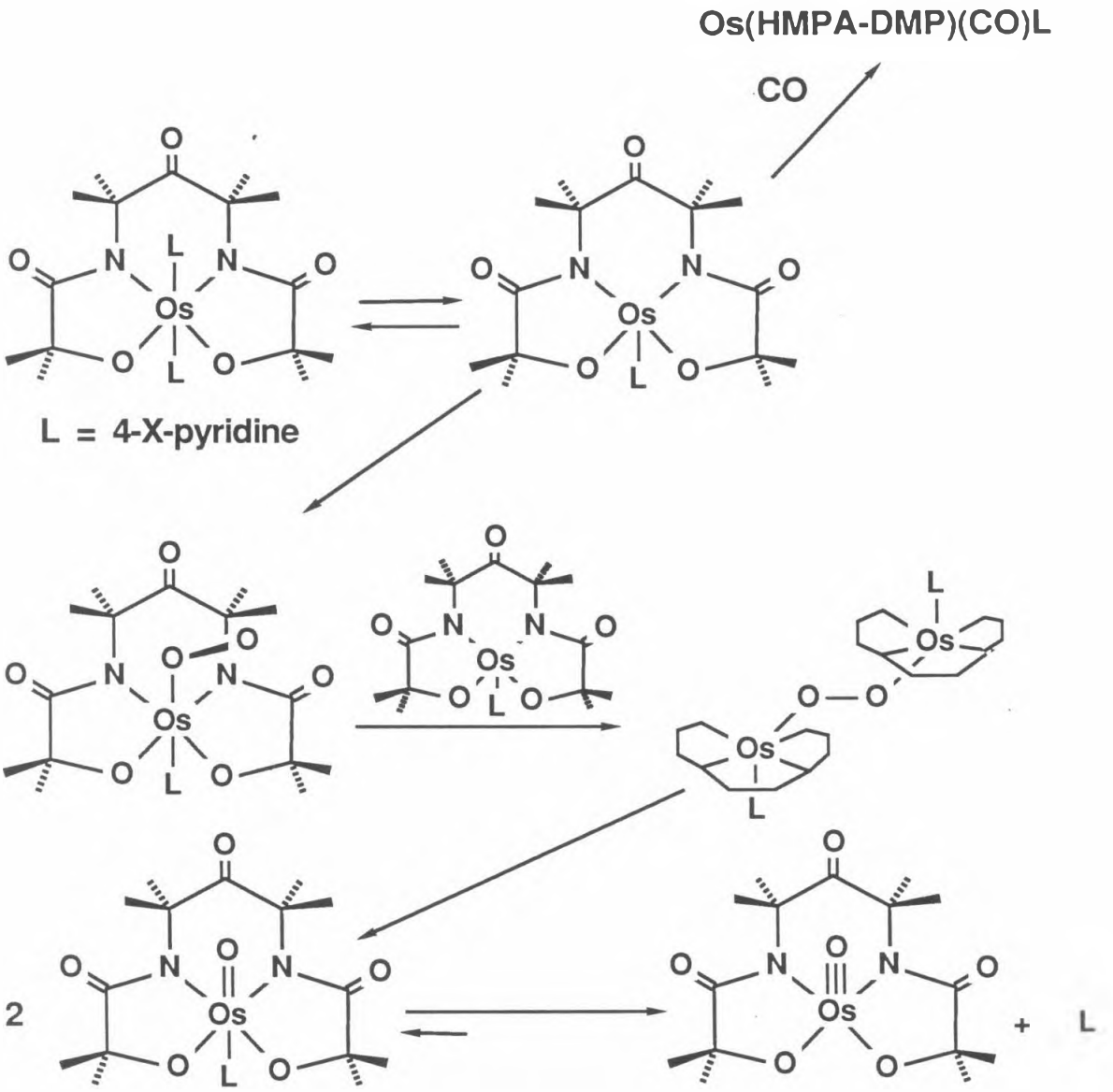
Figure 2-9: Schematic illustration of the interaction between the ortho hydrogens of the pyridine ligand and the methyl groups of the PAC ligand.

termediate either spectroscopically or electrochemically. A reasonable qualitative conclusion is that if indeed a pyridine is coordinating to the complex, the equilibrium constant is very small, as high concentrations of pyridine are necessary to bring about the color change (it also appears from these simple experiments that the more strongly donating the pyridine, the higher is the bonding constant). With no excess pyridine present, the complex would lose this ligand to produce the Os(η^4-HMPA-DMP)O species. Or, under conditions of excess pyridine and triphenylphosphine (catalytic conditions) a molecule of triphenylphosphine may interact with the oxo group, forming a weakly bound Os(η^4-HMPA-DMP)(pyridine)(triphenylphosphine oxide) complex. Dissociation of the triphenylphosphine oxide would regenerate the active, five-coordinate Os(η^4-HMPA-DMP)(pyridine)$_1$ intermediate.

Another possible course for the intermediate dioxygen adduct is to react with a second dioxygen adduct to produce a tetraoxide. Such a species would be expected to be very unstable, and would lead to production of two *trans*-Os(η^4-HMPA-DMP)O(pyridine) units and a molecule of dioxygen, as shown in Scheme (2-V). There is no evidence for such an intermediate (although such intermediates are known in organic autooxidations[6a]), but under conditions where the oxygen is in large excess, the concentration of the dissociated five-coordinate complex would be low. If this is indeed the case, the probability of two reactive intermediates in low concentrations coming together might be very low.

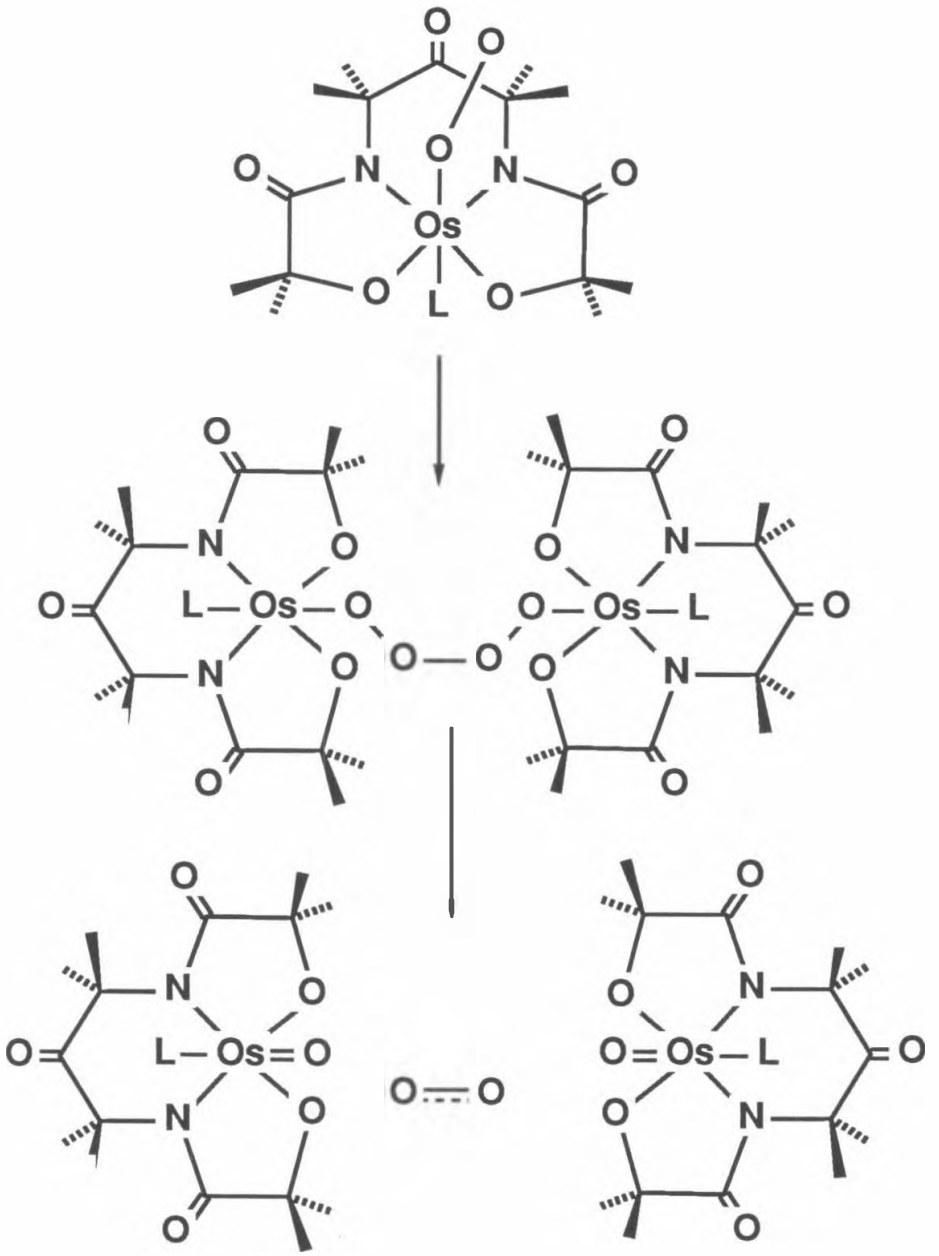
Both steric and electronic effects contribute to the reactivity of the *trans*-Os(η^4-PAC)(4-X-pyridine)$_2$ systems. Increased donation from the PAC ligands causes higher valent species to become air sensitive. Relative donor abilities of axial ligands govern bond strengths and therefore oxidation rates. Steric repulsions are largely responsible for the labilization of the pyridine ligands.

The changes that we observe in reactivity of Os(IV) polyanionic chelating ligand on varying the PAC ligand are dramatic. The key question is: Can the systems be modified in such a way that other species could be oxidized by the



Scheme 2-IV: Proposed mechanism of the conversion of trans-Os(HMPA-DMP)L_2 to Os(HMPA-DMP)O.

L = 4-X-pyridine

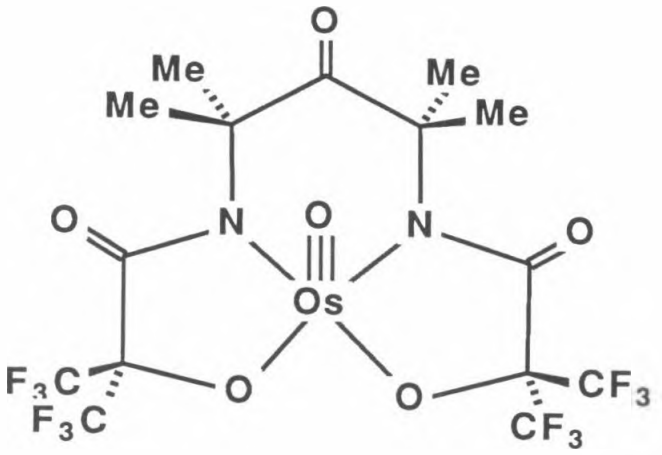


Scheme 2-V: A possible alternate pathway of oxidation involving a tetra-oxo intermediate

Os(VI)(PAC)O species? To achieve this, some means of destabilizing the Os(VI) species would be necessary. To destabilize the higher oxidation state, the electron donating methyl groups could be replaced with electron withdrawing trifluoromethyl groups.[37] Such a modification will raise the Os(VI/V) couple, and will therefore stabilize the reduced species. Oxygen atom transfer might become more facile, and harder-to-oxidize species may serve as substrates. Trifluoromethyl groups will offer steric repulsions similar to those of the methyl groups presently employed. A potential problem, however, is that the five-coordinate Os(IV) intermediate may not show as great reactivity with molecular oxygen as is seen with Os(η^4-HMPA-DMP)(4-X-pyridine)$_1$ species. This would not affect the initial atom transfer, but could drastically affect the overall course of catalysis.

Substitutions of methyl groups with trifluoromethyl groups is synthetically feasible.[41] Such substitutions could also be used to synthesize Os(IV) species which are optically active, possibly performing enantioselective catalysis. These represent promising directions for future ligand modification.

To summarize the interactions of the Class II polyanionic chelating ligands with osmium, we observe numerous examples of unusual Os(VI) monooxo compounds, which can be used to produce exceedingly rare five- and six-coordinate Os(V) compounds with interesting and varied reactivity. Some have potential use as tunable oxidants, some are very strongly reducing. We have altered the reactivity of common oxidation states and in so doing have produced an efficient catalyst which incorporates molecular oxygen as the stoichiometric oxidant. Our research into ligand design principles is continuing to yield novel compounds with interesting reactivity and valuable insight into the nature of high-valent metal centers.



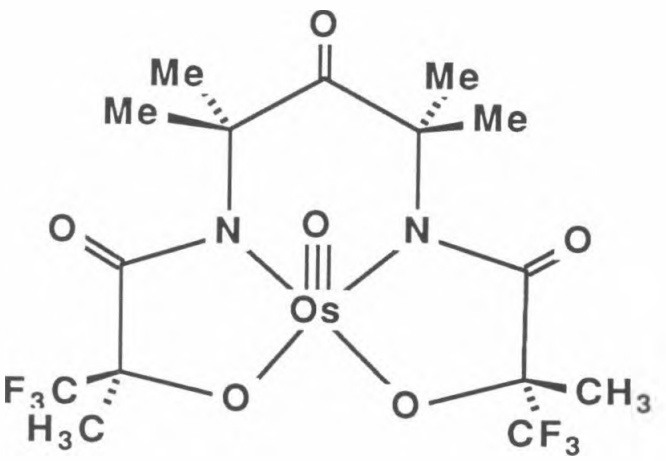


Figure 2-10: Possible ways to destabilize the Os(VI) monooxo species with the aim of extending the range of oxidizable substrates.

EXPERIMENTAL

Materials All solvents were reagent grade (Aldrich, Baker, Malinckrodt, M.C.B., or U.S.I.) and were used as received. Osmium tetroxide (99.8 percent, Alfa), trifluoroacetic acid (Baker), Bromine (Baker), sodium hydroxide (Baker), Pyridine (Baker), 4-^{tert}-butylpyridine (Aldrich), 4-dimethylaminopyridine (Aldrich), 4-pyrrolidinopyridine (Aldrich), 4-methylpyridine (Aldrich), 4-acetylpyridine (Aldrich), triphenlyphosphine (99 percent, Aldrich), ceric ammonium nitrate (Aldrich), and ferrocene (Aldrich) were used as received. 4-bromopyridine was prepared by dissolving the hydrochloride salt (Aldrich) in NaOH solution and extracting with diethyl ether. The free base pyridine polymerized on standing and was used immediately. 4-methoxypyridine was prepared from 4-methoxypyridine-N-oxide by the method of Ochaia[42]. 2-(4-pyridyl)-2-methyl-1,3-dioxolane was prepared by a modified three step procedure taken from Nielson.[43] (concentrated HCl was used in place of dry HCl gas). Potassium osmate ($K_2Os(O)_2(OH)_4$) was prepared from osmium tetroxide as described previously by Malin.[44]

Os(η^4-HMPA-Et)O Potassium osmate ($K_2OsO_2(OH)_4$), 1.58 g, 0.0043 mol) were dissolved in ethanol (200 ml) to yield a blue solution. To this was added H_4-HMPA-Et (1.00 g, 0.0043 mol) in acetone (200 ml). After 24 hours, the solution appeared dark orange. The reaction mixture was reduced to dryness on a rotary evaporator, and the orange-black solid remaining was purified by flash chromatography (90 CH_2Cl_2)/ 10 THF). The orange band was isolated and reduced to dryness on a rotary evaporator. The resulting orange powder was washed through celite with CH_2Cl_2. The orange filtrate was reduced to dryness on a rotary evaporator leaving a brick-red microcrystalline solid, 0.62 g (33 percent). ^{1}H NMR (δ, $CDCl_3$ 400 MHz) shift (multiplicity, int., assign.), 4.5-4.8 (AA'BB', 4H, N-CH_2), 1.35 (s, 6H, CH_3), 1.25 (s, 6H, CH_3). IR (cm^{-1}, nujol):

1700 ν(amide carbonyl), overtone at 3290 cm^{-1}; 970 ν(Os=O), shifts to 925 cm^{-1} (calc: 919 cm^{-1}) on exchange with $H_2{}^{18}O$; Anal. Calcd for $C_{10}H_{16}N_2O_5Os$: C, 27.65; H, 3.71; N, 6.45. Found: C, 27.40; H, 3.46; N, 6.14.

Os(η^4-HMBuA-Et)O 3-hydroxy-3-methylbutyric acid (1.00 g, 0.0086 mol) and ethylenediamine (0.26 g, 0.043 mol) were refluxed in toluene (1 week). An oil formed which was removed and reduced to dryness under vacuum (0.010 torr, RT). This oil was reacted with potassium osmate (0.056 g, 0.00021 mol) in methanol (20 ml). The reaction mixture was stirred (2 hr) with gentle warming (40-50° C). The reaction mixture was reduced to dryness on a rotary evaporator. A black solid remained. The black solid was stirred with CH_2Cl_2 (200 ml) to leach the desired product. The mixture was filtered and reduced to dryness on a rotary evaporator. An orange solid remained which was purified by preparative TLC (80 CH_2Cl_2/ 20 THF). The orange band was isolated and recrystallized from CH_2Cl_2/hexane to yield the desired product as orange crystals (0.010 g, 10 percent). 90 MHz ^1H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.3 (s, 6H, CH_3), 1.6 (s, 6H, CH_3), 3.0 (q, 4H, C(O)-CH_2), 4.0 (s, 4H, -CH_2-CH_2); 400 MHz NMR, 1.25 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 2.92 (d;J=18Hz, 2H, C(O)-CH_2), 3.32 (d;J=18Hz, 2H, C(O)-CH_2), 4.14 (mult;AA'BB', 4H, CH_2-CH_2).

Os(η^4-HMPA-DMP)O $K_2OsO_2(OH)_4$ (1.75g, 4.75 mmol) was dissolved in methanol (100 ml) and stirred under nitrogen. To this blue solution was added H_4-HMPA-DMP (1.0 g, 3.16 mmol). The reaction mixture was heated under reflux under a nitrogen atmosphere (4 hr). The reaction mixture was cooled and reduced to dryness on a rotary evaporator. To the black residue was added acetone (150 ml) and the suspension was stirred in air (1 hr). Insoluble impurities were removed by filtration leaving an orange filtrate. The filtrate was reduced to dryness on a rotary evaporator. To the resulting oil was added CH_2Cl_2 (100 ml). A tan precipitate immediately formed ($K_2Os(\eta^4$-HMPA-DMP)O_2) which was removed by filtration and set aside. The filtrate, a bright orange solution, was

again reduced to dryness on a rotary evaporator and purified by preparative TLC (90 CH_2Cl_2: 10 THF). The desired material was isolated as a deep orange powder. ^1H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.51 (s, 6H, methyls), 1.57 (s, 6H, methyls), 1.76 (s, 6H, methyls), 1.88 (s, 6H, methyls). IR (cm^{-1}, nujol): 970 ν(Os=O); 1700 ν(amides); 1715 ν(ketone). Anal. Calcd for $C_{15}H_{24}N_2O_5Os$: C, 34.75; H, 4.63; N, 5.40. Found: C, 35.08; H, 4.56; N, 5.32. The $K_2Os(\eta^4$-HMPA-DMP)O_2 (^1H NMR (δ, DMSO-d_6) shift (multiplicity, int., assign.), 1.18 (s, 12H, methyls), 1.62 (s, 12H, methyls). IR (cm^{-1}, nujol): 790 ν(O=Os=O); 1700 ν(ketone); 1600 ν(amides).) was treated with trifluoroacetic acid in THF to convert it to the Os(η^4-HMPA-DMP)O species, which was purified as described above. Combined yield, 0.57 g (35 percent). Ratios of $K_2Os(\eta^4$-HMPA-DMP)O_2 and Os(η^4-HMPA-DMP)O were not reproducible, and so the general procedure was to convert all the material to Os(η^4-HMPA-DMP)O without isolating the $K_2Os(\eta^4$-HMPA-DMP)O_2. Refluxing (2 days) Os(η^4-HMPA-DMP)O (100 mg) in $H_2{}^{18}O$(0.2 ml)/ THF (dry, 0.5 ml) effected partial (ca. 40 percent) ^{18}O labelling of the the oxo ligand. This was verified by IR: $\nu Os={}^{18}O$(calcd.); 719 cm^{-1}; observed; 719 cm^{-1}.

***trans*-Os(η^4-HMPA-DMP)$(py)_2$** Os(η^4-HMPA-DMP)O (0.200 g, 0.000386 mol) was dissolved in pyridine. The solution turned dark green. triphenylphosphine (0.600 g, 0.00229 mol) was added, whereupon the solution immediately turned bright orange-yellow. The solution was stirred under nitrogen (5 min, 21° C) and volatile impurities were removed under vacuum (21° C, 0.005 torr). A orange oil resulting which was washed three times with 100 ml portions of hexane. The resulting solid was recrystallized from CH_2Cl_2/hexane to give *trans*-Os(HMPA-DMP)$(py)_2$ as a yellow powder (0.230 g, 90 percent). ^1H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -22.19 (d J=7Hz, 4H, o-py), -7.58 (d;J=7Hz, 2H, p-py), 5.51 (s, 12H, methyls), 5.82 (d;J=7Hz, 4H, m-py), 11.48 (s, 12H, methyls). IR (cm^{-1}, nujol): 1692 ν(ketone); 1600 ν(amide); Anal. Calcd for $C_{25}H_{34}N_4O_5Os$: C, 45.47; H, 5.15; N, 8.48. Found: C, 45.42; H, 5.21;

N, 8.40.

trans-**Os(η^4-HMPA-DMP)(4-^{t}-butylpyridine)$_2$** This material was synthesized in 95 percent yield by the same method as for *trans*-Os(η^4-HMPA-DMP)(pyridine)$_2$. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -22.38 (d;J=7Hz, 4H, pyridine), -0.91 (s, 18H, ^{tert}-butyl), 5.39 (s, 12H, methyls), 5.59 (d;J=7Hz, 4H, pyridine), 11.45 (s, 12H, methyls). IR (cm^{-1}, nujol): 1681 ν(ketone); 1600 ν(amide); Anal. Calcd for $C_{33}H_{50}N_4O_5Os$: C, 51.28; H, 6.52; N, 7.25. Found: C, 51.76; H, 6.48; N, 6.81.

trans-**Os(η^4-HMPA-DMP)(4-methoxypyridine)$_2$** This was synthesized in 66 percent yield by the same method as for *trans*-Os(η^4-HMPA-DMP)(py)$_2$ ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -20.75 (d;J=7Hz, 4H,o-py), 2.76 (s, 6H, methoxy), 5.34 (s, 12H, methyls), 5.20 (s, 0.8H, CH_2Cl_2), 4.19 (d;J=7Hz, 4H, pyridine), 11.40 (s, 12H, methyls). IR (cm^{-1}, nujol): 1670 ν(ketone); 1610 ν(amide); Anal. Calcd for $C_{27}H_{38}N_4O_7Os$ 0.4 CH_2Cl_2(quantified by NMR) C, 43.55; H, 5.17; N, 7.41. Found: C, 43.77; H, 5.18; N, 7.44.

Os(η^4-HMPA-DMP)(4-acetylpyridine)$_2$ Os(HMPA-DMP)O (0.150 g, 285 μmol), triphenylphosphine (0.150 g, 550 μmol), and 4-acetylpyridine (0.5 ml) were stirred together. The reaction mixture became dark red. Volatile materials were removed under vacuum (0.005 torr, RT). As 4-acetylpyridine is very high boiling, several days of pumping under these conditions were required. The brown material which remained was washed with hexane (3 X 50 ml) and recrystallized from CH_2Cl_2/hexane. A brown-yellow powder (118 mg) was recovered in 40 percent yield. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.49 (s, 6H, CH_3), 1.54 (s, 6H, CH_3), 1.73 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 2.57 (s, 6H, -C(O)CH_3), 8.51 (d;J=5Hz, 4H, py), 8.78 (d;J=5Hz, 4H, py). IR (cm^{-1}, nujol): 1680 ν(ketone, acetyl); 1620 ν(amide); Anal. Calcd for $C_{29}H_{38}N_4O_7Os$: C, 46.78; H, 5.14; N, 7.52. Found: C, 46.56; H, 4.77; N, 7.15.

trans-**Os(η^4-HMPA-DMP)(4-dimethylaminopyridine)$_2$**. The same method was used as for *trans*-Os(η^4-HMPA-DMP)(py)$_2$, however, because 4-dimethylamino-pyridine is a solid, a small amount of THF was added to ensure homogeneity. On standing, the product crystallized out of solution in 90 percent yield. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 2.63 (d;J=7Hz, 4H, m-py), 5.14 (s, 12H, CH_3), 5.65 (s, 12H, CH_3), 11.36 (s, 12H, CH_3). IR (cm^{-1}, nujol): 1678 ν(ketone); 1622 ν(amide); Anal. Calcd for $C_{29}H_{44}N_6O_5Os$: C, 46.65; H, 5.90; N, 11.25. Found: C, 46.25; H, 5.75; N, 11.25.

trans-**Os(η^4-HMPA-DMP)(4-bromopyridine)$_2$** Os(HMPA-DMP)O (0.100 g, 193 μmol), triphenylphosphine (0.200 g, 763 μmol), and excess 4-bromopyridine were stirred (21° C, 1 hr) in THF (2ml). Volatiles were removed under vacuum (21° C, 0.005 torr) and the orange residue was washed three times with 100 ml aliquots of hexane. The resulting solid was purified by recrystallization (CH_2Cl_2/hexane) to yield the desired compound as a yellow powder (110 mg, 33 percent). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -21.71 (d;J=7Hz, 4H, pyridine), 5.48 (s, 12H, methyls), 6.30 (d;J=7Hz, 4H, pyridine), 11.27 (s, 12H, methyls). IR (cm^{-1}, nujol): 1681 ν(ketone); 1600 ν(amide); Anal. Calcd for $C_{25}H_{32}N_4O_5Br_2Os$: C, 36.70; H, 3.91; N, 6.84. Found: C, 36.49; H, 3.99; N, 6.67.

trans-**Os(η^4-HMPA-DMP)(2-(4-pyridyl)-2-methyl-1,3-dioxolane)$_2$** Os(HMPA-DMP)O (0.030g, 57.9 μmol), triphenylphosphine (0.070 g, 267 μmol), and 2-(4-pyridyl)-2-methyl-1,3-dioxolane (0.200 g) were added to a 10 ml round bottom flask. As all of these materials are solids, CH_2Cl_2 (3 ml) was added to effect homogeneity. The reaction mixture became a brilliant orange-yellow. The material was reduced to dryness on a rotary evaporator and washed exhaustively with hexane. Recrystallization from CH_2Cl_2/hexane yielded 0.048 g (quantitative yield) of the desired complex. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -22.20) (d; J=7Hz, 4H, o-py), 1.39-1.86 (mult, ca 8H, ethylene + Os(VI) CH_3), 0.25 (s, 6H, CH_3 (ketal)), 5.57

(s, 12H, CH_3(bridge)), 5.99 (d;J=7Hz, 4H, m-py) 11.43 (s, 12H, CH_3(arm)). IR (cm^{-1}, nujol): 1681 ν(ketone); 1588 ν(amide).

trans-**Os(η^4-HMPA-DMP)(4-pyrrolidinopyridine)$_2$**

Os(η^4-HMPA-DMP)O (0.100 g, 193 μmol) and triphenylphosphine (0.100 g, 382 μmol) were stirred in a mixture of excess (0.200 g) 4-pyrrolidinopyridine and 2 ml CH_2Cl_2. The CH_2Cl_2 was necessary to ensure homogeneity of the reaction mixture, as the reactants were all solids. The solution immediately became a bright orange yellow. The reaction mixure was reduced to dryness on a rotary evaporator and exhaustively washed with hexane to remove excess triphenylphosphine, triphenylphosphine oxide, and 4-pyrrolidinopyridine. A yellow solid remained which was recrystallized from CH_2Cl_2/hexane to yield 0.50 g (32 percent) of a bright yellow powder. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -19.90 (d;J=7Hz, 4H, o-py), 0.41 (br s, 8H, -CH_2-N-CH_2), 2.33 (d;J=7Hz, 4H, m-py), 5.14 (s, 12H, CH_3), 8.38 (br s, 8H, N-C-CH_2-CH_2-C), -19.90 (d;J=7Hz, 4H, o-py).

Os(η^4-HMBuA-B)O $K_2Os(OH)_4O_2$ (0.363 g, 987 μmol) was dissolved in methanol (200 ml) to form a blue solution. H_4-HMBuA-B (0.300g, 987 μmol) was added. The solution slowly turned brown. Stirring was continued (18 h, 21° C) and the solution was then reduced to dryness on a rotary evaporator. Acetone (200 ml) was added to the residue and the resulting slurry was stirred, filtered, and reduced to dryness on a rotary evaporator. THF (100 ml) was added, followed by 5 drops of trifluoroacetic acid. The mixture was filtered and the filtrate was again reduced to dryness on a rotary evaporator. The resulting oil was purified via preparative TLC eluting with CH_2Cl_2, which, after removal of solvents on a rotary evaporator, yielded the product as a brown solid (0.15 g, 31 percent).^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.47 (s, 6H, Me), 1.56 (s, 6H, Me), 2.98 (d;J=16Hz, 2H, methylene), 3.58 (d;J=16Hz, 2H, methylene), 7.03 (mult., 2H, aromatics), 8.61 (mult., 2H, aromatics). IR (cm^{-1}, nujol): 970 ν(Os=O); 1705,

1680, 1670; Anal. Calcd for $C_{16}H_{20}N_2O_5Os$: C, 37.66; H, 3.92; N, 5.49. Found: C, 38.42; H, 4.05; N, 5.29.

Os(η^4-HMBuA-DCB)O This compound was prepared in 34 percent yield in an analogous manner to Os(η^4-HMBuA-B) substituting H_4-HMBuA-DCB for H_4-HMBuA-B in the procedure, and purifying by preparative TLC eluting with 80 CH_2Cl_2/20 THF. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 1.45 (s, 6H, methyls), 1.55 (s, 6H, methyls), 2.94 (d;J=15Hz, 2H, methylene), 3.53 (d;J=15Hz, 2H, methylene), 8.83 (s, 2H, arom). IR (cm^{-1}, nujol): 960, 980 ν(Os=O); 1680, 1690 ν(amide); Anal. Calcd for $C_{16}H_{18}N_2O_5Cl_2Os$: C, 33.17; H, 3.11; N, 4.83. Found: C, 32.69; H, 3.22; N, 4.77.

***trans*-Os(η^4-HMBuA-B)(4-^{tert}-butylpyridine)$_2$** Os(HMBA-B)O (0.050 g, 0.000098 mol) was heated (ca. 100° C) in 4-^{tert}-butylpyridine (2ml) for thirty seconds. Triphenylphosphine (0.100 g, 0.000381 mol) was added. The reaction mixture immediately turned deep green. The reaction mixture was cooled and volatile impurities were removed under vacuum (21° C, 0.005 torr). The resulting green oil was washed with two aliquots of hexane (100 ml each) to remove residual 4-^{tert}-butylpyridine, triphenylphosphine, and triphenylphosphine oxide. A green solid formed which was recrystallized from CH_2Cl_2/hexane to give *trans*-Os(η^4-HMBuA-B)(4-^{tert}butylpyridine)$_2$ as green crystals (0.046 g, 50 percent). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -3.96 (s, 4H, methylenes), -0.23 (s, 18H, ^{t}butyl), 1.55 (s, 12H, methyls), 3.75 (m, 2H, arom), -4.72 (d;J=7Hz, 4H, pyridine), 7.85 (d;J=7Hz, 4H, pyridine), 9.15 (m, 2H, arom). IR (cm^{-1}, nujol): 1620 ν(amide); Anal. Calcd for $C_{34}H_{46}N_4O_4Os\cdot CH_2Cl_2$: C, 49.48; H, 5.65; N, 6.59. Found: C, 49.87; H, 5.63; N, 6.25. NMR shows that compound holds between 7/8 and 1 equivalent of CH_2Cl_2.

***trans*-Os(HMBuA-DCB)(4-^{tert}-butylpyridine)$_2$** Os(HMBuA-DCB)O (0.020 g, 34.5μmol) was dissolved in 4-^{tert}-butylpyridine. Triphenylphosphine (0.040 g, 153 μmol) was added and the mixture was heated to ca. 130° C. The

reaction mixture was cooled and excess 4-'tert'-butylpyridine was removed under vacuum (0.005 torr, RT). The resulting green residue was washed with hexane (2 x 50 ml) and recrystallized from CH_2Cl_2/hexane to yield the desired product as a green powder (0.015 g, 57 percent yield). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -5.56 (d;J=8Hz, 4H, py), -4.15 (s, 4H, methylene), 0.07 (s, 18H, 'butyl), 1.92 (s, 12H, CH_3), 7.89 (d;J=8Hz, 4H, py), 9.46 (s, 2H, arom). IR (cm^{-1}, nujol): 1630 ν(amide); Anal. Calcd for $C_{34}H_{44}N_4O_4Cl_2Os$: C, 48.99; H, 5.28; N, 6.72. Found: C, 48.49; H, 5.28; N, 6.72.

Os(η^4-HMPA-Pr)O Os(η^4-HMPA-Pr)O was prepared in 40 percent yield in an analogous manner to that of Os(HMPA-Et)O substituting H_4-HMPA-Pr for H_4-HMPA-Et. ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), 4.1-4.3 (mult, 2H, N-CH), 3.3-3.7 (mult, 2H, N-CH), 2.4-2.6 (mult, 2H,-C-CH_2-C-). IR (cm^{-1}, nujol): 1700 ν(amide carbonyl) overtone at 3385 cm^{-1}; 970 ν(Os=O); The compound analyzes for $C_{11}H_{18}N_2O_5Os$ 0.4 hexane solvate, quant. by NMR.

trans-**Os(η^4-HMPA-Pr)(py)$_2$** Os(η^4-HMPA-Pr)O (0.10 g, 223 μmol) and triphenylphosphine (0.30 g, 1.45 mmol) were stirred in neat pyridine (2 ml). The pale orange reaction mixture was heated (ca 100° C) for one minute. The color gradually changed to a brilliant orange-yellow. The reaction mixture was cooled and excess pyridine was removed under vacuum (0.005 torr, RT). A brown residue remained which was washed with three 50 ml aliquots of hexane. The resulting yellow solid was dissolved in CH_2Cl_2. Addition of hexane followed by slow removal of the CH_2Cl_2 on a rotary evaporator caused the desired complex to precipitate as a yellow powder (125 mg, 95 percent). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -16.26 (t; J=7Hz, 2H, p-py), -20.43 (d;J=7Hz , 4H, o-py), -15.26 (mult, 2H, -C-CH_2-C), +6.15 (t;J=7Hz, 4H, m-py), +12.15 (s, 12H, CH_3), +64.16 (mult, 4H, -CH_2-C-CH_2) . IR (cm^{-1}, nujol): 1581 ν(amide) Anal. Calcd for $C_{21}H_{28}N_4O_4Os$ C, 42.73; H, 4.74; N, 9.47. Found: C, 42.69; H, 4.88; N, 9.44.

trans-**Os(η^4-HMPA-Pr)(4-'butylpyridine)$_2$** Os(η^4-HMPA-pr)O (0.080

g, 0.179 mol) and triphenylphosphine (0.25 g, 954 μmol) were stirred in neat 4-^{t}butylpyrdine (2 ml). The pale orange reaction mixture was heated (ca 130° C) for one minute. The color gradually changed to a brilliant orange-yellow. After cooling, residual 4-^{t}butylpyridine was removed under vacuum (0.005 torr, RT). The resulting yellow-brown solid was washed with hexane (100 ml) and recrystallized from a mixture of CH_2Cl_2 and hexane. The desired *trans*-Os(HMPA-pr)(4-^{t}butylpyridine)$_2$ precipitated as a yellow powder (113 mg, 90 percent). ^{1}H NMR (δ, $CDCl_3$) shift (multiplicity, int., assign.), -20.33(d;J=7Hz, 4H, o-py), -4.85(mult, 2H, -C-CH_2-C), -0.48 (s, 18H, ^{t}Bu), 5.98 (d;J=7Hz, 4H, m-py), 12.57 (s, 12H, CH_3), 61.71 (mult, CH_2-C-CH_2). IR (cm^{-1}, nujol): 1600 ν(amide); Anal. Calcd for $C_{29}H_{44}N_4O_4Os$: C, 48.34; H, 6.38; N, 7.77. Found: C, 48.31; H, 6.26; N, 7.89.

Os(HMPA-DMP)pyCO *trans*-Os(η^4-HMPA-DMP)py$_2$ (0.15 g, 237 μmol) was dissolved in CH_2Cl_2 (50 ml). The solution was purged with nitrogen and saturated with gaseous carbon dioxide. The reaction vessel was sealed and allowed to stand (1 day). A gradual color change from yellow to red was observed. The reaction vessel was then opened to the atmosphere in a well ventilated fume hood and allowed to stand as such for 1 hour to dissipate the excess carbon monoxide. A red solid began to precipitate. The mixture was reduced to dryness on a rotary evaporator leaving a red powder in 40 percent yeild. Insolubility precluded NMR analysis. IR (cm^{-1}, nujol): 1941 ν(terminal carbonyl); 1705 ν(ketone); 1640 ν(pyridine); 1600 ν(amide). Elemental analysis is correct for the formulation Os(HMPA-DMP)pyCO, $C_{21}H_{29}N_3O_6Os$.

Magnetic moments were measured on a Cahn Faraday apparatus equipped with a permanent magnet. $HgCo(SCN)_4$ was used to calibrate the apparatus. Elemental analyses and mass spectra were obtained by Larry Henling at the Caltech analytical facility.

Electrochemical Data. Much of the electrochemical work was performed

with the assistance of James E. Toth at the California Institute of Technology. Cyclic voltammetry was performed on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer equipped with positive feedback IR compensation and a Model 175 universal programmer. Current voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. Controlled-potential electrolysis experiments were performed with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer using polite feedback IR compensation. For such experiments a three-compartment H-cell with a platinum-gauze counter electrode in one compartment was employed. A Corning Ag/AgCl double-junction reference electrode was employed.

Dichloromethane (EM Science) was distilled from calcium hydride on to activated 3 Å molecular sieves and stored under argon. Anhydrous sulfur dioxide (Matheson, 99.99 percent) was further purified by washing with concentrated sulfuric acid to remove SO_3 and residual water and passed through two 45-cm columns packed with P_2O_5 on glass wool for final drying. The sulfur dioxide was then condensed at -78° C into an electrochemical cell attached to a manifold. Tetrabutylammonium hexafluorophosphate was recrystallized twice from acetone/ether and vacuum dried at 80 °C. Sodium perchlorate was recrystallized twice from absolute ethanol and vacuum dried at 100 °C. Supporting electrolyte concentration in all cases was 0.1 M and osmium complex concentrations were typically 0.5-3 mM. The working electrode was a basal planar graphite electrode (Union Carbide). A new graphite surface was made for each sample by shaving a thin layer of graphite from the electrode surface. At the conclusion of each experiment ferrocene was added as an internal potential standard. All formal potentials were taken as the average of anodic and cathodic peak potentials and are reported vs. the ferrocinium/ferrocene couple which was consistently measured as +0.39 V vs. SCE in acetonitrile and +0.48 V vs SCE in methylene chloride unless otherwise noted. Peak-to-peak separation of the ferrocinium/ferrocene couple was similar to that of the osmium couples in all cases. Plots of peak current vs.

the square root of scan rate over the range 20-500 mV s^{-1} were made and found to be linear for couples that are stated to be reversible. All experiments were performed in standard two or three compartment electrochemical cells under an inert atmosphere. Where stated in the body the couples were checked for the number of Faradays transferred by bulk electrolysis.

General procedure for chemical preparation of Os(V)(η^4-HMPA-DMP)(4-X-pyridine)$_2{}^+NO_3{}^-$ 0.100 mg of a *trans*-Os(η^4-HMPA-DMP)(4-X-pyridine)$_2$ was dissolved in THF (10 ml) and CH_2Cl_2 (10 ml). Excess $Ce(IV)(NH_3)_6(NO_3)_2$ was added. The reaction mixture slowly turned to a deep red. The reaction mixture was filtered and reduced to dryness on a rotary evaporator. The residue was dissolved in CH_2Cl_2 and filtered. Hexane was added and slow removal of CH_2Cl_2 on a rotary evaporator caused precipitation of the oxidized product as a red solid. Characterization was extremely difficult due to paramagnetism and difficulties in purfication. IR shows a broad band between 1590 and 1650 corresponding to the multiple carbonyl groups in the molecule. The compounds could be re-reduced by addition of pyridine to solutions of the oxidized species in CH_2Cl_2, yielding the Os(IV) starting material. Electrochemical bulk oxidation of the Os(IV) yielded compounds with similar appearances to those produced chemically.

Os(V)(HMPA-DMP)O Os(VI)(η^4-HMPA-DMP)O was dissolved in THF distilled from Na/benzophenone. The solution was purged with nitrogen. This solution was added to a sodium amalgam mixture prepared by addition of sodium metal to liquid mercury under a steady stream of nitrogen. The pale orange solution changed to a deep green on stirring. The green solution was canulated into a flask containing pentane which had been purged with nitrogen for ten minutes. The reduced product precipitated as a pale green solid in 30 percent yield. IR: 1702 ν(carbonyl); 1600 ν(amide); 965 ν(Os=O). In solution, the compound is extremely air sensitive and is converted to the neutral starting material in a matter

of minutes. In the solid state the compound is only moderately air senstive.

General procedure to observe catalytic phosphine oxidation by *trans*-Os(η^4-HMPA-DMP)py$_2$ Os(η^4-HMPA-DMP)O (0.010 g) was dissolved in pyridine (3 ml). Triphenylphosphine (0.100 g) was added. The solution turned bright orange. The solution was allowed to stir in air for approximately 12 hours, after which TLC analysis showed no remaining triphenylphosphine nor any *trans*-Os(η^4-HMPA-DMP)py$_2$. At this time, another portion of 0.100 g of triphenylphosphine were added. The reaction mixture was again allowed to stir in air until no Os(IV) product nor triphenylphosphine remained. This required approximately 18 hours. The procedure was repeated. 24-36 hours were required to effect complete phosphine oxidation. TLC analysis at this time showed that there was little Os(IV) or Os(VI) complex remaining, indicative of some sort of catalyst deactivation pathway.

Crystal structure determination of Os(η^4-HMPA-DMP)O The crystal structure determination was carried out by Milton Smith with the help of Dr. Bernard Santarsiero at the Caltech crystallography facility. Bond lengths and bond angles may be found in the appendix.

Crystal data: monoclinic, space group $P2_1/c$, a = 10.022(1) Å, b = 15.417(2) Å, c = 12.187(3) Å, β = 100.935(15) °, V = 1848.9 Å^3, Z = 4. A crystal of dimensions 0.20x0.20x0.30 mm, bounded by the [100], [010] and [100] planes, was used to collect a hemisphere (+h, +/-k, +/-l) of data to /*theta* = 30° on an Enraf-Nonius CAD4 diffractometer with graphite monochromator and MoKα (λ = 0.7107 Å) radiation (11857 reflections, 100 hours). The three check reflections showed an average decrease in intensity of 1.5 percent and the intensity data were scaled accordingly. The data were reduced to $F-o^2$ and averaged over 2/m symmetry (5378 reflections, average goodness-of-fit of 1.19; average R^F of 0.069 for the 3528 paired reflections).

The osmium atom was derived from the Patterson map, and the remaining

structure was revealed by Fourier maps. Hydrogen atoms were calculated by assuming ideal geometry on the methyl units, and the remaining hydrogen atoms were located on difference Fourier maps; no hydrogen atoms were refined. Full-matrix least-squares refinement of atom coordinates and anisotropic Gaussian parameters, scale factor, and an isotropic secondary extinction parameter resulted in a goodness-of-fit S = 1.15 (n = 5378 reflections, v = 218 parameters), R_F = 0.064 (4449 reflections, I greater than 0), and R_F' = 0.021 (2697 reflections, I greater than 3σ). The final f value of the secondary extinction parameter was 0.454(11) x 10^6 (see Larson, *Acta Crystallogr.*, **23**, 664, 1967). Each shift less than 0.01 in final cycle, and the final difference map showed no peaks larger than 1.0 e/Å^3.

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CHAPTER THREE:
COPPER

Besides its significant role in biological processes, such as its involvement in methane monooxygenase,[1] tyrosinase,[2] galactose oxidase,[3] and hemocyanin,[4] copper is involved in a number of important chemical reactions. Important examples are the classic Cu(I) amine complexes which can oxidatively couple acetylenes, oxidize phenols and perform oxidative cleavage reactions among other conversions.[5]

Copper is stable in relatively few oxidation states. Except in the metallic form, Cu(0) is considered to be unstable. The vast majority of copper compounds involve copper in the +I or +II oxidation state.[6]

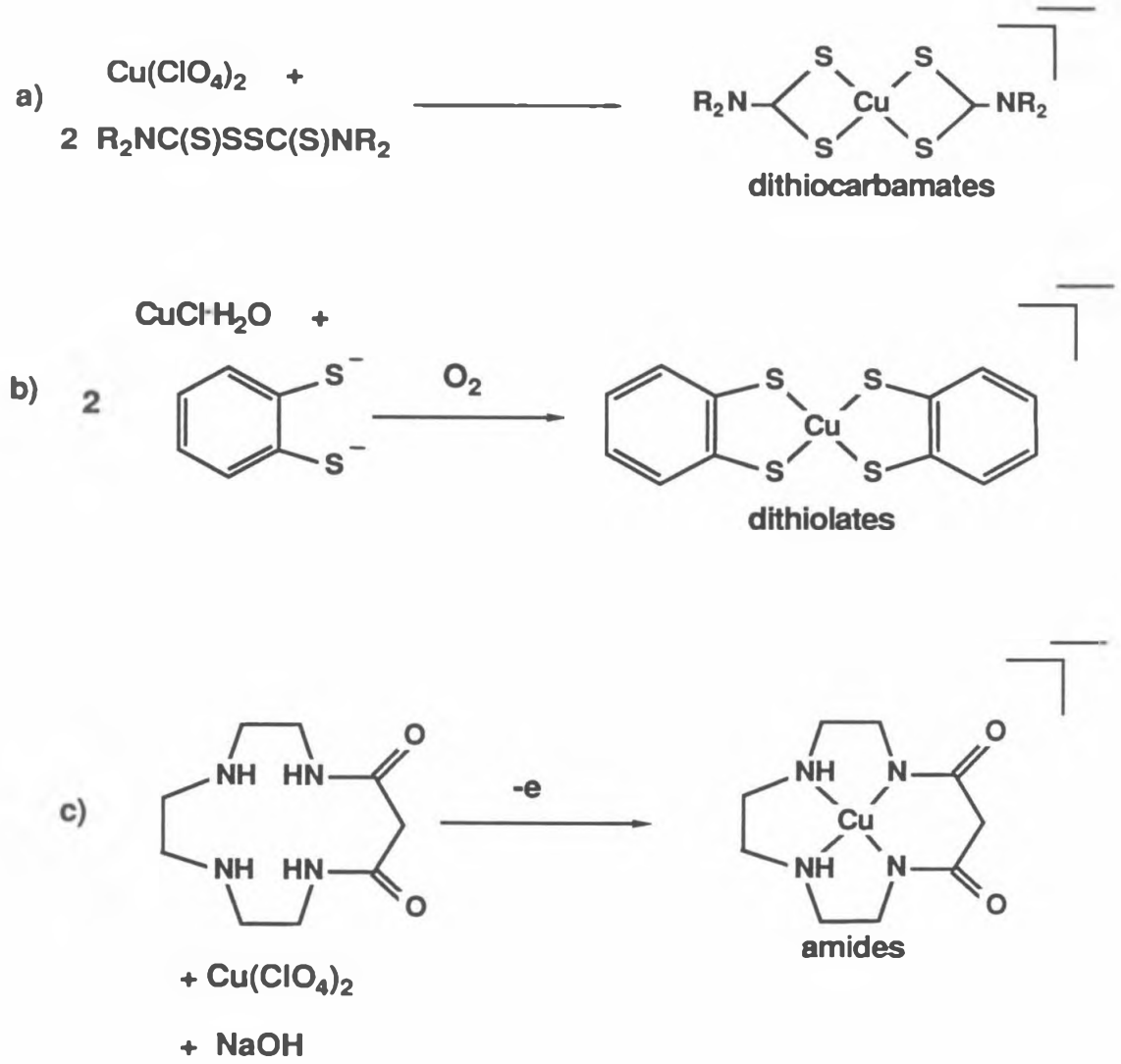
While Cu(III) has been known for over 170 years,[7] it is still considered an unusual valence for copper. With suitable ligand environments Cu(III) can be synthesized and isolated; numerous classes of such complexes exist. The simplest of these are the fluorides. Both octahedral CuF_6^{3-} and square planar CuF_4^- are obtained by high temperature and pressure fluorination of Cu(II) compounds.[8] A number of Cu(III) oxides are also known; for example $NaCuO_2$,[9] in addition to the newly discovered high-temperature superconductors.[10]

Many coordination complexes have been synthesized with a variety of first and second row donor atoms. The most common classes have sulfur and/or nitrogen donors.[11]

A large number of Cu(III) compounds have been synthesized from dithiocarbamates (Scheme 3-Ia). Since each ligand is anionic, the copper is surrounded by the equivalent of two anionic and two neutral sulfur donors. The Cu(III)/(II) potentials observed for such systems typically occur near +600 mV vs. SCE.[11,12]

Dithiolates have been successfully used to stabilize Cu(III).[11,13] Dithiolate complexes are made by the reaction shown in Scheme (3-Ib). The copper is surrounded by four anionic donor atoms. Correspondingly, the Cu(III)/(II) potential is observed to shift to significantly lower values. These complexes fit prominently in our discussion and are described in more detail below.

Nitrogen donors, both in the form of neutral amines and deprotonated



Scheme 3-I: Literature methods of Cu(III) synthesis.

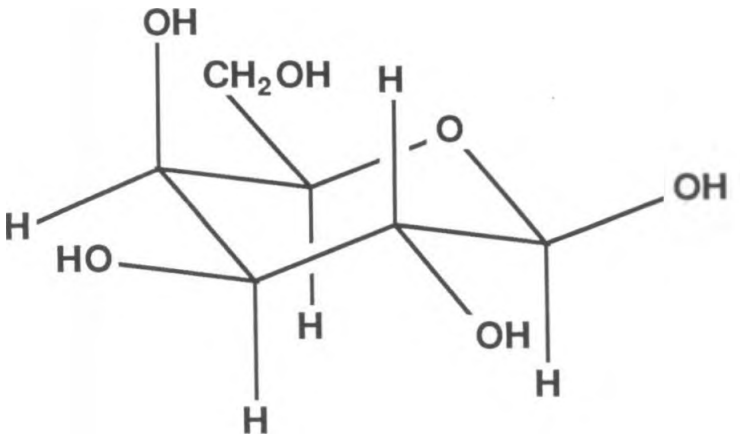
amides, have also been used to stabilize Cu(III). It has been observed that the deprotonated amido group stabilizes the higher valencies more than simple amine groups. When the four donor groups are all neutral amines (as in macrocyclic tetraamines) the Cu(III)/(II) potentials observed are very high, close to +1.0 V vs. SCE. Introduction of two amido groups into such a structure lowers the potential to approximately 0.0 V vs. SCE. A wide variety of complexes of these types including dozens of combinations and permutations of peptides have been synthesized.[11,14] A standard synthesis of Cu(III) peptides is shown in Scheme (3-Ic)

Cu(III) has also been synthesized using carboranes. Although these complexes are rare, one has been structurally characterized.[11,15,16] The strongly donating carbanionic donors lead to low potentials, approximately 0.15 V vs SCE.

In recent years Cu(III) has received increased attention. Cu(III) has been the postulated intermediate in a number of organic conversions (e.g. Ullmann coupling of aryl halides, air oxidation of copper alkoxides, cross coupling of alkyl groups, and decomposition of aromatic diazonium compounds).[17] Cu(III) oxides are an integral part of the exploding field of high-temperature superconductors.[10]

It has also been proposed that the active, oxidized form of galactose oxidase contains Cu(III), which serves as a two electron oxidant to convert an alcohol to an aldehyde.[18] Cu(III)'s involvement in galactose oxidase oxidations has been highly controversial. Hamilton, the chief proponent of such an intermediate, bases his postulate on the disappearance of an ESR signal on activation of galactose oxidase. He attributes this loss to the formation of diamagnetic Cu(III).[19]

Hamilton's views have been strongly criticized. Blumberg has put forth the view that instead of a Cu(III) intermediate, the active intermediate is a Cu(II) species with an oxidized ligand. The ligand centered radical would be very close to the Cu(II) center and strongly coupled to its spin. This would also explain the disappearance of the ESR signal. Hamilton argues that this is the same as a



GALACTOSE

formal Cu(III) intermediate. Others remain unconvinced. Margerum has argued that because a two electron process is suggested for a Cu(III) mediated galactose oxidase, similar two electron processes should be observed for synthetic Cu(III) complexes. Since such couples are not seen, it may be unrealistic to expect such a couple to exist in the enzyme.[19]

Part of the skepticism surrounding the possible role of Cu(III) from most of the observed potentials being very high. Kosman has suggested that to drive the oxidation of galactose, the Cu(III)/(II) potential could be no higher than 295 mV vs. SCE.[19] The nature of the copper site in galactose oxidase will be difficult to determine, and our experiments with PAC ligands will not resolve the argument. However, by introducing new ligand environments into Cu(III) chemistry, we can show how varied the chemistry of this oxidation state can be and how greatly the electrochemical potentials may be altered by varying the ligands. The pKa's of our PAC ligand donor atoms are much higher than those of the ligands which have typically been used to stabilize Cu(III), and thus our PAC ligands should

lead to extremly electron rich Cu(III) compounds.

In addition, most electrochemical studies of polyamide systems were performed in aqueous solution.[17] This will destabilize Cu(III) relative to Cu(II), as the Cu(II) starting materials are known to coordinate axial ligands. These ligands would have to dissociate in the formation of the d^8, square planar Cu(III).[6] Switching to less coordinating solvents, such as acetonitrile and especially methylene chloride will remove this stabilization of Cu(II) relative to Cu(III). The potentials should be lowered further.

Copper is a good choice for examining the higher valencies for other reasons. The highest lying electron in a square square planar d^9 system such as Cu(II) resides in the $d_{X^2-Y^2}$ orbital. Because the ligand donor atoms are located on the X and Y axes, any change in the ligand donors will greatly affect this orbital. Therefore, strongly donating ligands should dramatically lower the potentials.

With such questions in mind, we have studied the chemistry of copper with both Class I and Class II ligands. We have focused on the interaction of copper with H_4-CHBA-DCB, H_4-CHBA-Et, H_4-HMPA-DCB, H_4-HMPA-B, and H_4-HMPA-DMP. Reaction of the above ligands with $Cu(II)(OAc)_2 \cdot H_2O$ in basic ethanol/THF solution led to the formation of the $[Cu(II)(\eta^4\text{-PAC})]^{2+}$ complexes in high yield. The counterions depended on the base chosen. The $[Cu(\eta^4\text{-HMPA-DMP})]^{2+}$, $[Cu(\eta^4\text{-HMPA-DCB})]^{2+}$, and $[Cu(\eta^4\text{-HMPA-B})]^{2+}$ complexes could all be chemically oxidized to stable Cu(III) species with either inorganic (e.g. Ag(I)) or organic (e.g. benzoyl peroxide, *tert*-butyl hydrogen peroxide) oxidants. The Cu(II) species are paramagnetic and the ESR spectrum of $Na_2Cu(\eta^4\text{-HMPA-DMP})$ was measured. The expected pattern due to nitrogen hyperfine coupling is observed. The Cu(III) species are diamagnetic; unshifted, sharp NMR spectra can be observed for such complexes.[20]

The change from Class I to Class II ligands causes a large shift in the redox couple. The Cu(III)/(II) potentials for complexes of the type $[Cu(II)(\eta^4$-Class I

PAC)]$^{+2}$ are clustered about 0 V vs. Fc^+/Fc (+0.5 V vs SCE) while those for the analogous Class II complexes are clustered about -1.0 V vs. Fc^+/Fc (-0.5 V vs SCE) . In both Class I and Class II ligand complexes, the ligands are tetraanionic, and yet the redox couple differs in some cases by more than 1 volt. The Cu(III)/(II) couple for the Cu(η^4-HMPA-DMP)$^-$ species is -1.08 V vs Fc^+/Fc (-600 mV vs SCE) in methylene chloride. This is a remarkably low potential, more than half a volt lower than has been previously seen in polyamide complexes or any complexes incorporating first row donor atoms. Why the alkoxides should be such better donors than amides (when their pKa's are similar) is somewhat confusing. It is clear that simply equating the copper ion with a proton can be misleading. It is possible in the copper complexes that a significant portion of of the negative charge is delocalized on the carbonyl oxygen, more so than for the organic analog. Cu(III) amide complexes are usually drawn so that the negative charge is delocalized onto the carbonyl oxygen.[14] Such delocalization would attenuate the donor ability of the amido ligand. This would make the alkoxides comparatively better donors. Whether the delocalization explanation is valid or not, experiments recently performed in this group demonstrate that there is significant negative charge on the carbonyl oxygen atom of the deprotonated amide group.

It has been postulated that certain Cu(II) polyamide complexes should be air oxidized to Cu(III) complexes.[14] While the Cu(III)/(II) potentials have been in the correct range for this, no such oxidations were observed. In the copper complexes with Class II PAC ligands, we observe these compounds to be slowly air oxidized to the Cu(III) compounds.

In solution, Cu(η^4-HMPA-DMP)$^-$ appears to disproportionate to the Cu(II) species and an unidentified yellow material. It is tempting to suggest that this yellow species is a Cu(IV) complex, but on isolation we found this to be a ligand decomposition product of unknown structure. We had hoped that Cu(IV) would be accessible in these systems, but chemical oxidations have led to decomposition.

We have also failed to observe any electrochemical oxidations of Cu(III) solutions in methylene chloride, acetonitrile, or sulfur dioxide. Cu(IV) is extremely rare and has only been demonstrated to exist in CuF_6^{2-}; although it has been suggested that Cu(IV) is present in the material $BaCuO_{2.63}$. To date no examples of Cu(IV) coordination complexes have appeared.[6,11,21]

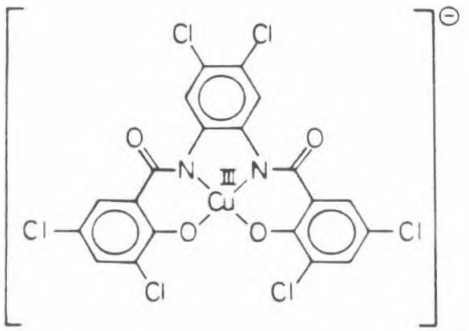
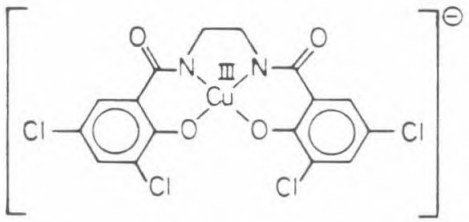
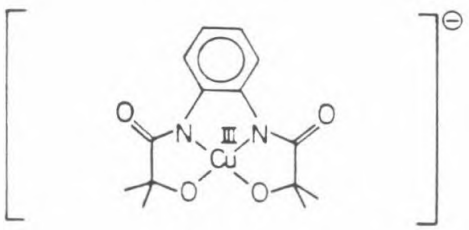
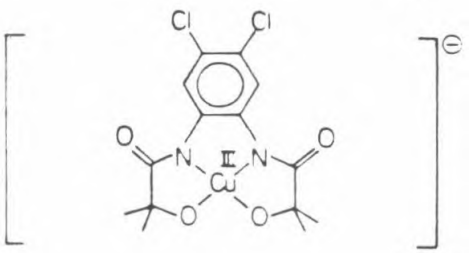
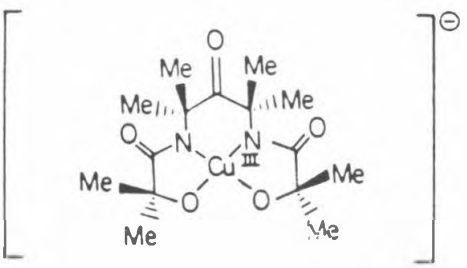
A complete table of Cu(III)/(II) potentials for all copper complexes synthesized in this work is shown as Table (3-I).

If we are correct in assuming that the Cu(III)/(II) potential in our systems is (to a good approximation) tied to the energy level of the $d_{x^2-y^2}$ orbital, the π-effects will be relatively unimportant and noninnocence arguments would not apply. We can test this by comparing the redox potentials of various PAC ligand copper complexes. If noninnocence operates through the π-ring system of the phenoxy donors, substitution of the *tert*-butoxy donors for phenoxy donors should raise the redox potential, because the possible stabilization imparted to the complex by the noninnocent aromatic system has been removed. The opposite is observed; the potential drops dramatically. If the aromatic bridge were being oxidized and quinoid and/or semiquinoid resonance structures were contributing, replacing this with the aliphatic bridge would raise the potential. Instead, the potential drops (although not as dramatically as with the arm substitution). These observations are consistent with the conclusion that the Class II PAC ligands coordinated to copper are not oxidized to any great extent and that the oxidized species may be best described as Cu(III).

We have also examined the effects of different solvents. Both methylene chloride and acetonitrile (two solvents which would be expected to differ greatly in their coordination and solvation properties) have been used as media for our experiments. In all cases, only small perturbations of the Cu(III)/(II) potentials are observed, suggesting that t any axial coordination of solvent is unlikely and that any effects due to different solvation properties affect both the copper complexes and the ferrocene internal standard similarly.

Table 3-I

COPPER(III/II) COUPLE FORMAL POTENTIALS (V vs. Fc^+/Fc)

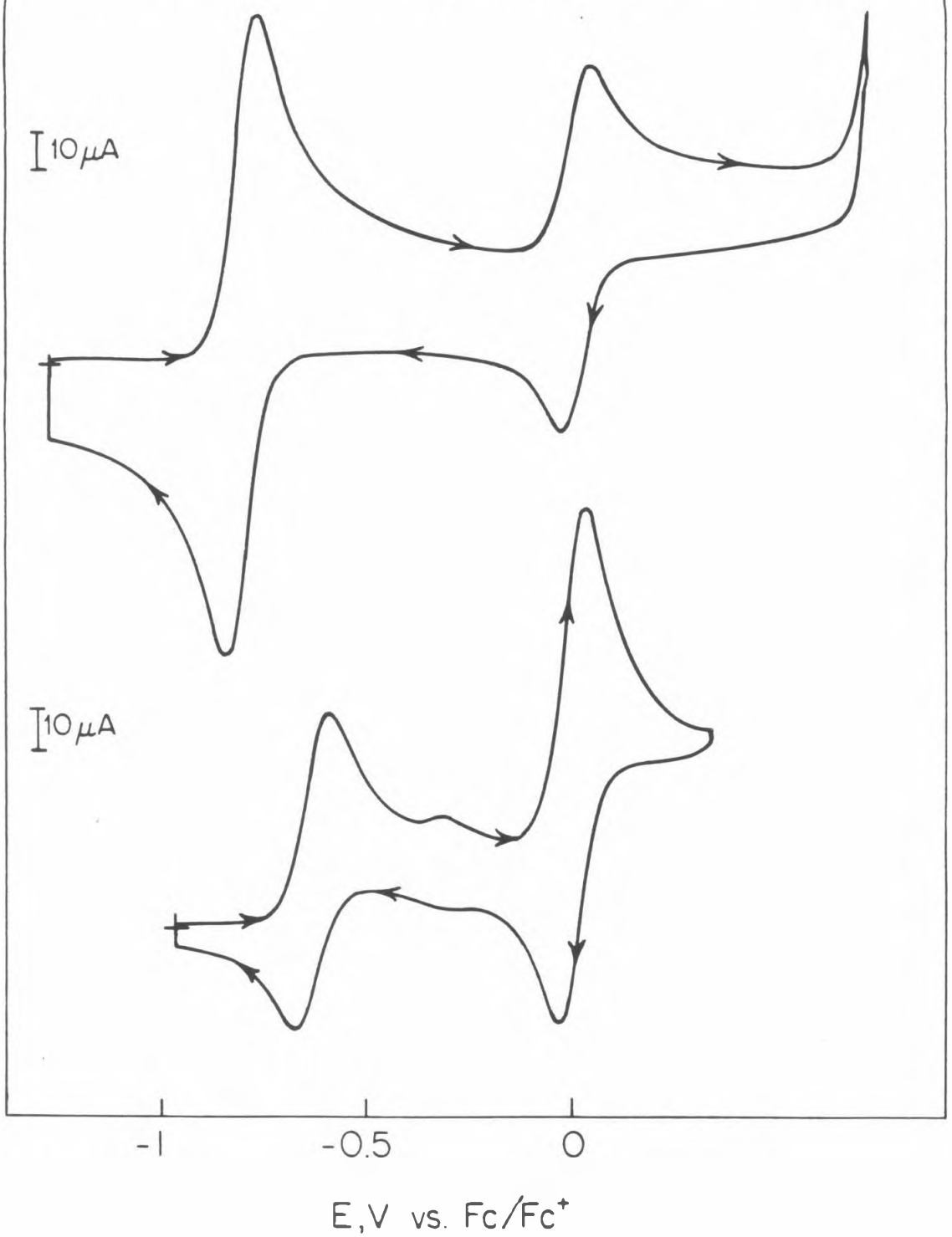
Copper(III) Complex	E^f (CH_2Cl_2)	E^f (CH_3CN)	Δ (mV)
	0.025	0.140	110 (20)
	-0.140	-0.100	45 (45)
	-0.945	-0.835	110 (20)
	-0.920	-0.848	70 (20)
	-1.080	-1.000	80 (10)

An interesting effect occurs when the tetraalkylammonium counterions are replaced with alkali metal cations. We first noticed irregular, irreproducible results when we examined the electrochemistry of the sodium salts of the Cu(II) or Cu(III) complexes. Two oxidation waves were observed. We hypothesized that rather than being due to impurities, the different peaks represented metal complexes in solution where the counterion varied, being either tetrabutylammonium (exchanged from the large excess of tetrabutylammonium perchlorate supporting electrolyte) or sodium. To address this problem, we synthesized all the complexes with tetraalkylammonium (or tetraphenylphosphonium) counterions, and it is the results for these compounds which are shown here. Where we saw two peaks, the lower potential observed corresponded to the complex synthesized with tetraalkylammonium counterions.

Cyclic voltammograms were taken before and after addition of 1.3 equivalents of $NaClO_4$ to a 0.1 M TBAP/methylene chloride solution of $(CH_3)_4N[Cu(III)(\eta^4$-HMPA-DMP)]. These are shown in Figure (3-2). The top and bottom portions of this figure show the cyclic voltammograms before and after addition of $NaClO_4$. Addition of the perchlorate salt caused the redox potential to shift 150 mV in a more positive direction. We believe that the alkali metal cation is acting as a Lewis acid, coordinated to the oxygen atoms of the alkoxide donor groups. Such coordination should shift the redox potential to a more positive value, since the donor ability of the ligand would be attenuated. Supporting evidence for this would be a crystal structure showing such coordination. In the next section a crystal structure of an analogous Co(III) complex is presented where sodium is indeed coordinated to the donor alkoxide atoms.

Other researchers have found that addition of sodium perchlorate to aqueous solutions of Cu(III) complexes *lowers* the Cu(III)/(II) potential. This appears to be in direct contradiction with our results. However, the cause of the shift in the potential is different in this case. These researchers propose that the perchlorate ion hydrogen bonds to the apical water molecules, thus weakening axial Cu(II)-

Figure 3-2: The effect of addition of $NaClO_4$ to an acetonitrile solution of $(CH_3)_4N[Cu(HMPA\text{-}DMP)]$



H_2O bonds. This leads to dissociation of the water ligands and so facilitates the formation of square planar Cu(III). The opposite effect is observed for Ni(III)/(II) couples, because loss of water ligands would destabilize octahedral Ni(III). These observations suggest that all such information concerning media effects must be examined very carefully, particularly in highly coordinating solvents.[11,22]

An X-ray crystal structure determination was performed for the complex $[PPh_4]Cu(\eta^4$-HMPA-B) (see Figure 3-3), where the cation would not coordinate to the donor atoms in the manner described above. A square planar environment for the metal center with normal bond distances and angles for the Cu(III) formulation is observed. The Cu-N bond distances (1.813(4) Å and 1.804(4) Å) are identical (within experimental error) to those found for the copper(III)-tripeptide complex of tri-α-amino-*iso*-butyric acid.[23]

It is interesting to compare our work with other work which has also produced Cu(III) complexes with very low formal potentials. Gray and coworkers synthesized a large number of Cu(III) complexes incorporating dithiolate ligands,[13] some of which are shown in Table (3-II). These complexes are synthesized from the corresponding dithiols, Cu(II), and base (Scheme (3-Ib)). The intermediate Cu(II) coordination compounds are air oxidized to (usually) green Cu(III) complexes. These complexes have been of great historical significance. The electronic structure of these compounds has been examined in detail experimentally and theoretically. Much of the evidence supporting the notion that Cu(III) assumes a square planar geometry comes from this early work.

These complexes exhibit potentials as low as -1.41 V vs. SCE (see Table 3-II)! This is more than 800 mV lower than the Cu(III)/(II) potential observed for $(CH_3)_4N[Cu(III)(\eta^4$-HMPA-DMP)].[13] We (and others) have observed a large lowering of the Cu(III)/Cu(II) potential with increased pKa's of the donor ligands. That a system with four aromatic thiolate donors (pKa's = 6-8) should be so much more electron rich than a system of 2 alkoxide donors (pKa = ca 19) and 2

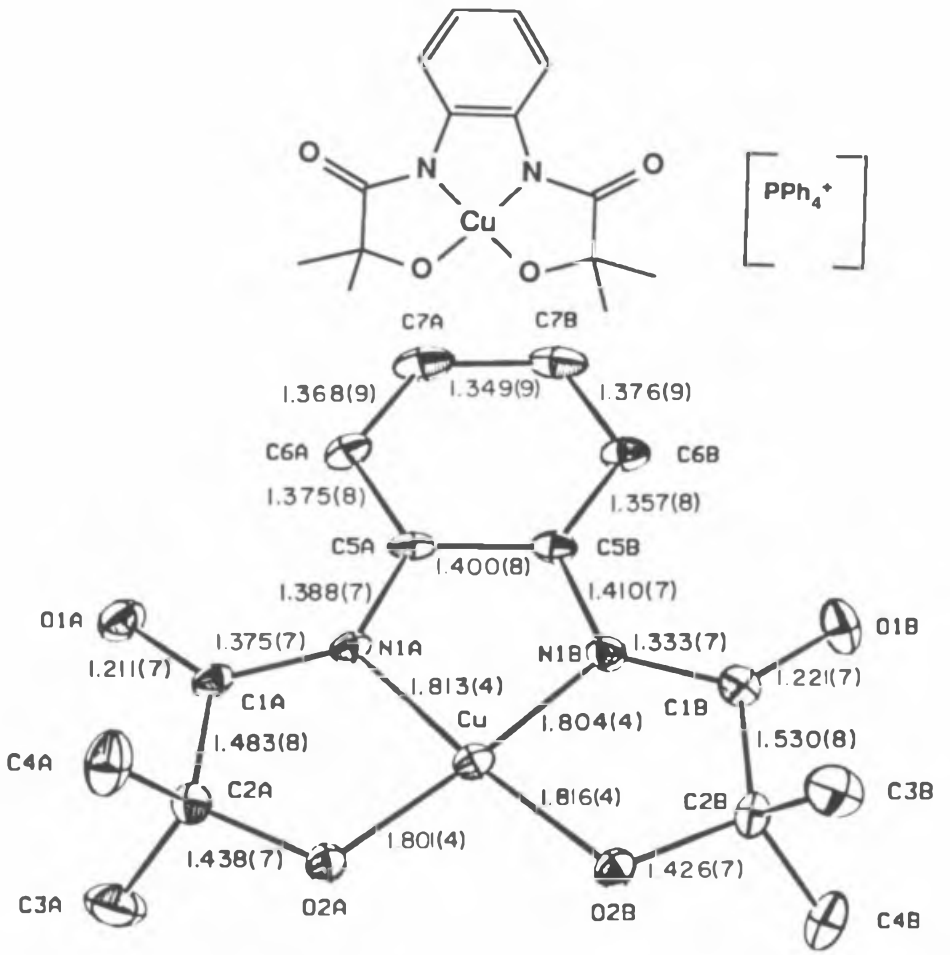


Figure 3-3: Crystal structure of [PPh_4]Cu(HMPA-B)

deprotonated amido donors (pKa = ca 17) was difficult to understand.[26]

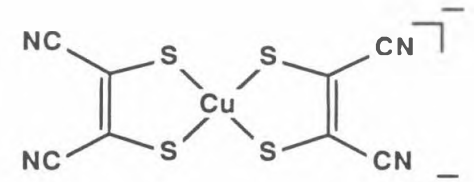
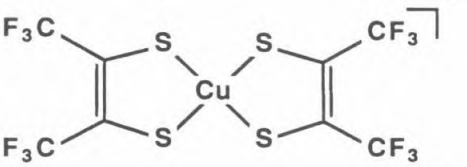
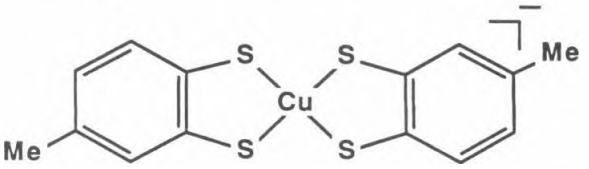
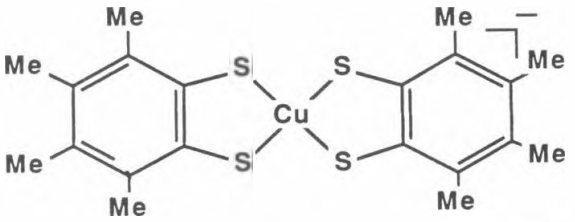
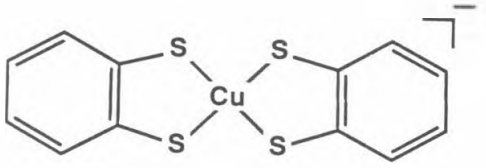
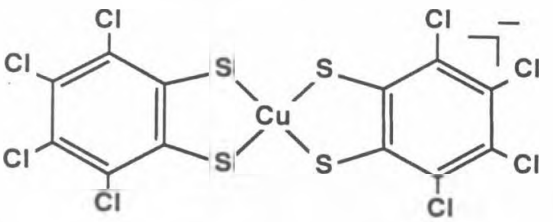
Because the copper dithiolate systems were studied polarographically in DMF, and our PAC systems were examined by cyclic voltammetry in methylene chloride and acetonitrile, we decided to reexamine Gray's dithiolate systems by cyclic voltammetry in methylene chloride and acetonitrile to better compare the two systems.

We chose the [tetrabutlyammonium]$^+$[Cu(1,2-benzenedithiolate)$_2$]$^-$ system, easily prepared by Gray's method. The cyclic voltammograms of this complex were examined in acetonitrile and methylene chloride. In methylene chloride, we observe the Cu(III)/Cu(II) wave at -1.07 vs. Fc^+/Fc (-0.59 V vs. SCE); in acetonitrile the wave occurs at -1.01 V vs. Fc^+/Fc (-0.62 V vs. SCE). (The sixty millivolt difference on switching solvents is normal.) The polarographic potential in DMF for this system is -1.14 V vs. SCE. On changing from DMF to dichloromethane, the formal potential shifts to a more positive value by more than half a volt. The redox potentials we have measured by cyclic voltammetry for the dithiolate systems are also very close to those we observe for our Class II PAC systems. Thus, the dithiolate systems do not significantly stabilize Cu(III) relative to the PAC systems. It remains, however, that the dithiolate ligands are as good donors as the Class II PAC ligands, despite the large difference in pKa's of the donor atoms of the ligand complements (see above). It is plausible that there is partial ligand oxidation which would lead to a lowering of the potential in the dithiolate systems. We have recognized this possibility in our systems and attempted to address this point by systematically removing the aromatic units from our PAC ligands. It would be revealing to follow a similar strategy with the dithiolate ligands, but unfortunately this is not feasible, since attempts to coordinate saturated alkyl thiolates to Cu(II) have led either to formation of di- or poly-nuclear compounds or to disulfide formation and reduction of Cu(II) to Cu(I).[24]

Although dithiolates are noninnocent, the assignment as formal Cu(III) com-

Table 3-II

Polarographic reduction potentials of copper bis-dithiolate complexes in DMF

Complex	$E_{1/2}$/V vs. SCE
	-0.201
	-0.010
	-1.15
	-1.41
	-1.14
	-0.752

pounds has been confirmed by molecular orbital calculations in a number of cases.[25] Workers in this field have been very concerned with the possible contributions of noninnocence to the nature of bonding in these systems, and have put much effort into applying various physical techniques to resolve the question. When feasible, it is worthwhile to examine the changes imparted to a metal center when the sources of noninnocence have been removed. This is what our work with copper-PAC systems has focused on. In removing the aromatic units and replacing them with aliphatic units, we have lowered the formal potentials in our systems by over a volt, and have achieved potentials which are lower than those previously observed in systems incorporating first row donor atoms by over half a volt. This is another example of Class II PAC ligands imparting new forms of reactivity to previously well-defined systems.

EXPERIMENTAL

All solvents were reagent grade (Aldrich, Baker, Malinckrodt, M.C.B., or U.S.I.) and were used as received except where noted for electrochemical purposes. Tetraphenylphosphonium chloride (Aldrich), tetra-*n*- butylammonium hydroxide (Aldrich), tetramethylammoniun hydroxide (Aldrich), silver acetate (Baker), benzoyl peroxide (Aldrich), *tert*-butyl hydroperoxide (Aldrich, 90%), and cupric acetate monohydrate (Malinckrodt) were used as received without further purification.

Electrochemical measurements were performed under conditions similar to those described in the experimental section of Chapter Two. Details may be found there or in reference 27, from which most of the material in this chapter has been taken.

$[(C_4H_9)_4N)]_2[Cu(\eta^4\text{-CHBA-Et})]$. H_4CHBA-Et (1.00 g, 2.28 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.45 g, 2.5 mmol) were mixed in ethanol (20 mL) and THF (20 mL) and the colorless solution with suspended copper acetate was stirred. A solution of tetrabutylammonium hydroxide in methanol (25%, 11.0 g, 42.5 mmol) was added and the reaction immediately became an intense translucent violet. The reaction mixture was stirred (1h), filtered, and the solvents were removed on a rotary evaporator. The residue was treated with THF (30 mL) and a purple solid formed which was collected by filtration and dried. Upon standing a second crop separated which was also collected and dried: combined yield, 2.20 g (90%). Anal. Calcd for $C_{24}H_{26}Cl_4CuN_4O$: C, 58.48; H, 8.52; N, 5.68. Found: C, 58.13; H, 8.56; N, 5.37.

$[(C_4H_9)_4N]_2[Cu(\eta^4\text{-CHBA-DCB})]$ This complex was prepared in an analogous manner to $[(C_4H_9)_4N]_2[Cu(\eta^4\text{-CHBA-Et})]$, substituting the ligand H_4-CHBA-DCB for H_4-CHBA-Et in the above preparation. Anal. Calcd for

$C_{28}H_{24}Cl_6CuN_4O_4$: C, 56.84; H, 6.55; N, 5.10. Found: C, 56.53; H, 6.92, N: 5.17.

$[(CH_3)_4N]_2[Cu(\eta^4\text{-HMPA-DCB})]$.
1,2-bis(2-hydroxy-2-methylpropanamido-3,4-dichlorobenzene (0.200 g, 573 μmol) and $Cu(OAc)_2 \cdot H_2O$ (0.115 g, 573 μmol) were mixed with $[(CH_3)_4N][OH] \cdot 5H_2O$ (0.104 g, 573 μmol) in absolute ethanol (25 mL) and stirred (1 h). The reaction mixture was filtered and the solvent was removed from the purple solution on a rotary evaporator. The remaining oil was treated with hexane to give a blue solid: yield 0.16 g (50%). A satisfactory elemental analysis was obtained for this hygroscopic compound if two waters of solvation were included in the molecular formula. However, independent verification of the solvate quantity was not obtained.

$[PPh_4][Cu(\eta^4\text{-HMPA-B})] \cdot 2H_2O$. $Cu(OAc)_2 \cdot H_2O$ (0.160 g, 797 μmol), H_4HMPA-B (0.200 g, 714 μmol), and NaOH (0.120 g) were stirred in ethanol (50 mL, 1 h). Addition of solid AgOAc (0.200 g) to the deep purple solution afforded a deep red solution which was filtered through celite to remove solids and the solvents were removed on a rotary evaporator. Redissolution in ethanol showed that some purple color remained so the oxidation with AgOAc was repeated. The product was dissolved in H_2O and addition of excess $[PPh_4]Cl$ in water caused precipitation. Recrystallization from acetone/water afforded plate-like crystals: yield 0.225 g (53%). Single crystals for X-ray diffraction were obtained from acetone/water. Anal. Calcd for $C_{38}H_{40}N_2CuO_6P$: C, 63.81; H, 5.64; N, 3.92. Found: C, 63.25; H, 5.33; N, 3.97. The sodium salt can be prepared by extraction of the $[PPh_4]^+$ salt into aqueous solution in the presence of 1 equivalent of $NaClO_4$. ^{1}H NMR of Na^+ salt (δ acetone-d_6) 7.85 (dd, 2H, C_6H_4), 6.75 (dd, 2H, C_6H_4), 1.23 (s, 12H, -$(CH_3)_2$C-).

$[(CH_3)_4N][Cu(\eta^4\text{-HMPA-DMP})]$. H_4HMPA-DMP (0.500 g, 1.58 mmol), $Cu(OAc)_2$ (0.287 g, 1.58 mmol) and $[(CH_3)_4N][OH] \cdot 5H_2O$ (1.140 g, 6.3 mmol) were stirred in ethanol (50 mL, 2 h). The ethanol was removed on a rotary

evaporator to leave a purple oil to which CH_2Cl_2 (50 mL) was added. The oil did not dissolve until excess *tert*-butyl hydroperoxide in toluene was added giving rapid formation of a red soluble product. The CH_2Cl_2 was removed on a rotary evaporator to leave a red oil which was recrystallized from CH_2Cl_2/cyclohexane to yield a red solid which was dried: yield 0.465g (63%). ^{1}H NMR (δ DMSO-d_6) 3.1 (s, 14.8H, $[(CH_3)_4N]^+$ and H_2O), 1.6 (s, 12H, -$(CH_3)_2$C-), 1.0 (s, 12H, -$(CH_3)_2$C-). IR (cm^{-1} nujol) 1600 ν_{CO} (amide), 1710 ν_{CO} (ketone). Anal. Calcd for $C_{19}H_{24}CuN_3O_5 \cdot 1.4(H_2O)$ (solvate quantified by ^{1}H NMR): C, 48.33; H, 7.81; N, 9.14. Found: C, 48.04; H, 8.16, N, 8.84.

Crystal Data for $[PPh_4][Cu(\eta^4\text{-}4)]\cdot 2H_2O$. Space group $P2_1/n$ (0k0 absent for k odd, h0l absent for h+l odd); the unit cell parameters at room temperature [a = 9.263 (1) Å, b = 14.446 (3) Å, c = 26.792 (4) Å, β = 96.056 (13)°, V = 3564 (1) Å^3, Z = 4] were obtained by least-squares refinement of 25 2θ values. The data were collected on a crystal at room temperature with an Enraf-Nonius CAD4 diffractometer (graphite monochromator and MoKα radiation λ = 0.7107 Å). The total in a hemisphere to 2θ = 50°, 14252 ($+h,\pm k,\pm \ell$), yielded an average data set of 6248 reflections; 5182 had $I > 0$ and 2329 had $I > 3\sigma_I$. The three check reflections indicated an average linear decrease of 8.8% in intensity over the 266 hours of data collection, and the intensity data were corrected accordingly and reduced to F^2. The coordinates of the Cu atom were derived from a Patterson map, and the remainder of the structure was revealed by Fourier maps. Hydrogen atoms were located from difference Fourier maps and introduced into the model with idealized positions and isotropic B = 4.0 A^2; they were not refined. Full-matrix least-squares refinement of atom coordinates and anisotropic U_{ij}'s for all non-hydrogen atoms minimizing $\Sigma w\Delta^2$ with weights $w = \sigma_{F^2}{}^{-2}$ and $\Delta = {F_o}^2 - ({F_c}^2/k)^2$ gave S (goodness-of-fit) $[\Sigma w\Delta^2/(n\text{-}p)]^{1/2}$ = 1.42 (p = 433), $R_F = (\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 0) = 0.144$, and $R_{3\sigma}$ (R for $I > 1_{\sigma I}$) = 0.061; average final shift/error < 0.10. Final atom coordinates are given in Table 1. All calculations were carried out on a VAX 11/750 computer using the **CRYRM**

system of programs. The form factors were taken from the *International Tables of X-ray Crystallography*, **Vol. IV**, Table 2.2B (1974); those for Cu and P were corrected for anomalous dispersion.

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(20) The ESR spectrum of the Na_2Cu(II)HMPA-DMP species was observed in frozen THF/ETOH solutions. The expected pattern indicative of the nitrogen hyperfine coupling was observed.

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CHAPTER FOUR:
COBALT

Cobalt has found great utility in chemical conversions. Even in comparatively simple forms, cobalt has exceptional utility. For example, simple cobalt amines can activate carbon-hydrogen bonds and hydroxylate aromatic rings; many other forms of reactivity are available, one of the most useful of which is hydroformylation of olefins.[1] A particularly fascinating example of cobalt's utility is its use in synthesizing the first aromatic ring with two ortho *tert*-butyl substituents.[2]

Cobalt compounds also serve as reversible dioxygen carriers. The properties of such carriers have been extensively reviewed.[3] Recently, a group of researchers has used an approach to enhancing efficiency of dioxygen carriers using a ligand design strategy somewhat similar to that described in this work.[4] These workers were only concerned about oxidative sensitivity and ignored the problem of ligand non-innocence.

The higher valencies of cobalt, if suitably stabilized, should yield useful forms of oxidative reactivity. The powerfully donating Class II PAC ligands seemed ideal for this purpose.

It is generally accepted that cobalt in oxidation states of +IV or higher is unstable and inaccessible except under extreme conditions.[5] The theory that high valent cobalt is unstable has been applied dogmatically in describing the mechanism of cobalt centered processes.[1a]

There are instances where the higher valencies of cobalt are known; these have been divided into three classes of compounds:[6] inorganic salts, organometallic species, and coordination complexes.

Inorganic Salts

In this category Co(IV) exists in both the tetrahedral Ba_2CoO_4[7] and octahedral Cs_2CoF_6.[8] These compounds are synthesized under high temperature and pressure conditions and have been well characterized.

While its existence has been claimed, it has proved more difficult to demonstrate the existence of Co(V) in similar complexes.

Organometallic Species

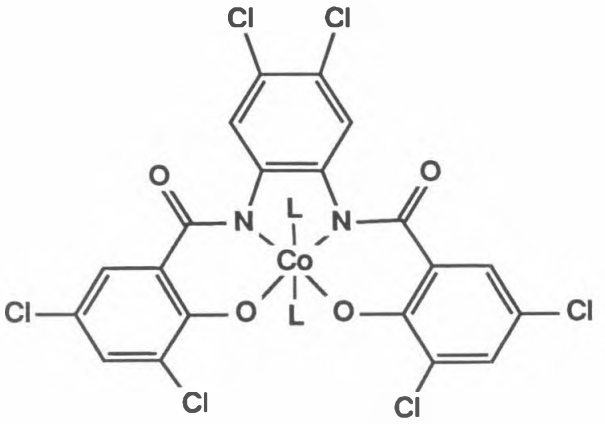
Organometallic compounds containing unusually high valent cobalt are well known. A well documented example is the extremely stable Co(1-norbornyl)$_4$ compound which has been structurally characterized (See Figure 4-1). In this compound, the cobalt is in the +IV oxidation state.[9,10] It is readily oxidized to Co(V) either chemically or electrochemically.[11] This system not only possesses extremely donating ligands (carbanions) but also an innocent ligand complement, therefore assignment of the metal's oxidation state is simple.

In addition there are the Co(IV) species synthesized by Halpern and coworkers.[12] While these species are unstable, they have been characterized in solution. In similar systems, Co(V) has been postulated as a high energy intermediate, but no supporting evidence has been obtained.[12c]

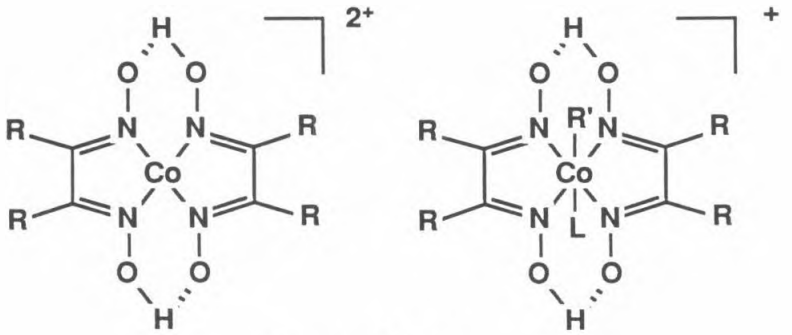
Coordination Complexes

In this class there have been very few examples of well-characterized stable Co(IV) complexes. Probably the best documented Co(IV) coordination complexes are those shown in Figure (4-1). These complexes are very similar to those studied by Halpern, the only difference being the former are devoid of axial ligands.[13]

It is to the coordination complexes that we can conceivably make a significant contribution. Using Class I ligands, complexes such as *trans*-Co(η^4-CHBADCB)L$_2$ (see Figure 4-1) have been produced which have been assigned as Co(IV) complexes.[15] Non-innocence dogs assignment of oxidation state in this work. It seemed logical to take a similar approach to cobalt as we did to copper, replacing the Class I ligands with innocent, more strongly donating Class II ligands and so eliminate the ambiguity in oxidation state assignment, further stabilize the Co(IV) complexes and allow access to still higher oxidation states.



L = 4-tert-butylpyridine



L = py , H_2O

R' = 4-X-Bz, Me, i-prop

R = Me, Ph

Figure 4-1: Examples of Co(IV) compounds
(for references, see text)

Our observations were surprising. While Class I ligands stabilize the octahedral geometry for Co(III), only square planar Co(III) complexes could be isolated in reactions of cobalt with Class II ligands.

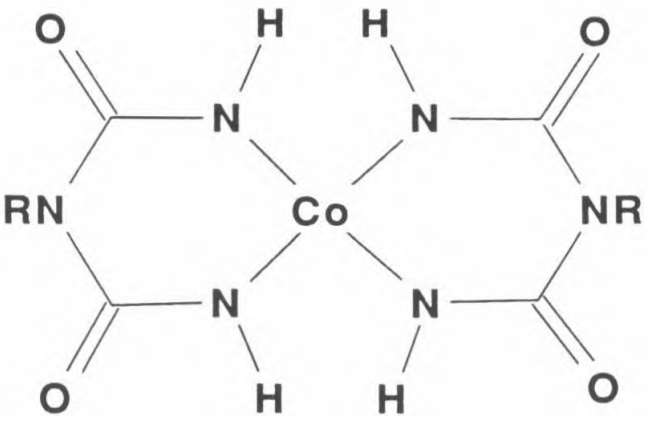
Co(III), a d^6 system, virtually always exhibits octahedral coordination geometry.[5] One rarely finds Co(III) in the square planar form. A handful of such compounds were known before this work, and some important examples are illustrated in Figure (4-2). The key to stabilizing this geometry is to have four strongly σ-donating anionic ligands and/or a complex π-system which will interact strongly with the metal d_{xz}, d_{yz}, and p_z orbitals.[16]

The square planar Co(III) complexes which have been synthesized with these Class II ligands are shown in Figure (4-3). The ligands all meet the σ- requirement; those ligands with aromatic bridges may meet the π- requirement. There seems to be some interaction with the aromatic bridge as all Co(III) square planar complexes which we have synthesized with aromatic bridges are deep green, while those with aliphatic bridges are bright orange. The interaction with the π-orbitals of the bridging unit shifts the absorption to longer wavelength.[17]

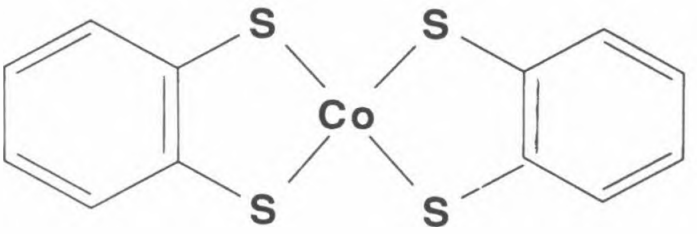
The change from octahedral geometry to square planar geometry may be seen as a continuous process. The Na[Co(III)(η^4-HMPA-B)] complex has an affinity, albeit low, for axial ligands. It is likely that small perturbations in the ligand could lead to large changes in the affinity for axial ligands.[17]

Structural determinations have been carried out for both Na[Co(III)(η^4-HMPA-B)][17] and Na[Co(III)(η^4-HMPA-DMP)].[19] These are illustrated in Figure (4-4). No significant shortening of C-N bond lengths is observed. Co(III) is the best description of the metal center. The magnetic moments of the Co(III) square planar compounds are consistent with the formulation as a system with two unpaired spins.[17-19]

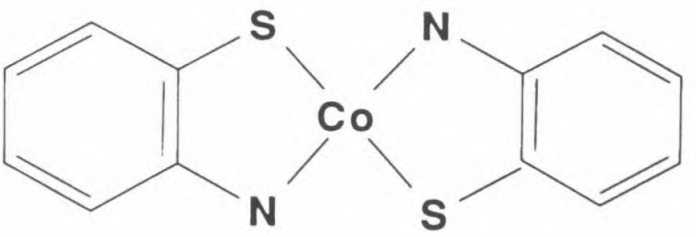
Although the species are paramagnetic, NMR spectra, while broadened and shifted, have been observed for all the species described in this section. Observa-



Birker, et al, Inorg. Chem., 12, 1973, 1254.



Van Der Put and Schilperoord, Inorg. Chem., 13, 1974, 2476.



Birker, et al, J. Coord Chem., 3, 1974, 175.

Figure 4-2: Examples of square planar Co(III) Note that all of the ligands are very strong sigma and/or pi donors.

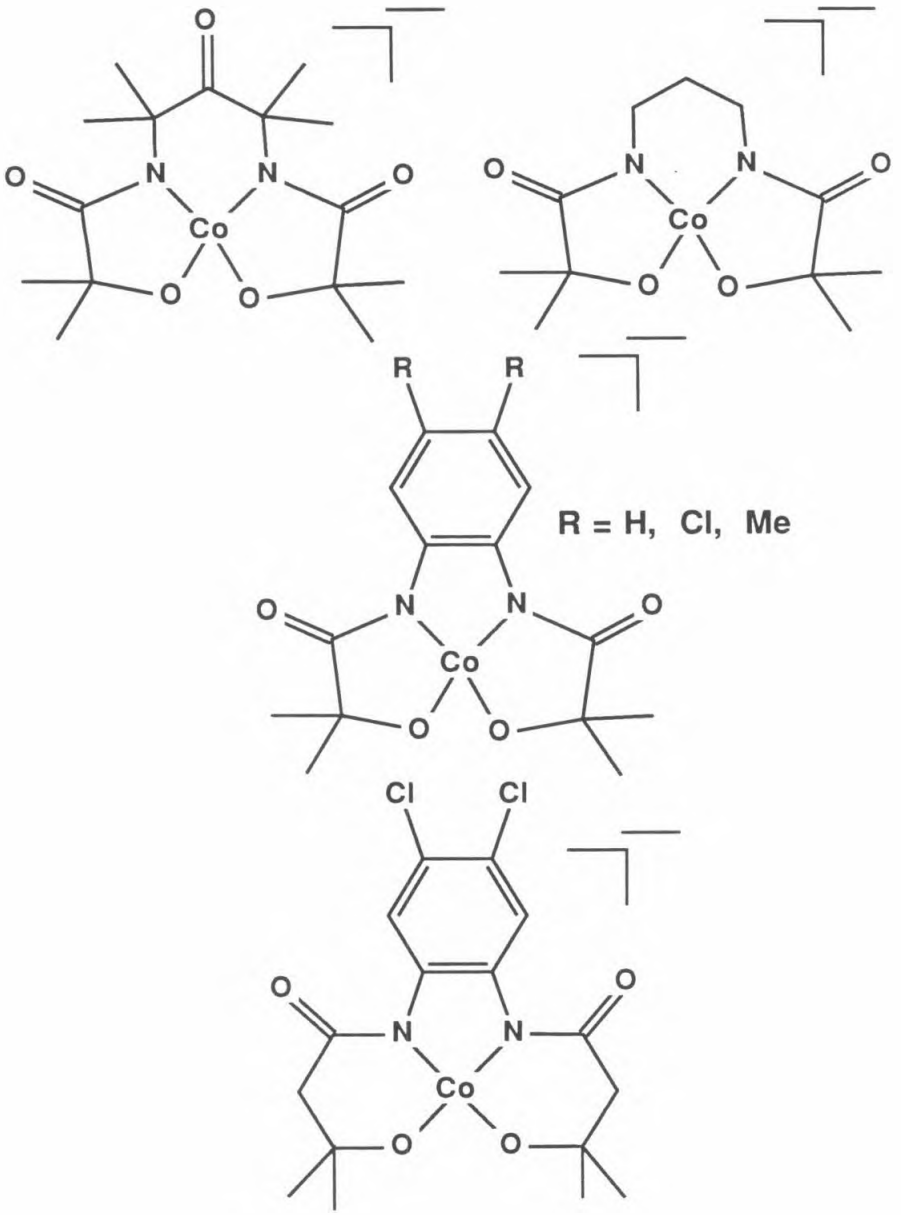


Figure 4-3: Co(III) square planar compounds incorporating Class II PAC ligands

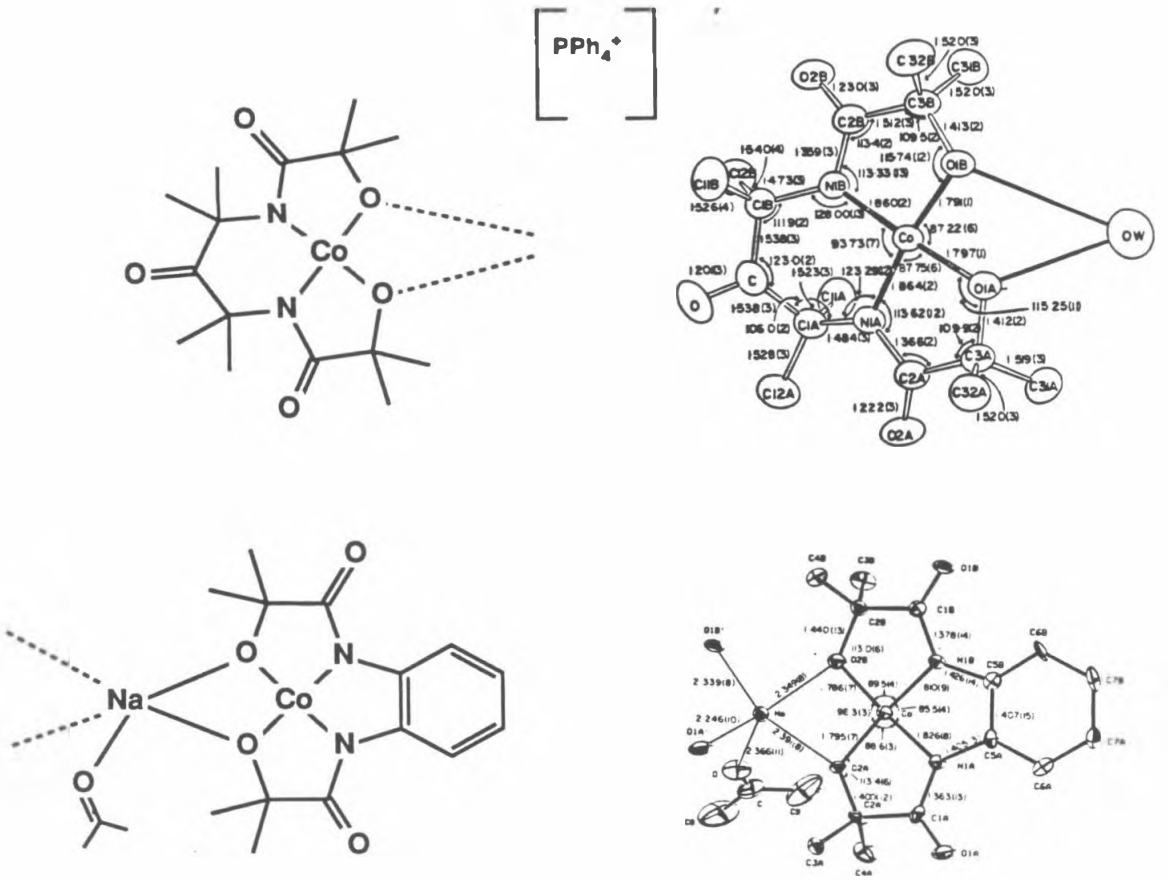


Figure 4-4: Crystal structures of PPh_4[Co(HMPA-DMP)] (top) and Na[Co(HMPA-B)] (bottom).

tion of NMR spectra for paramagnetic species has often been observed previously. The chemical shift values become meaningless, but the appearance of peaks, the number of peaks observed and their integrations remain useful for characterization purposes.[17]

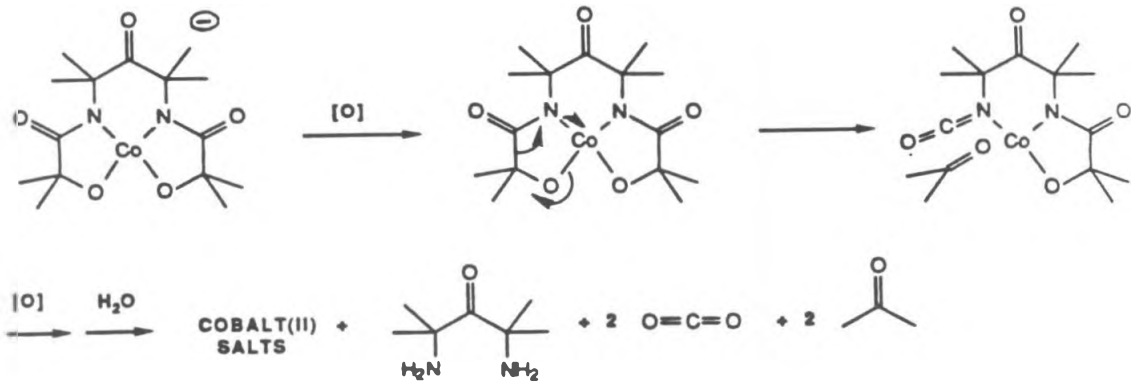
Electronic effects play a large role in determining these compounds affinity for axial ligands (or lack thereof). However, there is probably also a steric effect. The planar Class I ligands are far less sterically demanding than the Class II ligands which possess methyl groups which will interact with an ancillary ligand. Such interactions would lower the binding constants for such ligands. That the system where the ligand is most sterically demanding, Na[Co(III)(η^4-HMPA-DMP)], has no observable affinity for axial ligands is consistent with this argument;[6] Na[Co(III)(η^4-HMPA-B)], still a sterically demanding complex, but less so than Na[Co(III)(η^4-HMPA-DMP)] since there are no methyl groups on the aromatic bridge, has a small but measurable affinity for pyridine. For this system, the equilibrium constant for the square planar complex coordinating two pyridines to form the octahedral complex is 2.6 x 10^6 $mol^{-2}L^2$ in H_2O at 298 K and 37 $mol^{-2}L^2$ in ethanol at 298 K.[17] These observations are also consistent with the proposed steric labilization of pyridine axial ligands in Os(IV) complexes which was discussed in Chapter Two.

The square planar Co(III) complexes described here act as catalysts for styrene epoxidation using iodosoarenes as the stoichiometric oxidants.[20] The mechanism of the oxidation process is unclear. In similar processes, terminal oxo species have been proposed as the active intermediates.[22] Attempts to observe such a species in these systems have been unsuccessful. All of the catalysts slowly decompose. A plausible mechanism for this decomposition is acetone elimination, similar to that observed in the mass spectrum of Os(PAC)O species described in Chapter Two. In solution, this path would lead to a coordinated *iso*-cyanate complex, as shown in Scheme (4-1). We synthesized the ligands with the HMBuA (hydroxymethylbutamido) units so that this decomposition pathway could

be eliminated. While H_4-HMBuA-DMP fails to coordinate to cobalt, we have been able to synthesize Na[Co(III)(η^4- HMBuA-DCB)].[21,23]

These square planar compounds have been examined using cyclic voltammetric methods. In no case could any reversible oxidations be observed. It appears that square planar coordination will not be sufficient to stabilize Co(IV) or higher oxidation states. Axial ligands will probably be necessary to obtain high valent cobalt in these systems.

While the work described in this section was unsuccessful in producing stable Co(IV) compounds, we have made the square planar geometry for Co(III) more common and in doing so have demonstrated new forms of reactivity for cobalt, for example, the epoxidation of styrene. The square planar cobalt compounds also appear to have an interesting coordination chemistry. In related work in the Collins group, alkylation of the ligand has been effected to yield the first neutral square planar Co(III) compounds; the compounds also appear to react with sulfur dioxide and diatomic halogens, but these reactions are not yet understood.[6,19]



Scheme 4-I: A decomposition of an oxidized Co(Class II PAC) ligand proceeding by elimination of acetone followed by hydrolysis and further oxidation.

EXPERIMENTAL

MATERIALS Acetone (EM Science), hexanes (Aldrich), ethanol (USI), and pentane (EM Science) were used as received. Tetrahydrofuran was distilled from sodium benzophenone ketyl before use. Anyhydrous cobalt acetate (Alfa) and sodium hydroxide (Baker) were used as received. Analytical thin layer chromatography plates were 250 μm silica gel GF (Analtech).

Na[Co(η^4-HMPA-B)], Na[Co(η^4-HMPA-DCB)], and PPh_4[Co(η^4- HMPA-B)] are described in reference 17. Na[Co(η^4-HMPA-DMP)] and PPh_4[Co(η^4-HMPA-DMP)] are described in references 6 and 19. Experimental details may be found therein. Electrochemical measurements were performed under the conditions described in the experimental section of chapter three. Elemental analyses were performed by Larry Henling at the Caltech Analytical Facility. Magnetic moments were obtained on a Cahn Faraday balance equipped with a permanent magnet. The experimental apparatus was characterized with $HgCo(SCN)_4$ each day that a measurement was made. The moments were corrected using the moment of the free ligand and standard values for common atoms and ions. NMR spectra were obtained on a Varian EM-390 90 MHz CW spectrometer or on a Jeol 400 MHz FT spectrometer.

Na[Co(η^4-HMBuA-DCB)] H_4-HMBuA-DCB (0.100 g, 0.000265 mol) and $Co(OAc)_2$ (0.520 g, 0.000292 mol) were stirred in a mixture of THF (5 ml) and ethanol (5 ml). Both solvents were required as the the ligand is only sparingly soluble in ethanol and the cobaltous acetate is insoluble in THF. The reaction vessel was fitted with a drying tube and the reaction mixture was stirred (RT, 12 hr). The reaction mixture, which had been a pink suspension, became a deep green solution. This solution was filtered through a pad of celite to remove insoluble cobalt impurities. The pad was washed with acetone (20 ml). The solution was reduced to dryness on a rotary evaporator, redissolved in acetone,

and filtered once more through celite. The filtrate was reduced to a small volume whereupon methylene chloride was added. The desired complex precipitated as a green polycrystalline solid (0.050 g, 44 percent). ^{1}H NMR (EM-390, δ, Acetone-d_6) shift (multiplicity, int., assign.), 4.84 (br s, 2H, arom), -3.96 (br s, 12H, methyls), -6.82 (br s, 4H, methylene). Elemental analysis demonstrates that the material is isolated as a hemihydrate.

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(18) A magnetic moment of 3.5 BM was observed for NaCo(η^4-HMBuA- DCB). This value is somewhat higher than the spin only value for a system containing two unpaired electrons. It is, however, in the neighborhood of the values observed for similar complexes described in reference 17. A typical broadened and shifted NMR spectrum was observed for this species, as has been observed for the other square planar Co(III) compounds described.

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(21) Assays of the catalytic species of this and related 6,5,6 compounds will be performed in collaboration with Shigeko Ozaki at the Osaka Pharmaceutical Institute of Japan.

(22) Discussions may be found in (a) Cytochrome P-450. Structure, Mechanism, and Biochemistry, Ortiz de Montellano, P.R. Ed.; Plenum Press, New York, 1986; (b) VanAtta, R.B.; Franklin, C.C.; Valentine, J.S.; *Inorg. Chem.* **1984**, *23*, 4121; (c) Lee, W.A.; Bruice, T.C.; *Inorg. Chem.* **1986**, *25*, 131; (d) Koola, J.D.; Kochi, J.K.; *Inorg. Chem.* **1987**, *26*, 909.

(23) The reaction of H_4-HMBuA-B with cobalt is confusing. A color change

indicative of formation of the square planar trivalent cobalt complex is observed; however, we have been unsuccessful in isolating the product in pure form.

CONCLUSIONS AND OUTLOOK

While the project has been successful in a number of aspects, it appears that we have not yet observed the kinds of contributions to oxidation chemistry which we had originally expected, that is, in the production of extremely high and rare oxidation states. Rather, we have observed new and interesting reactivity from oxidation states which were generally regarded as well understood. The potentials observed for the copper systems show that π- interactions are not necessary to stabilize Cu(III). The cobalt square planar species which have been produced have reactivities similar to Fe(II) square planar systems. While the higher oxidation states of cobalt were not accessible via this route, the new forms of reactivity demonstrate that our efforts in ligand modification have been fruitful. The osmium systems also attest to this point: both electron transfer and atom transfer oxidants have been produced, and their reactivity can be controlled to a large degree by the appropriate choice of PAC and ancillary ligands.

The future of this project will certainly entail further improvements in ligand design. The use of Co(III)-6,x,6 square planar compounds in olefin epoxidation will demonstrate if by shutting down the acetone elimination pathway we can produce a longer lived catalyst. Of course, the methylene group may introduce new pathways of catalyst degradation. Copper compounds incorporating the HMBuA- B and HMBuA-DCB unit are highly unstable, possibly due to the presence of the weak C-H bonds. More experiments will need to be performed to answer this question. There is also the possibility of enantioselective catalysts. If asymmetry is introduced into the PAC ligand, then there is the potential for achieving asymmetric olefin epoxidation. Dr. Shigeko Ozaki, who spent a year in our group learning of our approach to oxidation chemistry, is presently pursuing this in Japan. Similar approaches also apply to the osmium atom transfer catalysis. As discussed in the end of Chapter Two, introduction of trifluoromethyl groups may not only introduce asymmetry into the catalytic species, but also may facilitate oxygen atom transfer. Such a change

may extend these species' catalytic activities into truly useful domains.

Finally, there is also the avenue of changing the donor atoms; the alkoxy donors may be replaced with N-amido donors, leading to tetraamide ligands. Such tetraamides are extremely poorly understood. All of the ligands studied in this work have been open chain ligands as opposed to macrocycles. The change from open to closed ligands greatly affects the availability of various oxidation states, in part due to size constraints (the macrocyclic ligands are not so permissive in terms of accommodating changes in ionic radius of the coordinated metal ion as are open chain ligands). Utilization of macrocyclic ligands would also be expected to introduce new forms of reactivity. These research strategies are being pursued by Erich Uffelmann.

Another aspect of this work which should be further pursued is the extension of these ligand systems to other metals. The rate limiting step in progress is is finding the correct ways to coordinate the ligands to new transition metals. However, there are reasons to be encouraged. Prof. Chi-ming Che has successfully coordinated a Class I PAC ligand to ruthenium. It also appears that James Toth has successfully coordinated a Class II ligand to iron. There are of course many transition metals which should be examined. If the proper starting materials and conditions are chosen, the chemistry described in this report may be extended to many other parts of the periodic table, and our modification of reactivity may be similarly extended to novel metal centers. This is a great challenge and perhaps one of the most promising areas for future research in oxidation chemistry as practiced in the Collins group.

This work was originally undertaken to remove points of oxidation state ambiguity. We have found that in most of the systems which we have examined, noninnocence is not a severe problem and that much of the concern with noninnocence is unnecessary. The best lesson is that the oxidation state formalism is a useful rough guide but should not be misused. The formal oxidation state of a metal should not be overinterpreted in an attempt to pigeonhole the reactivity. To say that an oxidation state is well understood may be unfairly closing the door to many

interesting phenomena. Any metal's reactivity depends strongly on the ligand donor environment, a factor this project has attempted to control. Becoming bogged down in the oxidation state formalism draws attention away from the true goal, which is to obtain new forms of reactivity from transition metals. Tying oneself to a particular ligand complement impedes creativity and limits the reactivity one can produce with a given metal.

APPENDIX A
STRUCTURAL DATA FOR OS(η^4-HMPA-DMP)O

In this appended section may be found the important bond length, bond angle, and torsion angle data for the structure of Os(η^4-HMPA-DMP)O. The experimental details of the data collection, refinement, and reduction may be found in the Experimental section of Chapter Two.

What follows is a series of tables referring to the crystal structure of Os(η^4-HMPA-DMP)O. In addition, included is an ortep drawing with the atoms labeled to serve as a key for interpreting the tables.

Labeled Ortep of Os(η^4-HMPA-DMP)O

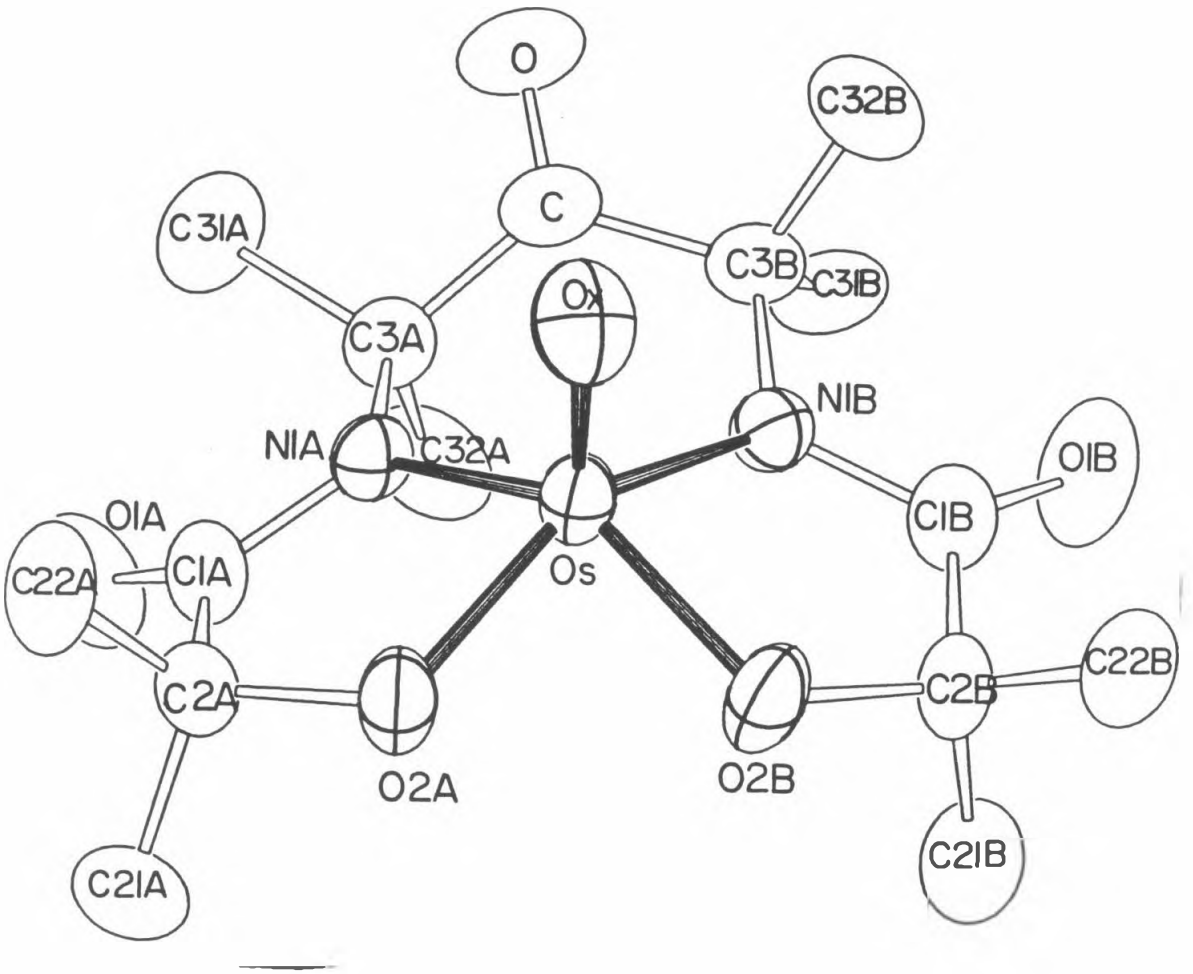


Table A1-1: Atom coordinates and U_{eq} (X 10^4)

Atom	x	y	z	U_{eq}
Os	1140.6(1)	2510.6(2)	2770.5(1)	354(1)
Ox	1182(3)	2416(2)	1412(2)	548(8)
N1A	2795(3)	3013(2)	3595(3)	380(8)
C1A	3710(4)	2430(4)	4247(4)	517(10)
O1A	4690(4)	2642(3)	4921(3)	822(12)
C2A	3310(5)	1493(3)	3995(4)	480(12)
O2A	1906(3)	1490(2)	3505(3)	494(9)
C21A	3495(6)	973(4)	5055(5)	809(18)
C22A	4138(5)	1136(4)	3183(5)	690(16)
N1B	140(4)	3572(2)	2931(3)	416(9)
C1B	−1224(5)	3474(3)	3001(5)	593(14)
O1B	−2053(4)	4047(3)	2920(4)	1010(16)
C2B	−1590(4)	2544(4)	3184(4)	496(10)
O2B	−424(3)	2006(2)	3139(3)	534(9)
C21B	−1919(5)	2741(4)	4339(4)	764(15)
C22P	−2739(5)	2256(4)	2273(5)	662(16)
C	2167(5)	4476(3)	2818(4)	440(11)
C3A	3108(5)	3964(3)	3747(4)	471(12)
C3B	603(5)	4449(3)	2661(4)	452(11)
C31A	4563(6)	4135(4)	3591(6)	840(20)
C32A	2863(7)	4253(4)	4901(5)	751(18)
C31B	220(6)	5174(3)	3410(5)	614(14)
C32B	8(6)	4635(3)	1431(4)	632(15)
O	2653(4)	4978(2)	2257(3)	695(10)

Table A1-2: Anisitropic Gaussian Parameters (X 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os	264(1)	315(1)	475(1)	−4(1)	47(1)	−34(1)
Ox	508(17)	591(21)	515(17)	48(21)	22(14)	−157(20)
N1A	304(18)	365(20)	458(22)	−44(17)	40(16)	−38(17)
C1A	362(20)	597(30)	569(24)	−22(33)	28(18)	23(30)
O1A	585(22)	804(33)	885(26)	−45(22)	−347(20)	−25(24)
C2A	335(24)	455(28)	644(34)	52(24)	75(23)	115(26)
O2A	285(15)	346(16)	819(24)	9(14)	22(16)	47(16)
C21A	689(40)	797(44)	926(47)	85(36)	117(37)	407(38)
C22A	465(32)	730(40)	889(43)	104(29)	165(31)	−48(34)
N1B	364(20)	345(19)	563(24)	53(16)	147(18)	57(18)
C1B	416(28)	488(31)	874(42)	87(25)	118(27)	62(29)
O1B	498(24)	622(26)	1967(51)	239(21)	380(29)	144(30)
C2B	286(17)	563(25)	639(26)	26(35)	90(17)	59(39)
O2B	297(16)	384(18)	930(27)	−40(15)	142(17)	9(18)
C21B	519(27)	1141(48)	636(30)	72(44)	121(24)	53(47)
C22B	372(25)	890(50)	715(35)	−28(26)	78(24)	−2(30)
C	588(30)	318(23)	452(26)	−78(22)	198(23)	−66(20)
C3A	441(28)	370(26)	573(31)	−132(23)	24(24)	−65(23)
C3B	531(27)	364(24)	500(28)	81(22)	194(24)	49(21)
C31A	462(34)	725(42)	1312(60)	−242(31)	117(37)	72(40)
C32A	1041(51)	592(36)	565(35)	0(36)	11(36)	−159(29)
C31B	763(39)	425(29)	722(39)	134(29)	317(32)	−17(27)
C32B	767(40)	500(33)	602(36)	165(30)	65(31)	84(28)
O	862(28)	535(22)	790(26)	−54(21)	414(23)	116(19)

Table A1-3: Hydrogen Atom Coordinates (X 10^4) and B's

Atom	x	y	z	B
H211A	2971	1245	5601	5.1
H212A	3199	396	4976	5.1
H213A	4428	979	5474	5.1
H211B	−1204	2601	4906	5.2
H212B	−2720	2783	4405	5.2
H213B	−2174	1839	4476	5.2
H221A	3983	1462	2454	4.8
H222A	5079	1124	3434	4.8
H223A	3851	541	2936	4.8
H221B	−2506	2324	1555	4.1
H222B	−2988	1666	2361	4.1
H223B	−3534	2610	2290	4.1
H311A	4696	3967	2869	6.0
H312A	4735	4769	3643	6.0
H313A	5223	3874	4145	6.0
H311B	566	5066	4179	5.1
H312B	532	5727	3214	5.1
H313B	−768	5212	3318	5.1
H321A	1963	4120	4994	4.8
H322A	3489	3971	5494	4.8
H323A	3001	4867	4992	4.8
H321B	291	4166	966	4.8
H322B	−943	4644	1287	4.8
H323B	358	5159	1182	4.8

Table A1-4: Bond Lengths (Å)

Os	Ox	1.670(3)			
Os	N1A	1.930(3)	Os	N1B	1.948(4)
Os	O2A	1.899(3)	Os	O2B	1.881(3)
N1A	C1A	1.416(6)	N1B	C1B	1.395(6)
N1A	C3A	1.504(6)	N1B	C3B	1.486(6)
C1A	O1A	1.200(6)	C1B	O1B	1.205(7)
C1A	C2A	1.515(7)	C1B	C2B	1.508(7)
C2A	O2A	1.421(6)	C2B	O2B	1.442(6)
C2A	C21A	1.502(8)	C2B	C21B	1.513(7)
C2A	C22A	1.510(8)	C2B	C22B	1.507(7)
C	C3A	1.545(7)	C	C3B	1.543(6)
C	O	1.196(6)			
C3A	C31A	1.529(8)	C3B	C31B	1.538(7)
C3A	C32A	1.538(8)	C3B	C32B	1.532(7)
C21A	H211A	1.013	C21B	H211B	0.930
C21A	H212A	0.936	C21B	H212B	0.975
C21A	H213A	0.977	C21B	H213B	0.986
C22A	H221A	1.006	C22B	H221B	0.953
C22A	H222A	0.935	C22B	H222B	0.955
C22A	H223A	0.991	C22B	H223B	0.968
C31A	H311A	0.950	C31B	H311B	0.950
C31A	H312A	0.993	C31B	H312B	0.953
C31A	H313A	0.942	C31B	H313B	0.978
C32A	H321A	0.953	C32B	H321B	0.991
C32A	H322A	0.966	C32B	H322B	0.936
C32A	H323A	0.960	C32B	H323B	0.952

Table A1-4 (cont.): Bond Angles (degrees)

N1A	Os	Ox	111.8(1)	N1B	Os	Ox	106.5(1)
O2A	Os	Ox	108.1(1)	O2B	Os	Ox	112.3(1)
O2A	Os	N1A	81.8(1)	O2B	Os	N1B	81.6(1)
N1B	Os	N1A	91.1(1)	O2B	Os	O2A	80.0(1)
O2B	Os	N1A	135.6(1)	N1B	Os	O2A	144.9(1)
C1A	N1A	Os	116.0(3)	C1B	N1B	Os	116.4(3)
C3A	N1A	Os	126.4(3)	C3B	N1B	Os	123.6(3)
C3A	N1A	C1A	116.9(4)	C3B	N1B	C1B	117.6(4)
O1A	C1A	N1A	124.7(4)	O1B	C1B	N1B	125.8(5)
C2A	C1A	N1A	111.9(4)	C2B	C1B	N1B	112.4(4)
C2A	C1A	O1A	123.5(5)	C2B	C1B	O1B	121.8(5)
O2A	C2A	C1A	106.9(4)	O2B	C2B	C1B	108.6(4)
C21A	C2A	C1A	110.5(4)	C21B	C2B	C1B	109.8(4)
C22A	C2A	C1A	108.8(4)	C22B	C2B	C1B	110.1(4)
C21A	C2A	O2A	108.1(4)	C21B	C2B	O2B	107.2(4)
C22A	C2A	O2A	110.3(4)	C22B	C2B	O2B	108.4(4)
C22A	C2A	C21A	112.1(4)	C22B	C2B	C21B	112.6(4)
C2A	O2A	Os	118.4(3)	C2B	O2B	Os	119.4(3)
C3B	C	C3A	122.8(4)				
O	C	C3A	119.4(4)	O	C	C3B	117.5(4)
C	C3A	N1A	108.9(4)	C	C3B	N1B	110.5(4)
C31A	C3A	N1A	109.5(4)	C31B	C3B	N1B	114.0(4)
C32A	C3A	N1A	109.2(4)	C32B	C3B	N1B	107.9(4)
C31A	C3A	C	106.6(4)	C32A	C3A	C	109.9(4)
C31A	C3A	C32A	112.7(4)	C31B	C3B	C32B	110.5(4)
C31B	C3B	C	105.5(4)	C32B	C3B	C	108.3(4)
H211A	C21A	C2A	110.4	H211B	C21B	C2B	113.0
H212A	C21A	C2A	115.7	H212B	C21B	C2B	110.4
H213A	C21A	C2A	113.3	H213B	C21B	C2B	111.4
H212A	C21A	H211A	105.5	H212B	C21B	H211B	109.1
H213A	C21A	H211A	102.5	H213B	C21B	H211B	108.1
H213A	C21A	H212A	108.5	H213B	C21B	H212B	104.6
H221A	C22A	C2A	112.6	H221B	C22B	C2B	110.9
H222A	C22A	C2A	116.0	H222B	C22B	C2B	112.1
H223A	C22A	C2A	111.8	H223B	C22B	C2B	109.6
H222A	C22A	H221A	106.1	H222B	C22B	H221B	108.8
H223B	C22B	H221B	107.7	H223B	C22B	H222B	107.6
H223A	C22A	H222A	107.3	H223A	C22A	H221A	102.0
H311A	C31A	C3A	111.9	H311B	C31B	C3B	111.9
H312A	C31A	C3A	108.6	H312B	C31B	C3B	111.8
H313A	C31A	C3A	113.2	H313B	C31B	C3B	109.7
H312A	C31A	H311A	105.9	H312B	C31B	H311B	109.2
H313A	C31A	H311A	110.2	H313B	C31B	H311B	107.2
H313A	C31A	H312A	106.6	H313B	C31B	H312B	106.9
H321A	C32A	C3A	111.5	H321B	C32B	C3B	108.8
H322A	C32A	C3A	111.2	H322B	C32B	C3B	112.3
H323A	C32A	C3A	110.3	H323B	C32B	C3B	111.8
H322A	C32A	H321A	107.9	H322B	C32B	H321B	107.2
H323A	C32A	H321A	108.5	H323B	C32B	H321B	105.9
H323A	C32A	H322A	107.4	H323B	C32B	H322B	110.5

Table A1-5: Torsion Angles (degrees)

Os	O2A	C2A	C1A	24.6(5)
O2A	C2A	C1A	N1A	-21.2(5)
O2A	C2A	C1A	O1A	158.8(5)
C2A	C1A	N1A	C3A	-178.3(4)
C2A	C1A	N1A	Os	10.4(5)
C1A	N1A	C3A	C	169.3(4)
N1A	C3A	C	O	-127.3(5)
N1A	C3A	C	C3B	59.7(5)
Os	O2B	C2B	C1B	-4.8(5)
O2B	C2B	C1B	N1B	-4.8(6)
O2B	C2B	C1B	O1B	174.6(5)
C2B	C1B	N1B	C3B	175.3(4)
C2B	C1B	N1B	Os	12.3(5)
C1B	N1B	C3B	C	170.2(4)
N1B	C3B	C	O	151.7(4)
C1A	N1A	Os	Ox	-104.0(3)
C2A	O2A	Os	Ox	94.2(3)
C1B	N1A	Os	Ox	122.8(2)
C2A	O2B	Os	Ox	116.3(2)

Table A1-6: Calculation of Dunitz Parameters

The Dunitz parameters ($\bar{\tau}$, χ_N and χ_C) were determined from the relevant torsion angles ω_1, ω_2 and ω_3 (computed using the program DISTAN) as described in references 32 and 33 of Chapter Two. Dunitz parameters and torsion angles are in degrees.

Amide 1:

ω_1=-178.24 $\bar{\tau}$=-6.18

ω_2=-169.40 χ_N=9.09

ω_3=1.51 χ_C=0.25

Amide 2:

ω_1=175.26 $\bar{\tau}$=4.05

ω_2=-167.16 χ_N=17

ω_3=-4.16 χ_C=-0.58

Table A1-7

Fractional and Orthogonalized Coordinates

	FRACTIONAL			ORTHOGONALIZED		
ATOM	X	Y	Z	X	Y	Z
OS	0.11406	0.25106	0.27705	0.5026	3.8707	3.3151
OX	0.11819	0.24156	0.14122	0.8580	3.7241	1.6899
N1A	0.27945	0.30129	0.35953	1.9694	4.6450	4.3021
C1A	0.37104	0.24296	0.42468	2.7368	3.7457	5.0816
O1A	0.46900	0.26422	0.49212	3.5627	4.0734	5.8885
C2A	0.33103	0.14926	0.39946	2.3941	2.3012	4.7798
O2A	0.19062	0.14898	0.35045	1.1002	2.2968	4.1934
C21A	0.34954	0.09726	0.50549	2.3345	1.4994	6.0485
C22A	0.41379	0.11364	0.31827	3.4113	1.7521	3.8083
N1B	0.01403	0.35717	0.29311	-0.5370	5.5065	3.5073
C1B	-0.12245	0.34738	0.30008	-1.9210	5.3556	3.5906
O1B	-0.20543	0.40474	0.29195	-2.7338	6.2398	3.4934
C2B	-0.15906	0.25435	0.31840	-2.3302	3.9214	3.8099
O2B	-0.04250	0.20061	0.31394	-1.1517	3.0928	3.7565
C21B	-0.19196	0.24412	0.43385	-2.9268	3.7636	5.1914
C22B	-0.27404	0.22563	0.22726	-3.2718	3.4785	2.7193
C	0.21670	0.44762	0.28183	1.5202	6.9010	3.3723
C3A	0.31079	0.39645	0.37467	2.2485	6.1120	4.4832
C3B	0.06032	0.44486	0.26611	-0.0106	6.8584	3.1842
C31A	0.45631	0.41348	0.35906	3.7430	6.3746	4.2964
C32A	0.28633	0.42528	0.49005	1.7366	6.5565	5.8638
C31B	0.02206	0.51743	0.34103	-0.5673	7.9772	4.0807
C32B	0.00084	0.46345	0.14306	-0.3224	7.1450	1.7118
O	0.26531	0.49778	0.22570	2.1372	7.6743	2.7006
211A	0.29714	0.12447	0.56005	1.6832	1.9190	6.7014
212A	0.31994	0.03964	0.49762	2.0560	0.6112	5.9544
213A	0.44279	0.09789	0.54744	3.1721	1.5092	6.5505
211B	-0.12036	0.26005	0.49055	-2.3403	4.0092	5.8697
212B	-0.27195	0.27828	0.44049	-3.7438	4.2903	5.2708
213B	-0.21743	0.18385	0.44756	-3.2137	2.8344	5.3553
221A	0.39828	0.14623	0.24543	3.4242	2.2544	2.9368
222A	0.50793	0.11237	0.34339	4.2967	1.7324	4.1089
223A	0.38508	0.05412	0.29357	3.1806	0.8343	3.5128
221B	-0.25057	0.23243	0.15552	-2.8708	3.5833	1.8609
222B	-0.29884	0.16660	0.23606	-3.5407	2.5685	2.8246
223B	-0.35337	0.26103	0.22900	-4.0708	4.0243	2.7401
311A	0.46964	0.39668	0.28689	4.0435	6.1156	3.4328
312A	0.47345	0.47693	0.36426	3.9028	7.3528	4.3586
313A	0.52225	0.38736	0.41454	4.2756	5.9720	4.9602
311B	0.05661	0.50660	0.41791	-0.3988	7.8103	5.0005
312B	0.05324	0.57269	0.32140	-0.2095	8.8291	3.8457
313B	-0.07683	0.52124	0.33184	-1.5372	8.0360	3.9707
321A	0.19634	0.41197	0.49942	0.8132	6.3514	5.9759
322A	0.34887	0.39709	0.54942	2.2263	6.1219	6.5743
323A	0.30008	0.48665	0.49915	1.8534	7.5027	5.9726
321B	0.02909	0.41662	0.09663	0.0682	6.4230	1.1562
322B	-0.09430	0.46440	0.12866	-1.2425	7.1597	1.5395
323B	0.03577	0.51585	0.11822	0.0852	7.9528	1.4146

APPENDIX B
UV-vis DATA FOR THE CONVERSION OF *trans*-Os(η^4-HMPA-DMP)(4-X- pyridine)$_2$ TO Os(η^4-HMPA-DMP)O

In this appendix may be found the UV-vis data obtained in the monitoring of the Os(IV) species described in the texts being converted to the Os(VI) monooxo species. Besides the half-lives, which were tabulated in the text, herein may also be found the k_{obs} values. UV-vis measurements were performed using a Hewlett-Packard HP8450A spectrophotometer using spectral grade chloroform. The solubility of oxygen in chloroform is approximately 0.02 M. Concentrations of Os(IV) species were less than 0.1 mM. The concentration of molecular oxygen was viewed as a large excess which did not change during the course of the experiment.

From the concentrations and the A values, ϵ's were also calculated for the complexes:

Table A2-1:Rates and Extinction coefficients

4-substituent	k_{obs} (22° C)	$\epsilon(\lambda$=410 nm)
Br	1.9(1) X 10^{-6} min^{-1}	10000
H	5.5(1) X 10^{-7} min^{-1}	12500
^{tert}Bu	9.7(2) X 10^{-8} min^{-1}	10200

The following pages contain the raw UV-vis data, along with the reduced data from which the above numbers were generated. On the final page of this appendix is a graph illustrating the relative rates of conversion of all three compounds.

Table A2-2: Data for unsubstituted pyridine complex

Data for Os(IV) bispyridine
conversion to Os(VI) monooxo
linear to three half lives
R = .999 T = 22 C
t(1/2) = 94 minutes

t(min)	A	A-Ainf	-ln(A-Ainf)
0	0.6958	0.4613	0.773706
30	0.6044	0.3699	0.994522
60	0.5341	0.2996	1.205307
90	0.4706	0.2361	1.443499
120	0.4333	0.1988	1.615455
150	0.398	0.1635	1.810942
180	0.369	0.1345	2.006191
210	0.3456	0.1111	2.197324
240	0.3271	0.0926	2.379466
270	0.312	0.0775	2.557477
300	0.2978	0.0633	2.759869
330	0.2883	0.0538	2.922481
360	0.2882	0.0537	2.924342
390	0.2774	0.0429	3.148883
420	0.2695	0.035	3.352407
450	0.2666	0.0321	3.438899

Table A2-3: Data for 4-bromopyridine complex

Absorbance data for conversion
of Os(HMPA-DMP)(4-Br-pyridine)2
to Os(HMPA-DMP)O In CHC13
T = 22 degrees C

ln(A-Ainf) vs. t
is linear to greater than three
half lives; R = 0.995
t(1/2) = 36 minutes

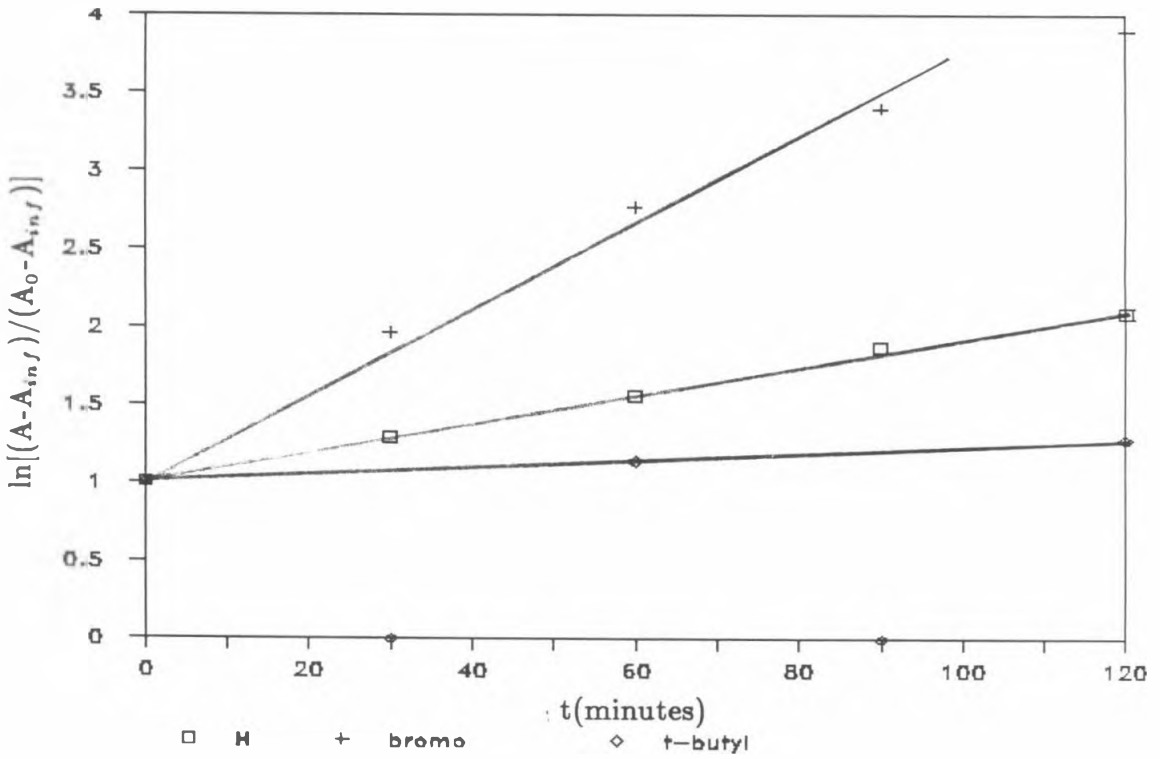
t(min)	A	A-Ainf	-ln(A-Ai)
0	0.7404	0.5424	0.611751
5	0.6835	0.4855	0.722575
10	0.6357	0.4377	0.826221
15	0.5943	0.3963	0.925583
20	0.5592	0.3612	1.018323
25	0.5272	0.3292	1.111089
30	0.4987	0.3007	1.201642
35	0.4731	0.2751	1.290620
40	0.4515	0.2535	1.372391
45	0.43	0.232	1.461017
50	0.4137	0.2157	1.533866
55	0.397	0.199	1.614450
60	0.3822	0.1842	1.691733
65	0.3706	0.1726	1.756778
70	0.3591	0.1611	1.825729
75	0.3485	0.1505	1.893792
80	0.3396	0.1416	1.954749
85	0.3309	0.1329	2.018158
90	0.3232	0.1252	2.077842
95	0.3168	0.1188	2.130313
100	0.3106	0.1126	2.183913
105	0.3051	0.1071	2.233992
110	0.2992	0.1012	2.290656
115	0.2947	0.0967	2.336141
120	0.2901	0.0921	2.384880

Table A2-4: Data for 4-tertiarybutylpyridine

t(min)	A	A-Ainf	−ln(A-Ainf)	
0	0.7578	0.5337	0.627921	
60	0.7146	0.4905	0.71233	UV-vis data for
120	0.6734	0.4493	0.800064	Os(IV)HMPA-DMP(t-b
180	0.6445	0.4204	0.866548	conversion to Os(V
240	0.6152	0.3911	0.938791	t1/2 = 636 min
300	0.5924	0.3683	0.998857	T = 22 degrees C
360	0.5716	0.3475	1.056990	
420	0.5537	0.3296	1.109875	
480	0.5363	0.3122	1.164111	
540	0.521	0.2969	1.214359	
600	0.5066	0.2825	1.264076	

Ainf = .2241

Graphical Illustration of the
Relative Rates of Conversion of
***trans*-Os(η^4-HMPA-DMP)(4-X-pyridine)$_2$**
Where X = H, Br, ^{tert}butyl



APPENDIX C
STARTING MATERIALS FOR FLUORINATED LIGANDS

At the end of Chapter Two, the synthesis of fluorinated PAC ligands was proposed as a means of destabilizing the monooxo compounds and introducing chirality. Some of the starting materials have been synthesized and they will be briefly described below.

The synthesis of the α-trifluoromethyl-lactic acid was achieved as described in (Darrall, R.A.; Smith, F.; Stacey, M.; Tatlow, J.C.; *J. Chem. Soc.* **1951**, 2329.). As suggested therein, the acid was purified by sublimation. The authors also describe the optical resolution by fractional recrystallization with brucine, but we did not do this. The acid (1.2 g, 7.59 mmol) was reacted with trimethylacetyl chloride (1.00 g, 8.35 mmol) with excess pyridine (0.90 g, 11.4 mmol). The reaction mixture quickly became hot and slowly cooled. After an hour of stirring, followed by removal of solvents, 1.8 g (90 percent) of the protected acid was recovered as a white powder. The PMR of this material shows a broad singled (10.0-10.1 ppm, 1H) corresponding to the acid proton, a sharp singlet (1.66 ppm, 3H) corresponding to the methyl group, and another sharp singlet, (1.25 ppm, 9H) corresponding to the pivolate group. A similar acylation was effected with acetyl chloride yielding the acetylated product. Exploratory experiments showed that this could be converted to the acid chloride with oxalyl chloride or thionyl chloride. A very small amount of what appears to be a Class II ligand was produced in this way, but it has not been sufficiently well characterized to warrant further discussion. Direct reaction of the unprotected acid (or its ester) with diamines was unsuccessful.

The synthesis of β-trifluoromethyl-β-hydroxybutyric acid was achieved as shown below and described in (Tarrant and Taylor, *J. Org. Chem.* **24**, *1959*, 1888.). Attempts to acylate the alcohol were unsuccessful (similar to what we observed for (1-10), as described in Chapter One. Acylation of the ester may be

more successful.

With these starting materials, the syntheses of appropriate fluorinated ligands should be straightforward. It should also be mentioned that the cyanohydrin reaction also works in the case of hexafluoroacetone. Of course, the chirality is lost, but so is the need to resolve optical isomers.

A recent report on asymmetric formation of cyanohydrins from aldehydes has appeared (Effenberger, F.; Ziegler, T.; Forster, Z.; *Angew. Chem., Int. Ed. Engl.* **26**, *1987*, 458.) Whether the enzymatic reaction described may be extended to ketones is uncertain. If so, this is an excellent opportunity to synthesize large quantities of chiral cyanohydrins which may later be used to synthesize chiral ligands.