HETEROLEPTIC PADDLEWHEEL COMPLEXES AND MOLECULAR ASSEMBLIES OF DIMOLYBDENUM AND DITUNGSTEN: A Study of Electronic and Structural Control

DISSERTATION

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By

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ABSTRACT

Molybdenum and tungsten have a rich chemistry in quadruply-bonded paddlewheel complexes that are very similar in many ways, yet significantly different in other ways. Details and findings from Density Functional Theory studies of homoleptic and heteroleptic ligand complexes as well as simple pairs of dimers linked by a bifunctional oxalate bridge are discussed. Special interest is given to metal-to-ligand interactions in paddlewheel complexes and metal-to-bridge interactions in simple pairs of dimers. Computational studies provide great insight, reliable explanations, and qualitative predictions of physicochemical properties.

A new series of dimolybdenum and ditungsten paddlewheel complexes with mixed amidinate-carboxylate ligands of the form \( \text{trans-M}_2(O_2CCH_3)_2'(\text{PrNC}(R)N'iPr)_2 \) where \( M = \text{Mo, W} \) and \( R = \text{Me, C≡C′Bu, C≡CPh, or C≡CFc} \) have been synthesized and characterized with the exception of the tungsten complex where \( R = \text{Me} \). The synthesis of a series of complexes with each metal allowed for the analysis and comparison of molecular structural features, spectroscopic properties, and electrochemical behavior. The dinuclear centers exhibit redox chemistry which is dependent upon the nature of the ancillary ligand, and the electrochemical properties can be tuned through ligand
modifications. DFT calculations on model complexes are used to help assign observable UV-vis absorptions and electrochemical redox behavior.

The use of amidate complexes of the form M$_2$(mhp)$_4$, where M = Mo, W and mhp is the anion of 2-hydroxy-6-methylpyridine, as building blocks in simple molecular assemblies including simple pairs of dimers and molecular squares is also explored. Metathesis reactions employing solvento derivatives of Mo$_2$(mhp)$_4$ and attempts to prepare solvento derivatives of W$_2$(mhp)$_4$ are discussed. For simple pairs of dimers, the cooperative effect of linkers to electronically couple dimetal units is observed through electrochemistry.

Finally, the preliminary findings of using the unique trans-geometry of mixed amidinate-carboxylate complexes to construct metallated conjugated oligomers or polymers when linked by a bifunctional bridge is explored. MALDI-TOF mass spectrometry was useful in resolving both the type and the number of species present. Based on solubility, only higher order assemblies are formed rather than true metallated conjugated polymers.
Dedicated to my family
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C.1 a) Differential pulse voltammogram and b) cyclic voltammogram of [Mo$_2$(mhp)$_3$]$_2$(O$_2$CCO$_2$) (2) in DMSO/0.1 M [Bu$_4$N][PF$_6$] 219

C.2 a) Differential pulse voltammogram and b) cyclic voltammogram of [Mo$_2$(mhp)$_3$]$_2$(O$_2$CC$_6$F$_4$CO$_2$) (3) in DMSO/0.1 M [Bu$_4$N][PF$_6$] 220
LIST OF ABBREVIATIONS

* anti-bonding
α alpha
Å angstrom
Ac acetyl
AE all electron
Anth anthracene
br broad (IR and NMR)
β beta
B3LYP hybrid Becke-3 parameter exchange functional and the Lee-Yang-Parr nonlocal correlation functional
n′Bu normal-butyl
t′Bu tert-butyl
°C degrees Celsius
C≡C acetyl unit
calcd calculated
CH₃CN acetonitrile
δ chemical shift in parts per million downfield from tetramethylsilane; delta orbital
d doublet (spectra); day(s)
DCM dichloromethane
DFT Density Functional Theory
DMSO  dimethylsulfoxide
E  potential
ECP  effective core potential
EPR  Electron Paramagnetic Resonance
eq.  equivalent
Et  ethyl
Fc  ferrocence
γ  gamma
G  Gibbs free energy
g  gram(s)
H  hydrogen
h  hour(s)
HOMO  highest occupied molecular orbital
I  nuclear spin
IVCT  inter-valence charge transfer
IR  infrared
J  coupling constant in Hz (NMR)
K  degrees Kelvin
K_c  Comproportionation constant
L  ligand; liter(s)
LUMO  lowest unoccupied molecular orbital
M  moles per liter
m  multiplet (NMR)
M$_2$  dimetal unit
MALDI-TOF  Matrix Assisted Laser desorption Ionization Time of Flight
MLCT  metal-to-ligand charge transfer
MMCT  metal-to-metal charge transfer
Mo  molybdenum
$\lambda$  Marcus reorganization energy
Me  methyl
MeCN  acetonitrile
mg  milligrams
MHz  megahertz
min  minute(s)
ml  milliliters
mmol  millimoles
mol  mole(s)
MS  mass spectrometry
mV  millivolts
$m/z$  mass to charge ratio (MS)
NIR  near-infrared
nm  nanometer
NMR  nuclear magnetic resonance
OTTLE  optically transparent thin-layer electrochemical
$p$  para
$\pi$  pi orbital
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>PES</td>
<td>potential energy surface</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>q</td>
<td>quartet (NMR)</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>σ</td>
<td>sigma orbital</td>
</tr>
<tr>
<td>S</td>
<td>spin multiplicity</td>
</tr>
<tr>
<td>s</td>
<td>singlet (NMR); second(s)</td>
</tr>
<tr>
<td>SDD</td>
<td>Stuttgart/Dresden basis set</td>
</tr>
<tr>
<td>t</td>
<td>tertiary (tert)</td>
</tr>
<tr>
<td>t</td>
<td>triplet (NMR)</td>
</tr>
<tr>
<td>TBAF</td>
<td>tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>TDDFT</td>
<td>time-dependent DFT</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>Thio</td>
<td>thiophene</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>vis</td>
<td>visible</td>
</tr>
<tr>
<td>W</td>
<td>tungsten</td>
</tr>
<tr>
<td>X</td>
<td>generic atom; conjugated organic group</td>
</tr>
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CHAPTER 1

INTRODUCTION

1.1 The discovery of the metal-metal multiple bonds

In the early 1960’s, the recognition of metal-metal multiple bonds heralded a new era in the development of inorganic transition metal chemistry. The structural determination of the \([\text{Re}_2\text{Cl}_8]^{2-}\) ion by F. A. Cotton established the existence of a direct quadruple bond between two metal centers.[1] Since then, multiple bonds between metal atoms have been systematically identified across the transition metal series of the periodic table. Today, this bonding mode is no longer considered an anomaly but rather seen as a major bonding pattern in low oxidation state transition metal compounds.[2] The synthesis and investigation of new compounds containing metal-metal multiple bonds continue to receive a high level of interest.

1.2 Structural motifs

Transition metal compounds incorporating metal-metal multiple bonds often adopt a “paddlewheel” conformation, sometimes also referred to as a lantern-type
structure.[3] The paddlewheel structural motif (Figure 1.1) adopted by these compounds has three important features:[4]

1. Transition metal atoms of groups 5-10 can form M-M bonds with formal bond orders varying from four to zero.

2. The equatorial ligands (green) can be μ-bridging such as carboxylates (a), or monodentates such as halide ions and even coordinated solvent molecules (b).

3. Some metals have a strong preference for additional axial coordination. The axial ligands (blue) frequently contain N- or O- donating atoms.

![Figure 1.1](image)

**Figure 1.1** (a) A generic structure of a bridging paddlewheel complex with two axially coordinated ligands. (b) A similar structure with equatorial monodentate ligands and two axially coordinated ligands. (Reproduced from Reference [4])

### 1.3 Dimolybdenum and ditungsten tetracarboxylate compounds

One of the most common in the class of μ-bridging paddlewheel compounds are dimetal tetracarboxylates, $M_2(O_2CR)_4$, where R is an organic functional group. Dimetal tetracarboxylates of various transition metals (including Mo, W, Tc, Re, Ru and Rh) have
been studied extensively since the early 1960s[2]. The unique four bridging ligands provide an interesting framework for metal-metal and metal-ligand interactions. Let us focus on what is currently known about dimolybdenum and ditungsten tetracarboxylate compounds of the form shown in Figure 1.2.

![Figure 1.2](image_url)

**Figure 1.2** The general structure adopted by compounds of the formula $M_2(O_2CR)_4$.

### 1.3.1 The quadruple bond

To a first order approximation, each metal atom uses a set of $s$, $p_x$, $p_y$, $d_{x^2-y^2}$ hybrid orbitals to form its square planar ligand bonds. The remaining d valence shell orbitals form multiple metal-to-metal bonds. The $d^8-d^4$ metal cores in these compounds are quadruply bonded.[5] There are three different types of bonds forming this quadruple bond. The first type involves the direct overlap of the metal $d_{z^2}$ orbitals to form a strong $\sigma$ bond. The second type is side-to-side overlap of both the $d_{xz}$ or $d_{yz}$ orbitals to form a set of degenerate $\pi$ bonds. The $\sigma$ and $\pi$ bonds impose no restriction on rotation about the metal-metal axis. The last type involves the face-to-face overlap of $d_{xy}$ orbitals to form a
weak $\delta$ bond that now restricts rotation about the metal-metal axis and establishes the eclipsed configuration. Therefore, the metal-metal quadruple bond consists of metal $\sigma$, $2\pi$, and $\delta$ orbitals as illustrated in Figure 1.3.

![Orbital interactions](image)

**Figure 1.3** Orbital interactions associated with multiple bonding of metal core.

### 1.3.2 $M_2$ manifold

The metal-metal and metal-ligand orbital interactions result in a unique splitting pattern as seen in a simplified qualitative molecular diagram. See Figure 1.4 which has been generated under $D_{4h}$ symmetry for simplicity. As rationalized by the Huckel concept, Molecular Orbital (MO) energies are proportional to the degree of overlap for similar types of orbitals.[2] Therefore, from the expected increase in overlap $\delta << \pi < \sigma$, the orbital energies increase in energy from $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. In practice, this ordering of metal manifold may differ based on second-order, metal-ligand interactions. The bonding orbitals can be represented as $\sigma^2 \pi^4 \delta^2$ in this configuration. The actual
energy of the RCO₂ π* orbitals has been arbitrarily determined since the nature of any alkyl or aryl substituents must be considered.

Figure 1.4 Qualitative molecular orbital diagram for M₂(O₂CR)₄ under D₄h symmetry.

1.3.3 Tungsten vs molybdenum

The ionic radii of molybdenum tungsten are essentially identical due to the lanthanide contraction.[6] The metal-metal multiple bond distance, however, does slightly increases as a function of increasing electron density and the resulting increase in core-core repulsion. The greater bond length considerably reduces the δ overlap and has a smaller, but still significant, adverse effect on the π overlaps resulting in a weaker W-W
quadruple bond.[7] This also translates into shorter metal-ligand bond lengths for tungsten analogs.

A common characteristic of both Mo\(_2\) and W\(_2\) species is that they are closed-shell and diamagnetic. The \(\text{M}_2^{4+}\) centers facilitate redox activity and readily undergo reversible one-electron oxidations.[8] The M-M distance increases as the bond order decreases from 4 to 3.5 to 3 and the electronic configuration changes from \(\sigma^2\pi^4\delta^2\) to \(\sigma^2\pi^4\delta^1\) to \(\sigma^2\pi^4\delta^0\), respectively.[9] The tungsten compounds are much easier to oxidize. This can be explained by a comparison of the frontier molecular orbitals of \(\text{M}_2(\text{O}_2\text{CR})_4\) compounds. The W\(_2\) \(\delta\) orbitals are about 0.5 eV higher in energy than their Mo\(_2\) \(\delta\) counterparts. Therefore, the higher energy \(\delta\)-orbitals in tungsten compounds are easier to oxidize as shown in Figure 1.5.

![Figure 1.5 Energies of the frontier molecular orbitals of \(\text{M}_2(\text{O}_2\text{CR})_4\). (Reproduced from Reference [3])](image-url)
1.3.4 General synthesis

The most common method of preparing $\text{Mo}_2(O_2\text{CR})_4$ species is the thermal reaction of $\text{Mo(CO)}_6$, with the appropriate carboxylic acid, either neat or, preferably, in an inert high boiling solvent such as diglyme or $o$-dichlorobenzene.[10] The reaction of $\text{W(CO)}_6$ in an analogous way is unsuitable to synthesize $\text{W}_2(O_2\text{CR})_4$ compounds and affords either polymeric or high-oxidation-state tungsten trinuclear species.[11] For this reason, it took nearly twenty years for the tungsten analogs of carboxylates to be made. Instead, the $\text{W}_2(O_2\text{CR})_4$ species is normally synthesized by the reduction of $\text{WCl}_4$ with 2 equiv of sodium amalgam in THF at -25 $^\circ$C and subsequent addition of the sodium salt of a carboxylic acid.[7] In 1985, Santure and co-workers reported the first structural characterization of a ditungsten tetracarboxylate.[10]

$$\text{Mo(CO)}_6 + \text{Excess HO}_2\text{CR} \xrightarrow{\Delta \ \text{inert solvent}} \text{Mo}_2(O_2\text{CR})_4$$

$$\text{WCl}_4 + 2\text{Na/Hg} + 2\text{NaO}_2\text{CR} \xrightarrow{-25 \ ^\circ\text{C} \ \text{THF}} 0.5\text{W}_2(O_2\text{CR})_4 + 4\text{NaCl}$$

**Scheme 1.1** Comparison of synthetic strategies for molybdenum and tungsten leading to $\text{M}_2(O_2\text{CR})_4$ compounds.
1.3.5 Substitutional chemistry.

Labile ligands are important for substitutional chemistry. Several simple routes to mixed carboxylate complexes are possible. Refer to Scheme 1.1. The first is carboxylate exchange reactions where one ligand is replaced by the free acid of another ligand. This is often an equilibrium reaction that does not yield a discreet product. Next is a metathesis reaction. This is an exchange reaction that can be driven to the right by the removal of a less soluble product. The third is a metathesis reaction employing solveto complexes. Dications and sometimes mono-cations can be formed to greatly increase the solubility of the products. The latter reactions tend to be driven by thermodynamic factors and are kinetically faster. These same techniques can also be used for other non-carboxylate ligands that will be discussed later.

Carboxylate Exchange Reactions

\[
M_2(O_2CR)_4 + xHO_2CR' \rightleftharpoons M_2(O_2CR)_{4-x}(O_2CR')_x + xHO_2CR
\]

where \( x = 1-4 \)

Metathesis Reactions

\[
M_2(O_2CR)_4 + xQ^+ [O_2CR']^- \rightarrow M_2(O_2CR)_{4-x}(O_2CR')_x + xQ^+ [O_2CR']^-
\]

Metathesis Reactions employing solveto complexes

\[
[M_2(O_2CR)_2(CH_3CN)_4]^{2+}[BF_4]^- + 2Q^+ [O_2CR']^- \rightarrow M_2(O_2CR)_2(O_2CR')_2 + 2Q^+ [O_2CR']^-
\]

where \( Q = Na, Li, ^nBu_4N \)

Scheme 1.2 Common substitutional chemistry routes.
1.3.6 Electronic Absorptions

These compounds are typically colored with strong electronic absorptions in or near the visible region of the electromagnetic spectrum.[2] Dinuclear species of quadruply-bonded metal atoms have a unique metal-based absorption band entirely different from mononuclear compounds. This transition arises from the extensive d-orbital overlap of the metal atoms. The electronic absorption is a $\delta \rightarrow \delta^*$ transition in the metal core. The intensity of this transition in molybdenum and tungsten compounds is, however, often very weak. This is a direct consequence of the weak $\delta$-bond overlap between the metal atoms. In the case of tungsten compounds, this transition is also masked by a MLCT electronic absorption of greater intensity due to the high metal $\delta$-orbital manifold as shown in Figure 1.4.

Another metal-based electronic absorption normally observed in these compounds is a low energy $M_2 \delta \rightarrow CO_2 \pi^*$ metal-to-ligand charge transfer (MLCT). The $M_2 \delta \rightarrow CO_2 \pi^*$ transition shows up as a very intense MLCT band in the visible spectra. This absorption most strongly influences the color of the compound. Color is therefore a good indication of the energy gap between the $M_2 \delta$ and the $CO_2 \pi^*$ orbitals and greatly affects the electronic properties of the compounds. Since the $W_2 \delta$ orbital is already higher in energy than the $Mo_2 \delta$ orbital, the $W_2 \delta$ orbital is closer in energy to the $CO_2 \pi^*$ and the energy of the $W_2 \delta \rightarrow CO_2 \pi^*$ transition is lower. It is this red-shifted transition in tungsten that effectively masks the weak $\delta \rightarrow \delta^*$ transition previously discussed.

Adjusting the position of the $CO_2 \pi^*$ orbitals is an effective means of tuning the electronic properties of these compounds. The presence of a $\pi$-conjugating as in PhCO$_2$ organic functional group causes the $CO_2 \pi^*$ orbitals to become lower in energy and
decrease the absorption energy. This can be seen as a red-shift in the absorption of the compounds. Unfortunately, modification of the electronic properties of carboxylates is limited to changing of the organic functional group only.

Another electronic absorption that may also be seen in ligands with chromophores consists of a higher energy ligand $\pi \rightarrow \pi^*$ charge transfer that can be affected by the metal-ligand interaction. The intensity of this transition is often comparable to the MLCT band previously discussed. These electronic transitions are illustrated in Figure 1.6.

![Diagram of electronic transitions](attachment:electronic_transitions.png)

**Figure 1.6** Typical visible electronic transitions in $M_2(O_2CR)_4$ complexes.

### 1.3.7 Physical properties

In the solid state, most $M_2(O_2CR)_4$ compounds have been shown to be weakly bonded to their neighboring molecules through long dative O--M bonds (Figure 1.7).[3, 12] The carboxylates form extended lattice structures as a result of these weak intermolecular interactions involving the axial sites of the metal atoms. Crystals of these
compounds are often thin plates or long thin hairs unsuitable for single crystal X-ray crystallography.[3]

Figure 1.7 Typical extended lattice structure of $\text{M}_2(\text{O}_2\text{CR})_4$. (Reproduced from Reference [3])

The $\text{M}_2(\text{O}_2\text{CR})_4$ compounds tend to have low solubility but coordinating solvents such as THF are often best in breaking the weak intermolecular interaction. They are kinetically labile in solution to ligand exchange and ligand scrambling.[3, 13] Normally, less acidic or basic ligands can be substitutionally exchanged for one or more carboxylate ligands. Reaction equilibria have to be driven to the right to favor product either by thermodynamic factors such as $\text{pK}_a$ or La Chatelier’s principle by precipitation of a lesser soluble product.
1.3.8 Other ancillary ligands

Today, there are many $\mu$-bridging ligands to choose from. More recently discovered supporting or ancillary ligands of interest are amidates, formamidinates, and amidinates. Their chemical structures are shown in Figure 1.8.

![Chemical structures of amidates, formamidinates, and amidinates](image)

Figure 1.8 Structures of (a) amidates, (b) formamidinates, and (c) amidinates where R and R' are organic functional groups.

The first examples of amidate ligands as bridges across multiple metal-metal bonds were published in 1979, using $\text{Cr}_2^{4+}$ and $\text{Mo}_2^{4+}$ cores.[14] The amidate ligand is sterically and electronically similar to the carboxylate group. The striking difference is the overall symmetry in the arrangement of the ligands around the dimetal unit. Due to steric factors associated with the nitrogen substituent, the orientation of the ligand normally alternates around the metal core to reduce steric interactions (Figure 1.9).
More recently, the coordination chemistry of formamidinate ligands has been extensively investigated.\[15, 16\] Research has shown that \(N,N^{\prime}\)-donor bridging ligands are particularly good as non-labile ligands stabilizing \(M_2\) units (Figure 1.10). Paddlewheel molecules in which the bridging ligands employ two nitrogen atoms to bind to the metal atoms have allowed the preparation of several cationic species.\[17\] The more basic formamidinate ligands form stronger, more covalent bonds that stabilize oxidation. The nitrogen substituents also prevent the formation of axial dative bonds with neighboring molecules as is common with carboxylates and allows for the formation of good single crystals for X-ray crystallography. Unfortunately, even formamidinate ligands cause problems since they cleave under certain reaction conditions into \(R'N\) and RNC fragments.\[18\]
Amidinates have been significantly investigated as ligands for various transition metals in recent years but their use as ligands in Mo$_2$ and W$_2$ complexes has been very limited.[19] Amidinates are one of the most versatile bridging ligands used to stabilize a wide variety of dinuclear transition metal complexes with various orders of M-M bonds.[19] This is due to the ease with which the steric and electronic properties of the resultant metal complexes can be tuned by means of substitution at the nitrogen atoms and the central carbon atom.[20] The electronic tuning of nitrogen based ligands can also help tuning the energy gap in the M$_2$ $\delta \rightarrow$ CN$_2$ $\pi^*$ transition. Additionally, amidinates can be easily functionalized to either increase the solubility of the metal complexes or to provide additional spectroscopic handles within the ligand framework.[20] Steric bulk at the central carbon atom may also prevent fragmentation that is common to formamidinates. Symmetric or asymmetric ligands can be synthesized for both amidinates and formamidinates.

Generally speaking, as you move from carboxylates to amidinates, the metal-oxygen interactions decrease; the alkyl substituents on the nitrogen increase solubility; and the more basic nitrogen ligands are less labile.
1.3.9 Mixed ligands

Up until now, the discussion has been based on homoleptic complexes. More recently work has been underway on mixed ligand or heteroleptic complexes.[21-24] Introducing two or different types of ligands to a dimetal unit may drastically change its utility. The idea of using one ligand to increase solubility while using another labile ligand for substitutional chemistry is not new.[25, 26] These designer or hybrid complexes offer new and unique properties not seen in homoleptic complexes.

The synthesis, structure and characterization of heteroleptic complexes offer new challenges and new methodologies that build off what is already know about homoleptic complexes. Mixed ligand compounds are still subject to ligand redistribution. This often leads to an equilibrium of a range of substituted products rather than a thermodynamically favored one. Therefore, ligand scrambling and isomerization are much more critical in heteroleptic complexes. This thesis will explore, amongst other things, the synthesis, structure and characterization of heteroleptic complexes of dimolybdenum and ditungsten paddlewheel complexes.

1.4 Simple pairs of dimers

Although paddlewheel complexes serve as model compounds, it is their linked or coupled derivatives that have the greatest potential for electronic applications. The earliest effort to link pairs of dimetal units was published in 1989 by Chisholm and coworkers.[27] Dimetal tetracarboxylates, $M_2(O_2CR)_4$, can be linked equatorially, axially, or in combinations as shown in Figure 1.11.[4] Equatorial linkers coordinate in a perpendicular bridging manner while axial linkers coordinate in a parallel monodentate
manner. This nomenclature is based on the relative orientation of the M-M axis with respect to the linker. The most common is linking in a perpendicular manner through the use of a bridging ligand to give “dimers of dimers” \([M_2(O_2CR)_3]_2\) (bridge), or extended molecular entities.\(^3\) This is the preferred method for molybdenum and tungsten since it will result in stronger coupling since both metals have a weak affinity for axial coordination.

![Diagram of different linker types](image)

**Figure 1.11** Basic modes of assembling dinuclear units. (Reproduced from Reference [4])

### 1.4.1 General synthesis

The formation of simple pairs of dimers can also be accomplished by substitutional chemistry. In this case, a dicarboxylic acid or its salt is used as a linker via the mono-carboxylate acid or salt. Refer to Scheme 1.3. The first typical reaction is the carboxylate exchange reaction previously described. The second is the metathesis reaction also previously described.
Carboxylate Exchange Reactions

\[2M_2(O_2CR)_4 + HO_2C(X)CO_2H \rightarrow [M_2(O_2CR)_3]_2(O_2C(X)CO_2) + 2HO_2CR\]

Metathesis Reactions

\[2[M_2(O_2CR)_3(MeCN)_2][BF_4] + Na_2[O_2C(X)CO_2] \rightarrow [M_2(O_2CR)_3]_2(O_2C(X)CO_2) + 2NaBF_4\]

where \(X = \text{conjugated linker}\)

**Scheme 1.3** Common routes to simple pairs of dimers

1.4.2 Metal-bridge interaction

The majority of linked \(M_2\) (\(M = \text{Mo, W}\)) compounds synthesized to date contain dicarboxylate linkers.[27-29] Compounds bridged by dicarboxylate linkers have been extensively studied and are well understood. Dimetal units can be linked by a dicarboxylate linker to allow electron communication between the two metal cores.[27] Electronic coupling of the metal cores arises from the interaction of the dimetal units \(\delta\) orbital and the \(CO_2\) \(\pi\) orbitals of the ligand.[30] The primary interaction comes from the mixing of the filled \(\delta\) orbital of the metal with the filled \(CO_2\) \(\pi\) and the empty \(CO_2\) \(\pi^*\) orbital of the bridge. This gives rise to the out-of-phase and in-phase orbital combination of the dimetal unit and the ligand \(CO_2\), and of these, the most important is the interaction shown in Figure 1.12 because of orbital energetics.
1.4.3 Electronic coupling

There are many ways of probing electronic communication between components connected by linkers, such as studying their response to electromagnetic radiation, their electrochemical behavior or their magnetic properties.[28] Bridged compounds are often intensely colored with absorptions that are red-shifted in comparison to the starting material. For example, the starting materials, $M_2(O_2C^tBu)_4$ ($M = Mo, W$), are yellow, while the oxalate bridged versions of these compounds are red ($M = Mo$) and blue ($M = W$), respectively.[3] This is a result of decreasing the $M_2 \delta \rightarrow$ bridging $CO_2 \pi^*$ absorption energy due to increased conjugation and orbital mixing. The higher energy of the $W_2 \delta$ orbitals again means they are closer in energy to the $CO_2 \pi^*$ orbital, and the $W_2$ compounds are red shifted in comparison to the $Mo_2$ analogues. The degree of coupling or communication between the dimetal cores can therefore be explored experimentally.
1.4.4 Typical bridges

Through recent studies, it has been shown that the coupling falls off as the length of the bridge increases or conjugated overlap decreases.[28] It was also shown that the greater basicity and hence tighter binding of the diamidate linkers may permit measurably better electrochemical communications between dimetal units.[14] Clearly, it is the nature of the linker that controls the extent of communication.[4] Examples of dicarboxylate linker are shown in Figure 1.13.

![Figure 1.13 Common dicarboxylate linkers (Reproduced from Reference [31])](image)

19
1.5 Mixed valence species

Since the late 1940s, the field of electron-transfer processes has been a scientific curiosity.[32] In 1967, significant awareness was provided by the physical properties of mixed-valence (MV) systems.[33] Since then, MV complexes have served as models for both theoretical and experimental research in this area.

The most extensively studied systems containing MV complexes are those consisting of two potentially identical metal-containing units which differ by one electron and are linked by a bridge that allows the odd electron to move back and forth between the two metal centers.[34] One of the first designed and best studied examples is the pyrazine-bridged decaamminediruthenium ion, \([(\text{NH}_3)_5\text{Ru(pyrazine)}\text{Ru(NH}_3)_3]^{5+}\) shown in Figure 1.14.[35] It is also known as the Creutz-Taube (C-T) complex.

![Figure 1.14 Creutz-Taube Ion. (Reproduced from Reference [35])](image)

The interest with MV complexes is understanding the location of the electron and how it transfers from one metal unit (donor) to the other (acceptor). The problem is best attacked by employing a number of physical techniques. There are many ways of probing electronic communication between metal units connected by a linker, such as
studying their response to electromagnetic radiation, their electrochemical behavior or their magnetic properties.[28] The degree of coupling or communication between the metal units can therefore be explored experimentally by use of electrochemistry, electronic absorption spectroscopy, and EPR spectroscopy.

1.5.1 Robin-Day Classification

The crucial issue of electron transfer is the assessment of the degree of electronic coupling between the two ligand-bridged metal units.[36] In general, the electronic coupling (V) between the two linked metal units is dependent upon their intranuclear distance and the nature of the bridge.[28] Depending on the bridge’s ability to transmit electronic communication, the complexes can be placed in one of three classifications according to the Robin-Day classification scheme.[37] In class I, the interaction between the M and M\(^+\) units is so weak that the observed properties are consistent with isolated mononuclear M and M\(^+\) complexes. The opposite extreme is found in class III. The interaction between the two metal units under these conditions is so great that the isolated metal properties are lost and new concerted properties emerge. Class II lies on the continuum between these extremes and exhibits mixed properties.

Depending on the timescale of the experiments, the determination of the class may vary.[38] The timescale of electron transfer as measured by electrochemistry is in the range of \(10^{-7}\) to 1 second. EPR spectroscopy has a timescale of \(10^{-4}\) to \(10^{-8}\) seconds. In UV-vis spectroscopy, the timescale is much faster on the order of \(10^{-14}\) to \(10^{-15}\) seconds. For this reason, it is best to use multiple techniques when characterizing the class of a compound.
1.5.2 Electrochemistry

Dimetal units can be monitored electrochemically as a function of the linker.[39] The degree of electronic coupling of two dimetal centers through a linker is determined by the separation of their oxidation potentials ($E_{1/2}$).[4] The two extremes are illustrated in Scheme 1.4. After the first oxidation [$E_{1/2}$(I)], the charge can remain localized on one metal core or be delocalized over both cores. If the positive charge is localized on one metal core, the second metal core is unaffected and a small difference is seen in the second oxidation potential [$E_{1/2}$(II)]. If the charge is delocalized over both $M_2$ cores, each unit shares the charge and the second oxidation potential will then be significantly larger.

**Scheme 1.4** Extreme cases of oxidation states in linked dinuclear units. (Reproduced from Reference [4])
This fundamental relationship between oxidation potentials can also be written as an equilibrium constant. Linked dimers undergo multistep charge-transfer reactions of the type

\[
\begin{array}{c}
A \quad n_1e^-, E_1^\circ \\
\quad \xrightarrow{\text{equilibrium}} \\
B \quad n_2e^-, E_2^\circ \\
\quad \xleftarrow{\text{equilibrium}} \\
C
\end{array}
\]  

(Equation 1.1).[40]

The relation of the concentrations of A and C to B at equilibrium is expressed by the comproportionation constant \(K_c\) where

\[
K_c = \frac{[B]^{n_1+n_2}}{[C]^{n_1}[A]^{n_2}} = \exp\left[\frac{(E_1^\circ - E_2^\circ)n_1n_2F}{RT}\right]  
\]  

(Equation 1.2).[40]

\(K_c\) is therefore a measure of the degree of mixed oxidation species by cyclic or differential pulse voltammetry. \(K_c\) increases as electrostatic interaction or charge delocalization increases. After entering the thermodynamic parameters for a one electron process, the \(K_c\) expression can simplified to the difference between the first and second oxidation potentials (in mV) according to equation 1.3.

\[
K_c = \exp\left[\frac{\Delta E^\circ}{25.6\text{mV}}\right]  
\]  

(Equation 1.3)[40]
An approximate relationship between $\Delta E^0$, $K_c$, and the Robin-Day classification is shown in Table 1.1.

<table>
<thead>
<tr>
<th>$\Delta E^0$ (mV)</th>
<th>$K_c$</th>
<th>Robin-Day classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;150 mV</td>
<td>&lt;350</td>
<td>Class I</td>
</tr>
<tr>
<td>~150 – 350 mV</td>
<td>~350 – $10^6$</td>
<td>Class II</td>
</tr>
<tr>
<td>&gt;350 mV</td>
<td>&gt;$10^6$</td>
<td>Class III</td>
</tr>
</tbody>
</table>

**Table 1.1** Electrochemical parameters according to the Robin-Day classification.

If a linker is a poor transmitter of the effect of oxidation from one $M_2$ unit to another, the interaction would be essentially electrostatic (Coulombic) in nature. Under these conditions, a plot of $\Delta E_{1/2}$ versus $d^2$ ($d =$ distance between the centers of the $M_2$ units) would be linear.

### 1.5.3 UV-vis spectroscopy

The Hush model is often the preferred method of analyzing mixed valence complexes because of its readily understandable derivation and overlap with the Marcus theory of intermolecular electron transfer.[33] According to Marcus theory, the potential energy surfaces (PESs) of a degenerate mixed valence system can be represented by parabolic functions.[41, 42] See Figure 1.15.

If no coupling is present, the PESs are nonadiabatic (non-interacting).[37, 42] Thermal electron transfer under these conditions is unlikely. In other words, the system
tends not to cross from the left-hand state to the right-hand state at the intersection. Since the optical electron transfer also depends on coupling, it may not be observed under these conditions.

This two-state analysis will therefore assume varying degrees of coupling between two adiabatic PESs that are being modeled as parabolas. Other assumptions include:

(1) The vibrational levels are assumed to be close in energy.

(2) The population of the vibrational levels of the ground state is weighted by a Boltzmann distribution.

(3) Direct electronic coupling of the terminal metal units is negligible since there is no direct bonding.

Figure 1.15 PES model related to electron transfer coordinate. (Reproduced from Reference [41])
Electronic coupling of the two PESs leads to an avoided crossing in the intersection region of the two parabolas. The splitting at the avoided intersection is twice the electronic coupling. The two electron-transfer pathways are now possible:[42]

(1) The thermal path where the system moves from one minimum of the lower surface over a transition state ($\Delta G^*$) along the electron-transfer coordinate to the other minimum.

(2) The optical path where the system is photoexcited from one minimum of the lower surface to the Franck-Condon state of the upper adiabatic surface. The energy of the path is the Marcus reorganization energy ($\lambda$) and can be broken down to an inner vibronic contribution ($\lambda_v$) and an outer solvent contribution ($\lambda_s$).

![Class I, Class II, Class III PESs](image)

**Figure 1.16** From left to right, PESs for class I, class II, and the class II/III border for symmetric mixed valence complexes. (Reproduced from Reference [35])
Referring to Figure 1.16, the Robin-Day classification scheme can be graphically represented for symmetric mixed valence complexes.[35] For class I, the odd electron is valence trapped on one of the two metal units because of a high energy barrier for thermal ($E_{th}$) and optical ($E_{op}$) electron transfer. For class II, electron delocalization is promoted by mixing the electronic donor and acceptor wave functions via the bridging ligand. As mixing or coupling increases, the discrete oxidation state character at the metal sites decreases. If electronic coupling is sufficient, there is a blending of the oxidation states and the odd electron is partially delocalized over both metal sites. For class I and class II complexes, the odd electron is restricted to one of the two metal units due to the thermal energy barrier for electron transfer.[34] Finally at the class II/III border, the magnitude of coupling becomes so great that $E_{th}=0$, the odd electron moves freely between metal centers.[33]

Hush applied this conceptual framework to understanding the inter-valence transitions in mixed valence complexes.[33] Unfortunately, the ability to generate mixed valence states for class I complexes is limited since both metal units are independent of each other. For example, under electrochemical conditions both metal units reduce or oxidize at the same potential and prevent the formation of a mixed valence complex. For this reason, the discussion will now be limited to class II and class III for simplicity.
Referring to Figure 1.17, the weakly coupled mixed valence complexes should exhibit a photoexcited transition between PESs at an energy $\lambda$. \[33\] This results in the transfer of an electron between states or between metal units. This is an inter-valence charge transfer (IVCT) and in this case is often referred to as a metal-to-metal charge transfer (MMCT).\[33\] If the potential energy surfaces are true parabolas, the absorption spectra has almost an exact Gaussian shape with $\nu_{\text{max}} = \lambda$.\[42\] The high energy side has the true Gaussian shape. On the low energy side, the smallest vertical excitation energy is limited to twice the coupling ($2V$).\[42\] Therefore, the theoretical Gaussian-shaped absorption band is cutoff at this lower energy. Since the band envelope consists of many sub-bands due to vibrational fine structure, the actual band envelope drops off smoothly.
at the lower energy side as shown by the dotted line.[42] For symmetric species, the bandwidth at half-intensity should be a function of the band maximum. The prediction for this absorption band for a class II system using the Hush Formula is $\Delta v_{1/2} = (2310v_{\text{max}})^{1/2} \text{ cm}^{-1}$. [34]

Class II complexes are generally recognized by the weak intensity of their MMCT absorption band, a larger than theoretical peak width at half height and a dipole moment.[33] The experimental bandwidth, however, is usually greater than the theoretical bandwidth due to anharmonicity and other effects.

Upon transition to class III, the minimum excitation energy is $2V$ and the theoretical absorption spectrum can be described as a low energy half band.[42] Vibrational fine structure in this case results in the same lower energy drop off as previously discussed. Since the ground state is fully delocalized between metal centers, it is not appropriate to describe this absorption as a metal-to-metal charge transfer.[33]

Class III complexes are generally recognized by the strong intensity of its charge resonance band, a smaller than theoretical peak width at half height, and no dipole moment.[33] From this model, experimental researchers can even work backwards to estimate the electronic coupling from the IVCT band maximum and shape after making sufficient assumptions.

1.5.3.1 OTTLE cell

Under normal conditions, the radical cations can be formed by chemical oxidation with an appropriate oxidizing agent such as $\text{Cp}_2\text{Fe}^+$ or $\text{Ag}^+$ salts. Under certain conditions, the oxidized species may not be stable long enough for prolonged sample
handling. Experimentally, spectroelectrochemistry allows for the rapid detection and classification of an IVCT band in the near-infrared region of the spectrum. This is commonly accomplished by use of an optically transparent thin-layer electrochemical (OTTLE) cell similar to that shown in Figure 1.18.[44] The OTTLE cell allows for the stepwise oxidation of the complexes to the mixed valence state and concurrent monitoring of the UV-vis-NIR absorption spectrum.[45]

**Figure 1.18** Typical optically transparent thin-layer electrode cell. (Reproduced from Reference [44])
1.5.4 EPR spectroscopy

EPR is also a powerful technique for studying molecular species that possess unpaired electrons.[46] Although most synthesized compounds will be diamagnetic, they are redox active and one-electron radical cations can again be prepared by chemical oxidation with an appropriate oxidizing agent such as Cp₂Fe⁺ or Ag⁺ salts.

An EPR spectrum contains several descriptive identifiers including g-value, coupling constants, and intensities.[46] The g-value and coupling constants reflect the environment of the unpaired electron with the metal center. The g-value represents the energy of the electron as compared to the free electron value of 2.023. Typical g-values for dimolybdenum and ditungsten compounds are approximately 1.9 and 1.8, respectively.[47] This is fundamentally attributed to increased spin-orbit coupling going from second to third row elements. The interaction of the unpaired electron with the nuclear spin of the nuclei can cause spin coupling. This electron-nuclear interaction is termed hyperfine splitting and is characterized by the coupling constant A. The intensities represent the probability of various states or the degree of interaction. As the degree of delocalization increases, the magnitude of the interaction with any specific nuclei decreases along with its intensity.

In the case of molybdenum compounds, ⁹⁵Mo and ⁹⁷Mo have a nuclear spin of I=5/2 (25.5% of the combined natural abundance isotopes with comparable magnetic moments) and the electronic coupling of the unpaired electron to the spin-active M₂
center would result in hyperfine lines.[6] The number of hyperfine lines is derived from
\[2nI + 1,\] where \(n\) is the number of nuclei of a given isotope.

Theoretically, the resultant EPR spectrum consists of a central resonance arising
from Mo\(_{2}\)\(^{5+}\) centers where each Mo has \(I=0\). The probability or intensity of this line can
be expressed as:

\[
(0.746^{98}\text{Mo} \times 0.746^{98}\text{Mo}) \times 100 = 55.6%. 
\]

This line is flanked by six lines arising from one of the Mo atoms being spin
active with \(I=5/2\). The total probability or intensity of these lines can be expressed as:

\[
2 \times (0.254^{95/97}\text{Mo} \times 0.746^{98}\text{Mo}) \times 100 = 37.9%. 
\]

The center line is again flanked by eleven lines arising from both the Mo atoms
being spin active with \(I=5/2\). The total probability or intensity of these lines can be
expressed as:

\[
(0.254^{95/97}\text{Mo} \times 0.254^{95/97}\text{Mo}) \times 100 = 6.4%. 
\]

These eleven lines will overlap with the previously discussed center and six lines.
In practice, these eleven lines are not normally observed. The probability that both metal
atoms in the M\(_2\) center being spin active is small and often beyond the resolution of the
instrument.
In the case of tungsten compounds, $^{183}$W has a nuclear spin of $I=1/2$ (14.3% of a natural abundance isotope) and electronic coupling of the unpaired electron to the spin-active M$_2$ center would result in hyperfine splitting.[6] Theoretically, the resultant EPR spectrum consists of a central resonance arising from W$_2^{5+}$ centers where each W has $I=0$. The probability or intensity of this line can be expressed as:

$$(0.857^{18x}W \times 0.857^{18x}W) \times 100 = 73.4\%.$$ 

This line is flanked by two lines arising from one of the W atoms being spin active with $I=1/2$. The total probability or intensity of these lines can be expressed as:

$$2 \times (0.143^{183}W \times 0.857^{18x}W) \times 100 = 24.5\%.$$ 

The center line is again flanked by five lines arising from both the W atoms being spin active with $I=1/2$. The total probability or intensity of these lines can be expressed as:

$$(0.143^{183}W \times 0.143^{183}W) \times 100 = 2.0\%$$ 

These five lines will overlap with the previously discussed center and two lines. In practice, these five lines also have a low probability of being observed.

Simulated EPR spectra for molybdenum and tungsten paddlewheel complexes are shown in Figure 1.19. As delocalization increases between dimetal cores via a
conjugated bridge, the spin coupling will increase and the spectrum line pattern will become more complex. This hyperfine coupling can therefore be used as a diagnostic tool to monitor the unpaired electron’s degree of delocalization.

Figure 1.19  Simulated EPR spectra of a) Mo$_2$ paddlewheel complex (parameters $g_{av} = 1.941$, $A_{iso} = 27.0$) and b) W$_2$ paddlewheel complex (parameters $g_{av} = 1.814$, $A_{iso} = 51.0$)

1.5.5 Superexchange

The bridging ligand mediates the interaction between the two metal units and plays an important role in the proposed mechanisms for electron transfer.[37] When the metal donor wave function has dominant mixing with the empty $\pi^*$ LUMO of the bridging ligand, the mechanism for metal-metal coupling is termed electron transfer superexchange.[33] When the metal acceptor wave function has dominant mixing with
the filled π orbital of the bridging ligand, the mechanism for metal-metal coupling is
termed hole transfer superexchange.[33] In other words, optical excitation from one
minimum of a PES causes the transfer of an electron or a hole from one metal unit to the
other metal unit.[43] One or both of these superexchange pathways contribute to the
overall metal-metal coupling.[33] See Figure 1.20.

Figure 1.20 Graphical representation of superexchange mechanisms.

1.6 Molecular wires

In general terms, molecular wires can be described as a one-dimensional molecule
that allows for exchange of electrons or holes between remote terminal groups via a
bridge.[48] This definition includes compounds with two redox active metal units
connected through a pi-system to allow intramolecular electron (hole) transfer.
Therefore, dimers of dimers are the simplest of molecular wires and serve as model
compounds for electron transfer mechanisms. Electronic interactions between the metal units and the bridge can be examined and provide insight into tuning properties. Model complexes in which two metal units are bridged by a conjugated bridge also provide a possible understanding of expected properties in higher order species.

1.7 Molecular assemblies

The use of dimetal units to build higher order structures was pioneered in 1998. It has been shown that by using suitably chosen \( \text{M}_2 \) units and linkers, a variety of product geometries can be obtained including loops, triangles, squares and polyhedra.[49] Molecular self-assemblies incorporating dinuclear metal species as rigid or semi-rigid corner units have become an intensely active research area.[50] See Figure 1.20 for illustrations.

The electronic coupling of larger molecular assemblies with greater than two dimetal centers has also attracted a high level of interest. In theory, dimetal centers can be linked together to have unique and interesting electronic properties. Unfortunately, as the molecular weights of these molecular assemblies increase, their solubility decreases. This limits their usefulness and requires new synthetic precursor or strategies to maximize solubility.
Figure 1.21 Structures of (a) molecular loop, (b) molecular triangle, (c) molecular square, and (d) molecular polyhedra. (Reproduced from Reference [4])
1.8 Statement of purpose

The overall goal of this thesis is to gain a greater insight into heteroleptic ligand complexes, molecular assemblies, and metallated conjugated polymers of metal-metal quadruply-bonded paddlewheel complexes of dimolybdenum and ditungsten. A systematic study of electronic and structural control is used in hopes of optimizing these types of complexes as models in the study and application of electron transfer processes.

Chapter Two contains details and findings from Density Functional Theory studies of homoleptic and heteroleptic ligand complexes as well as simple pairs of dimers linked by a bifunctional oxalate bridge. Special interest is given to metal-to-ligand interactions in paddlewheel complexes and metal-to-bridge interaction in simple pairs of dimers. A variety of model complexes have been studied theoretically to understand their electronic properties. Computational techniques provide molecular orbital construction and predictions of observable properties.

Chapter Three contains details of a new series of dimolybdenum and ditungsten paddlewheel complexes with mixed amidinate-carboxylate ligands of the form \( \text{trans-M}_2\text{O}_2\text{CCH}_3\text{PrNC(R)NPr}_2 \) where \( M = \text{Mo, W} \) and \( R = \text{Me, C≡CBu, C≡CPh, or C≡CFc} \) have been synthesized and characterized with the exception of the tungsten complex where \( R = \text{Me} \). These heteroleptic complexes exhibit unique and interesting properties including reduced ligand lability, increased solubility and the ability to tune electronic properties such as oxidation potential and metal-to-ligand charge transfer bands. The ability to expand this chemistry to other mixed amidinate-carboxylate ligands complexes is also addressed.
Chapter Four investigates the use of amidate complexes of the form $M_2(mhp)_4$ where $M = \text{Mo, W}$ and mhp is the anion of 2-hydroxy-6-methylpyridine as building blocks in simple molecular assemblies including simple pairs of dimers and molecular squares. The controlled synthesis of higher order molecular assemblies and the cooperative interaction of dimetal centers linked by conjugated bifunctional bridges are investigated.

Chapter Five reports the preliminary findings of using the unique trans-geometry of mixed amidinate-carboxylate complexes from Chapter Three to construct metallated conjugated oligomers or polymers when linked by a bifunctional bridge. Their suitability and properties as building blocks in hybrid co-polymer materials are investigated.
1.9 References


CHAPTER 2

DENSITY FUNCTIONAL THEORY (DFT) STUDIES OF PADDLEWHEEL COMPLEXES AND BRIDGED DIMERS.

2.1 Introduction.

Computational chemistry and molecular modeling have made significant progress and today, there is a unique synergy between theory and experiment. While spectroscopy is invaluable for actual physical measurements of properties, theoretical calculations have provided a means of explaining or predicting these same properties. Computational techniques have become a standard by providing molecular orbital construction and the prediction of allowed electronic transitions.

Computational studies of transition metal complexes with metal-metal bonds have attracted great interest. Traditional \textit{ab initio} studies of large electron complexes can be very challenging and sometimes impractical. Developments in DFT have shown this method to be a powerful computational alternative to the conventional quantum chemical methods.\cite{1} DFT calculations are much less computationally demanding and have greater electron correlation. The quality of computation, however, is best judged by comparison to known physical measurements.
This chapter will be divided into four distinct parts. Section 2.3 will validate the DFT methodology by comparing calculated results to known physical measurements. Section 2.4 will then explore the general theory of metal-ligand interactions in homoleptic paddlewheel complexes. Section 2.5 will calculate expected heteroleptic paddlewheel properties from sequential ligand substitution. Lastly, Section 2.6 will attempt to understand and predict the electronic communication found in bridged dimers using DFT.

2.2 Computational Methodology

A variety of modern density-functional techniques can be utilized in studying $\text{M}_2$ paddlewheel systems. Calculations were performed using the hybrid Hartree-Fock density functional B3LYP[2] (as implemented in the Gaussian 03 suite).[3] Recent studies have shown this method to be accurate for theoretical studies of second-row transition metal dinuclear complexes.[1, 4] In an effort to be cost-effective, the hybrid B3LYP functional was primarily used in conjunction with the 6-31G* basis set for all non-metal atoms and the SDD basis set with effective core potential (ECP) for all metal atoms.[5] Pure 5d functions were used versus Cartesian (6d) functions. All calculations were run in the highest possible symmetry. All calculations yielded a self-consistent set of results that were verified to be a minimum on the potential energy surface (PES) by vibrational frequency analysis unless otherwise noted.

Calculations were carried out with Gaussian 03: IA64-Linux-G03RevB.04 on the Itanium Cluster at the Ohio Supercomputing Center (OSC). Input files, isosurfaces,
spectrum, structures including bond distance and bond angles were produced with GaussView 3.09.[6]

2.3 Benchmarking

Initial results were used to benchmark the models shown in Figure 2.1 with previously reported theoretical and experimental data on Mo$_2$(O$_2$CH)$_4$ and Mo$_2$(HNCHNH)$_4$.[1, 4] All-electron (AE) calculations were also done with the standard 3-21G* basis sets for all atoms for trend analysis.[5]

![Figure 2.1 Model structures, assigned identification letter, chemical formula, and applied symmetry.](image)

Calculations compared well to the previously reported theoretical and experimental data. The AE calculations showed that accurate geometry optimization could be achieved even with a small basis set. The ECP calculations showed that the approximation could be incorporated for computational efficiency without losing significant accuracy. The 6-31G*/SDD basis set slightly overestimates the metal-metal bond distance but appears to be accurate to within 0.05 Å. This basis set also appears to
be accurate for bond angles to within approximately 1.5 degrees. The high mirror plane symmetry of all models resulted in a fixed ligand to dinuclear core dihedral angle of zero degrees. Actual experimental data supports a small dihedral angle of approximately 3.2°.[1, 4] See Tables 2.1 and 2.2.

<table>
<thead>
<tr>
<th></th>
<th>AE</th>
<th>ECP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3-21G</td>
<td>3-21G*</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2.108  2.104</td>
<td>2.150  2.119</td>
</tr>
<tr>
<td>Mo-O</td>
<td>2.107  2.108</td>
<td>2.118  2.120</td>
</tr>
<tr>
<td>O-C</td>
<td>1.295  1.295</td>
<td>91.51  91.68</td>
</tr>
<tr>
<td>MoMoO</td>
<td>92.11  92.16</td>
<td>91.51  91.68</td>
</tr>
<tr>
<td>MoOC</td>
<td>117.02 116.98</td>
<td>91.51  91.68</td>
</tr>
<tr>
<td>OMoO</td>
<td>89.92  89.92</td>
<td>91.51  91.68</td>
</tr>
<tr>
<td>OMoMoO</td>
<td>0.0 (fixed) 0.0 (fixed)</td>
<td>0.0 (fixed) 0.0 (fixed)</td>
</tr>
</tbody>
</table>

a Previously reported calculations were performed with the B3LYP functional and the Gaussian 94 program.[1]
b Average bond distances and angles from crystal structure data of Mo₂(O₂CH)₄.[7]

Table 2.1 Optimized and experimental structural parameters for bond lengths [Å] and angles [deg] of Mo₂(O₂CH)₄ model dimer.

<table>
<thead>
<tr>
<th></th>
<th>AE</th>
<th>ECP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3-21G</td>
<td>3-21G*</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>2.093  2.089</td>
<td>2.141  2.132</td>
</tr>
<tr>
<td>Mo-N</td>
<td>2.157  2.159</td>
<td>2.141  2.132</td>
</tr>
<tr>
<td>N-C</td>
<td>1.335  1.335</td>
<td>1.344  1.328</td>
</tr>
<tr>
<td>MoMoN</td>
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<td>92.32  92.17</td>
</tr>
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<td>118.89 117.98</td>
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<tr>
<td>NCN</td>
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<td>118.89 119.70</td>
</tr>
<tr>
<td>NMoMoN</td>
<td>0.0 (fixed) 0.0 (fixed)</td>
<td>0.0 (fixed) 0.0 (fixed)</td>
</tr>
</tbody>
</table>

a Previously reported calculations were performed with the B3LYP functional and the Gaussian 98 program.[4]
b Average bond distances and angles from crystal structure data of Mo₂(RNCHNR)₄ where (R = p-CH₃C₆H₄).[8]

Table 2.2 Optimized and experimental structural parameters for bond lengths [Å] and angles [deg] of Mo₂(HNCHNH)₄ model dimer.
Overall, this comparison indicates that DFT calculations with a less computer
demanding 6-31G*/SDD basis set with an ECP yielded comparable results. The
agreement between the optimized geometries and the experimental values indicates the
reliability of at least a qualitative interpretation.

2.4 Homoleptic paddlewheel complexes.

As in most cases, the sum of the pieces makes the whole. Therefore, it is useful to
examine the key pieces of a typical paddlewheel complex. These pieces include the M₂
manifold, the ligand π system, and the effects of their interaction. The metals of interest
will remain dimolybdenum and ditungsten. The ligands of interest are simple formate,
formamidate, and formamidinate. Since formamidate is an asymmetric ligand, we will
concentrate on paddlewheel complexes derived from formate and formamidinate. This
will allow for easy comparison under the same D₄h symmetry. Paddlewheel complexes
of these two ligands will serve as models for these calculations.

2.4.1 M₂ manifold

As previously discussed, the metal manifold consists of MOs known as σ, π, δ,
δ*, π*, σ*. The MO isosurfaces illustrating these typical orbitals have been calculated
and are shown in Figure 2.2.
Figure 2.2 Molecular orbital isosurfaces for the metal manifold of the model complex Mo$_2$(O$_2$CH)$_4$. Only one example of each degenerate $\pi$ and $\pi^*$ orbitals are shown. (Isovalue for surfaces set at 0.04 au)
2.4.2 µ-bridging ligands

The electronic structures of these µ-bridging ligands are easily understood in terms of their valence electrons.[9] The simplest carboxylate moiety, O=C(H)-O⁻, is formate and has 18 valence electrons. Six electrons are involved in the three σ bonds between the four atoms. Eight electrons are located in the two lone pairs on each oxygen atom. The remaining four electrons are part of the delocalized π network of the ligand.

The simplest formamidate moiety, HN=C(H)-O⁻, also has 18 valence electrons. Six electrons are involved in the three σ bonds (N-C, C-H, and C-O bonds). Six electrons are located in two lone pairs on the oxygen atom and one lone pair on the nitrogen atom. Two electrons that are analogous to the lone pair on oxygen atoms are now used in the formation of a N-H σ bond. The remaining four electrons are part of the delocalized π network of the ligand. The simplest formamidinate moiety, HN=C(H)-NH⁻, again has 18 valence electrons. Six electrons are involved in the three σ bonds (C-H and two N-C bonds). Four electrons are located in a lone pair on each nitrogen atom. Four electrons that are analogous to lone pairs on oxygen atoms are now used in the formation of two N-H σ bonds. The remaining four electrons are part of the delocalized π network of the ligand. In this manner, we can show these ligands to be isoelectronic but they are not isoenergetic.

2.4.3 Ligand π system

Concentrating on the formate and formamidinate ligand models, there are three possible π symmetry combinations for X-C-X ligands illustrated in Figure 2.3.[9] The lowest energy combination is a bonding π-orbital formed by the three central p-orbitals
being in-phase. The next combination is a non-bonding $\pi$-orbital formed only by the X p-orbitals being out-of-phase. The last combination is an anti-bonding $\pi$-orbital formed by p-orbitals being in-phase but the C p-orbital being out-of-phase. The four electrons in the $\pi$ network occupy the two lowest energy orbitals.

![Energy](image)

**Figure 2.3** Three $\pi$ symmetry combinations possible for X-C-X and calculated isosurfaces for O=C-O$^-$anion (isovalue for surfaces set at 0.04 au).

### 2.4.4 Symmetry-allowed linear combinations.

When these simple formate or formamidinates ligands interact with the dimetal unit to form an $M_2(X\text{-}C\text{-}X)_4$ complex, the highest possible symmetry is $D_{4h}$. Under this
symmetry, each X-C-X (also to be written as X^X) \( \pi \) orbital forms four linear combinations of molecular orbitals.[9] Refer to Figure 2.4. The bonding \( \pi \)-orbitals form linear combinations of \( a_{2g} \), \( e_u \), and \( b_{2g} \) symmetries. The non-bonding \( \pi \)-orbitals form linear combinations of \( a_{1u} \), \( e_g \), and \( b_{1u} \) symmetries. The anti-bonding \( \pi \)-orbitals form linear combinations of \( a_{2g}^* \), \( e_g^* \), and \( b_{2g}^* \) symmetries.

![Diagram](image)

**Figure 2.4** Linear combinations of ligand \( \pi \) orbitals and ligand geometry under \( D_{4h} \) symmetry.
2.4.5 Metal-ligand interaction

We can now examine the key orbital interactions that arise from the $M_2$ manifold interaction with the linear combinations of the ligand $\pi$ system. It is now important to know that the $M_2 \delta$ orbital transforms under the irreducible representation $b_{2g}$, while the $M_2 \delta^*$ orbital transform under the irreducible representation $b_{1u}$. In the bonding and antibonding linear combinations of the ligand $\pi$ system, only the $b_{2g}$ and $b_{2g}^*$ combinations have the proper symmetry and orientation to interact with the $M_2 \delta$ orbital. In the nonbonding linear combination, only the $b_{1u}$ combination has the proper symmetry and orientation to interact with the $M_2 \delta^*$ orbital. These interactions provide additional splitting and electron donation to the metal center. Figure 2.5 is a qualitative MO diagram that summarizes these interactions.

The strongest metal-ligand interaction occurs between the $M_2 \delta^*$ and ligand $b_{1u}$ orbitals because of the close energy match between fragment orbitals. Based on the $M_2 \delta^*$ fragment orbital being slightly higher in energy than the $b_{1u}$ fragment orbital, this results in the metal-ligand bonding combination being stabilized to lower energy and the corresponding metal-ligand anti-bonding being destabilized to higher energy. The next metal-ligand interaction occurs between the $M_2 \delta$ and the ligand $b_{2g}$ and $b_{2g}^*$ combinations. This interaction is much weaker due to poor energy matching and the effects are competitive.Depending on which interaction is stronger, the $M_2 \delta$ fragment may be stabilized or destabilized by the interaction with the $b_{2g}$ and $b_{2g}^*$ fragment orbitals.[9]
Figure 2.5 Frontier molecular orbital diagram illustrating ligand π-type interaction with $M_2 \delta$ and $\delta^*$ orbitals. The arrows represent the HOMO of the $M_2(X^X)_4$ system.


2.4.6 Ligand effects

DFT calculations show that the ligands of interest are not isoenergetic. As the O-donor atom becomes N-H, the ligand becomes less electronegative and more electron donating. This effect on the ligand $\pi$ system is illustrated in Figure 2.6 along with the calculated isosurfaces. Specifically, the bonding and non-bonding are moved to higher energy by approximately 1.5 eV in going from formate to formamidinate.

Figure 2.6 Qualitative comparison of ligand $\pi$-orbital of O=C(H)-O$^-$, HN=C(H)-O$^-$, and HN=C(H)-NH$^-\$ anions (isovalue for surfaces set at 0.04 au).
The overall effect on the $M_2(X-C-X)_4$ complex in going from formate to formamidinate ligands is to raise the energy of the frontier molecular orbitals of the paddlewheel complex. This is illustrated in Figure 2.7. The relative energies of orbitals are consistent with formamidinate being a better electron-donor than carboxylate ligands. The more basic formamidinate ligand raises the $M_2$ manifold of $Mo_2(HNCHNH)_4$ by approximately 2 eV relative to the $Mo_2(O_2CH)_4$. A similar trend is also found in the tungsten comparison that is already approximately 0.5 eV higher than its $Mo_2$ analogs. Based on this information, it would appear that the ionization potential of these paddlewheel complexes could be tuned by several eV based on the choice of metal and ligand.
Figure 2.7 Qualitative comparison of metal manifold and ligand $\pi^*$ energies between Mo$_2$(O$_2$CH)$_4$ and Mo$_2$(HNC(H)NH)$_4$. 
2.5 Heteroleptic paddlewheel properties.

Detailed theoretical studies of paddlewheel bonding scheme have been mainly limited to molecules of the general formula $\text{M}_2\text{L}_4$ with an approximate $\text{D}_{4h}$ symmetry for ligands around the dimetal core.\[4, 9\] Structural properties of second-row transition metal complexes of this type can be quantitatively predicted using theoretical methodologies.\[4\] Good estimates for other physical properties based on several different density functionals have also been shown.\[9\]

A primary concern of these complexes is the effect that chemical tuning of the metal and ligand has on their reactivity and electronic properties. An interesting set of isoelectronic complexes have been chosen to examine ligand effects on dimolybdenum paddlewheel complexes. This study will draw on work previously done with $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{HNCHNH})_4$ to study the $\text{Mo}_2(\text{O}_2\text{CH})_{4-x}(\text{HNCHNH})_x$ series of complexes where $x = 0, 1, 2, 3, \text{ or } 4$ to understand ligand exchange effects on observable properties. Figure 2.8 illustrates this series as a sequential carboxylate exchange.
Figure 2.8 Sequential ligand exchange (nitrogen hydrogen substituents omitted for clarity).

Computational studies include geometry optimization, molecular orbital analysis, and molecular/thermochemical properties such as gas-phase ionization potentials, vibrational (IR and Raman) frequencies, and nuclear magnetic resonance chemical shifts. Time-dependent DFT (TD-DFT) calculations are used to determine low energy electronic transitions. The model complexes are shown in Figure 2.9. The overall goal is to understand the expected observable properties of these model complexes and any significant trends in the series.
Figure 2.9 Model structures, assigned identification letter, chemical formula, and applied symmetry.
2.5.1 Optimized Geometry

The predicted geometries of the model complexes were paddlewheel complexes as expected with several interesting trends. The first trend in going across the series from $\text{Mo}_2(\text{O}_2\text{CH})_4$ to $\text{Mo}_2(\text{HNCHNH})_4$ is the progressive increase in the metal-metal bond distance. Another trend showed the more basic formamidinate ligands to have shorter bond distances to the dimetal core than the formate ligands. In fact, formate ligands that were trans to formamidinate ligands were even longer on average. This suggests a trans-influence that may be anticipated based on the order $N > O$.[10] Comparison of the enthalphy and free energy between models C1 and C2 shows that the cis complex is thermodynamically favored by about 1 kcal/mol. The trans complex, however, may be kinetically favored by a trans effect.[11] The optimized geometry parameters for all model complexes are listed in Table 2.3.
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C1</th>
<th>C2</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Mo</td>
<td>2.119</td>
<td>2.122</td>
<td>2.125</td>
<td>2.126</td>
<td>2.130</td>
<td>2.132</td>
</tr>
<tr>
<td>Mo-O</td>
<td>2.120</td>
<td>2.133(2)</td>
<td>2.145</td>
<td>2.159</td>
<td>2.178</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.149(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-N</td>
<td>2.114</td>
<td>2.141</td>
<td>2.123</td>
<td>2.153(2)</td>
<td>2.133(1)</td>
<td>2.165</td>
</tr>
<tr>
<td>O-C</td>
<td>1.273</td>
<td>1.272(2)</td>
<td>1.271</td>
<td>1.270</td>
<td>1.269</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.271(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C</td>
<td>1.330</td>
<td>1.329</td>
<td>1.330</td>
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<td>MoMoO</td>
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<td>91.65</td>
<td>91.61</td>
<td>91.58</td>
<td></td>
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<td>91.63(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MoMoN</td>
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<td>92.24</td>
<td>92.22</td>
<td>92.20(2)</td>
<td>92.17</td>
<td></td>
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<td></td>
<td>92.18(1)</td>
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<td></td>
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<tr>
<td>MoOC</td>
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<td>116.33(2)</td>
<td>116.14</td>
<td>116.17</td>
<td>115.98</td>
<td></td>
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<td>116.36(1)</td>
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<tr>
<td>MoNC</td>
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<td>118.17</td>
<td>118.25</td>
<td>118.05(2)</td>
<td>117.98</td>
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<td></td>
<td></td>
<td>118.21(1)</td>
<td></td>
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<td>OCO</td>
<td>123.57</td>
<td>124.02</td>
<td>124.43</td>
<td>124.41</td>
<td>124.89</td>
<td></td>
</tr>
<tr>
<td>NCN</td>
<td>118.69</td>
<td>119.16</td>
<td>119.00</td>
<td>119.45(2)</td>
<td>119.70</td>
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<td>119.22(1)</td>
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<td>OMoO</td>
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<td>176.71</td>
<td>85.95</td>
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<td></td>
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<tr>
<td>OMoN</td>
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<td>89.94</td>
<td>89.68</td>
<td>87.54</td>
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<td></td>
</tr>
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<td>176.12</td>
<td></td>
<td></td>
<td>176.24</td>
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<td>NMoN</td>
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<td>94.44</td>
<td>92.32</td>
<td>173.48</td>
<td>175.66</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.3** Optimized structural parameters for bond lengths [Å] and angles [deg] of mixed ligand dimers.

### 2.5.2 Molecular Orbitals

A series of isosurfaces were generated for the orbitals above and below the highest occupied molecular orbitals (HOMO) for the model complexes. This allowed for
the characterization of each orbital. In all cases, the HOMO was a $M_2 \delta$ orbital.

However, the trend in going from $\text{Mo}_2(\text{O}_2\text{CH})_4$ to $\text{Mo}_2(\text{HNCHNH})_4$ was that the energy of the HOMO was raised by approximately 2 eV. This suggests that the type of ligand plays an important role in incrementally tuning the ionization potential of these complexes.

Another trend was observed with the ligand $\pi^*$ orbitals. For model complexes A, C2, and E, the ligand $\pi^*$ orbitals were degenerate. For model complexes B, C1, and D, the ligand $\pi^*$ orbitals were not degenerate or isoenergetic. Unfortunately, the metal-to-ligand charge transfer band as shown in Figure 2.10 was relatively unaffected.

![Molecular Orbital Comparison](image)

**Figure 2.10** MO comparison of $M_2 \delta$ and $L \pi^*$ energies of the model complex series.
2.5.3 Ionization Potentials

Gas-phase ionization potentials were calculated for the model complexes using three different approximations. The first is an adiabatic approximation using the zero point energy difference between the optimized geometries of the neutral molecule and the corresponding radical cation energy. The second is a vertical approximation using the bottom-of-the-energy well energy difference with the optimized geometries of the neutral molecule and the single-point calculation of the radical cation at the geometry of the neutral molecule. The third is an approximation of the Koopmans’ theorem[12] as applied to Hartree-Fock methods. In exact DFT, the first ionization potential should be a direct analogy to the Koopmans’ theorem.[12] Specifically, the energy of the highest occupied Kohn-Sham MO is the negative of the ionization potential.

The results in Table 2.4 show a similar trend. Qualitatively, the ionization potentials step down the series in going from Mo$_2$(O$_2$CH)$_4$ to Mo$_2$(HNCHNH)$_4$. This illustrates that formamidinate complexes are easier to oxidize than carboxylate complexes. Quantitatively, the results of the adiabatic and vertical approximation are better than the Koopmans’ approximation. This suggests that the functional used is only approximate. Unfortunately, the adiabatic and vertical methods generally do not agree closely with experimental results. The fact that the adiabatic and vertical ionization potentials are close does suggest another interesting possibility. Since the energy difference before geometry optimization is close to the energy difference after geometry optimization, the reorganization energy appears to be small. In other words, the geometry of the neutral molecule and the radical cation are very similar. This may lead to interesting excited state properties.
Table 2.4 Predicted gas-phase ionization potentials in eV.

<table>
<thead>
<tr>
<th>Model</th>
<th>Adiabatic</th>
<th>Vertical</th>
<th>Koopmans’ approx.</th>
<th>exptl[9]</th>
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</thead>
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<tr>
<td>$\text{Mo}_2\text{(O}_2\text{CH)}_4$ (A)</td>
<td>7.20</td>
<td>7.30</td>
<td>5.47</td>
<td>6.89</td>
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<tr>
<td>$\text{Mo}_2\text{(O}_2\text{CH)}_2\text{(HNCHNH)}$ (B)</td>
<td>6.60</td>
<td>6.68</td>
<td>4.91</td>
<td></td>
</tr>
<tr>
<td>$\text{trans-Mo}_2\text{(O}_2\text{CH)}_2\text{(HNCHNH)}_2$ (C1)</td>
<td>6.06</td>
<td>6.10</td>
<td>4.40</td>
<td></td>
</tr>
<tr>
<td>$\text{cis-Mo}_2\text{(O}_2\text{CH)}_2\text{(HNCHNH)}_2$ (C2)</td>
<td>6.05</td>
<td>6.09</td>
<td>4.39</td>
<td></td>
</tr>
<tr>
<td>$\text{Mo}_2\text{(O}_2\text{CH)}\text{(HNCHNH)}_3$ (D)</td>
<td>5.56</td>
<td>5.59</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>$\text{Mo}_2\text{(HNCHNH)}_4$ (E)</td>
<td>5.12</td>
<td>5.11</td>
<td>3.49</td>
<td>5.63</td>
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</tbody>
</table>

2.5.4 UV-vis Calculations

Time-dependent DFT was used to calculate the first 25 excited states for the model complexes. The electronic transitions were correlated to the character of the molecular orbital. Most excited states showed very weak oscillator strength including all $\text{M}_2\delta \rightarrow \text{M}_2\delta^*$ transitions. The weak $\text{M}_2\delta \rightarrow \text{M}_2\delta^*$ transition can be attributed to poor d-d orbital overlap within the dimetal core involving the $d_{xy}$ orbitals. The most significant and intense observable transitions corresponded to one or more $\text{M}_2\delta \rightarrow \text{L}\pi^*$ transitions as expected. The lowest energy transition is predicted for the C1 complex. Results are shown in Table 2.5.
<table>
<thead>
<tr>
<th>Model (Electronic State)</th>
<th>transition</th>
<th>energy</th>
<th>wavelength</th>
<th>intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₂(O₂CH)₄ (A) (1¹A₁g)</td>
<td>1¹Eₓ*</td>
<td>4.17 eV</td>
<td>297.24 nm</td>
<td>0.1286</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo₂(O₂CH)₃(HNCHNH) (B) (1¹A₁)</td>
<td>1¹B₁*</td>
<td>4.06 eV</td>
<td>305.06 nm</td>
<td>0.1203</td>
</tr>
<tr>
<td></td>
<td>2¹A₁*</td>
<td>4.17 eV</td>
<td>297.08 nm</td>
<td>0.0814</td>
</tr>
<tr>
<td></td>
<td>3¹A₁</td>
<td>4.63 eV</td>
<td>267.93 nm</td>
<td>0.0640</td>
</tr>
<tr>
<td>trans-Mo₂(O₂CH)₂(HNCHNH)₂ (C1) (1¹A₁g)</td>
<td>1¹B₂ₓ*</td>
<td>3.99 eV</td>
<td>310.57 nm</td>
<td>0.1098</td>
</tr>
<tr>
<td></td>
<td>1¹B₃ₓ*</td>
<td>4.18 eV</td>
<td>296.87 nm</td>
<td>0.0291</td>
</tr>
<tr>
<td>cis- Mo₂(O₂CH)₂(HNCHNH)₂ (C2) (1¹A₁)</td>
<td>1¹B₂*</td>
<td>4.04 eV</td>
<td>306.93 nm</td>
<td>0.0537</td>
</tr>
<tr>
<td></td>
<td>2¹A₁*</td>
<td>4.08 eV</td>
<td>303.80 nm</td>
<td>0.1129</td>
</tr>
<tr>
<td>Mo₂(O₂CH)(HNCHNH)₃ (D) (1¹A₁)</td>
<td>2¹A₁*</td>
<td>4.03 eV</td>
<td>307.61 nm</td>
<td>0.0735</td>
</tr>
<tr>
<td></td>
<td>1¹B₁*</td>
<td>4.19 eV</td>
<td>295.91 nm</td>
<td>0.0541</td>
</tr>
<tr>
<td></td>
<td>1¹B₂</td>
<td>4.39 eV</td>
<td>282.38 nm</td>
<td>0.0580</td>
</tr>
<tr>
<td>Mo₂(HNCHNH)₄ (E) (1¹A₁g)</td>
<td>1¹Eₓ*</td>
<td>4.16 eV</td>
<td>297.83 nm</td>
<td>0.0516</td>
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<tr>
<td></td>
<td>1¹A₂ₓ</td>
<td>4.20 eV</td>
<td>295.22 nm</td>
<td>0.0806</td>
</tr>
</tbody>
</table>

Table 2.5 Computed low energy vertical excitation energies. * indicates M₂δ → L π* transitions.

2.5.5 Additional calculations.

For brevity, additional calculation results have been including in Appendix A.

For vibrational frequency analysis, refer to Appendix A.1. For nuclear magnetic resonance results, refer to Appendix A.2. For comparison of methyl substituents to hydrogen substituents model complexes, refer to Appendix A.3.
2.6 Bridged dimers.

Again, it is useful to examine the key pieces of typical bridged dimers. These pieces include the $[\text{M}_2]_2$ manifold, the bridge $\pi$ system, and the effects of their interaction. We will continue to concentrate on paddlewheel complexes derived from formate and formamidinate. The bridges of interest will be a simple oxalate dianion. Hydrogen-substituted complexes will also serve as models for these calculations. This will allow for easy comparison under the same $D_{2h}$ symmetry.

2.6.1 $[\text{M}_2]_2$ manifold.

When two $\text{M}_2$ units are linked by the oxalate bridge in $D_{2h}$ symmetry, the metal manifold combines as two sets of $\sigma$ and $\sigma^*$, four sets of $\pi$ and $\pi^*$, and two sets of $\delta$ and $\delta^*$. In the absence of oxalate bridge interactions, each unique set of MOs are essentially isoenergetic.

2.6.2 Oxalate $\pi$ system.

The six $\pi$ molecular orbitals of the planar oxalate dianion and the calculated molecular orbital isosurfaces are shown in Figure 2.11. The $\pi_1$ and $\pi_2$ orbitals are bonding. The $\pi_1$ orbital represents a total bonding mode. The $\pi_2$ orbital is bonding with respect to the four C-O bonds but anti-bonding with respect to the C-C bond. The $\pi_3$ and $\pi_4$ orbitals are essentially non-bonding. Each represents non-bonding oxygen lone pair orbitals. The $\pi_5$ and $\pi_6$ orbitals are anti-bonding. The $\pi_5$ orbital is anti-bonding with respect to the four C-O bonds but bonding with respect to the C-C bond. The $\pi_6$ orbital represents a total anti-bonding mode. The eight electrons in the $\pi$ network occupy the
four lowest energy orbitals. The oxalate anion’s HOMO is therefore $\pi_4$ and the LUMO is $\pi_5$.

**Figure 2.11** Qualitative $\pi$ MO diagram and calculated isosurfaces for oxalate$^{2-}$ dianion (isovalue for surfaces set at 0.04 au).
2.6.3 Metal-bridge interaction.

Let’s now examine the key orbital interactions that arise from linking $\text{M}_2$ units via an oxalate bridge.[10, 13] It is important to know that the $[\text{M}_2]_2 \delta$-orbitals transform under the irreducible representations of $b_{1g}$ and $b_{2u}$. This is the same symmetry as $\pi_2$ and $\pi_5$ oxalate orbitals, respectively. Through calculations, the $\text{M}_2 \delta$-orbitals significantly interact with the $\pi_2$ and $\pi_5$ MOs of the oxalate anion. In fact, the $\text{M}_2 \delta$-orbitals are split by the symmetry allowed interactions. A qualitative MO diagram illustrates these interactions in Figure 2.12.

![Figure 2.12 Qualitative MO diagram showing the interaction of the frontier orbitals of a $[\text{M}_2]_2$ fragment with the $\pi_2$ and $\pi_5$ oxalate orbitals.](image_url)
Splitting of the M\textsubscript{2} δ orbitals by a symmetry-allowed combination of the appropriate oxalate π orbitals can be referred to as a filled metal to filled oxalate orbital and a filled metal to empty oxalate orbital interaction or simply a filled-filled and filled-empty interaction. Mixing of the bridge and metal-based orbitals result in the formation of the four new and important MOs as illustrated in a qualitative MO diagram with molecular orbital isosurfaces for [(HCO\textsubscript{2})\textsubscript{3}Mo\textsubscript{2}](oxalate) in Figure 2.13.

The two lowest energy MOs are metal-to-bridge bonding combinations while the two higher energy MOs are metal-to-bridge anti-bonding combinations. Typically, the lowest energy MO is essentially filled bridge π in character. The character of the next two MOs is mostly an in-phase and out-of-phase combination of the filled δ-orbitals. The in-phase combination of these two MOs is stabilized by the metal back-bonding to the empty bridge π* orbital while the out-of-phase combination of these two MOs is destabilized by the filled metal orbital interaction with the filled bridge π orbital. These MOs are normally also identified as the HOMO-1 and HOMO, respectively. From visual inspection, it can be seen that the greatest metal-to-bridge interaction occurs in HOMO-1 from a filled metal to empty oxalate orbital interaction. Lastly, the highest energy MO is mostly empty bridge π* in character.
Figure 2.13 Qualitative bridge $\pi$ and metal $\delta$ MO diagram and calculated isosurfaces for $[(\text{HCO}_2)_3\text{Mo}_2]_2$(oxalate) (isovalue for surfaces set at 0.04 au).
2.6.4 Electronic communication.

When bridged dimers are singly oxidized, the nature of electronic communication between M₂ units via a conjugated bridge can be anticipated through molecular orbital analysis. The mixing of the M₂ δ-orbitals with the ligand bridge is believed to be an essential requirement for electronic coupling of the M₂ units. With effective overlap between the bridge π-orbitals and the [M₂]₂ δ-based orbitals, the δ-orbitals are split into an in-phase and out-of-phase combination as previously discussed. This essentially allows the bridge to act as a conduit for electron or hole transfer between M₂ units. Therefore, the degree of splitting between the [M₂]₂ δ-orbital is an indicator for electronic communication. The closer in energy the [M₂]₂ δ-orbitals and appropriate symmetry-allowed bridge π orbitals are, the better the interaction or mixing. This results in better splitting between the [M₂]₂ δ-orbitals. Larger splitting between [M₂]₂ δ-orbitals implies a greater possibility for electronic communication. Unfortunately, the degree of electronic communication or electron delocalization cannot be quantified without experimental techniques.

The mechanism of electronic communication in a mixed-valence bridged dimer can be described by the superexchange mechanism.[14] The ligand bridge provides a means for either electron hopping through the empty bridge π* orbital or hole hopping through the filled bridge π orbital. Both means may contribute to the total electronic coupling between M₂ units but one path generally dominates. Based on the relative energy separation of the HOMO-1 and HOMO from the essentially filled and empty bridge π orbitals, it is also possible to predict the dominant superexchange mechanism of hole or electron hopping, respectively.
For simplicity, the DFT calculations of the bridged dimers model will be calculated from the neutral species. This will assume a negligible re-organizational energy that would be expected in fast electron transfer. One should also note that these gas-phase calculations ignore solvent effects.

For $[(\text{HCO}_2)_3\text{Mo}_2]_2$(oxalate), the separation in energy of the HOMO and HOMO-1 is approximate 0.4 eV. Based on the MO energy level diagram in Figure 2.14, the dominant superexchange mechanism should be electron hopping through the empty bridge $\pi$ orbital.

![Figure 2.14](image)

**Figure 2.14** Qualitative MO energy level diagram with calculated isosurfaces for $[(\text{HCO}_2)_3\text{Mo}_2]_2$(oxalate) (isovalue for surfaces set at 0.04 au).
For \([(HNCHNH)_{3}Mo_{2}]_{2}(oxalate)\), the separation in energy of the HOMO and HOMO-1 is approximate 0.3 eV. This implies less communication than the previous formate model. Based on the MO energy level diagram in Figure 2.15, the dominant superexchange mechanism also should be electron hopping through the empty bridge $\pi$ orbital.

**Figure 2.15** Qualitative MO energy level diagram with calculated isosurfaces for \([(HNCHNH)_{3}Mo_{2}]_{2}(oxalate)\) (isovalue for surfaces set at 0.04 au).
For $[(\text{HCO}_2)_3\text{W}_2]_2$(oxalate), the separation in energy of the HOMO and HOMO-1 is approximate 0.6 eV. This implies greater communication than in the molybdenum analog. Based on the MO energy level diagram in Figure 2.16, the dominant superexchange mechanism remains electron hopping through the empty bridge $\pi$ orbital.

**Figure 2.16** Qualitative MO energy level diagram with calculated isosurfaces for $[(\text{HCO}_2)_3\text{W}_2]_2$(oxalate) (isovalue for surfaces set at 0.04 au).
For \([\text{HNCHNH}_3\text{W}_2\text{](oxalate)}\), the separation in energy of the HOMO and HOMO-1 is approximate 0.45 eV. This implies less communication than in the previous tungsten model but more communication than any of the molybdenum models. Based on the MO energy level diagram in Figure 2.17, the dominant superexchange mechanism should also be electron hopping through the empty bridge \(\pi\) orbital.

**Figure 2.17** Qualitative MO energy level diagram with calculated isosurfaces for \([\text{HNCHNH}_3\text{W}_2\text{](oxalate)}\) (isovalue for surfaces set at 0.04 au).
The greater splitting of the set of \([M_2]_2\) \(\delta\) orbitals for tungsten than molybdenum reflects the normally accepted greater 5d orbital overlap with the oxalate anion. Additionally, the higher energy set of \(\delta\) orbital in tungsten lie closer in energy to the \(\pi_s\) oxalate orbital and therefore simply mix better.

DFT calculations support greater splitting and electronic communication in formate complexes than formamidinates complexes. From examination of the MO diagrams, visual comparisons appear to be very informative. Since the formamidinate ligands are higher in energy, it appears they are closer in energy to the \(M_2\) manifold and mix better than formate ligands. This results in greater formamidinate ligand character in the \([M_2]_2\) \(\delta\) orbital. This adversely affects the metal-to-bridge mixing and decreases the \([M_2]_2\) \(\delta\) splitting. The overall effect is to decrease the expected electronic communication in formamidinate complexes.

Many of these trends have been shown experimentally. For example, the electrochemistry of \([\left(\text{tBuCO}_2\right)_3\text{Mo}_2\text{(oxalate)}]\) shows less communication than \([\left(\text{tBuCO}_2\right)_3\text{W}_2\text{(oxalate)}]\) where \(K_c\) is \(5.4 \times 10^4\) and \(1.3 \times 10^{12}\), respectively. The electrochemistry of \([\left(\text{BuCO}_2\right)_3\text{Mo}_2\text{(oxalate)}]\) also shows more communication than \([\left(D\text{AniF}\right)_3\text{Mo}_2\text{(oxalate)}]\) where DAniF is \(N,N'\)-di-anisylformamidinate and the latter \(K_c\) is \(5.9 \times 10^3\). Unfortunately, no electrochemistry of any \([\left(formamidinate\right)_3\text{W}_2\text{(oxalate)}]\) was found for a final comparison.

Additional calculations were done for diformamidinate bridged dimers. Electronic structure calculations on the diformamidinate bridged models predicted a non-planar geometry across the bridge. This was due to a strong hydrogen-hydrogen interaction from opposing N-H groups. The ground state geometry is predicted to have a
90° twist angle about the C-C bond of the bridge. In this twisted D$_{2d}$ symmetry, the [M$_2$]$_2$ δ orbitals are degenerate and do not significantly mix through the diformamidinate π system. This twisting essentially causes the bridge to restrict the previously mentioned conduit analog for electron or hole transfer between M$_2$ units. Specifically, the C p-orbitals of the bridge π system are orthogonal and restrict the superexchange mechanism. Although, there may be some rotation to a more planar bridge geometry in solution, the utility of diformamidinate bridge appears limited unless the bridge can be restricted to a near planar geometry.

2.7 Summary and conclusion

Theoretical and computational studies can provide a great deal of insight, reliable explanations, and qualitative predictions. Unfortunately, there is no clear consensus of the appropriate DFT methodology to use in problems of transition metal chemistry for quantitative confidence. Through these DFT calculations, a great deal of valuable information and insight about metal-to-ligand interaction in both paddlewheel complexes and bridged dimers has been gained. Formate and formamidinate ligands are useful for the fundamental studies of the relationship between ligands and transition metals. In general more electron donating ligands raise the M$_2$ manifold to higher energy and mix better. The M$_2$ manifold and the ligand π orbitals interact to change the stability of the M$_2$ δ and δ* orbitals.

DFT calculations provide qualitative predictions for a range of experimentally observable properties. The investigations of heteroleptic model complexes have provided a great deal of insight into their more complex electronic nature. This series of
iso-electronic complexes revealed similar properties with uniquely different energetics. Their electronic properties were modified by changes to ligands and ligand substituents that most significantly impacted the ionization potential and the number of metal-to-ligand charge transfer bands. The fundamental expectation is that fine-tuning of intrinsic chemical characteristics of ligands can lead to improved electronic and excitonic performance as well as furthering our understanding of the mechanisms involved. Interestingly, different ligands with unique properties may also be combined in a heteroleptic complex to add favorable qualities and enhanced hybrid properties.

While the degree of electronic communication in bridged dimers cannot be quantified with experimental techniques, DFT calculations can make many valuable predictions including tungsten complexes exhibiting better delocalization than molybdenum complexes. The filled and empty bridge π orbitals interact with an in-phase and out-of-phase combination of the \([M_2]_2\) δ orbitals. The degree of splitting between the \([M_2]_2\) δ-orbital is an indicator for electronic communication. Without effective overlap between the bridge π-orbitals and the \([M_2]_2\) δ-orbitals, the electronic communication would be limited to electrostatic interactions.

In formate complexes, the mixing of the oxalate bridge and metal-based orbitals result in a splitting of the \([M_2]_2\) δ-based MOs by approximately 0.4 eV for Mo and 0.6 eV for W. In formamidinate complexes, the mixing of the oxalate bridge and metal-based orbitals result in a splitting of the \([M_2]_2\) δ-based MOs by approximately 0.3 eV for Mo and 0.45 eV for W. The greater splitting of the \([W_2]_2\) δ-based MOs reflects that the tungsten-based orbitals are closer in energy to the π\(_5\) oxalate orbital and better tungsten 5d-to-oxalate π* overlap. The lesser splitting of formamidinate complexes relative to
formate complexes is a ligand effect. The greater formamidinate ligand character in the $[\text{M}_2]_2 \delta$ orbital adversely affects the metal-to-bridge mixing and decreases the $[\text{M}_2]_2 \delta$ splitting. It follows from this study that the greatest electronic coupling between M₂ units will be when the metal-based $\delta$-orbitals are closest in energy and provide the best overlap with the appropriate bridge $\pi$ orbital.

This DFT study has shed significant light on qualitative understanding, designing and controlling the properties of both paddlewheel complexes and bridged dimers.
2.8 References


CHAPTER 3

DIMOLYBDENUM AND DITUNGSTEN PADDLEWHEEL COMPLEXES WITH MIXED AMIDINATE-CARBOXYLATE LIGANDS.

3.1 Introduction

$\text{M}_2(\text{O}_2\text{CR})_4$ complexes of molybdenum and tungsten are kinetically labile as evidenced by ligand scrambling.[1, 2] These complexes, however, are suitable starting materials since they are kinetically labile to ligand exchange which may be brought about by adventitious $\text{H}^+$ or $\mu$-bridging $\text{L}^-$. [3] These tetracarboxylate complexes were chosen as starting material since they could be readily made in substantial gram quantities and their properties have been extensively studied. It was reasoned that the use of a more basic ligand lacking the active lone pairs of carboxylates would be more kinetically persistent and thus enhance their possible application.

Formamidinate ligands have been extensively investigated in recent years.[4-10] The use of formamidinate ligands proved great insight but still showed susceptibility towards C-N scission degradation because of the relatively unprotected central carbon in the $\mu$-bridging ligand.[11] Amidinate ligands comprise a class of ligand currently finding many applications in mononuclear main group and transition metal chemistry. Their
isolobal relationship with carboxylates allows for ligand exchange or metathesis reactions. A new series of dimolybdenum and ditungsten paddlewheel complexes with mixed amidinate-carboxylate ligands of the form \( \text{M}_2(\text{O}_2\text{CCH}_3)_2(\text{iPrNC(R)N}^\prime\text{Pr})_2 \) where M = Mo, W and R = Me, C≡CtBu, C≡CPh, or C≡CFc have been synthesized and characterized with the exception of the tungsten complex where R = Me.

This chapter will be divided into five distinct parts. Section 3.2 will look at the fundamentals and approaches used to develop a series of amidinate ligands. Section 3.3 will report the findings of mixed amidinate-carboxylate complexes of molybdenum and tungsten. Section 3.4 will discuss efforts to expand the chemistry to other mixed amidinate-carboxylate complexes by changing the amidinate ligand and the tetracarboxylate starting material. Section 3.5 is an overall summary and conclusion while section 3.6 is the experimental section.

### 3.2 Amidinate ligands

Initial research was aimed at synthesizing lithium amidinate salts for ligand exchange reactions on molybdenum tetracarboxylate compounds.[12] The lithium amidinate salts were prepared from interaction of a carbodiimide (RN=C=NR) and an alkyllithium reagent. Nucleophilic addition of organolithium reagents to a carbodiimide to yield the corresponding amidinate salt is a well established process. In this fashion, carbodiimide can be extremely useful to prepare a wide variety of amidinate ligands.

This type of modular assembly of amidinate salts was thought to be ideal for tuning its electronic structure and controlling solubility. This same technique has been extensively used in both organic and inorganic chemistry.
(\textsuperscript{i}PrN=N\textsuperscript{i}Pr) and \textit{N,N'}-diphenylcarbodiimide (\textsuperscript{t}BuN=N\textsuperscript{t}Bu) were both commercially available. Diisopropylcarbodiimide was chosen due to its lower steric bulk at the nitrogen atoms.

Lithium amidinate salts were prepared \textit{in situ} from the corresponding carbodiimide and alkyl lithium reagents as shown in Scheme 3.1.[13] Several lithium amidinate salts including methyl and phenyl acetylide derivatives were prepared. In cases where the alkyl lithium was not directly available, \textit{n}-butyllithium was used as a deprotonating agent to obtain the desired alkyl lithium reagent.

\[
\begin{align*}
\text{iPrN=N\textsuperscript{i}Pr} & \quad + \quad \text{Li-R} & \quad \xrightarrow{0 \circ C} & \quad \text{Li-} \quad \text{THF} \\
\text{where R = Me, C≡C\textsuperscript{t}Bu, C≡CPh, C≡CFc, C\textsubscript{4}H\textsubscript{4}S}
\end{align*}
\]

\textbf{Scheme 3.1} Synthesis of lithium amidinate salts

The lithium amidinate salts readily formed large crystals suitable for single crystal x-ray diffraction. Figure 3.1 and 3.2 illustrate the common lithium amidinate salt features in Li\textsuperscript{+}[\textsuperscript{i}PrN\textsubscript{2}CC≡CPh\textsuperscript{−}] and Li\textsuperscript{+}[\textsuperscript{i}PrN\textsubscript{2}CC\textsubscript{4}H\textsubscript{4}S\textsuperscript{−}], respectively. Complete crystallographic details can be found in Appendix B.3. The structures are of a lithium dimer that sits on a crystallographic inversion center. The lithium atom is in a tetrahedral
coordination environment with a bidentate or chelating amidinate and one coordinating THF solvent molecule per asymmetric unit.

**Figure 3.1** ORTEP diagram of asymmetric unit (left) and centrosymmetric dimer (right) of Li$^+[(^{'}PrN)_2CC≡CPh]^-$ with coordinating THF drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

In both crystal structures, the aromatic rings do not lie in the N-C-N plane. Each aromatic ring has a significant dihedral angle relative to the amidinate backbone that would limit $\pi$ conjugated interaction. In the case of the phenyl acetylide amidinate salt, this dihedral angle is a function of crystal packing since no $\pi-\pi$ stacking is observed. In
the case of the thiophene amidinate salt, this 90° dihedral angle is necessary to reduce steric interactions with the isopropyl groups on each nitrogen atom.

![Figure 3.2 ORTEP diagram of centrosymmetric dimer of Li⁺[(iPrN)₂CC₄H₄S]⁻ with coordinating THF drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.]

Figure 3.2 ORTEP diagram of centrosymmetric dimer of Li⁺[(iPrN)₂CC₄H₄S]⁻ with coordinating THF drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.

The ability of amidinates to act as a bidentate ligand is well established.[14-16] Amidinate ligands have been used extensively in this fashion for main group, transition metal, and f-block coordination chemistry.[15] Steric factors influence the preference for
chelating versus bridging structures. Steric crowding between C-R and N-R’ groups tends to decrease the N-C-N angle and limit the ability of the ligand to bridge as shown in Figure 3.3.

Figure 3.3 a) bridging and b) chelating modes of amidinates. (Extract from reference [16])

The challenge was therefore to design a series of amidinate ligands that would bridge the dimetal units of molybdenum and tungsten.

3.3 Mixed amidinate-carboxylates: results and discussion.

The initial interest was in synthesizing a series of molybdenum and tungsten complexes of the general form $\text{M}_2(\text{O}_2\text{CCH}_3)_{4-x}(\text{iPrN})_2\text{CR}_x$ where $x = 1-4$ by a carboxylate exchange reaction employing the previously mentioned molybdenum tetraacetate and lithium amidinate salts.
3.3.1 General Methodology

A metathesis reaction with $\text{M}_2(\text{O}_2\text{CCH}_3)$ and an *in situ* lithium amidinate resulted in an initial color change and the formation of a visible salt by-product. The reactants were stirred in tetrahydrofuran (THF) for 2-20 hours. The solvent was then stripped off and the dried product was extracted with $\text{CH}_2\text{Cl}_2$ and filtered over Celite to remove salt by-product contamination. After reducing the volume of solvent to a minimum, product precipitated or ethanol was added to force the precipitation of a colored product that was collected on a frit. Prolonged exposure of tungsten complexes to ethanol was detrimental and avoided where possible. All reactions were carried out on a millimolar scale.

Initial characterization was done by $^1\text{H}$ NMR spectroscopy and matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry. NMR spectra showed a 1:1 ratio of amidinate to carboxylate ligands. The methyls of the isopropyl group were also found to be equivalent. Based on this spectroscopic handle, the geometry was believed to be a *trans* bis-amidinate bis-carboxylate complex. Molecular ions with the characteristic weight and isotopic pattern for a bis-amidinate bis-carboxylate complex were detected in the MALDI-TOF mass spectra.

Regardless of the concentration of the amidinate ligand, products always corresponded to a bis-amidinate bis-carboxylate complex. It was proposed that the steric bulk of the isopropyl groups around the metal core prevented the formation of tri- and tetra-amidinate compounds via this synthetic route. The poor solubility of the $\text{M}_2(\text{O}_2\text{CCH}_3)_4$ starting material also insured its concentration relative to the amidinate ligand concentration did not favor mono-amidinate formation. Controlled ligand
substitution via metathesis reactions was therefore primarily limited to the synthetic path illustrated in Scheme 3.2

\[ \text{Scheme 3.2 Synthesis of trans-} M_2(O_2CCH_3)_2(\text{PrN})_2CR_2 \]

To our advantage, all mixed amidinate-carboxylate complexes have significantly increased solubility in comparison to the \(M_2(O_2CR)_4\) starting material due in part to the isopropyl substituents. This characteristic was important and crucial to exploring possible applications and higher order assemblies.

A new series of mixed amidinate-carboxylate complexes of the form \(M_2(O_2CCH_3)_2(\text{PrNC}(R)N^{\prime}\text{Pr})_2\) where \(M = \text{Mo, W}\) and \(R = \text{Me, C≡C}^{\prime}\text{Bu, C≡C}^{\prime}\text{Ph or C≡C}^{\prime}\text{F}^{\prime}\) have been synthesized and characterized with one exception noted earlier. For simplicity, these complexes will be identified as complexes \(3X, 4X, 5X\) and \(6X\) respectively where \(X = A\) for molybdenum or \(B\) for tungsten. The physicochemical properties of the series of complexes \(3X-5X\) were compared using electronic absorption
spectroscopy and electrochemistry. DFT calculations on model complexes are also discussed and used to help assign observable UV-vis absorptions and electrochemical redox behavior. Complexes 6X are used to probe electronic communication or coupling associated with the dimetal unit.

3.3.2 UV-vis Spectroscopy

All compounds have significant absorptions in the visible region of the spectrum as a result of the fully allowed metal-to-ligand charge-transfer (MLCT) transition. Their color arises from this electronic absorption. Unlike homoleptic complexes, it was anticipated that the mixed ligand complexes would have more than one MLCT based on ligand energetics and symmetry. Specifically, two electronic transitions corresponding to an M_2 δ to O_2C π* absorption as well as a new M_2 δ to N_2C π* absorption were expected.

Comparison of the spectra for the molybdenum complexes 3A, 4A, and 5A are shown in Figure 3.4. Inspection of the spectra revealed several absorption features. The higher energy (shorter wavelength) transitions (< 300 nm) are attributed to ligand π→π* transition of both carboxylate and amidinate ligands. The lower energy (longer wavelength) transitions correspond to M_2 δ to ligand π* MLCT transitions.
Figure 3.4 UV-vis spectra of Mo$_2$(O$_2$CCH$_3$)$_2$($^{i}$PrN)$_2$CMe)$_2$ (3A-majenta), Mo$_2$(O$_2$CCH$_3$)$_2$($^{i}$PrN)$_2$CC≡C$^t$Bu)$_2$ (4A-red), and Mo$_2$(O$_2$CCH$_3$)$_2$($^{i}$PrN)$_2$CC≡CPh)$_2$ (5A-blue) complexes in THF at room temperature.

The spectrum of complex 3A shows a small plateau corresponding to MLCT band from approximately 300 to 350 nm. The spectrum of complex 4A shows two MLCT peaks at approximately 400 and 425 nm. Lastly, the spectrum of complex 5A shows a broad non-gaussian MLCT with a maximum absorption at approximately 490 nm. The width of the 5A transition probably reflects a varying dihedral angle between the N$_2$C plane and the plane of the phenyl ring.

Based on this series, it can be recognized that the lowest energy absorption corresponds to the metal to amidinate ligand charge-transfer transition in at least complexes 4A and 5A. Comparison of these spectra also reveals that the electronic
absorption occurs at lower energy and with greater intensity as ligand conjugation increases. This is consistent with conjugation lowering the ligand $\pi^*$ orbital energy and better M$_2$ $\delta$ to amidinate $\pi^*$ orbital mixing.

In the case of complex 4A, low temperature UV-vis spectroscopy was utilized to rule out vibronic coupling. Upon lowering the temperature, vibronic features are expected to shift to lower energy and sharpen to show greater resolution. The Boltzmann distribution of rotamers present in solution or glass will also more closely resemble the minimum energy structure that maximizes $\pi$ conjugation. We observed no red shift or increase in resolution of absorption features upon cooling the sample in 2-MeTHF. Consequently, we concluded that the appearance of the two absorption bands is not a result of vibrational features.

The spectral features of the analogous tungsten complexes are complementary. The MLCT transitions are red shifted and higher in intensity than the corresponding molybdenum complexes. This is consistent with the fact that the W$_2$ $\delta$ orbitals are higher in energy and therefore closer in energy to the ligand $\pi^*$. This is illustrated in a comparison of complex 5A and 5B shown in Figure 3.5.
Figure 3.5 UV-vis spectra of $\text{M}_2(\text{O}_2\text{CCH}_3)_2((\text{i-PrN})_2\text{CC}≡\text{CPh})_2$ where $\text{M} = \text{Mo (red-5A)}$ and $\text{M} = \text{W (blue-5B)}$ in THF at room temperature.

UV-vis spectra are included in Appendix B.1.

3.3.3 Electrochemistry

The metal-metal bond is a quadruple bond of configuration $\sigma^2\pi^4\delta^2$ and readily undergoes a one-electron oxidation. The complexes in THF showed one reversible oxidation wave associated with the removal of a $\delta$-electron in the $\text{M}_2^{4+/5+}$ cycle. The dinuclear centers exhibit a range of oxidation potentials which are dependent on both the metal and the ancillary ligand as shown in Figure 3.6.
Figure 3.6 Normalized differential pulse voltammograms of synthesized complexes and estimated voltammogram for complex 3B in THF/0.1 M [tBu₄N][PF₆] and referenced to the FeCp₂⁰⁺⁺ couple.

The oxidation potentials of these complexes have been tuned through raising or lowering of the metal orbital manifold. As ligand conjugation decreases, the electron donating ability of the amidinate ligand increases. This results in more electron donation to the dimetal center and translates into lower oxidation potentials. Within a Mo series of complexes, the oxidation potential was shifted by about 0.3 eV.

The available W analogs show the same trends but are approximately 0.5 eV more easily oxidized. This is consistent and almost quantitative with the W δ orbitals being 0.5 eV higher in energy as shown in Table 3.1. The oxidation potential of complex 3B was therefore estimated as being 0.5 eV easier to oxidize than complex 3A.
Table 3.1 Summary of electrochemical data for $M_2$ oxidation potentials in mV. Potentials were recorded in THF/0.1 M $[t\text{Bu}_4\text{N}][\text{PF}_6]$ and referenced to the FeCp$_2$ 0/+ couple.

Unfortunately, complex 3B has not been isolated. There are two possible explanations for this. The first is based on the relative ease of oxidation that may result in the complex being simply oxidized in solution. The second possibility is related to steric factors. Of all the ligands in this series, the methyl amidinate has the greatest steric interaction with the isopropyl groups and the W$_2$ unit has the greatest bridging distance. Therefore, the methyl amidinate may have exceeded its ability to bridge the W$_2$ unit. One or both of these explanations are believed to have prevented the isolation of complex 3B.

The electrochemistry of complexes 6A and 6B will be discussed in further details in Section 3.3.8 on electronic communication. Electrochemistry data are included in Appendix B.2.
3.3.4 Electronic Structure Calculations

DFT calculations complement frontier molecular orbital theory and assist in the interpretation of physicochemical properties of these complexes. Calculations were performed using simplified models of complexes 3A, 4A, and 5A. In each model, the isopropyl groups were substituted with hydrogen atoms to increase symmetry and achieve a set of self-consistent results that were verified to be a minimum on the potential energy surface. Molecular orbital analysis was used to verify the character of individual orbitals. It should be recognized that these gas-phase calculations are qualitative, but not quantitative, guides in interpreting the spectral properties of the complexes. Observed UV-vis and oxidation potential properties were shifted to slightly lower energy due to charge-transfer stabilization in coordinating solvents and probably the greater stabilizing influence of the isopropyl groups on the amidinates.

Findings are summarized in Figure 3.7. In all three models, the HOMO was identified as the Mo$_2$ δ orbital as expected. DFT calculations correctly predict the nearly 0.3 eV increase in Mo$_2$ δ orbital energy as amidinate ligand conjugation decreases and electron donation increases.
Time-dependent DFT calculations on the geometry optimized models were performed to ascertain the nature of expected electronic transitions. Unlike homoleptic complexes, the calculations predict three different MLCT transitions. One transition is to an amidinate-based ligand $\pi^*$ set; one transition is to a carboxylate-based ligand $\pi^*$ set; and one transition is to a mixed amidinate-carboxylate ligand $\pi^*$ set.

These DFT calculations were fundamental in explaining the observed UV-vis absorption features. In the case of model complex 3A, calculations predicts three relatively high energy absorptions between 310 and 340 nm that coincide well with the
small plateau actually observed. In the case of complex 4A, calculations predict two moderately separate transition bands that agree nicely with the experimental and absorption data. In the case of complex 5A, calculations predict the lowest energy highest intensity absorption in the series as a metal to amidinate-based ligand \( \pi^* \) transition. The calculated transition energy at 509 nm agrees reasonably well with the observed excitation at 490 nm. It appear that this electronic absorption trails to higher energy due to the contribution of the carboxylate-based ligand set and mixed amidinate-carboxylate ligand set absorptions. The broad nature of this spectral feature is still attributed to the varying dihedral angles between the \( \text{N}_2\text{C} \) plane and the plane of the phenyl ring.

It is also interesting to note that the expected excitation energy to the acetate ligand \( \pi^* \) orbital across the model series is nearly constant. This implies that the tunable amidinate ligands have little effect on the acetate ligands. DFT calculations show that the electronic absorptions are polarized in the plane of the ligand sets. Therefore, the metal-to-amidinate MLCT absorbs at one wavelength, while the metal-to-acetate MLCT absorbs at another wavelength that is 90° off of the original axis. If the orientation of the complex is preserved in crystal packing, the crystal should show polarization or birefractents effects. Intermolecular \( \pi-\pi \) stacking should aid in this preferred orientation in crystal growth.

3.3.5 Crystal Structures

Crystal growth suitable for single crystal X-ray diffraction analysis of all complexes was readily available. This is due to the nitrogen substituents on the
amidinate ligand preventing metal-oxygen intermolecular interactions that normally plague homoleptic carboxylate complexes. The molecular structures of several complexes were further characterized by X-ray diffraction analysis. In general, crystal structures showed that each M$_2$ unit retains a paddlewheel conformation consisting of two trans-amidinate groups and two trans-carboxylate groups.

The crystal structure of complex 3A is shown in Figure 3.8. It is proposed that the steric bulk of the isopropyl groups around the metal core prevents the formation of a tetraamidinate compound via this synthetic route. This is also consistent with the unique formation of a trans species versus a cis species.

**Figure 3.8** ORTEP diagram of the centrosymmetric Mo$_2$(O$_2$CCH$_3$)$_2$((tPrN)$_2$CMe)$_2$ molecule (3A) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.
Structurally, molybdenum and tungsten analogs are very similar. The crystal structure of complex 5B is shown in Figure 3.9. Only small changes in bond length and bond angles are seen. The trends are also consistent with previously reported comparisons of homoleptic molybdenum and tungsten complexes. The metal-metal bond length is approximately 0.1 Å longer in tungsten complexes as compared to molybdenum analogs. This is due in part to the greater core-core repulsion for the 3rd row elements. The metal-ligand bond lengths are also slightly shorter in tungsten complexes when compared to molybdenum analogs. This is indicative of the greater degree of metal-ligand orbital mixing and increased bond strength due to the greater radial extension of the metal 5d orbitals.

Figure 3.9 ORTEP diagram of the centrosymmetric W₂(O₂CCH₃)₂((^iPrN)₂CC≡CPh)₂ molecule (5B) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarrred atom by the crystallographic inversion center.
Another fundamental trend is seen in comparing the metal to amidinate bond length of complex 5A with complex 3A. The less electronegative amidinate ligands of complex 3A have shorter bond length than the more electronegative amidinate ligands of complex 5A. This is indicative of a stronger more covalent bond between the M$_2$ unit and methyl amidinate ligand.

The last detail can be illustrated by the structure of complex 6A in Figure 3.10. In the case of both molybdenum and tungsten, the redox active ferrocene iron centers are pendent at opposite sides of the M$_2$ unit. The iron-iron distance in both complexes is approximately 16.5 Å.

![Figure 3.10 ORTEP diagram of the centrosymmetric Mo$_2$(O$_2$CCH$_3$)$_2$([PrN]$_2$CC≡CFc)$_2$ molecule (6A) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.](image)
Complete crystallographic details for complexes 1, 2, 3A, 5A, 5B, 6A, and 6B can be found in Appendix B.3.

3.3.6 Ligand Scrambling

The solution behavior of carboxylate complexes is well known and problematic.[17] $^1$H NMR spectroscopy has been used to study the kinetics and equilibrium properties of carboxylate ligand scrambling.[1, 2] In our case, the ability to form specific mixed ligand complexes could be thwarted by deleterious side reactions caused by carboxylate or general ligand scrambling. For this reason, it was important to probe ligand scrambling in these mixed ligand complexes.

The reaction between Mo$_2$(O$_2$CCH$_3$)$_2$((^3PrN)$_2$CC≡C^tBu)$_2$ (4A) and Mo$_2$(O$_2$CCF$_3$)$_4$ has been studied by $^1$H NMR spectroscopy and MALDI-TOF mass spectrometry. These two complexes were chosen since they have similar solubility. The two principal goals of this study were a) to determine if ligand scrambling occurred in mixed amidinate-carboxylate complexes and if so b) to determine if there was temperature dependence.

In the reaction, relatively equimolar quantities of complex 4A and Mo$_2$(O$_2$CCF$_3$)$_4$ were weighed using an analytical balance accurate to 0.1 mg in a drybox. A 1:1 solution of complexes was then prepared by adding approximately 0.7 ml of deuteriated benzene. Based on previous scrambling studies, the rate of scrambling was expected to be of higher order in a non-coordinating solvent such as benzene. The sample was then maintained in an inert environment by using a J. Young® NMR tube.

The initial methodology was to monitor the acetate and butyl peaks of 4A by $^1$H NMR. It was anticipated that the signals for acetate would move downfield (i.e., towards
less shielding) as the number of CF$_3$CO$_2$ ligands increased. Unlike previous work where equilibriums were reached within hours, exchange was much slower and initially limited to carboxylate exchange only based on $^1$H NMR data. Refer to Figure 3.11.

![Figure 3.11](image)

**Figure 3.11** Stacked $^1$H NMR plot of acetate scrambling reaction involving 4A and Mo$_2$(O$_2$CCF$_3$)$_4$ showing the slow disappearance of 4A (main peak) over time and after heating.

During the first few hours at room temperature, only small changes of the NMR spectra in the acetate region could be observed. By day three, the majority of 4A was still present and only three other minor peaks were present in the acetate region. Based on sequential carboxylate only exchange as shown in Scheme 3.3, five peaks would be anticipated. Complexes Mo$_2$(O$_2$CCF$_3$)$_3$(O$_2$CCH$_3$) and
Mo₂(O₂CCH₃)(O₂CCF₃)((RPrN)₂CC≡CtBu)₂ are formed concurrently with the first acetate/trifluoroacetate exchange. Complexes Mo₂(O₂CCF₃)₂(O₂CCH₃)₂ and Mo₂(O₂CCF₃)₂((RPrN)₂CC≡CtBu)₂ are then formed on subsequent acetate scrambling. The formation of Mo₂(O₂CCF₃)₂(O₂CCH₃)₂ was expected in a 2:1 cis:trans preference on a purely statistical basis. From this, it was apparent that the spectra were complicated by the presence of one or more overlapping resonances but limited to carboxylate exchange only.

\[
\text{Mo}_2(O_2CCF_3)_4 + \text{Mo}_2(O_2CCH_3)_2((RPrN)_2CC≡CtBu)_2 \rightarrow \text{Mo}_2(O_2CCF_3)_3(O_2CCH_3) + \text{Mo}_2(O_2CCH_3)(O_2CCF_3)((RPrN)_2CC≡CtBu)_2
\]

\[
\text{Mo}_2(O_2CCF_3)_2(O_2CCH_3)_2 + \text{Mo}_2(O_2CCF_3)_2((RPrN)_2CC≡CtBu)_2
\]

1 acetate peak

\[
\text{cis or trans}
\]

2 acetate peaks

**Scheme 3.3** Sequential carboxylate only scrambling of products of **4A** and Mo₂(O₂CCF₃)₄. Number of unique acetate peaks are identified in red below the complex.

After three days at room temperature, the mixture was heated to 70 °C for several hours. The subsequent NMR spectra identified at least eleven acetate peaks and a significant reduction in complex **4A**. This number of peaks could only be explained if
amidinate scrambling had now occurred but further interpretation by NMR was not possible. The sample was again heated overnight at 70 °C and further NMR spectra showed no shift in equilibrium concentrations. MALDI-TOF mass spectrometry was now employed to verify amidinate ligand scrambling. The qualitative results are shown in Figure 3.12. Although only six species were identified, molecular weights correspond to both mono-amidinate and bis-amidinate complexes.
Figure 3.12 MALDI-TOF mass spectra of scrambling reaction involving 4A and Mo$_2$(O$_2$CCF$_3$)$_4$ at heating at approximately 70 °C for 3 hours. The chemical formula and molecular weights of identified species are labeled.
From this, we concluded that mixed amidinate-carboxylate complexes are generally more kinetically persistent than homoleptic carboxylate complexes at room temperature. Unfortunately, even amidinate ligands are subject to scrambling in mixed amidinate-carboxylate complexes at moderately elevated temperature.

3.3.7 Electronic Communication

Charge transfer (CT) processes have been extensively researched over the last half century.[18] The experimental and theoretical study of intramolecular electron transfer is paramount in chemistry, biology, and the emerging field of molecular electronics. Probing the efficiency of charge transfer through a dimetal unit is of fundamental importance. One of the commonly used techniques is to attach a pair of identical electroactive groups at opposite sides of the dimetal unit and use electrochemistry to gauge electron mobility.

A straightforward probe is to covalently attach two ferrocenyl (Fc) units at opposite ends of the molecular fragment (X) and use the free energy of comproportionation ($\Delta G_c$) of the mixed-valence ion to gauge the electron delocalization across X.[19, 20] This interaction is defined by equations 1 and 2.

\[
\text{Fc}^{II} - X - \text{Fc}^{II} \quad \overset{-e^-}{\underset{E_{1/2}(I)}{\longrightarrow}} \quad [\text{Fc}^{II} - X - \text{Fc}^{III}]^+ \quad \overset{-e^-}{\underset{E_{1/2}(II)}{\longrightarrow}} \quad [\text{Fc}^{III} - X - \text{Fc}^{III}]^{2+} \quad (1)
\]

\[
\Delta G_c = F[E_{1/2}(II) - E_{1/2}(I)] \quad (2)
\]
The electrochemistry of complexes 6A and 6B are shown in Figures 3.13 and 3.14, respectively. Both complexes show essentially two reversible oxidation waves. The first wave (right) is the oxidation of the \( M_2 \) unit. The second wave (left) is the ferrocene centers in each complex undergoing oxidation at a similar potential. The two one-electron oxidations overlap to give a single CV or DPV wave that corresponds to two simultaneous one-electron oxidations. A small side feature at lower potential on the ferrocene center DPV wave of the tungsten complex may represent a small degree or onset of electronic communication at a distance of nearly 16.5 Å.

It is interesting to note that the ferrocene centers oxidize at a higher potential (+192 mV) than free ferrocene. This represents that the oxidation of the \( M_2 \) units probably influences the ferrocene centers as a function of metal-to-ligand orbital mixing. This is further supported by comparing the tungsten complex to its molybdenum analog. The ferrocene center oxidation potential is approximately 0.4 eV higher for the tungsten complex than its molybdenum analog. The shift to higher oxidation potential of the ferrocene centers is consistent with better mixing with the higher energy W 5d orbitals and better W5d-to-ligand \( \pi^* \) overlap.

Based on electrochemistry, one would conclude that the ferrocene centers are in electronic communication with the \( M_2 \) unit but not in significant communication with each other through the \( M_2 \) unit. Since previous studies using this methodology have shown ferrocene communication across other materials at this distance, we conclude that the charge delocalization is impeded by an energy barrier across the \( M_2 \) unit. This barrier is further complicated by preferential oxidation of the \( M_2 \) unit.
Figure 3.13 a) Differential pulse voltammogram and b) cyclic voltammogram of Mo$_2$(O$_2$CCH$_3$)$_2$((^PrN)$_2$CC≡CFc)$_2$ (6A) in THF/0.1 M [^Bu$_4$N][PF$_6$].
Figure 3.14 a) Differential pulse voltammogram and b) cyclic voltammogram of $W_2(O_2CCH_3)_2((^{i}PrN)C≡CFc)_2$ (6B) in THF/0.1 M $[^{4}Bu_4N][PF_6]$. 
3.4 Expanding mixed amidinate-carboxylate chemistry

Efforts in synthesizing mixed amidinate-carboxylate complexes led to several early limitations. As previously mentioned, the substitution chemistry, when successful, is limited to bis-amidinate bis-carboxylate complexes. Since the sterically demanding isopropyl amidinate appeared to limit substitution to the \textit{trans}-geometry, it was reasoned that less sterically demanding nitrogen substituents could favor controlled ligand substitution. The direct synthesis of other amidinate ligands with less bulky nitrogen substituents such as dimethylbenzylamidinate (DMBA) was explored. Solubility differences between molybdenum tetraacetate and the lithium DMBA salt resulted in tetra-substitution of the acetate ligands and an alternative synthetic path to Mo$_2$(DMBA)$_4$. This supported the idea of greater substitution by less demanding amidinate ligands but showed no substitutional control.

Several attempts to prepare the molybdenum bis-thiophene-amidinate bis-carboxylate complex were unsuccessful. It appears that the steric size of the thiophene functional group would not allow the ligand to bridge the dimetal core as previously discussed. For this reason, an acetylene spacer group was invaluable in reducing steric interactions with the isopropyl group on the amidinates. The acetylene group acts as a linear spacer to move bulky functional groups away from the central carbon backbone of the amidinate while maintaining an extended $\pi$ conjugation. The idea of steric crowding was further supported by the inability to apply this chemistry to the bulkier $N,N'$-diterbutylcarbodiimide even with the use of an acetylene spacer.

Using more soluble M$_2$(O$_2$CR)$_4$ such as molybdenum tetrapivalate ($R = 'Bu$) was also explored. The larger alkyl chains greatly increased the solubility of the starting
material. Unfortunately, the lithium salt by-product of the reaction (i.e., lithium pivalate) was more soluble and thus complicated product purification. The separation of unreacted starting material from soluble products was also difficult. This made tetraacetate complexes much better starting material than tetravalerate complexes. The tetraacetate complexes and the by-product lithium acetate could be easily separated from products in polar solvents such as dichloromethane.

This lead us to believe that turning less soluble starting materials into more soluble products was fundamentally achievable and valuable to applications. Since aromatic carboxylate complexes are generally less soluble than alkyl carboxylate complexes, the substitutional chemistry of Mo$_2$(O$_2$C-2-thiophene)$_4$ and Mo$_2$(O$_2$C-9-anthracene)$_4$ were explored. Substitutional chemistry on Mo$_2$(O$_2$C-2-thiophene)$_4$ yielded a $\text{trans}$-Mo$_2$(O$_2$C-2-thiophene)$_2$($('\text{PrN})_2\text{CMe}$)$_2$ (7) as expected. Substitutional chemistry on Mo$_2$(O$_2$C-9-anthracene)$_4$ was unique and did not yield a $\text{trans}$-complex. $^1$H NMR showed a 1:1 ratio of amidinate to carboxylate ligands but the methyl groups on the nitrogen atoms were now diastereotopic. This suggested the amidinate ligands were $\text{cis}$. The complex was later identified as Mo$_2$(cis-$\mu$-O$_2$C-9-anthracene)$_2$($\eta^2$-($'\text{PrN})_2\text{CMe}$)$_2$ (8) by single crystal x-ray diffraction. The crystal structure is shown Figure 3.15. Complex 8 has two $\mu$-bridging 9-anthracene carboxylate ligands that are in a $\text{cis}$-geometry and two chelating amidinate ligands (one on each molybdenum). The formation of a $\text{cis}$-species versus a $\text{trans}$-species was quite unique and now offers cis-templating possibilities. Both complexes showed increased solubility when compared to the homoleptic starting material.
Figure 3.15 ORTEP diagram of Mo$_2$(cis-µ$_3$-O$_2$C-9-anthracene)$_2$(η$_2$-(iPrN)$_2$CMe)$_2$ (8) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Complete crystallographic details for complex 8 can be found in Appendix B.3.

Molybdenum carboxylates were initially explored since their synthetic routes are normally easier than tungsten carboxylates. In most cases, the tungsten analogs are
expected to mirror the molybdenum carboxylate chemistry. Continued work in this area with tungsten analogs would provide valuable comparisons and is on-going.

3.5 Summary and conclusion

Amidinate ligands for molybdenum and tungsten paddlewheel complexes are relatively unexplored but useful for fundamental studies of the relationship between ligands and transition metals. Lithium amidinates are readily prepared by the reaction of an alkylthium reagent with the appropriate carbodiimide. Since a variety of symmetric and asymmetric carbodiimides are synthetically available, the modular assembly of a wide assortment of amidinate ligands is possible. Their steric and electronic properties can be modified by means of the C- and N-substituents. Their isolobal relationship with the well established carboxylate chemistry has facilitated their rapid development.

A new series of paddlewheel complexes with mixed amidinate-carboxylate ligands of the form $M_2(O_2CH_3)_2(PrNC(R)N'Pr)_2$ and other mixed amidinate-carboxylate were synthesized and characterized. Although substitutional control was not seen, a wealth of fundamental information and new possibilities are recognized. Mixed amidinate-carboxylate complexes exhibit rich physicochemical properties. The synthesis of a series of complexes with each metal allowed for the analysis and comparison of molecular structural features, spectroscopic properties and electrochemical behavior. Density functional theory (DFT) calculations provide further insight into their electronic and physical properties.

All complexes have significant absorption in the visible region of the spectrum due to a fully allowed MLCT transition. The dinuclear centers exhibit redox chemistry
which is dependent upon the nature of the ancillary ligand. The electrochemical
properties can be tuned through ligand modifications. The use of both molybdenum and
tungsten complement each other and allows for fundamental comparisons.

Mixed amidinate-carboxylate complexes are more kinetically persistent at room
temperature than homoleptic carboxylate complexes. The greater basicity and hence
stronger covalent binding of amidinate ligands permit stronger metal-ligand interactions.
The substituents on the nitrogen atoms tend to block the axial positions of the
paddlewheel complex to reduce both intermolecular association and coordination of
additional ligands. Reductions in intermolecular association are advantageous to
increasing solubility and good single crystal growth. Reduction in additional ligand
coordination may be, however, detrimental to further ligand substitution since axial
coordination is believed to be involved in the exchange mechanism.

Mixed amidinate-carboxylate complexes are a new hybrid class of paddlewheels
that offer the best properties of both ligands. *Trans-* and *cis*-geometry templating has
been observed based on the $M_2(O_2CR)_4$ starting materials. Their unique geometries may
be useful building blocks for molecular assemblies such as “molecular wires” or
“molecular squares”, respectively. The ability to increase solubility alone, opens new
possibilities for previously insoluble homoleptic complexes.

### 3.6 Experimental details

All reactions were carried out under an inert atmosphere of UHP-grade argon or
nitrogen using standard Schlenk techniques and under a dry oxygen-free nitrogen
atmosphere using standard glovebox techniques. All solvents were dried and degassed
by standard methods prior to use. THF was dried by refluxing over sodium/benzophenone while toluene and hexanes were dried by refluxing over sodium metal. Dichloromethane (DCM) was dried by refluxing over calcium hydride. Ethanol was dried by refluxing over magnesium ethoxide.

Starting materials \(\text{Mo}_2\left(\text{O}_2\text{CCH}_3\right)_4\)[21], \(\text{Mo}_2\left(\text{O}_2\text{CCF}_3\right)_4\)[22], \(\text{W}_2\left(\text{O}_2\text{CCH}_3\right)_4\)[23], \(\text{W}_2\left(\text{O}_2\text{CCF}_3\right)_4\)[24], \(\text{Mo}_2\left(\text{O}_2\text{C-2-Th}\right)_4\)[25], and \(\text{Mo}_2\left(\text{O}_2\text{C-9-anthracene}\right)_4\)[26] were prepared according to the literature procedures. \(\text{Mo(CO)}_6\), \(\text{W(CO)}_6\), \(\text{WCl}_6\), glacial acetic acid, acetic anhydride, trifluoroacetic acid, \(\text{NaO}_2\text{CCF}_3\), \([\text{nBu}_4\text{N}]\left(\text{O}_2\text{CCH}_3\right)\), \(\text{N,N'}\)-diisopropylcarbodiimide, \(\text{N,N'-diterbutylcarbodiimide}\), methyllithium (1.6 M in diethyl ether), thiophene, \(\text{t}^\text{rer}-\text{butylacetylene}\), lithium phenylacetylide (1.0 M in THF), ethynylferrocene, \(\text{HO}_2\text{C-2-Thiophene}\), \(\text{HO}_2\text{C-9-anthracene}\), and \(\text{n-butyllithium}\) (2.5 M in hexanes) were purchased from commercial sources and used as received.

**Physical Measurements.** NMR spectra were recorded on a 400 MHz Bruker DPX spectrometer. All \(^1\text{H}\) NMR chemical shifts are reported in ppm relative to the protio impurity in THF-\(d_8\) at 3.58 ppm or benzene-\(d_6\) at 7.15 ppm from a 90% benzene /10% THF mixture by weight. UV-visible spectra were recorded at room temperature using a Perkin-Elmer Lambda 900 spectrometer. Spectra in THF solution were obtained using an air-tight 1 mm quartz cell. Microanalyses were carried out by Atlantic Microlab, Inc.

Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded at OSU’s Campus Chemical Instrument Center (CCIC) using a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were run pure or mixed with dithrinol matrix to aid in the flight of the molecule. All complexes were kept in an inert atmosphere.
Electrospray ionization (ESI) was also recorded at CCIC using a Micromass Q-TOF II mass spectrometer with auto-injector.

Cyclic voltammetric and differential pulse voltammetric data were collected with the aid of a Princeton Applied Research (PAR) 173A potentiostat-galvanostat equipped with a PAR 176 current-to-voltage converter with \(iR\) compensation capability. A single compartment voltammetric cell was equipped with a platinum working electrode, a platinum wire auxiliary electrode, and a pseudo reference electrode consisting of a silver wire in 0.5 M \(\text{Bu}_4\text{NPF}_6/\text{THF}\) separated from the bulk solution by a Vycor tip. The standard three electrode cell was utilized in a drybox with an inert atmosphere. Ferrocene was added as an internal reference and typically was found at +0.75 V under these conditions.

**Computational Details.** Density functional theory (DFT) calculations were performed with the hybrid Becke-3 parameter exchange functional and the Lee-Yang-Parr nonlocal correlation functional (B3LYP)[27] implemented in the Gaussian03 (Revision B.04) program suite[28] in conjunction with the 6-31G* basis set for all non-metal atoms and the SDD basis set with effective core pseudo-potential (ECP) for all metal atoms.[29] The calculations were carried out on simplified models in which each isopropyl substituent was replaced with a hydrogen atom. All geometries were fully optimized at the above levels using the default optimization criteria of the program. Each stationary point was confirmed to be a minimum on the potential energy surface (PES) by a vibrational frequency analysis. Orbital analyses were completed with GaussView.[30] To gain insight into the electronic transitions responsible for the observed UV-vis spectrum of all compounds, time-dependent density functional theory (TD-DFT)
calculations were performed using the Gaussian program suite. All calculations were run on an Itanium 2 Cluster running Linux version 2.4.18 located at the Ohio Supercomputer Center.

**X-ray Structure Determination.** All single crystals were coated with Paratone oil and mounted on a quartz fiber or a nylon cryoloop affixed to a goniometer head. All diffraction data was collected using a Nonius Kappa CCD diffractometer. All work was done at between 150 to 200 °K using an Oxford Cryosystem Cryostream Cooler. Data integration was done with Denzo. Scaling and merging of data was done with Scalepack. The structures were solved by the Direct or Patterson method in SHELXS-86 or SHELXS-97.

**Preparation of Li⁺[\(\text{PrN})_2\text{CC≡CPh}\]^− (1)** 1.25 ml of \(N,N\)-diisopropylcarbodiimide (8.0 mmol) was dissolved in approximately 25 ml of THF and cooled to 0 °C. 5 ml of 1.6 M methyllithium (8.0 mmol) in THF was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, the solvent was stripped to dryness to give a tan solid in quantitative yield.

**Preparation of Li⁺[\(\text{PrN})_2\text{CC}_4\text{H}_4\text{S}\]^− (2)** 2.0 ml of thiophene (10.0 mmol) was dissolved in approximately 25 ml of THF and cooled to 0 °C. 10 ml of 1.0 M n-butyllithium (10.0 mmol) in THF was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, the solution was again cooled to 0 °C and 3.9 ml of \(N,N\)-diisopropylcarbodiimide was slowly added to the mixture and allowed to warm to room temperature.
Preparation of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2((\text{iPrN})_2\text{CMe})_2$ (3A). 1.25 ml of $N,N'$-diisopropylcarbodiimide (8.0 mmol) was dissolved in approximately 25 ml of THF and cooled to 0 °C. 5 ml of 1.6 M methyllithium (8.0 mmol) in THF was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, it was used in situ for the next reaction. A slurry of 1.72 g of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (4.0 mmol) in approximately 25 ml of THF was cooled to 0 °C. The in situ solution was cooled again to 0 °C and slowly added to the slurry. The initial color change was red but darkened. After stirring at room temperature overnight, the mixture was stripped to dryness and redissolved in approximately 50 ml of DCM. The solution was filtered over Celite. The volume of the red solution was reduced to a minimum (~ 3 ml) and ethanol (~ 5 ml) was added to crash out product. The yellow product was collected on a glass frit, washed with 10 ml of ethanol, and yielded 825 mg. The filtrate was stripped to dryness and 10 ml of ethanol was added. This resulted in a yellow suspension. The solid was washed three times with approximately 10 ml of ethanol and allowed to settle (each time the wash was canulared off). The remaining solid was dried and yielded a second crop of 500 mg. Overall yield: 1.325 g (55.9%)

Microanalysis found: C 40.22; H 6.67; N 9.18%. $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_4\text{Mo}_2$ requires: C 40.55; H 6.81; N 9.46%. NMR (Benzene-$d_6$): $^1\text{H}$ (400 MHz) 4.19 (septet, $J_{HH} = 6.4$ Hz, 4H, CHMe$_2$), 2.32 (s, 6H, CMe), 2.21 (s, 6H, CMe), 0.92 (d, $J_{HH} = 6.4$ Hz, 24H, CHMe$_2$). The methyl groups of the acetate and amidinate have not been assigned. MALDI-MS: 593.1 (100%, M$^+$).
**Attempted preparation of W₂(O₂CCH₃)₂(PrN)₂CMe₂ (3B).** The reaction was carried out under similar conditions outlined for the molybdenum analogue using 600 mg of W₂(O₂CCH₃)₄ (1.0 mmol), 0.31 ml of N,N'-diisopropylcarbodiimide (2.0 mmol) and 1.25 ml of 1.6 M methyllithium (2.0 mmol). Within minutes, the solution turned gray. After 2 h, the solvent was stripped to dryness but the mixture yielded no tractable product.

**Preparation of Mo₂(O₂CCH₃)₂(PrN)₂CC≡CtBu₂ (4A).** 3.2 ml of 2.5 M n-butyllithium (8.0 mmol) was slowly added to a mixture of 1 ml of tert-butylacetylene (8.0 mmol) in 25 ml of THF at -78 °C. The solution was allowed to stir at room temperature for 2 h. The solution appeared almost colorless. It was used *in situ* for the next reaction. 1.25 ml of N,N'-diisopropylcarbodiimide (8.0 mmol) was slowly added to the *in situ* mixture at 0 °C. The solution was allowed to stir at room temperature for 2 h. The solution appeared colorless. It was used *in situ* for the next reaction. A slurry containing 1.72 grams of Mo₂(O₂CCH₃)₄ in 25 ml of THF was cooled to 0 °C. The *in situ* amidinate salt was cooled again to 0 °C and slowly added to the slurry. The solution rapidly turned red. Within the first hour the solution was dark. After stirring overnight, the solvent was stripped to dryness and redissolved in approximately 50 ml of DCM. The solution was filtered over Celite. The volume of the solution was reduced to a minimum and ethanol was added to crash out product. The solid was collected using a glass frit and washed with 2 x10 ml of hexane. The yield was 810 mg. The filtrate was stripped to dryness and redissolved in pure ethanol. The second crop of product was collected using a glass frit and yielded 220 mg. Overall yield: 1.030 g (35.5%)
Microanalysis found: C 49.12; H 7.26; N 7.65%. C_{30}H_{52}N_4O_4Mo_2 requires: C 49.72; H 7.23; N 7.73%. NMR (Benzene-d_6): ^1H (400 MHz) 4.90 (septet, J_{HH} = 6.5 Hz, 4H, CHMe_2), 2.23 (s, 6H, O_2CMe), 1.19 (s, 18H, CMe_3) 1.10 (d, 24H, CHMe_2). MALDI-MS: 724.2 (100%, M^+).

**Preparation of W_2(O_2CCH_3)_2((^iPrN)_2CC≡C'Bu)_2 (4B).** The reaction was carried out under similar conditions outlined for the molybdenum analogue using 600 mg of W_2(O_2CCH_3)_4 (1.0 mmol), 0.8 ml of 2.5M n-butyllithium (2.0 mmol), 0.25 ml of tertbutylacetylene (8.0 mmol), and 0.31 ml of N,N'-diisopropylcarbodiimide (2.0 mmol). An orange solid (310 mg, 34.3% yield) was isolated by filtration.

Microanalysis found: C 39.41; H 5.96; N 6.02%. C_{30}H_{52}N_4O_4W_2 requires: C 49.72; H 7.23; N 7.73%. NMR (Benzene-d_6): ^1H (400 MHz) 5.16 (septet, J_{HH} = 6.5 Hz, 4H, CHMe_2), 2.44 (s, 6H, O_2CMe), 1.23 (s, 18H, CMe_3) 1.20 (d, 24H, CHMe_2). MALDI-MS: 900.3 (100%, M^+).

**Preparation of Mo_2(O_2CCH_3)_2((^iPrN)_2CC≡CPh)_2 (5A).** 1.25 ml of N,N'-diisopropylcarbodiimide (8.0 mmol) was dissolved in 25 ml of THF and cooled to 0 °C. 8.0 ml of 1 M lithium phenylacetylide (8.0 mmol) was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, It was used *in situ* for the next reaction. A slurry of 1.72 g of Mo_2(O_2CCH_3)_4 in 25 ml of THF was made and cooled to 0 °C. The *in situ* solution was cooled again to 0 °C and slowly added to the slurry. The initial color change was red but darkened. After stirring at room temperature overnight, the solvent was stripped to dryness and redissolved in approximately 50 ml of
DCM. The solution was filtered over Celite. The volume of the red solution was reduced to a minimum and ethanol was added to crash out product. The product was collected on a glass frit, washed with 10 ml of ethanol, and yielded 1.85 g. The filtrate was stripped to dryness and 10 ml of ethanol was added. This resulted in an orange suspension. The solid was washed three times with approximately 10 ml of ethanol and allowed to settle (each time the wash was canulared off). The remaining solid was dried and yielded a second crop of 0.5 g. Overall yield: 2.35 g (76.8%).

Microanalysis found: C 51.52; H 5.63; N 6.74%. C_{34}H_{44}N_{4}O_{4}Mo_{2} requires: C 53.41; H 5.80; N 7.33%. NMR (Benzene-\textit{d}_6): \textsuperscript{1}H (400 MHz) 7.56 (m, 4H, Phenyl H), 7.37 (m, 6H, Phenyl H), 4.77 (septet, J_{HH} = 6.5 Hz, 4H, C_\text{HMe}_2), 2.39 (s, 6H, O_2CMe), 0.90 (d, J_{HH} = 6.5 Hz, 24H, CHMe_2). MALDI-MS: 765.2 (100%, M^+).

**Preparation of W_2(O_2CCH_3)_2((^i\text{PrN})_2CC≡CPh)_2 (5B).** The reaction was carried out under similar conditions outlined for the molybdenum analogue using 604 mg of W_2(O_2CCH_3)_4 (1.0 mmol), 0.31 ml of \textit{N},\textit{N}'-diisopropylcarbodiimide (2.0 mmol) and 2.0 ml of 1.0 M lithium phenylacetylide (2.0 mmol). A single crop of blue solid (0.340 g, 36.2% yield) was isolated by filtration.

Microanalysis found: C 42.65; H 4.70; N 5.90%. C_{34}H_{44}N_{4}O_{4}W_{2} requires: C 43.42; H 4.72; N 5.96%. NMR (Benzene-\textit{d}_6): \textsuperscript{1}H (400 MHz) 7.38 (d, J_{HH} = 7.4 Hz, 4H, Phenyl o-H), 7.05 (t, J_{HH} = 7.6 Hz, 4H, Phenyl m-H), 6.93 (d, J_{HH} = 7.5 Hz, 2H, Phenyl p-H), 5.30 (septet, J_{HH} = 6.5 Hz, 4H, CHMe_2), 2.45 (s, 6H, O_2CMe), 1.24 (d, J_{HH} = 6.5 Hz, 24H, CHMe_2). MALDI-MS: 940.2 (100%, M^+).
Preparation of Mo$_2$(O$_2$CCH$_3$)$_2$((PrN)$_2$CC≡CFc)$_2$ (6A). 0.8 ml of 2.5M n-butyllithium was slowly added the a mixture of 430 mg of ethynylferrocene in approximately 50 ml of THF at 0 °C. The solution was allowed to stir at room temperature for 2 h. It was used in situ for the next reaction. 0.31 ml of N,N-diisopropylcarbodiimide was slowly added to the in situ mixture at 0 °C. The solution was allowed to stir at room temperature for 2 h. It was used in situ for the next reaction. A slurry containing 428 mg of Mo$_2$(O$_2$CCH$_3$)$_4$ in 25 ml of THF was cooled to 0 °C. The in situ solution was cooled again to 0 °C and slowly added to the slurry. The solution initially turned red. Within the first hour the solution was dark. After stirring overnight, the mixture was stripped to dryness and redissolved in approximately 50 ml of DCM. The solution was filtered over Celite. The volume of the solution was reduced to a minimum and product crashed out. The orange solid was collected using a glass frit and washed with hexane. Overall yield: 385 mg (39.3%)

Microanalysis found: C 51.53; H 5.29; N 5.69%. C$_{42}$H$_{52}$N$_4$O$_4$Fe$_2$Mo$_2$ requires: C 51.45; H 5.35; N 5.71%. NMR (Benzene-$d_6$): $^1$H (400 MHz) 5.06 (septet, $J_{HH} = 6.4$ Hz, 4H, CHMe$_2$), 4.43 (s, 4H, Fc), 4.10 (s, 10H, Fc), 3.97 (s, 4H, Fc), 2.28 (s, 6H, O$_2$CMe), 1.16 (d, $J_{HH} = 6.4$ Hz, 24H, CHMe$_2$). MALDI-MS: 980.1 (100%, M$^+$).

Preparation of W$_2$(O$_2$CCH$_3$)$_2$((PrN)$_2$CC≡CFc)$_2$ (6B). The reaction was carried out under similar conditions outlined for the molybdenum analogue using 604 mg of W$_2$(O$_2$CMe)$_4$ (1.0 mmol), 430 mg of ethynylferrocene (2.0 mmol), 0.8 ml of 2.5 M n-butyllithium (2.0 mmol) and 0.31 ml of N,N-diisopropylcarbodiimide (2.0 mmol). 280 mg of a dark red solid yield was isolated by filtration. The filtrate was stripped to
dryness and redissolved in 10 ml of THF. This solution was placed in the -40 °C refrigerator to grow crystals. After several days, the mother liquor was removed and a 100 mg crop of crystals were collected. Overall yield: 380 mg (32.9%)

Microanalysis found: C 40.71; H 4.49; N 4.65%. C_{42}H_{52}N_{4}O_{4}Fe_{2}W_{2} requires: C 43.63; H 4.53; N 4.85%. NMR (Benzene-d_6): \(^1\)H (400 MHz) 5.33 (septet, J_{HH} = 6.4 Hz, 4H, CHMe₂), 4.39 (s, 4H, Fc), 4.09 (s, 10H, Fc), 3.98 (s, 4H, Fc), 2.45 (s, 6H, O₂CMe), 1.27 (d, J_{HH} = 6.4 Hz, 24H, CHMe₂). MALDI-MS: 1156.2 (100%, M⁺).

**Preparation of Mo₂(O₂C-2-thiophene)₂((PrN)₂CMe)₂ (7).** 0.31 ml of N,N-diisopropylcarbodiimide (2.0 mmol) was dissolved in 25 ml of THF and cooled to 0 °C. 1.25 ml of 1.6 M methyllithium (2.0 mmol) was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, it was used in situ for the next reaction. A slurry of 0.7 g of Mo₂(O₂C-2-thiophene)₄ in 25 ml of THF was made and cooled to 0 °C. The in situ solution was cooled again to 0 °C and slowly added to the slurry. The initial color change was black but changed to a deep red. After stirring at room temperature for two days, the solvent was stripped to dryness and redissolved in approximately 25 ml of DCM. The solution was filtered over Celite. The volume of the red solution was reduced to a minimum to crash out an orange-red solid. The product was collected on a glass frit and washed with 2 x 5 ml of hexane. Additional hexane was added to the filtrate which caused secondary precipitation. This second batch was also collected on a frit and washed with 2 x 5ml hexane. The solid was dried under vacuum for several hours. Overall yield: 130 mg (17.9%).
Microanalysis found: C 37.86; H 5.93; N 3.86%. C_{26}H_{40}Mo_2N_4O_4S_2 requires: C 42.86; H 5.53; N 7.69%. NMR (Benzene-\textit{d}_6): ^1\text{H} (400 MHz) 7.67 (d, 2H, Thio), 6.79 (d, 2H, Thio), 6.63 (t, 2H, Thio), 4.16 (septet, 4H, CHMe_2), 2.01 (s, 6H, N_2CMe), 0.95 (d, 24H, CHMe_2). MALDI-MS: 728.1 (100%, M\textsuperscript{+}).

**Preparation of Mo_2(cis-\mu-O_2C-9-anthracene)_2(\eta^2-\text{PrN})_2CMMe_2 (8).** 0.31 ml of \(N,N\)-diisopropylcarbodiimide (2.0 mmol) was dissolved in 25 ml of THF and cooled to 0 °C. 1.25 ml of 1.6 M methyllithium (2.0 mmol) was added to the mixture. The solution was allowed to warm slowly to room temperature. After 2 h, it was used in situ for the next reaction. A slurry of 1.08 g of Mo_2(O_2C-9-anthracene)_4 in 25 ml of THF was made and cooled to 0 °C. The in situ solution was cooled again to 0 °C and slowly added to the slurry. The initial color change was black but changed to a deep red. After stirring at room temperature for two days, the solvent was stripped to dryness and redissolved in approximately 25 ml of DCM. The solution was filtered over Celite. The volume of the solution was reduced to a minimum and ethanol was added to crash out a purple solid. The product was collected on a glass frit and washed with 10 ml of ethanol. The solid was dried under vacuum for several hours. Overall yield: 360 mg (39.2%).

Microanalysis found: C 63.21; H 5.26; N 3.77%. C_{46}H_{54}Mo_2N_4O_4 requires: C 60.13; H 5.92; N 6.10%. NMR (Benzene-\textit{d}_6): ^1\text{H} (400 MHz) 9.25 (d, 4H, Anth), 8.23 (s, 2H, Anth), 7.74 (d, 4H, Anth), 7.09 (t, 4H, Anth), 6.95 (t, 4H, Anth) 3.83 (septet, 4H, CHMe_2), 1.75 (s, 6H, N_2CMe), 1.58 (d, 12H, CHMe_2) 1.09 (d, 12H, CHMe_2). MALDI-MS: 919.2 (100%, M\textsuperscript{+}).
3.7 References


DIMOLYBDENUM AND DITUNGSTEN AMIDATE COMPLEXES AS BUILDING BLOCKS FOR SIMPLE MOLECULAR ASSEMBLIES.

4.1 Introduction

The term “supramolecular” is defined as consisting of more than one molecule or of greater complexity than a single molecule.[1, 2] Supramolecular species are constructed by combining molecular building blocks in a manner similar to the way molecules are constructed of atoms. The conceptual feature that distinguishes supramolecular assemblies from molecular assemblies is the individual existence of the building blocks in the former. Supramolecular assemblies utilize interactions such as hydrogen bonding[3], π-π stacking[4], electrostatics, and van der Waals forces[5] while molecular assemblies break and/or form new covalent bonds.

Transition metal complexes can be versatile building blocks in supramolecular chemistry.[6-8] Since the early 1990’s, significant research has been directed towards the synthesis of polynuclear coordination complexes with interesting electronic, optical, or magnetic properties. The use of metal atoms or ions as key elements in the formation of supramolecular chemistry first emerged. Mono-nuclear transition metal complexes of square planar Pd$^{II}$ and Pt$^{II}$ as well as tetrahedral Zn$^{II}$ have already been shown to be
versatile building blocks in supramolecular chemistry.[7] These materials, however, have high ionic charges and are not normally electrochemically active.

Attempts to develop molecular assemblies utilizing dimetal building blocks were almost concurrent. The first efforts to link simple pairs of dimetal units as model complexes for molecular wires were underway as early as 1989.[9] Beginning in 1998, molecular assemblies incorporating dinuclear metals as corner units to build higher order structures was groundbreaking.[10] Work in these areas, however, has been limited to a select group of building blocks and not without significant difficulties.

The intention of this research was to identify a new series of $M_2$(amidate)$_4$ derivatives for molybdenum and tungsten that could be used as building blocks to construct molecular assemblies including simple pairs of dimers and a molecular square. This chapter will be divided into four distinct parts. Section 4.2 looks at the rationalization and systematic approach used to develop a new series of amidate derivatives as building blocks. Section 4.3 reports the findings of $M_2$(amidate)$_4$ derivatives where $M = Mo$ and $W$ as well as their ability to form higher order assemblies. Section 4.4 is a summary and conclusion while section 4.5 is the experimental section.

4.2 Molecular assemblies

Using suitable $M_2$ units and linkers, a variety of product geometries including simple pairs of $M_2$ units, loops, triangles, squares, clusters, and three-dimensional arrays can be obtained.[10-14] Of paramount importance is the proper selection of both dimetal units and linker. The most common $M_2$ units of molybdenum form building blocks with the aid of ancillary carboxylate or formamidinate ligands.[9, 15] Specifically, the
Chisholm group has commonly utilized dimolybdenum tetrapivalate, Mo₂(Piv)₄, and its derivatives while the Cotton group has commonly utilized dimolybdenum tetra-\(N,N'-p\)-anisylformamidinate, Mo₂(DAniF)₄, and its derivatives. The work with tungsten building blocks has been limited to ditungsten tetracarboxylates of which ditungsten tetrapivalate, W₂(Piv)₄, is the most common.

Since molybdenum and tungsten complexes normally exhibit only weak axial coordination, efforts focused on linking dimetal units with suitable equatorial linkers for stronger covalent interactions.[16] The typical synthetic paths are carboxylate exchange and methathesis reactions as previously discussed in Chapter 1. The typical derivatives of homoleptic dimolybdenum complexes are mono- and di-cations as well as mono- or di-substituted carboxylate and di-substituted chloride derivatives for dimolybdenum tetraformamidinate complexes.

### 4.2.1 Mo₂(O₂CR)₄ derivatives

The replacement of carboxylate ligands in dimolybdenum tetracarboxylate complexes with solvent ligands has been extensively studied.[17-19] Di-cations and in some case mono-cations are readily obtained by the treatment of homoleptic molybdenum carboxylate complexes with Meerwein’s reagent (Et₃OBF₄) in acetonitrile.[20] Triethylxonium tetrafluoroborate is an electrophilic alkylating reagent for esterification of sterically hindered carboxylic acids. After esterification, the ligand is replaced by coordinating solvent to form an active solvated complex. Solvated complexes of the general form [Mo₂(O₂CR)₃(CH₃CN)₂]⁺(BF₄⁻) and [Mo₂(O₂CR)₂(CH₃CN)₄]²⁺(BF₄)₂ have been versatile in the preparation of simple pairs of
dimers of the formula [Mo\(_2\)(O\(_2\)CR)\(_3\)](linker)[Mo\(_2\)(O\(_2\)CR)\(_3\)] and higher oligomers of the formula [Mo\(_2\)(O\(_2\)CR)\(_2\)(linker)]\(_n\), respectively.[19]

**4.2.2 Mo\(_2\)(DA\textit{niF})\(_4\) derivatives**

The replacement of amidinate ligands in Mo\(_2\)(DA\textit{niF})\(_4\) has also been extensively studied.[20] Mono-, di-, and even tri-cations of Mo\(_2\)(DA\textit{niF})\(_4\) have been readily obtained with the same or similar reagents as previously discussed. Metathesis reactions of cationic species can also be used to obtain mixed formamidinate-carboxylate complexes. In other cases, labile di-substituted chloride derivatives are useful. Both mixed ligand and di-chloride complexes allow for preferential reactions at the more labile carboxylate/chloride site while maintaining geometry with the less labile formamidinate ligands.[21-23] These complexes have been versatile in the preparation of simple pairs of dimers and higher oligomers to most notably include molecular squares and triangles.

**4.2.3 W\(_2\)L\(_4\) derivatives**

Unfortunately, little progress has been made in applying the above chemistry to tungsten analogs. The tungsten work has been limited to carboxylate exchange reactions since key tungsten derivatives have not been obtainable. It would therefore be highly desirable to devise a synthetic path to cationic species of the general form W\(_2\)L\(_{4-n}\)\(_n^+\) where \(n = 1\) or \(2\) and \(L\) is a \(\mu\)-bridging ancillary ligand.
4.2.4 Common limitations

Significant synthetic limitations have been previously identified when using $\text{M}_2(\text{O}_2\text{CR})_4$ complexes in the formation of higher order oligomers. These problems most notably include reversibility of the substitution and equilibrium processes that prevent isolation of targeted products.[21] Similar issues exist when using $\text{Mo}_2(\text{DAniF})_4$ in the formation of higher order oligomers. With linear linkers, the formation of squares is favored by the $90^\circ$ angle subtended by the dimetal corner piece. Kinetically, intermolecular reactions are favored, especially in cases of dilution, which may result in the formation of triangles. With non-linear linkers, the formation of loops, triangle and other clusters is often preferred.[10] In many cases, spontaneous self assembly does not always result in a single product but also results in a mixture of species in equilibrium.[24] The idea of generating a kinetic product that rapidly forms, drops out of solution, and limits subsequent side reactions was very desirable.

4.2.5 Solvent effects

Further substitution or side reactions can be limited by the choice of a solvent that preferentially removes the desired complex by precipitation from solution.[25] Hydrocarbons such as acetonitrile or dichloromethane are preferred for metathesis reactions with solveto complexes. The cationic species are normally readily soluble in these solvents while the neutral product often precipitates out of solution immediately. For carboxylate exchange reactions, a hydrocarbon such as toluene is more preferred than a coordinating solvent like tetrahydrofuran which may form higher order assemblies due to increased solvation effects.[25]
4.2.6 New molecular assemblies

The greatest challenges are to control geometry and solubility. The synthesis of molecular assemblies dictates the need for geometry control. The use of dimetal units that are partly encumbered by less labile ancillary ligands is important. Solubility is normally inversely related to molecular mass. As a molecular assembly’s size and mass increases, its solubility tends to decrease. This can adversely affect the characterization as well as application of the product.

As previously stated, the intention of this research was to identify a new series of M$_2$(amidate)$_4$ derivatives for molybdenum and tungsten that could be used as building blocks to construct molecular assemblies including simple pairs of dimers and a molecular square. The first step was to prepare suitable dimetal building blocks to act as end caps or corner pieces for molecular assemblies. It was desirable to synthesize both molybdenum and tungsten derivatives in order to compare their physiochemical properties. The next step would be to link these pieces with an appropriate bifunctional linker to maximize the electronic communication.

4.2.6.1 Amidate complexes

Carboxylate ligand scrambling led to investigating the feasibility of using other less labile homoleptic complexes. The amidate ligand is structurally similar to the carboxylate ligand in forming a three-atom bridge across the M$_2$ unit but the more basic ligand does differ electronically as previously discussed. Therefore, dimetal complexes containing ancillary amidate ligands might be more useful by suppressing ligand scrambling and other side reactions.
Amidate complexes fall into two broad classes or types: 1) cyclic amidate complexes (I) using ligands such as 2-oxopyridine and 2) non-cyclic amidate complexes (II) using ligands such as acetamide. [26]

Based on previous work done by the Chisholm Group with 2-hydroxy-6-methylpyridine, (Hmhp) (III), our desire was to extend this chemistry. [19] The anion of Hmhp is unique ligand in that it can be used to easily synthesize the Group 6B triad of Cr, Mo, and W complexes of the form $M_2(mhp)_4$. [27] All three homoleptic complexes are readily accessible in gram quantities and have been fully characterized.
Unlike the previous discussion of tungsten carboxylate complexes, the thermal reaction of either molybdenum or tungsten hexacarbonyl with Hmhp in an inert high boiling solvent forms the homoleptic complex of the molecular formula $M_2$(mhp)$_4$ as shown in Scheme 4.1. These complexes are relatively stable with robust metal-ligand interaction. Their crystallographic characterization shows a unique arrangement of ligands around the $M_2$ unit.[28] The methyl group on the pyridine influences the geometry of the product. In these complexes, there are two cis-ligands with opposite orientation of the methyl groups along the MM axis while the trans-ligands are in the same direction to each other. This allows for the greatest separation and least methyl group interaction.

$$\text{M(CO)}_6 \quad + \quad \text{(Hmhp)} \quad \xrightarrow{\Delta} \quad \text{inert solvent}$$

where $M = \text{Mo, W}$

**Scheme 4.1** Common synthetic path to $M_2$(mhp)$_4$.

In 1992, Cayton and co-workers prepared and characterized the mono-cation $[\text{Mo}_2(\text{mhp})_3(\text{CH}_3\text{CN})_2]^+(\text{BF}_4^-).[19]$ Its application for simple pairs of dimers in
molecular assemblies was intriguing. No reports, however, identified the preparation and characterization of the di-cation complex. It was rationalized that the di-cation should be obtainable with methods similar to those already used for other di-cation species as previously discussed. The di-cation complex could be a suitable building block for molecular squares. Lastly, similar methodology may also provide a synthetic path to the mono- and di-cation derivatives of $W_2$(mhp)$_4$. Further investigation was warranted.

4.2.6.2 Linkers

The most common bifunctional linkers are dianions of dicarboxylic acids.[21, 29, 30] Dicarboxylate-based linkers with an extended π-network of the form $(O_2C-X-CO_2)_2^-$ where $X = $ conjugated organic group have been extensively employed to promote cooperative interaction between dimetal units. Work in the area of linkers has also expanded to include diamidates and diaminodinate linkers.[31, 32]

Of the dicarboxylate linkers available, the oxalate (IV) and tetrafluoroterephthalate (V) dianion seemed well suited for the initial task at hand. Both are well studied π-conjugated linkers that are planar in the ground state to maximize electronic coupling. It has been previously identified that linking of two dimetal units linked by the oxalate dianion causes strong electronic coupling.[24, 29] The two CO$_2^-$ units are directly connected since there is no X. The electronic coupling with tetrafluoroterephthalate should be less due to the increased separation of dimetal units with insertion of the $C_6F_4$ moiety. The linear nature of both linkers should aid in the formation of the desired molecular assemblies. Additionally, oxalate and
tetrafluoroterephthalate form quaternary salts such as an $n$-butylammonium salt when mixed with $^n$Bu$_4$NOH in methanol.[30]

\[
\begin{align*}
\text{Oxalate} & \quad \text{Tetrafluoroterephthalate} \\
\text{IV} & \quad \text{V}
\end{align*}
\]

4.2.7 Synthetic strategy

The synthetic strategy for simple pairs of dimers is based on metathesis reactions employing solvento complexes and carboxylate exchange reactions as illustrated in Scheme 4.2. The metathesis reaction established the need to synthesize the known monocation of Mo$_2$(mhp)$_4$, [Mo$_2$(mhp)$_3$(CH$_3$CN)$_2$]$^+[\text{BF}_4^-]$, and investigate the synthesis of the corresponding tungsten analog. The carboxylate exchange reaction could be utilized for other dicarboxylic acids when quaternary salts are not possible. Under these circumstance, the mono-substituted carboxylate derivatives of both molybdenum and tungsten tetra-mhp would be required. It was envisioned that the mono-substituted acetate derivatives would be accessible through the metathesis reaction of the corresponding mono-cation and the $n$-butylammonium acetate salt.
Scheme 4.2 Proposed synthetic routes to simple pairs of dimers.

The synthetic strategy for the molecular squares was slightly different as illustrated in Scheme 4.3. In these cases, the di-cation or di-substituted carboxylate derivatives of both molybdenum and tungsten could be required. If the di-cation was accessible, the di-substituted acetate derivative should be available through a metathesis reaction similar to that previously discussed for mono-substituted acetate derivatives with the $n$-butylammonium acetate salt.
\[
[M_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}[\text{BF}_4^-]_2 + [\text{"Bu}_4\text{N}]_2(\text{O}_2\text{C-X-CO}_2)_{\text{CH}_3\text{CN}}
\]

\[
[M_2(\text{mhp})_2(\text{O}_2\text{C-X-CO}_2)]_n + 2[\text{"Bu}_4\text{N}][\text{BF}_4^-]
\]

\[
M_2(\text{mhp})_2(\text{O}_2\text{CCH}_3)_2 + \text{HO}_2\text{C-X-CO}_2\text{H} \xrightarrow{\text{toluene}} [M_2(\text{mhp})_2(\text{O}_2\text{C-X-CO}_2)]_n + 2\text{HO}_2\text{CCH}_3
\]

where M = Mo, W and n = 4

**Scheme 4.3** Proposed synthetic routes to molecular squares.

### 4.2.8 Electronic communication

The goal in this research was to prepare model complexes of interest where the electronic coupling of dimetal units could be systematically investigated. Electronic communication between two atoms or groups of atoms is a fundamental curiosity.[30] The presence of dinuclear units facilitates redox processes and the use of \(\pi\)-conjugated linkers allow for electronic communication or so-called coupling.[33] A major point of interest for these molecular assemblies is the cooperative effect of various linkers to communicate the effects of one dimetal unit to another dimetal unit.[12, 34] Simple pairs of dimers and molecular squares are well suited as model complexes for the investigation of the cooperative effect associated with the interaction of two or more dimetal units. The simple pairs of dimers or so-called dimers of “dimers” represent a model for molecular wires as previously discussed in Chapter 1 as well as a dimeric subunit in one-dimensional polymers.[9]
Ultimately, it was desirable to expand this study to molecular squares where the cooperative effects can be significantly different as well as informative. A point of considerable interest is the degree of electron delocalization in oxidized species (Scheme 4.4). For example in a homogeneously-linked molecular square, the first oxidation of the square (A) may result in a localized positive charge (B) or a delocalized positive charge (C) depending on the ability of the linker to communicate. If the charge is delocalized, the first and second oxidation potentials should be significantly different due to charge stabilization. The second oxidation may also result in a localized charge (B'//B") or a delocalized charge (C'). If the second oxidation results in a localized charge, there may be a preferred orientation to minimize electrostatic interactions (B"). In a heterogeneously-linked square, where one pair of linkers communicates significantly better than the other pair of linkers, different characteristic should be expected. The first oxidation of the square (D) may still result in a localized positive charge (E) or a partially delocalized positive charge (F) based on the linkers. The first and second oxidation potentials should be similar. The second oxidation may result in a localized charge (E'/E") or a partially delocalized charge (F'). If the second oxidation results in a localized charge, there may be a preferred orientation to minimize electrostatic interactions (E").
4.3 Mixed amidate-carboxylate complexes

The investigation started with the known synthesis of the mono-cation

\[ [\text{Mo}_2(\text{mhp})_3(\text{CH}_3\text{CN})_2]^+ (\text{BF}_4^-) \] as shown in Scheme 4.5. The di-cation

\[ [\text{Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+} (\text{BF}_4^-)_2 \] (I) was easily obtained by the treatment of the homoleptic \text{Mo}_2(\text{mhp})_4 complex with an excess of Meerwein’s reagent as also shown in Scheme 4.5. The formation of the di-cation was, however, uniquely interesting when fully characterized by single x-ray crystallography. This will be discussed later in section 4.3.3.
We then turned our investigation towards synthesizing mono- or di-cations of W\(_2\)(mhp)\(_4\) with Meerwein’s reagent. Although initial efforts looked hopefully, the complexes isolated appeared to be adducts of the original complex by \(^1\)H NMR and subsequent reactions with this product resulted in the reformation of the thermodynamically stable starting material W\(_2\)(mhp)\(_4\). Additional reagents were also investigated.

Work with another esterification reagent was next explored. Because of its powerful Lewis acidity, boron triiodide, BI\(_3\), is an effective reagent in promoting the conversion of acids to esters.[35] Attempts with this reagent were also unsuccessful and resulted in loss of starting material probably due to oxidation of the W\(_2\) unit.

We also predicted the mhp ligand may be cleaved for the dimetal unit with another appropriate reagent. Trimethylsilyl iodide, Me\(_3\)SiI, (also known as iodotrimethylsilane) is one of many compounds commonly used to cleave carboxylic esters.[35] This reaction could be analogous to saponification and convert the mhp ligand to its salt derivative. The salt derivative may then be replaced by a bridging iodide.
to form a species of the general form $W_2(mhp)_3(\mu-I)$. Unfortunately, this reaction did not afford the desired product.

The last approach was analogous to mono-cation formation with $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$. The di-chloride derivative of $W_2(mhp)_4$ was prepared according to literature preparation.[36] In our case, the $W_2(mhp)_3\text{Cl}_2$ reaction as shown in Scheme 4.6 resulted in the reformation of $W_2(mhp)_4$.

$$\text{CH}_3\text{CN}_2W_2(mhp)_3\text{Cl}_2 + \text{Zn} \rightarrow 2[W_2(mhp)_3(\text{CH}_3\text{CN})_2]^+ + \text{ZnCl}_4^{2-}$$

**Scheme 4.6** Failed synthetic route to $W_2(mhp)_3^+$ cation.

At this point, the ability to form an active complex of the form $W_2(mhp)_4-n^{n+}$ where $n = 1$ or 2 does not appear to be feasible. Work with tungsten complexes was suspended and efforts were directed towards the formation of simple pairs of molybdenum dimers.

As expected, the reaction of the mono-cation $[\text{Mo}_2(mhp)_3(\text{CH}_3\text{CN})_2]^+(\text{BF}_4^-)$ with half an equivalent of the $n$-butylammonium salt of the corresponding dicarboxylic acid in acetonitrile resulted in the rapid formation and precipitation of a simple pair of dimers. The microcrystalline precipitate was collected by centrifugation or filtration and washed
with acetonitrile and/or hexanes. Problems with the solubility of products immediately arose. These complexes are air sensitive and practically insoluble in most solvents including THF but are sparingly soluble in dimethyl sulfoxide (DMSO). The characterization of these dicarboxylate-linked complexes has been limited due to their relative insolubility.

Mixed amidate-carboxylate complexes of molybdenum were investigated next. The mono-cation \([\text{Mo}_2(\text{mhp})_3(\text{CH}_3\text{CN})_2]^+ (\text{BF}_4^-)\) and \(n\)-butylammonium acetate did yield the desired mixed amidate-carboxylate complex, \(\text{Mo}_2(\text{mhp})_3(\text{O}_2\text{CCH}_3)\) (4), through precipitation in acetonitrile. Mass spectroscopy, however, of product 4 showed the co-formation of \(\text{Mo}_2(\text{mhp})_4\) as an impurity as shown in Figure 4.1. The di-cation complex 2 did not directly yield the desired mixed amidate-carboxylate complex, \(\text{cis-}\text{Mo}_2(\text{mhp})_2(\text{O}_2\text{CCH}_3)_2\) (5), through precipitation in acetonitrile. Complex 5 was surprisingly soluble in acetonitrile and only precipitated after reduction of solvent or addition of hexanes. The desired product 5 also showed the co-formation of \(\text{Mo}_2(\text{mhp})_3(\text{O}_2\text{CCH}_3)\) by mass spectroscopy. This was attributed to the relatively polar products being soluble in polar solvents such as acetonitrile and DCM. It also appears that equilibrium processes are preventing the isolation of targeted complexes in both cases.
The ability to synthesize molecular squares as previously discussed was lastly investigated. The reaction of the di-cation \([\text{Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)^{-}_2\) and \(n\)-butylammonium salt of oxalic acid did not produce a solid precipitate in acetonitrile. This reaction instead yielded oil that could only be characterized as a mixture of products. The reaction of the di-cation \([\text{Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)^{-}_2\) and \(n\)-butylammonium salt of tetrafluoroterephthalate acid did yield a solid precipitate in acetonitrile. Through mass spectrometry, it was determined that the reaction yielded a mixture of higher order species that specifically consisted of simple pairs of dimers.
molecular triangles, and molecular squares as shown in Figure 4.2. The observed formation of simple pairs of dimers is the likely result of side reactions or mono-cation impurity in the di-cation starting material. The formation of both molecular triangle and molecular squares indicates the semi-rigid nature of the $cis$-$Mo_2(mhp)_2^{2+}$ building block.

**Figure 4.2** MALDI-TOF spectrum of 1 and ($^n$Bu$_4$N)$_2$(O$_2$CC$_6$H$_4$CO$_2$) reaction generating a mixture of simple pairs of dimers, molecular squares, and molecular squares.

The existence of both molecular triangles and squares can be rationalized in terms of kinetic and thermodynamic factors. The formation of molecular triangles can be
viewed as a kinetically and entropically favored product while the formation of molecular squares can be viewed as thermodynamically favored product. In previous studies, it has been shown that both molecular triangles and molecular squares can be found in equilibrium.\[37\] The formation of a mixture of products prevents the isolation of targeted complex while poor solubility prevents its complete characterization.

4.3.1 UV-vis spectroscopy

Complexes 2 and 3 have low energy absorptions attributed to fully allowed metal-to-bridge electronic transition in the visible light spectrum. Their intense colors are derived from fully allowed MLCT transitions involving the linker. Due to the relative insolubility and lack of purity of most of the products in this section, UV-vis spectroscopy was postponed.

4.3.2 Electrochemistry

A major interest of this chapter is the ability of bridging linker to communicate the effects of oxidation of a dimetal unit at one end to the dimetal unit at the other end. Electrochemical measurements of complexes 2 and 3 revealed two quasi-reversible oxidation waves separated by 282 and 240 mV, respectively. Refer to table 4.1, the separation of oxidation waves was greater for the oxalate-bridged complex than the tetrafluoroterephthalate-bridged complex by approximately 40 mV. This show a stronger coupling between the dimetal units with the shorter bridge as expected. The large $K_c$ values of both complexes implies a partial delocalization of charge that should fall in the
class II or class II/III border of mixed valence complexes in the Robin and Day scheme.

The first oxidation wave of complex 2 occurs at a lower potential than the more electron withdrawing bridged complex 3. The second oxidation waves occur at similar potentials.

<table>
<thead>
<tr>
<th></th>
<th>$E_{1/2}$(I)</th>
<th>$E_{1/2}$(II)</th>
<th>$\Delta E_{1/2}$</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo$_2$(mhp)$_3$]$_2$(O$_2$CCO$_2$) (2)</td>
<td>-238</td>
<td>44</td>
<td>282</td>
<td>6.0 x 10$^4$</td>
</tr>
<tr>
<td>[Mo$_2$(mhp)$_3$]$_2$(O$_2$CC$_6$F$_4$CO$_2$) (3)</td>
<td>-188</td>
<td>52</td>
<td>240</td>
<td>1.2 x 10$^4$</td>
</tr>
</tbody>
</table>

**Table 4.1** Summary of electrochemical data for [Mo$_2$(mhp)$_3$]$_2$(O$_2$C-X-CO$_2$) oxidation potentials in mV. Potentials were recorded in DMSO/0.1 M [Bu$_4$N][PF$_6$] and referenced to the FeCp$_2^{0/+}$.

Based on poor solubility, electrochemistry was only available in DMSO versus a more common solvent such as THF. This makes comparisons with other simple pairs of dimers limited. The 282 mV separation of oxidation waves in complex 2 is, however, very consistent with other oxalate-bridged complexes. Cyclic voltammetric measurements of complexes [Mo$_2$(Bu-CO$_2$)$_3$]$_2$(oxalate)[29] and [Mo$_2$(DAniF)$_3$]$_2$(oxalate)[12] show oxidation waves separated by 280 and 223 mV, respectively. The 240 mV separation of oxidation waves in complex 3 is larger than expected. Cyclic voltammetric measurements of complexes [Mo$_2$(Bu-CO$_2$)$_3$]$_2$(tetrafluoroterephthalate)[29] and [Mo$_2$(DAniF)$_3$]$_2$(tetrafluoroterephthalate)[12] show oxidation waves separated by only 65 and 87 mV, respectively. This implies that complex 4 has significantly greater electronic coupling relative to other known
tetrafluoroterephthalate-bridged molybdenum complexes. However, the $\Delta E_{1/2}$ and hence $K_c$ are very dependent on the solvent. This relatively high electronic coupling for tetrafluoroterephthalate-bridged complex 3 is further explored by DFT calculations using model complexes.

Electrochemistry data are included in Appendix C.1.

4.3.3 Crystal structure

The crystal structure of complex 1 is shown in Figure 4.3. Contrary to previous discussions about the orientation of the cis-amidate ligands in the parent complex, the two cis-ligands have the same orientation of the methyl groups along the MM axis. This means that the amidate ligands have scrambled to this new configuration during synthesis. Since the initial synthesis of complex 1 was conducted at 70 °C, it was hypothesized that the elevated temperature resulted in re-configuration of the ligands. A subsequent preparation of complex 1 was therefore conducted at room temperature. The resulting crystallographic unit cell was identical. The relative electronic stability of dication complexes with cis-amidate ligands on the same and opposite orientation along the MM axis were further explored by DFT calculations using model complexes.
Figure 4.3 ORTEP diagram of $[\text{Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4^-)_2$ (1) drawn with 50% probability displacement ellipsoids. Hydrogen atoms, space-filling CH$_3$CN solvent molecules and BF$_4^-$ counter ions are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atoms by the crystallographic mirror plane.

Crystallographic data are included in Appendix C.2.

4.3.4 Electronic structure calculations

DFT calculations were used in an effort to understand the reasons for several atypical results including the unique geometry of complex 1 and the relatively higher than expected electronic coupling in complex 3. The unique geometry of complex 1 was first explored with the use of model complexes A and B as shown in Figure 4.4. Models A and B are isomers related by the relative position of the methyl groups on the mhp
ligands. The *anti*-isomer of the model complex has an inversion center and $C_{2h}$ symmetry while *syn*-isomer of the model complex has a mirror plane and $C_{2v}$ symmetry. Gas-phase and solvated PCM[38] calculations of both model complexes identified that model A with the opposite orientation across the MM axis to be slightly favored in terms of thermodynamic stability. The only factor that appeared to favor the same orientation across the MM axis was related to dipole moments. The model B showed a slightly higher dipole moment than model A. This may imply that model B forms due to polar solvent effects. No conclusive evidence supports the preferred geometry of Complex 1.

![Model structures](image)

**Figure 4.4** Model structures, assigned identification letter, chemical formula, and applied symmetry. Hydrogen atoms omitted for clarity.

Before examining the electronic coupling of the simple pairs of dimers, it should be recognized that the potential for two isomers exists. The two isomers are related by rotation about the linear linker to one of two planar configurations. The *syn*-isomer of the
model complex has a mirror plane and $C_{2v}$ symmetry while anti-isomer of the model complex has an inversion center and $C_{2h}$ symmetry. In all cases, the model complexes have been simplified by removal of the methyl group on the amidate ligand. This allowed for increased symmetry and a reduction in computational time. The model complexes are shown in Figure 4.5.

![Figure 4.5](image)

**Figure 4.5** Model structures, assigned identification letter, chemical formula, and applied symmetry. Hydrogen atoms are omitted for clarity.
Frequency analysis of the optimized geometries of the tetrafluoroterephthalate-bridged model complexes showed them to be a transition state with 1 imaginary frequency each. Analysis of this imaginary frequency showed it to be related to the rotation of the phenyl ring out of the plane of the carboxylates. Effort to optimize the model structures to a local minimum were considered unnecessary. The model complexes are expected to have a shallow energy well due to the phenyl ring rotation. The geometry of these optimized model complexes are, therefore, expected to be close enough in energy to a local minimum for use in qualitative analysis.

Based on DFT calculations, the two isomers are essentially the same in terms of predicted thermodynamic stability. We will therefore only use one of the two isomers to compare the DFT results between bridges. The syn-isomers were arbitrarily chosen for this comparison. As previously discussed in Chapter 2, the in-phase and out-of-phase splitting of the M$_2$ $\delta$ orbitals predicts the electronic coupling through the bridge in simple pairs of dimers. These orbitals are represented by DFT calculations as the HOMO and HOMO-1 orbitals.

For the syn-$[\text{C}_3\text{H}_4\text{NO})_3\text{Mo}_2]_2$(oxalate), the separation in energy of the HOMO and HOMO-1 is approximately 0.33 eV. This is comparable to the oxalate-bridged models from Chapter 2. Based on the energy level diagram in Figure 4.6, the dominant superexchange mechanism should be electron hopping through the empty bridge $\pi$ orbital.
Figure 4.6 Qualitative MO energy level diagram with calculated isosurfaces for \([\text{[(C}_5\text{H}_4\text{NO)}_3\text{Mo}_2\text{]_2(oxalate)}}\) (isovalue for surfaces set at 0.02 au with the exception of the filled bridge \(\pi\) which is set at 0.01 au). Hydrogen atoms are omitted for clarity.

For the \(\text{syn-[(C}_5\text{H}_4\text{NO)}_3\text{Mo}_2\text{]_2(tetrafluoroterephthalate)}}\), the separation in energy of the HOMO and HOMO-1 is approximately 0.16 eV. This relatively weak splitting predicted by the HOMO and HOMO-1 does not correlate to the relatively high \(K_c\) value observed in electrochemistry. These DFT calculations do not provide an understanding of the observed electronic coupling. Based on the energy level diagram in Figure 4.7, the
dominant superexchange mechanism should be electron hopping through the empty bridge $\pi$ orbital.[25, 39] Although the filled bridge $\pi$ orbital is relatively close to the HOMO and HOMO-1 orbitals, it shows no dimetal character for effective electron transfer. Based on the relatively small splitting of the HOMO and HOMO-1 orbitals, no conclusive evidence supports the relatively large electronic coupling observed by electrochemistry of Complex 3.

**Figure 4.7** Qualitative MO energy level diagram with calculated isosurfaces for $[(\text{C}_5\text{H}_4\text{NO})_3\text{Mo}_2](\text{tetrafluoroterephthalate})$ (isovalue for surfaces set at 0.02). Hydrogen atoms are omitted for clarity.
4.3.5 EPR measurements

On the EPR timescale, the single electron oxidized radical cations of oxalate-bridged Mo$_2$ units supported by ancillary carboxylate [40] and formamidinate [13, 21] ligands show electron delocalization over all four metal atoms. Based on the strong electronic coupling in complex 2 and 3 by electrochemistry, both complexes should observe similar electron delocalization over all four metal atoms. Unfortunately, the lack of solubility prevented exploring this expectation. The high dielectric constant of DMSO has been problematic in EPR analysis. Efforts to use smaller diameter tubes to minimize dielectric effects improved tunability of the EPR instrument but concentration of samples then became problematic. No supporting EPR datum is currently available.

4.4 Summary and conclusion

The preparation of new building blocks for the construction of molecular assemblies has been explored. Although the strategy of this project was sound, the results are less than desirable. The several desired target complexes were synthesized but purity and solubility were always detrimental to the overall goals. Initially, both the mono- and di-cation showed slight impurities that could not be removed through washing or re-crystallization. The impurities were normally found to be unreacted starting material that appeared to be co-crystallizing with the desired mono-cation or mono-cation that co-crystallized with the desired di-cation. An equilibrium process is probably responsible for this in both cases.
Subsequent reactions with either cation did favor the desired product but did not allow for the easy isolation of that product. In the case of simple pairs of dimers, the solubility of cyclic amidate complexes worked in our favor to precipitate a relatively pure product but subsequent characterization was extremely limited due to relative insolubility. Relative insolubility also prevented the characterization of any higher order oligomers such as the desired molecular square.

It appears evident that equilibrium processes in this chemistry are detrimental to the isolation of targeted complexes. The use of Mo$_2$(mhp)$_4$ derivatives as building blocks in molecular assemblies was extremely limited due to the relative insolubility of the oligomers. The use of non-cyclic amidate ligands as ancillary ligands of dimolybdenum complexes may more productive. Alkyl chains off the nitrogen and central carbon atoms of the amidate ligand in Mo$_2$(amidate)$_4$ complexes may have increased solubility. The introduction of large aliphatic chains could drastically change the solubility and associated chemistry.

Like many chemists before me, the ability of synthesizing an active solvento derivative of a tungsten analog has been unsuccessful. The tungsten ligand bonds are relative stronger than the corresponding molybdenum ligand bonds. This can be attributed to better metal-to-ligand overlap with the more diffuse 5d orbitals of tungsten. The overall effect is the relative stability and unreactive nature of the tungsten complexes to ligand replacement by a neutrally charged species.
4.5 Experimental details

All reactions were carried out under an inert atmosphere of UHP-grade argon or nitrogen using standard Schlenk techniques and under a dry oxygen-free nitrogen atmosphere using standard glovebox techniques. All solvents were dried and degassed by standard methods prior to use. THF was dried by refluxing over sodium/benzophenone while toluene and hexanes were dried by refluxing over sodium metal. Acetonitrile and dichloromethane (DCM) was dried by refluxing over calcium hydride.

Starting materials Mo$_2$(mhp)$_4$[27], [Mo$_2$(mhp)$_3$(MeCN)$_2$]$^+(BF_4)^{-}$[19], W$_2$(mhp)$_4$[27], and W$_2$(mhp)$_3$Cl$_2$[36] were prepared according to the literature procedures. 2-hydroxy-6-methylpyridine, triethylxonium tetrafluoroborate (1.0 M in DCM), n-butylammonium acetate, n-butylammonium hydroxide (1.0 M), oxalalic acid, tetrafluoroterephthalic acid, trimethylsilyl iodide, boron triiodide, and zinc metal were purchased from commercial sources and used as received. Other n-butylammonium salts were prepared by the 1:1 reaction of the appropriate acid with a 1 M solution of n-butylammonium hydroxide in methanol. After stirring for 1 hr at room temperature, the mixture was stripped to dryness and dried under vacuum at 50 °C for several hrs.

Physical Measurements. NMR spectra were recorded on a 400 MHz Bruker DPX spectrometer. All $^1$H NMR chemical shifts are reported in ppm relative to the protio impurity in MeCN-$d_3$ at 1.53 ppm, THF-$d_8$ at 3.58 ppm, or DMSO-$d_6$ at 2.50 ppm. UV-visible spectra were recorded at room temperature using a Perkin-Elmer Lambda 900 spectrometer. Spectra in THF solution were obtained using an air-tight 1 mm quartz cell. Microanalyses were carried out by Atlantic Microlab, Inc.
Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded at OSU’s Campus Chemical Instrument Center (CCIC) using a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were run pure or mixed with dithrinol matrix to aid in the flight of the molecule. All complexes were kept in an inert atmosphere.

Cyclic voltammetric and differential pulse voltammetric data were collected with the aid of a Princeton Applied Research (PAR) 173A potentiostat-galvanostat equipped with a PAR 176 current-to-voltage converter with $iR$ compensation capability. A single compartment voltammetric cell was equipped with a platinum working electrode, a platinum wire auxiliary electrode, and a pseudo reference electrode consisting of a silver wire in 0.1 M $[^n\text{Bu}_4\text{N}]\text{[PF}_6]\text{/DMSO}$ separated from the bulk solution by a Vycor tip. The standard three electrode cell was utilized in a drybox with an inert atmosphere. Ferrocene was added as an internal reference and typically was found at +0.75 V under these conditions.

**Computational Details.** Density functional theory (DFT) calculations were performed with the hybrid Becke-3 parameter exchange functional and the Lee-Yang-Parr nonlocal correlation functional (B3LYP)[41] implemented in the Gaussian03 (Revision B.04) program suite[42] in conjunction with the 6-31G* basis set for all non-metal atoms and the SDD basis set with effective core pseudo-potential (ECP) for all metal atoms.[38] The calculations were carried out on simplified models in which each isopropyl substituent was replaced with a hydrogen atom. All geometries were fully optimized at the above levels using the default optimization criteria of the program. Each stationary point was confirmed to be a minimum on the potential energy surface (PES) by a vibrational frequency analysis unless otherwise noted. Orbital analyses were completed
with GaussView.[43] To gain insight into the electronic transitions responsible for the observed UV-vis spectrum of all compounds, time-dependent density functional theory (TD-DFT) calculations were performed using the Gaussian program suite. All calculations were run on an Itanium 2 Cluster running Linux version 2.4.18 located at the Ohio Supercomputer Center.

**X-ray Structure Determination.** All single crystals were coated with Paratone oil and mounted on a quartz fiber or a nylon cryoloop affixed to a goniometer head. All diffraction data was collected using a Nonius Kappa CCD diffractometer. All work was done at between 150 to 200 °K using an Oxford Cryosystem Cryostream Cooler. Data integration was done with Denzo. Scaling and merging of data was done with Scalepack. The structures were solved by the Direct or Patterson method in SHELXS-86 or SHELXS-97.

**Preparation of \([\text{cis-Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)_2\) (1).** To a stirred solution of Mo₂(mhp)₄ (600 mg, 0.96 mmol) in 40 ml of MeCN was added 5 ml of 1.0 M Et₃OBF₄. The solution immediately turned purplish and after stirring for 1.5 hrs at 70 °C all the starting material appeared consumed. After stirring at room temperature overnight, the solvent was reduced to approximately 5 ml. Approximately 10 ml of toluene was then added to force the product to precipitate out of solution. The blue precipitate was collected on a frit, washed three times with approximately 20 ml of toluene and dried under vacuum. Overall yield: 575 mg (80%)
Microanalysis found: C 31.80; H 3.24; N 10.97; F 21.31%. B$_2$C$_{20}$F$_8$H$_{24}$N$_6$O$_2$Mo$_2$
requires: C 32.20; H 3.24; N 11.27; F 20.38%. NMR (MeCN-$d_6$): $^1$H (400 MHz) 1.57 (s, 3H), 6.68 (d, 1H), 7.16 (d, 1H), 7.65 (t, 1H). MALDI-MS: Not available

**Preparation of [Mo$_2$($mhp$)$_3$](O$_2$CCO$_2$) (2).** To a stirring solution of [Mo$_2$(C$_6$H$_6$NO)$_3$(CH$_3$CN)$_2$]$^+$BF$_4^-$ (0.300 g, 0.438 mmol) in approximately 10 ml of MeCN was added to a solution of ($^6$Bu$_4$N)$_2$(O$_2$CCO$_2$) (0.125 g, 0.219 mmol) in approximately 10 ml of MeCN. An immediate reaction took place with the formation of a red precipitate. After stirring for 30 minutes, the red precipitate was collected by filtration, washed several times with CH$_3$CN, and dried under vacuum. Overall yield: 205 mg (84%)

Microanalysis found: C 37.16; H 3.31; N 6.57%. C$_{38}$H$_{36}$N$_6$O$_{10}$Mo$_4$ requires: C 40.73; H 3.24; N 7.50%. NMR (DMSO-$d_6$): $^1$H (400 MHz) 1.62 (s, 6H), 1.75 (s, 3H), 6.40 (d, 1H), 6.49 (d, 2H), 6.73 (d, 1H), 6.83 (d, 2H), 7.34 (t, 1H), 7.42 (t, 2H). MALDI-MS: 1120.9 (100%, M$^+$_).

**Preparation of [Mo$_2$($mhp$)$_3$]$_2$(O$_2$CC$_6$F$_4$CO$_2$) (3).** The reaction was carried out under similar conditions outlined for complex 2 using 300 mg of [Mo$_2$($mhp$)$_3$(CH$_3$CN)$_2$]$^+$BF$_4^-$ (0.438 mmol) and 158 mg of ($^6$Bu$_4$N)$_2$(O$_2$CCO$_2$) (0.219 mmol). 171 mg of a purple precipitate was isolated. Overall yield: 171 mg (78%)

Microanalysis found: C 40.77; H 2.77; N 6.44; F 5.91%. C$_{44}$F$_4$H$_{36}$N$_6$O$_{10}$Mo$_4$ requires: C 41.66; H 2.86; N 6.62; F 5.99%. NMR (DMSO-$d_6$): $^1$H (400 MHz) 1.78 (s, 3H), 1.94 (s, ...
6H), 2.35 (s, 3H), 6.30 (d, 1H), 6.38 (d, 2H), 6.67 (d, 1H), 6.81 (d, 2H), 7.21 (t, 1H), 7.32 (t, 2H). MALDI-MS: 1266.9 (100%, M⁺).

**Preparation of Mo₂(mhp)₃(O₂CCH₃) (4).** To a stirring solution of Mo₂(C₆H₆NO)₃(CH₃CN)₂⁺(BF₄⁻) (450 mg, 0.657 mmol) in approximately 10 ml of MeCN was added a solution of (°Bu₄N)₂(O₂CCO₂) (198 mg, 0.657 mmol) in approximately 10 ml of MeCN. The solution immediately turned from red to orange. After stirring for 30 minutes, the orange precipitate was washed three times with approximately 20 ml of MeCN and dried under vacuum for 3 hrs. Overall yield: 320 mg (85%)

Microanalysis found: C 42.35; H 3.84; N 8.81%. C₂₀H₂₁N₃O₅Mo₂ requires: C 41.76; H 3.68; N 7.30%. NMR (THF-d₈): ¹H (400 MHz) 1.78 (s, 3H), 1.94 (s, 6H), 2.35 (s, 3H), 6.30 (d, 1H), 6.38 (d, 2H), 6.67 (d, 1H), 6.81 (d, 2H), 7.21 (t, 1H), 7.32 (t, 2H). MALDI-MS: 575.0 (100%, M⁺).

**Preparation of cis-Mo₂(mhp)₂(O₂CCH₃)₂ (5).** To a stirred solution of [cis-Mo₂(mhp)₂(CH₃CN)₄]²⁺(BF₄)₂ (160 mg, 0.21 mmol) in 10 ml of CH₃CN was added (°Bu₄N)(O₂CCH₃) (160 mg, 0.53 mmol) in 10 ml of CH₃CN. An immediate reaction took place as observed by a color change to yellow but no precipitate formed. After stirring for 30 minutes, the solvent was reduced to a minimum to precipitate a yellow product that was collected by filtration, and dried under vacuum. Overall yield: 67 mg (59.4%)
Microanalysis found: C 36.51; H 3.87; N 5.08%. \( C_{16}H_{18}N_2O_6\) requires: C 36.52; H 3.45; N 5.32%. NMR (THF-\(d_8\)): \( ^1H \) (400 MHz) 1.71 (s, 3H), 2.49 (s, 3H), 6.34 (d, 1H), 6.79 (d, 1H), 7.27 (t, 1H). MALDI-MS: 525.9 (100%, \( M^+ \)).

**Attempted preparation of \([\text{Mo}_2(\text{mhp})_2(\text{O}_2\text{CCO}_2)]_4\).** To a stirred solution of \([\text{cis-Mo}_2(\text{mhp})(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)_2\) (426 mg, 0.64 mmol) in 10 ml of CH\(_3\)CN was added \((\text{Bu}_4\text{N})_2(\text{O}_2\text{CCO}_2)\) (367 mg, 0.64 mmol) in 10 ml of CH\(_3\)CN. An immediate reaction took place with the formation of an apparent red precipitate. After stirring for 30 minutes, the crude product could not be collected by filtration and was re-evaluated to be an oil. The oil was collected by separation for analysis. \(^1H\) NMR and MALDI-TOF spectroscopy could only identify the product as a mixture of species.

**Attempted preparation of \([\text{Mo}_2(\text{mhp})_2(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)]_4\).** To a stirred solution of \([\text{cis-Mo}_2(\text{mhp})(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)_2\) (400 mg, 0.60 mmol) in 10 ml of CH\(_3\)CN was added \((\text{Bu}_4\text{N})_2(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)\) (387 mg, 0.60 mmol) in 10 ml of CH\(_3\)CN. An immediate reaction took place with the formation of a red precipitate. After stirring for 30 minutes, the crude product was collected by filtration, washed several times with CH\(_3\)CN, and dried under vacuum. The reaction yielded 207 mg of a red solid that was determined to be a mixture of simple pairs of dimers, molecular triangles, and molecular squares by MALDI-TOF spectroscopy.

Microanalysis found: C 36.35; H 1.98; N 4.81%. \( C_{80}H_{48}F_{16}Mo_8N_8O_{24} \) requires: C 37.29; H 1.88; N 4.35%.

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**Attempted preparation of \([\text{W}_2(\text{mhp})_4]^{n+}\).**

Method A: To a solution of \(\text{W}_2(\text{mhp})_4\) (800 mg, 1.000 mmol) in 25 mL of \(\text{CH}_2\text{Cl}_2\) and 1 mL of MeCN was added 5 ml of 1.0 M \(\text{Et}_3\text{BF}_4\). The solution immediately turned reddish green and within the first hour was green. After 2 hours, stirring was stopped and the solution was allowed to sit at room temperature overnight. No green solid was isolated by cannula removal of the mother liquor. The solution was split into two halves. Diethyl ether (~ 25 ml) was added to one half. This resulted in the precipitation of a green solid that could not be cannulated. The solvent was then removed by cannular and the green solid was dried under vacuum for 3 hrs. The yield was 440 mg of an unknown adduct of the starting material that could not be identified as the desired complex. The second half was placed in a -20 °C refrigerator over the weekend. No crystals formed.

Method B: To a stirred solution of \(\text{W}_2(\text{mhp})_4\) (400 mg, 0.500 mmol) in approximately 40 ml of acetonitrile was added iodotrimethylsilane (0.068 ml, 0.500 mmol). After stirring overnight, the volume of the solvent was reduced to a minimum. A red solid was collected by filtration and washed 2 x 10 ml of hexanes. The red solid was characterized by \(^1\text{H}\) NMR as unreacted starting material.

Method C: To a stirred solution of \(\text{W}_2(\text{mhp})_4\) (400 mg, 0.500 mmol) in approximately 40 ml of acetonitrile was added boron triiodide (0.068 ml, 0.500 mmol). After stirring overnight, the solvent was stripped to dryness. The mixture yielded no tractable product.
Method D: Approximately 40 ml of acetonitrile was added to a reaction vessel containing W$_2$(mhp)$_3$Cl$_2$ (400 mg, 0.500 mmol) and excess Zn dust (7.2 g, 110 mmol). After stirring for 1 hour, the orange solution turned red. The mixture was allowed to continue stirring overnight before working up. The mixture was then filtered over Celite and the solvent of the filtrate stripped to dryness. The red solid was characterized by $^1$H NMR as reformed W$_2$(mhp)$_4$. 
4.6 References


[38] Frisch, Æ; Frisch, M.J.; Trucks, G.W. *Gaussian 03 User's Reference*; Gaussian Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 06492.


CHAPTER 5

HIGHER ORDER OLIGOMERS USING DIMOLYBDENUM COMPLEXES WITH MIXED AMIDINATE-CARBOXYLATE LIGANDS.

5.1 Introduction

Applications for conjugated polymers such as polyacetylene, poly-p-phenylenes, and poly-p-phenylene vinylenes have been well recognized over the past few decades.[1] These materials are semiconductors with tunable band gaps that may be doped to show significant conductivity. They offer many interesting properties, such as nonlinear optical properties, electronic conductivity, and luminescence. Organic light-emitting diodes, OLEDs, have already achieved significant success in manufacturing.[2] Other conjugated polymers could be useful in a wide range of applications including chemical sensors, electroluminescent devices, electrocatalysis, batteries, smart windows, and memory devices.[1, 3, 4]

Metallated conjugated polymers are an important new class of materials due to the coupling of chemical, optical and electronic properties of the metal moiety to the polymer.[5] The inclusion of metal units into organic polymers offers potential in the area of hybrid organic-inorganic materials. A significant number of metallated conjugated polymers have already been prepared and studied.[4, 6, 7] Wolf categorized
metallated conjugated polymers into three classes as shown in Figure 5.1.[4] Class A and B represent conjugated polymers with side chains that are electronically insulated or coupled metal units, respectively. In Class A, the polymer acts as a conductive support and the original properties of the metal unit are relatively undisturbed. In Class B, the polymer and the metal unit are electronically coupled and each can influence the properties of the other. Class C represents incorporating metal units into the backbone of the polymer. This makes strong electronic interactions possible.

![Diagram of metallated conjugated polymers](image)

**Figure 5.1** Class representations of metallated conjugated polymers.

The idea of connecting $M_2$ units together with bifunctional linkers to form Class C polymers has been studied over the last few decades.[8-11] The $M_2$ units can be incorporated through equatorial or axial coordination as shown in Figure 5.2. These will be referred to as perpendicular and parallel polymers based on the relative orientation of the M-M axis to the direction of the polymer chain, respectively.
It was reasoned that the use of mixed amidinate-carboxylate complexes from Chapter 3 may be suitable starting materials for perpendicular metallated conjugated polymers. Chapter 5 will briefly outline the preliminary findings of this work. Section 5.2 looks at the methodology used and section 5.3 reports the preliminary findings of building metallated conjugated oligomers. Section 5.4 identifies initial conclusions while section 5.5 is the experimental section.

5.2 Methodology

The building of higher order oligomers is often thwarted by loss of geometry control and/or solubility as previously discussed. The mixed amidinate-carboxylate complexes from Chapter 3 had several advantageous characteristics. First, the isopropyl groups on the amidinates increased the solubility of the complexes. Second, ligand scrambling reactions showed the more basic amidinate ligands were less labile than the carboxylate ligands. This would aid in preferred carboxylate ligand exchange and help
maintain geometry control. Third, the unique *trans*-geometry of ligands should favor linear propagation and deter against the formation of cyclic oligomers such as loops, triangles, or squares.

The synthetic strategy was to employ a carboxylate exchange reaction using a bifunctional diacid bridge to replace the acetate ligands on the starting material and form linear oligomers or metallated conjugated polymers as shown in Scheme 5.1. The acetate groups were expected to be replaced preferentially over the more basic amidinate ligands. For the purpose of this study, the use of *trans*-Mo$_2$(O$_2$CCH$_3$)$_2$((iPrN)$_2$CC≡CPh)$_2$ and terephthalic acid were arbitrarily chosen. For simplicity, the M$_2$ units with supporting ancillary ligands will be illustrated as M$_2$ while the bifunctional bridge will be illustrated as B. The product would therefore be a co-polymer of the general shorthand form [-M$_2$-B-]$_n$.

\[\text{trans-M}_2(\text{amidinate})_2(\text{O}_2\text{CCH}_3)_2 + \text{HO}_2\text{C-X-CO}_2\text{H} \xrightarrow{\text{solvent}} [\text{M}_2(\text{amidinate})_2(\text{O}_2\text{C-X-CO}_2)_2]_n + 2\text{HO}_2\text{CCH}_3\]

\[\text{M}_2(\text{O}_2\text{CCH}_3)_2 + \text{H}_2\text{B} \xrightarrow{\text{solvent}} [-\text{M}_2\text{-B-}]_n\]

where M = Mo, W and n = number of repeating units

**Scheme 5.1** Carboxylate exchange route to proposed metallated conjugated polymers with corresponding shorthand notation (blue).
As the chain length grew, it was anticipated that the solubility of the product would decrease and precipitate out of solution. The overall chain length would therefore be determined by the solubility of the product. Hopefully, this would correspond to a discreet product with a fixed chain length and not a mixture of similar chain lengths. This fixed chain length should also be dependent on the solvent. Since the mixed amidinate-carboxylate complexes are soluble to some degree in any solvent, the effects of various solvents such as ethanol and hexane could be studied.

5.3 Metallated conjugated oligomers

Nuclear magnetic resonance, mass spectroscopy and elemental analysis were chosen to provide initial verification and characterization of products. From the first reaction, it quickly became apparent that mixtures of products were being formed. $^1$H NMR spectroscopy was unable to resolve the type or number of species due to overlapping resonances. MALDI-TOF mass spectrometry, however, was very useful in resolving both the type and the number of species present. Unfortunately, this information is qualitative but not quantitative in nature. The isotopic patterns of an $M_2$ unit and multiples of $M_2$ units are unique and could be used as a fingerprinting tool.

The first reaction was run in THF for 20 days. Analysis of this reaction by MALDI-TOF mass spectrometry showed a series of molecular weights corresponding to the progressive construction of a metallated conjugated oligomer with one to four $M_2$ units as shown in Figure 5.3. The isotopic patterns and molecular weights correspond to
the formation of a simple pair of dimers (M₂-B-M₂), the start of a trimer (M₂-B-M₂-B), a trimer (M₂-B-M₂-B-M₂), the start of a tetramer (M₂-B-M₂-B-M₂-B), and a tetramer (M₂-B-M₂-B-M₂-B-M₂). The formation of molecular loops, triangles, or squares was not observed. This implies the rigid trans-geometry of the starting material was being preserved. Elemental analysis of this reaction mixture using a polymer molecular formula corresponding to the co-polymer repeating unit (M₂-B) did not agree well with theoretical predictions. The percentage of carbon, hydrogen and nitrogen were all lower than expected indicating no conclusive trend for analysis.

Figure 5.3 MALDI-TOF spectrum of trans-Mo₂(O₂CCH₃)₂(PrN)₂CC≡CPh₂ and terephthalic acid reaction in THF generating a mixture of chain lengths with one, two, three, and four M₂ units.
The second reaction was run in ethanol for 20 days. Analysis of this reaction by MALDI-TOF showed several molecular species including those corresponding to the formation of a simple pair of dimers and a trimer as shown in Figure 5.4. The isotopic patterns and molecular weights correspond to the formation of a simple pair of dimers ($M_2$-$B$-$M_2$), and a trimer ($M_2$-$B$-$M_2$-$B$-$M_2$). Precursors to higher order products (i.e., those with an additional bridge) were not observed. The other MALDI-TOF peaks could not be positively identified. No elemental analysis was conducted.

**Figure 5.4** MALDI-TOF spectrum of *trans*-Mo$_2$(O$_2$CCH$_3$)$_2$((PrN)$_2$CC≡CPh)$_2$ and terephthalic acid reaction in ethanol generating a mixture of chain lengths with one, two, and three $M_2$ units.
The third reaction was run in hexanes for 20 days. Analysis of this reaction by MALDI-TOF showed several molecular species including those corresponding to the formation of a simple pair of dimers as shown in Figure 5.5. The isotopic patterns and molecular weights correspond to the formation of a simple pair of dimers \((M_2-B-M_2)\). Precursors to higher order products (i.e., those with an additional bridge) are not observed. The other MALDI-TOF mass spectrometry peaks could not be positively identified. Elemental analysis of this reaction mixture using an average molecular formula corresponding to a simple pair of dimers agreed well with theoretical predictions.

![MALDI-TOF spectrum](image)

**Figure 5.5** MALDI-TOF spectrum of \(\text{trans-Mo}_2(O_2CCH_3)_2((^i\text{PrN})_2CC\equiv\text{CPh})_2\) and terephthalic acid reaction in hexanes generating a mixture of starting material and simple pair of dimers.
Solvent effects therefore played an important role in chain growth but, in all cases, reactions did not go to completion. Significant amounts of starting material were always present after weeks of stirring. This may be due to several factors including poor solubility of the diacid bridge, reduced ligand lability of mixed amidinate-carboxylate complexes, and steric factors associated with mixed amidinate-carboxylate complexes. In the later, the isopropyl groups of the amidinate ligands block to a degree the axial sites of the paddlewheel complexes. Axial coordination of the bridge is believed to be mechanistically important for ligand exchange.[12]

Based on these initial findings, it was rationalized that a new strategy employing a metathesis reaction with solvento complexes may be more advantageous. In a metathesis reaction, the reaction rate should be kinetically faster and there should be less likelihood of equilibrium mixtures or side reactions as previously discussed. The required building block for this strategy would be a \( [\text{trans-Mo}_2(\text{amidinate})_2(\text{CH}_3\text{CN})_4]^{2+} \) dication species. This synthetic reaction path is illustrated in Scheme 5.2. Based on the inability to form ditungsten cations in Chapter 4, this synthetic scheme was not considered viable for the tungsten analogs but its investigation is warranted.

\[
[\text{trans-Mo}_2(\text{amidinate})_2(\text{CH}_3\text{CN})_4]^{2+}[\text{BF}_4^-]_2 + Q^+2(\text{O}_2\text{C-X-CO}_2)^{2-} \xrightarrow{\text{CH}_3\text{CN}} [\text{M}_2(\text{amidinate})_2(\text{O}_2\text{C-X-CO}_2)]_n + 2Q^+[\text{BF}_4^-]
\]

Where \( M = \text{Mo} \) and \( Q^+ = \text{quartenary ion} \)

**Scheme 5.2** Metathesis reaction with solvento complexes route to proposed metallated conjugated polymers.
Although these types of *trans*-geometry solvento complexes are not known, there were two possible synthetic paths that appeared plausible. The first path was the treatment of a *trans*-Mo$_2$(amidinate)$_2$(O$_2$CCH$_3$)$_2$ complex with Meerwein’s reagent similar to the work done with dications in Chapter 4. The desire was to preferentially replace the more labile acetate ligands over the more basic amidinate ligands in the mixed amidinate-carboxylate complexes with coordinating CH$_3$CN molecules. It was also hoped that the amidinate ligands with the isopropyl groups would maintain the *trans*-geometry due to steric factors.

The second path was the treatment of the known [Mo$_2$(CH$_3$CN)$_{10}$]$^{4+}$(BF$_4$)$_4$ tetracation with two equivalences of the lithium salt of an amidinate ligand similar to the work done in Chapter 3. This required being able to control ligand substitution and maintaining a *trans*-geometry once again with the isopropyl groups of the amidinate ligand due to steric factors.

Both reaction paths to form the required *trans*-building block with the previously selected *trans*-Mo$_2$(O$_2$CCH$_3$)$_2$((iPrN)$_2$CC≡CPh)$_2$ were conducted with unfavorable results. In the first case, treatment of the mixed amidinate-carboxylate complex with Meerwein’s reagents formed a dication species. By $^1$H NMR spectroscopy, however, the product can be formulated as a [Mo$_2$(O$_2$CCH$_3$)((iPrN)$_2$CC≡CPh)(CH$_3$CN)$_4$][(BF$_4$)$_2$ species. Full characterization of this product was deferred since it was not the target complex. In the second case, the addition of a lithium salt of an amidinate ligand to the tetracation in solution lead to apparent decomposition of starting materials and yielded no tractable product. The initial failure to synthesize the [*trans*-
Mo$_2$(amidinate)$_2$(CH$_3$CN)$_4$$^{2+}$ dication species prevented the investigation of building the desired metallated conjugated polymers via a metathesis reaction with solvento complexes.

5.4 Summary and conclusion

Preliminary results indicate that molecular assemblies of the general form L(L')$_2$Mo$_2$-[Mo$_2$(L')$_2$-bridge]$_n$-Mo$_2$(L')$_2$(L) where L is a carboxylate group such as acetate, L' is an amidinate group such as (iPrN)$_2$CC≡CPh, M is molybdenum and n is 0, 1, or 2 can be prepared. The product regrettably is not discreet and a mixture of chain lengths is observed. Based on solubility, only higher order assemblies are formed rather than true metallated conjugated polymers. The preliminary investigation used only mixed amidinate-carboxylate complexes of dimolybdenum since they were more readily available than the tungsten analogs. The use of ditungsten complexes are, however, expected to have similar results in carboxylate exchange reactions. Work is continuing towards the synthesis of metallated conjugated polymers using mixed amidinate-carboxylate complexes.

5.5 Experimental details

All reactions were carried out under an inert atmosphere of UHP-grade argon or nitrogen using standard Schlenk techniques and under a dry oxygen-free nitrogen atmosphere using standard glovebox techniques. All solvents were dried and degassed by standard methods prior to use. THF and diethyl ether was dried by refluxing over
sodium/benzophenone while toluene and hexanes were dried by refluxing over sodium metal. Ethanol was dried by refluxing over magnesium ethoxide.

The starting material, \( \text{trans-Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{iPrN})_2\text{CC}≡\text{CPh})_2 \), was prepared according to the literature procedures in Chapter 3. Starting material, \([\text{Mo}_2(\text{CH}_3\text{CN})_{10}]^{4+}(\text{BF}_4^-)_4[13]\), was prepared according to the literature procedures. Terephthalic acid was purchased from commercial sources and used as received.

**Physical Measurements.** NMR spectra were recorded on a 400 MHz Bruker DPX spectrometer. All \(^1\)H NMR chemical shifts are reported in ppm relative to the protio impurity in MeCN-\(d_3\) at 1.53 ppm, THF-\(d_8\) at 3.58 ppm, or benzene-\(d_6\) at 7.15 ppm from a 90% benzene / 10% THF mixture by weight. UV-visible spectra were recorded at room temperature using a Perkin-Elmer Lambda 900 spectrometer. Microanalyses were carried out by Atlantic Microlab, Inc. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded at OSU’s Campus Chemical Instrument Center (CCIC) using a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were run pure or mixed with dithrinol matrix to aid in the flight of the molecule.

**Attempted preparation of [-Mo\(_2\)\((\text{iPrN})_2\text{CC}≡\text{CPh})_2(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)\)-\(n\).**

Solvent 1: 230 mg of \( \text{trans-Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{iPrN})_2\text{CC}≡\text{CPh})_2 \) (0.3 mmol) and 50 mg of terephthalic acid (0.3 mmol) were mixed at room temperature in approximately 25 ml of THF. The solution was red in color and showed terephthalic acid suspended. After 20 days, the solution remained red but no terephthalic acid was visible. The mixture was centrifuged, solvent was canulared off, and the remaining solid was dried under vacuum. \(^1\)H NMR spectrum indicated a mixture of products with overlapping resonances.
Analysis by MALDI-TOF indicated low weight oligomers with mono-, di-, tri- or tetra-Mo$_2$ units.

Microanalysis found: C 50.94; H 4.88; N 5.55%. $C_{38}H_{42}N_4O_4Mo_2$ (polymer) requires: C 56.30; H 5.22; N 6.91%.

Solvent 2: This reaction was carried out under similar conditions outlined for the initial reaction using 230 mg of trans-Mo$_2$(O$_2$CCH$_3$)$_2$((iPrN)$_2$CC≡CPh)$_2$ (0.3 mmol) and 50 mg of terephthalic acid (0.3 mmol) in approximately 25 ml of ethanol. A red solid was isolated by centrifugation. $^1$H NMR spectrum indicated a mixture of products with overlapping resonances. Analysis by MALDI-TOF indicated low weight oligomers with mono-, di-, and tri-Mo$_2$ units. No elemental analysis was conducted.

Solvent 3: This reaction was carried out under similar conditions outlined for the initial reaction using 230 mg of trans-Mo$_2$(O$_2$CCH$_3$)$_2$((iPrN)$_2$CC≡CPh)$_2$ (0.3 mmol) and 50 mg of terephthalic acid in approximately 25 ml of hexanes. A red solid was isolated by centrifugation. $^1$H NMR spectrum indicated a mixture of products with overlapping resonances. Analysis by MALDI-TOF indicated low weight oligomers with mono- and di-Mo$_2$ units.

Microanalysis found: C 55.25; H 5.51; N 6.59%. $C_{72}H_{86}N_8O_8Mo_4$ (simple pairs of dimers) requires: C 54.90; H 5.50; N 7.11%.
**Attempted preparation of [trans-Mo$_2$((^PrN)$_2$CC≡CPh)$_2$]$^{2+}$.**

Method A: To a solution of 380 mg of *trans*-Mo$_2$(O$_2$CCH$_3$)$_2$((^PrN)$_2$CC≡CPh)$_2$ (0.5 mmol) in 10 ml of CH$_2$Cl$_2$ and 2.5 ml of MeCN was added 330 mg of Me$_3$OBF$_4$ (2.25 mmol). Within 1h all of the solid material had dissolved and the solution was bright red. After stirring overnight, the reaction mixture was concentrated and cooled to -20 °C. After several days, red crystals formed. The product was isolated by removal of the mother liquor, washing with diethyl ether, and drying under vacuum. $^1$H NMR characterized the product as a [Mo$_2$(O$_2$CCH$_3$)((^PrN)$_2$CC≡CPh)(CH$_3$CN)$_4$](BF$_4$)$_2$ species. Full characterization of this product was deferred since it was not the target complex.

Method B: 0.16 ml of N,N'-diisopropylcarbodiimide (1.0 mmol) was dissolved in approximately 25 ml of THF and cooled to 0 °C. 5 ml of 1.0 M lithium phenylacetylide (1.0 mmol) in THF was added to the mixture. The solution was allowed to warm slowly to room temperature. After stirring overnight, it was used in situ for the next reaction. A solution of 0.475 g of dimolybdenum tetracation, [Mo$_2$(CH$_3$CN)$_{10}$]$^{4+}$(BF$_4$)$_4$, (0.5 mmol) in approximately 25 ml of CH$_3$CN was made and cooled to 0 °C. The in situ solution was cooled again to 0 °C. The in-situ solution was slowly added to the solution. The initial color change was gray-black. After stirring at room temperature overnight, the solvent was stripped to dryness and extracted with approximately 25 ml of hexanes. The solution was filter over Celite. The filrate was near colorless with no apparent product.
5.6 References


APPENDIX A

SUPPORTING INFORMATION FOR DENSITY FUNCTIONAL THEORY (DFT) STUDY OF PADDLEWHEEL COMPLEXES AND BRIDGED DIMERS
A.1 Vibrational frequency analysis

Vibrational frequency analysis including IR and Raman was performed on each model complex. Frequencies with oscillator strength of greater than 35 are reported in Table A.1. Models A, C1 and E are centrosymmetric molecules and show no coincidence of IR and Raman bands. Models B, C2 and D are non-centrosymmetric molecules and show Raman-active vibrations coincident to IR-active vibrations. These gas-phase calculations would have to be analyzed with condensed phase effects to match normal experimental data.
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**Table A.1** Selected computed IR and Raman vibrational frequency bands. * indicates IR-active and Raman-active vibration.
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<td>3082.95*</td>
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<td>3094.68</td>
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<td></td>
<td>3102.58*</td>
<td>202.8</td>
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<td>3561.99</td>
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<td>442.82</td>
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<td>Raman</td>
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<td>3557.70</td>
<td>716.7</td>
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A.2 Nuclear magnetic resonance

NMR analysis of active isotopic elements including H, C, N, O, and Mo were conducted using the Gauge-Independent Atomic Orbitals (GIAO) method to compute isotropic shielding constants. Reference molecules of CH$_4$, NH$_3$, and H$_2$O were also run in order to calculate relative chemical shifts for H, C, N, and O respectively. The natural abundance of $^1$H and $^{13}$C isotopes would allow for the easy comparison of theoretical predictions to experimental data. $^{17}$O and $^{15}$N, on the other hand, would only be available with enriched complexes due to their very low natural abundances of 0.048% and 0.37%, respectively.[1]

The results should not be considered quantitative for several reasons. These gas-phase calculations would have to be analyzed with condensed phase effects to match normal experimental data. The chosen model basis sets were not ideal for quantitative analysis. The general recommendation calls for at least a triple-$\zeta$ quality with both diffuse and polarization functions.[2] The use of an ECP also prevents the accurate analysis of absolute shielding for molybdenum atoms since the remaining basis function will have an incorrect behavior at the nuclear position.[2] See Table A.2.
<table>
<thead>
<tr>
<th>Model</th>
<th>atom</th>
<th>$\sigma$ (ppm)</th>
<th>$\delta$ (ppm)</th>
</tr>
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<td>$\text{Mo}_2(\text{O}_2\text{CH})_4$ (A)</td>
<td>H</td>
<td>22.6701 (4)</td>
<td>9.2313 (4)</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>34.6551 (4)</td>
<td>158.9667 (4)</td>
</tr>
<tr>
<td></td>
<td>O</td>
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<td>352.7691 (8)</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>-958.6355 (2)</td>
<td></td>
</tr>
<tr>
<td>$\text{Mo}_2(\text{O}_2\text{CH})_3(\text{HNCHNH})$ (B)</td>
<td>H</td>
<td>22.9015 (1)</td>
<td>8.9999 (1)</td>
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<td></td>
<td></td>
<td>22.9228 (2)</td>
<td>8.9786 (2)</td>
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<td>23.5531 (1)</td>
<td>8.3483 (1)</td>
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<td></td>
<td></td>
<td>23.1969 (2)</td>
<td>8.7045 (2)</td>
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<tr>
<td></td>
<td>C</td>
<td>35.6212 (1)</td>
<td>158.0006 (1)</td>
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<tr>
<td></td>
<td></td>
<td>36.6511 (2)</td>
<td>156.9707 (2)</td>
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<td></td>
<td>49.5651 (1)</td>
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<td>Mo</td>
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<td>trans-$\text{Mo}_2(\text{O}_2\text{CH})_2(\text{HNCHNH})_2$ (C1)</td>
<td>H</td>
<td>23.7996 (4)</td>
<td>8.1018 (4)</td>
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<tr>
<td></td>
<td></td>
<td>23.1320 (2)</td>
<td>8.7694 (2)</td>
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<td>23.7020 (2)</td>
<td>8.1994 (2)</td>
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<td>C</td>
<td>38.6719 (2)</td>
<td>154.9499 (2)</td>
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<td></td>
<td>49.0108 (2)</td>
<td>144.6110 (2)</td>
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<td>N</td>
<td>57.4764 (4)</td>
<td>198.1763 (4)</td>
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<td></td>
<td>O</td>
<td>-9.9182 (4)</td>
<td>327.3676 (4)</td>
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<td></td>
<td>Mo</td>
<td>-903.5965 (2)</td>
<td></td>
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<tr>
<td>cis-$\text{Mo}_2(\text{O}_2\text{CH})_3(\text{HNCHNH})_2$ (C2)</td>
<td>H</td>
<td>23.7714 (4)</td>
<td>8.1300 (4)</td>
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<td></td>
<td>23.0081 (2)</td>
<td>8.8933 (2)</td>
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<tr>
<td></td>
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<td>23.6907 (2)</td>
<td>8.2107 (2)</td>
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<tr>
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<td>C</td>
<td>37.4100 (2)</td>
<td>156.2118 (2)</td>
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<td>51.8921 (2)</td>
<td>141.7297 (2)</td>
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<tr>
<td></td>
<td>Mo</td>
<td>-902.4927 (2)</td>
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*Table A.2* Computed isotropic absolute shielding constants ($\sigma$) and relative chemical shifts ($\delta$) in ppm. Values in parentheses indicated the degeneracy in complex.
<table>
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<tr>
<th>Model</th>
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<th>σ</th>
<th>δ</th>
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<td>Mo₂(O₂CH)(HNCHNH)₃ (D)</td>
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<tr>
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<td></td>
<td>23.8525 (2)</td>
<td>8.0489 (2)</td>
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<tr>
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<td></td>
<td>23.9192 (1)</td>
<td>7.9822 (1)</td>
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<tr>
<td></td>
<td></td>
<td>24.2150 (2)</td>
<td>7.6864 (2)</td>
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<tr>
<td></td>
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<td>24.3248 (4)</td>
<td>7.5766 (4)</td>
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<td></td>
<td>C</td>
<td>38.9277 (1)</td>
<td>154.6941 (1)</td>
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<td></td>
<td>50.7663 (2)</td>
<td>142.8555 (2)</td>
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<td></td>
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<td>53.9153 (1)</td>
<td>139.7065 (1)</td>
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<td>63.7323 (4)</td>
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<td>O</td>
<td>-3.1697 (2)</td>
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<td></td>
<td>Mo</td>
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<td></td>
</tr>
<tr>
<td>Mo₂(HNCHNH)₄ (E)</td>
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<td>24.7896 (8)</td>
<td>7.1118 (8)</td>
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<td>23.9733 (4)</td>
<td>7.9281 (4)</td>
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<td>C</td>
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<td>N</td>
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<tr>
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<td>Mo</td>
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Absolute shielding constants for reference molecules

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<th>exptl[3]</th>
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<td>CH₄</td>
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<td>C</td>
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<td>NH₃</td>
<td>N</td>
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<tr>
<td>H₂O</td>
<td>O</td>
<td>317.4494</td>
<td>344.0</td>
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A.3 Methyl effect

Some additional calculations were done with methyl substituents vice hydrogen on models A and E to assess the impact of alkyl substituents as shown in Figure A.1 on observable properties.

Figure A.1 Additional model structures, assigned identification letter, chemical formula, and applied symmetry.

<table>
<thead>
<tr>
<th>A'</th>
<th>Mo₂(O₂CMe)₄</th>
<th>C₄h</th>
<th>E'</th>
<th>Mo₂(MeNCMeNMe)₄</th>
<th>C₄h</th>
</tr>
</thead>
</table>

The A' model yielded self-consistent results that were verified to be a minimum. The E' model gave self-consistent results in both C₄h and C₅ symmetry. Frequency analysis of these optimized geometries, however, showed them to be a transition state with 4 imaginary frequencies each. Analysis of all imaginary frequencies showed them to be related to methyl group fluctuation. Attempts to optimize the E' model in C₁ symmetry was unsuccessful and resulted in atomization of the complex. The E' model is expected to have a very shallow energy well due the methyl group fluctuation.

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expected geometry of the $C_{4h}$ optimization is expected to be close enough in energy to a
local minimum for use in qualitative analysis. An effort to optimize the structure to a
local minimum is on-going.

The effect of the methyl substituents on the basic paddlewheel geometry was
minimal as seen in Table A.3. This suggests that the observable properties of these
methyl complexes will be qualitatively similar.

<table>
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<tr>
<th></th>
<th>Mo$_2$(O$_2$CR)$_4$</th>
<th></th>
<th>Mo$_2$(RNCRNR)$_4$</th>
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<tr>
<td></td>
<td>R=H</td>
<td>R=Me</td>
<td>R=H</td>
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<tr>
<td>Mo-Mo</td>
<td>2.119</td>
<td>2.114</td>
<td>2.132</td>
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<td>Mo-O</td>
<td>2.120</td>
<td>2.119</td>
<td>2.165</td>
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<td>O-C</td>
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<td>1.279</td>
<td>1.328</td>
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<td>MoMoO</td>
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<td>91.63</td>
<td>92.17</td>
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<tr>
<td>MoOC</td>
<td>116.54</td>
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<td>OCO</td>
<td>123.57</td>
<td>121.65</td>
<td>119.70</td>
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<tr>
<td>OMoO</td>
<td>89.95</td>
<td>89.95</td>
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<td>OMoMoO</td>
<td>0.0 (fixed)</td>
<td>0.0 (fixed)</td>
<td>0.0 (fixed)</td>
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Table A.3 Comparison of model complex hydrogen and methyl substituents.

A comparison of molecular orbitals shows a similar trend as well as a new unique
trend. The MO energies are higher for the $M_2 \delta$ orbitals in both methyl models as shown
in Figure A.2. Although this change is not as significant as that predicted in going from
carboxylates ligands to formamidinates ligands, it suggests that alkyl substituents also
play a role in tuning the ionization potential of these complexes.

The new trend is seen in the $L \pi^*$ orbitals. In the methyl carboxylate complex, the
$L \pi^*$ orbital is slightly closer in energy to the corresponding $M_2 \delta$ orbital than that
observed in the formate complex. This fact is easily observed for methyl amidinate. In
the methyl amidinate complex, the L π* orbital is even lower in energy than the formamidinate L π* orbital. This suggests that the methyl substituents play a role in tuning the metal-to-ligand charge transfer band. This is most likely the result of the methyl group mixing with the ligand orbitals to lower the overall π* orbital energy. This suggests that electron donor and acceptor substituents on amidinate ligands may have significant impact on the metal-to-ligand charge transfer band as well the overall electronic properties of the complexes.

![Molecular Orbital Comparison](image)

**Figure A.2** MO comparison of M₂ δ and L π* energies of hydrogen and methyl model complexes.
A.4 References


APPENDIX B

SUPPORTING INFORMATION FOR DIMOLYBDENUM AND DITUNGSTEN PADDLEWHEEL COMPLEXES WITH MIXED AMIDINATE-CARBOXYLATE LIGANDS
B.1 UV-vis spectrum

![UV-vis spectrum](image)

**Figure B.1.** UV-vis spectra of Mo$_2$(O$_2$CCH$_3$)$_2$((^iPrN)$_2$CMe)$_2$ (3A) complex in THF at room temperature.
Figure B.2. UV-vis spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{i}^3\text{PrN})_2\text{C}≡\text{CtBu})_2$ (4A) complex in THF at room temperature.

Figure B.3. UV-vis spectra of $\text{W}_2(\text{O}_2\text{CCH}_3)_2(\text{i}^3\text{PrN})_2\text{C}≡\text{CtBu})_2$ (4B) complex in THF at room temperature.
Figure B.4. UV-vis spectra of Mo\(_2\)(O\(_2\)CCH\(_3\))\(_2\)((i$^\dagger$PrN)\(_2\)C≡C\(^t\)Bu)\(_2\) (5A) complex in THF at room temperature.

Figure B.5. UV-vis spectra of W\(_2\)(O\(_2\)CCH\(_3\))\(_2\)((i$^\dagger$PrN)\(_2\)C≡C\(^t\)Bu)\(_2\) (5B) complex in THF at room temperature.
**Figure B.6.** UV-vis spectra of Mo$_2$(O$_2$CCH$_3$)$_2$((^iPrN)$_2$CC≡CFc)$_2$ (6A) complex in THF at room temperature.

**Figure B.7.** UV-vis spectra of W$_2$(O$_2$CCH$_3$)$_2$((^iPrN)$_2$CC≡CFc)$_2$ (6B) complex in THF at room temperature.
B.2 Electrochemistry data

Figure B.8. a) Differential pulse voltammogram and b) cyclic voltammogram of Mo$_2$(O$_2$CCH$_3$)$_2$(('PrN)$_2$CMe)$_2$ (3A) in THF/0.1 M [Bu$_4$N][PF$_6$].
Figure B.9. a) Differential pulse voltammogram and b) cyclic voltammogram of Mo$_2$(O$_2$CCH$_3$)$_2$((’PrN)$_2$CC≡C’Bu)$_2$ (4A) in THF/0.1 M [’Bu$_4$N][PF$_6$].
Figure B.10. a) Differential pulse voltammogram and b) cyclic voltammogram of \( \text{W}_2(\text{O}_2\text{CCH}_3)_2(\text{'PrN})_2\text{CC}==\text{CtBu})_2 \) (4B) in THF/0.1 M \([\text{'Bu}_4\text{N}][\text{PF}_6]\).
Figure B.11. a) Differential pulse voltammogram and b) cyclic voltammogram of Mo₂(O₂CCH₃)₂(PrN)₂CC≡CPh₂ (5A) in THF/0.1 M [Bu₄N][PF₆].
Figure B.12. a) Differential pulse voltammogram and b) cyclic voltammogram of W$_2$(O$_2$CCH$_3$)$_2$((PrN)$_2$CC≡CPh)$_2$ (5B) in THF/0.1 M [Bu$_4$N][PF$_6$].
Figure B.13. a) Differential pulse voltammogram and b) cyclic voltammogram of Mo$_2$(O$_2$CCH$_3$)$_2$((PrN)$_2$CC≡CFc)$_2$ (6A) in THF/0.1 M [Bu$_4$N][PF$_6$].
Figure B.14. a) Differential pulse voltammogram and b) cyclic voltammogram of $W_2(O_2CCH_3)_2((^iPrN)_2CC\equiv CFc)_2$ ($6B$) in THF/0.1 M $[^{t}Bu_4N][PF_6]$. 

Potential vs ferrocene$^{0+/mV}$
B.3 Crystallographic data

Molecular formula                   C38 H54 Li2 N4 O2
Formula weight                      612.73
Temperature                         200(2) K
Wavelength                         0.71073 Å
Crystal system                      Triclinic
Space group                         P 1
Unit cell dimensions                a = 9.724(1) Å   α = 93.575(5) °
b = 10.008(1) Å   β = 91.225(5) °
c = 19.713(2) Å   γ = 90.848(4) °
Volume                              1914.0(3) Å³
Z                                    2
Density (calculated)                1.063 Mg/m³
Absorption coefficient              0.065 mm⁻¹
F(000)                              664
Crystal size                        0.27 x 0.35 x 0.38 mm
Theta range for data collection    2.04 to 25.05 °
Index ranges                        -11≤h≤11, -11≤k≤11, -23≤l≤23
Reflections collected               36676
Independent reflections            6769 [R(int) = 0.028]
Refinement method                  Full-matrix least-squares on F²
Data / restraints / parameters     6769 / 2 / 428
Goodness-of-fit on F²               1.007
Final R indices [I>2σ(I)]          R1 = 0.0518, wR2 = 0.1348
R indices (all data)               R1 = 0.0676, wR2 = 0.1471
Largest diff. peak and hole        0.184 and -0.248 e/Å³

Table B.1. Crystallographic details for Li⁺[(PrN)₂CC≡CPh]⁻ (1)
File: Chisholm 1141
Empirical formula  
C15 H25 Li N2 O S  
Formula weight  
288.37  
Temperature  
200(2) K  
Wavelength  
0.71073 Å  
Crystal system  
Monoclinic  
Space group  
P21/c  
Unit cell dimensions  
a = 9.173(1) Å  
b = 10.970(1) Å  
β = 95.953(7) °  
c = 17.190(2) Å  
Volume  
1720.5(3) Å³  
Z  
4  
Density (calculated)  
1.113 Mg/m³  
Absorption coefficient  
0.185 mm⁻¹  
F(000)  
624  
Crystal size  
0.15 x 0.23 x 0.31 mm  
Theta range for data collection  
2.21 to 25.04 °  
Index ranges  
-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20  
Reflections collected  
27382  
Independent reflections  
3031 [R(int) = 0.036]  
Refinement method  
Full-matrix least-squares on F²  
Data / restraints / parameters  
3031 / 9 / 221  
Goodness-of-fit on F²  
1.040  
Final R indices [I>2σ(I)]  
R1 = 0.0472, wR2 = 0.1249  
R indices (all data)  
R1 = 0.0659, wR2 = 0.1361  
Largest diff. peak and hole  
0.189 and -0.185 e/Å³

Table B.2. Crystallographic details for Li⁺[(iPrN)₂CcH₄S]⁻ (2)
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<tr>
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<td>Wavelength</td>
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<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
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<td>Unit cell dimensions</td>
<td>a = 8.3023(10) Å, α = 68.840(4)°</td>
</tr>
<tr>
<td></td>
<td>b = 9.0596(10) Å, β = 77.080(4)°</td>
</tr>
<tr>
<td></td>
<td>c = 9.5252(10) Å, γ = 65.805(5)°</td>
</tr>
<tr>
<td>Volume</td>
<td>607.03(12) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>1, 1.621 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.065 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>304</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.38 x 0.31 x 0.19 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.99 to 27.46 °</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10≤h≤10, -11≤k≤11, -12≤l≤12</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>17872 / 2771 [R(int) = 0.027]</td>
</tr>
<tr>
<td>Completeness to theta = 27.46</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Empirical from Scalepack</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2771 / 0 / 136</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.084</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0169, wR2 = 0.0432</td>
</tr>
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<td>R indices (all data)</td>
<td>R1 = 0.0180, wR2 = 0.0436</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.345 and -0.436 e/Å⁻³</td>
</tr>
</tbody>
</table>

**Table B.3.** Crystallographic details for Mo₂(O₂CCH₃)₂(Pr₂N₃CMe)₂ (3A)  
File: Chisholm1328.
Figure B.15 ORTEP diagram of the centrosymmetric Mo$_2$(O$_2$CCH$_3$)$_2$((^iPrN)$_2$CC≡CPh)$_2$ molecule (5A) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.
Molecular formula                  C34 H44 Mo2 N4 O4 and 3 THFs
Formula weight                     980.92
Temperature                        200(2) K
Wavelength                         0.71073 Å
Crystal system                     Triclinic
Space group                        P ¯1
Unit cell dimensions               a = 9.311(1) Å   α = 66.083(3) °
b = 11.735(1) Å   β = 74.895(3) °
c = 12.973(1) Å   γ = 68.780(5) °
Volume                              1197.1(2) Å³
Z                                   1
Density (calculated)               1.361 Mg/m³
Absorption coefficient             0.574 mm⁻¹
F(000)                              512
Crystal size                        0.15 x 0.31 x 0.38 mm
Theta range for data collection    2.74 to 27.44 °
Index ranges                       -12≤h≤11, -15≤k≤15, -16≤l≤16
Reflections collected              32426
Independent reflections            5452 [R(int) = 0.028]
Refinement method                  Full-matrix least-squares on F²
Data / restraints / parameters      5452 / 4 / 273
Goodness-of-fit on F²              1.036
Final R indices [I>2σ(I)]          R1 = 0.0300, wR2 = 0.0797
R indices (all data)               R1 = 0.0336, wR2 = 0.0818
Largest diff. peak and hole         0.774 and -0.742 e/Å³

Table B.4. Crystallographic details for Mo₂(O₂CCH₃)₂((iPrN)₂CC≡CPh)_2(5A)
File: Chisholm 1144
Empirical formula C34 H44 N4 O4 W2
Formula weight 940.43
Temperature 150(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P ̅1
Unit cell dimensions 
\[ a = 8.279(1) \text{ Å} \quad \alpha = 75.741(1) ^\circ \]
\[ b = 9.371(1) \text{ Å} \quad \beta = 71.498(1) ^\circ \]
\[ c = 12.082(1) \text{ Å} \quad \gamma = 78.558(1) ^\circ \]
Volume 854.18(2) Å³
Z 1
Density (calculated) 1.828 Mg/m³
Absorption coefficient 6.770 mm⁻¹
F(000) 456
Crystal size 0.12 x 0.19 x 0.27 mm³
Theta range for data collection 2.62 to 27.51°
Index ranges \(-10 \leq h \leq 10, -12 \leq k \leq 12, -15 \leq l \leq 15\)
Reflections collected 26489
Independent reflections 3913 \([R(int) = 0.0173]\)
Completeness to theta = 27.51° 99.7 %
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 3913 / 0 / 199
Goodness-of-fit on F² 1.065
Final R indices \([I>2\sigma(I)]\) R1 = 0.0169, wR2 = 0.0398
R indices (all data) R1 = 0.0190, wR2 = 0.0404
Largest diff. peak and hole 1.152 and -1.393 e.Å⁻³

Table B.5. Crystallographic details for W₂(O₂CCH₃)₂(PrN)₂CC≡CPh)₂ (5B)
File: Chisholm1317
Empirical formula: \( \text{C42 H52 Fe2 Mo2 N4 O4 and 4 THFs} \)
Formula weight: 1268.87
Temperature: 200(2) K
Wavelength: 0.71073 Å
Crystal system: Triclinic
Space group: \( P\bar{1} \)
Unit cell dimensions:
\[ a = 11.135(1) \text{ Å}, \quad \alpha = 67.157(1) ^\circ \]
\[ b = 11.862(1) \text{ Å}, \quad \beta = 78.161(1) ^\circ \]
\[ c = 12.321(1) \text{ Å}, \quad \gamma = 85.503(1) ^\circ \]
Volume: 1467.97(2) Å³
Z: 1
Density (calculated): 1.435 Mg/m³
Absorption coefficient: 0.956 mm⁻¹
F(000): 660
Crystal size: 0.12 x 0.27 x 0.27 mm³
Theta range for data collection: 2.35 to 27.51°.
Index ranges:
\[ -14 \leq h \leq 14, \quad -15 \leq k \leq 15, \quad -15 \leq l \leq 16 \]
Reflections collected: 40640
Independent reflections: 6736 [R(int) = 0.0175]
Completeness to theta = 27.51°: 99.7%
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 6736 / 0 / 371
Goodness-of-fit on F²: 1.049
Final R indices [I>2σ(I)]:
\[ R1 = 0.0355, \quad wR2 = 0.0939 \]
R indices (all data):
\[ R1 = 0.0471, \quad wR2 = 0.0996 \]
Largest diff. peak and hole: 0.957 and -0.576 e.Å⁻³

Table B.6. Crystallographic details for \( \text{Mo2(O2CCH3)2(\{iPrN\}_2CC≡CFc)}_2 (6A) \)
File: Chisholm1272.
Figure B.16 ORTEP diagram of the centrosymmetric \( \text{W}_2(\text{O}_2\text{CCH}_3)_2(\text{\\textit{i}PrN})_2\text{CC}\equiv\text{CFc})_2 \) molecule (6B) drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the corresponding unstarred atom by the crystallographic inversion center.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C42 H52 Fe2 N4 O4 W2 and 4 THFs</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1444.69</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, ( P \bar{1} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 11.051(1) \text{ Å} ), ( \alpha = 67.331(4) ^\circ )</td>
</tr>
<tr>
<td></td>
<td>( b = 11.816(1) \text{ Å} ), ( \beta = 77.860(4) ^\circ )</td>
</tr>
<tr>
<td></td>
<td>( c = 12.251(1) \text{ Å} ), ( \gamma = 85.531(4) ^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>1443.13(2) Å(^3)</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>1, 1.662 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>4.521 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>724</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.38 x 0.38 x 0.15 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.55 to 27.48 (^\circ)</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-14( \leq h \leq 14), -15( \leq k \leq 15), -15( \leq l \leq 15)</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>40553 / 6607 [R(int) = 0.051]</td>
</tr>
<tr>
<td>Completeness to theta = 27.48</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Empirical from Scalepack</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F(^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6607 / 7 / 318</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>1.032</td>
</tr>
<tr>
<td>Final R indices [I&gt;2(\sigma(I))]</td>
<td>R1 = 0.0307, wR2 = 0.0748</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0391, wR2 = 0.0781</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.419 and -1.180 e.Å(^{-3})</td>
</tr>
</tbody>
</table>

**Table B.7.** Crystallographic details for \( W_2(O_2CCH_3)_2((^{('Pr)N}_2CC\equiv CFc)_2 \) (6B)

File: Chisholm 1321
Empirical formula  C46 H52 Mo2 N4 O4 and THF
Formula weight  988.90
Temperature  293(2) K
Wavelength  0.71073 Å
Crystal system  Monoclinic
Space group  P21/n
Unit cell dimensions a = 21.482(2) Å
b = 9.609(1) Å
β = 97.634(4)°
c = 22.527(3) Å
Volume  4608.9(9) Å³
Z  4
Density (calculated)  1.425 Mg/m³
Absorption coefficient  0.595 mm⁻¹
F(000)  2048
Crystal size  0.23 x 0.18 x 0.08 mm³
Theta range for data collection  2.33 to 27.47°
Index ranges -27 ≤ h ≤ 27, -12 ≤ k ≤ 12, -29 ≤ l ≤ 29
Reflections collected  82643
Independent reflections  10574 [R(int) = 0.083]
Completeness to theta = 27.47°  99.9%
Absorption correction  Empirical from Scalepack
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  10574 / 0 / 566
Goodness-of-fit on F²  0.981
Final R indices [I>2σ(I)]  R1 = 0.0548, wR2 = 0.1214
R indices (all data)  R1 = 0.0989, wR2 = 0.1383
Largest diff. peak and hole  1.603 and -0.784 e.Å⁻³

Table B.8. Crystallographic details for Mo₂(cis-µ-O₂C-9-anthracene)₂(η²-(iPrN)₂CMe)₂ (8) File: Chisholm1390.
APPENDIX C

SUPPORTING INFORMATION FOR DIMOLYBDENUM AND DITUNGSTEN AMIDATE COMPLEXES AS BUILDING BLOCKS FOR SIMPLE MOLECULAR ASSEMBLIES
C.1 Electrochemistry data

Figure C.1. a) Differential pulse voltammogram and b) cyclic voltammogram of [Mo$_2$(mhp)$_3$]$_2$(O$_2$CCO$_2$) (2) in DMSO/0.1 M [Bu$_4$N][PF$_6$].
Figure C.2. a) Differential pulse voltammogram and b) cyclic voltammogram of $[\text{Mo}_2(\text{mhp})_3]_2(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)$ (3) in DMSO/0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$. 

Potential vs ferrocene$^{0/+}$/mV
C.2 Crystallographic data

Empirical formula  C22 H24 Mo2 N6 O2, 2(C2 H3 N), 2(B F4)
Formula weight  828.06
Temperature  150(2) K
Wavelength  0.71073 Å
Crystal system  Orthorhombic
Space group  P2₁
Unit cell dimensions  
  a = 7.26150(10) Å  \( \alpha = 90^\circ \)
  b = 12.0539(2) Å  \( \beta = 90^\circ \)
  c = 19.1113(3) Å  \( \gamma = 90^\circ \)
Volume  1672.9(4) Å³
Z  2
Density (calculated)  1.644 Mg/m³
Absorption coefficient  0.830 mm⁻¹
F(000)  824
Crystal size  0.04 x 0.08 x 0.38 mm³
Theta range for data collection  3.28 to 27.49°.
Index ranges  -9 ≤ h ≤ 9, 0 ≤ k ≤ 15, 0 ≤ l ≤ 24
Reflections collected  19161
Independent reflections  3950 [R(int) = 0.0336]
Completeness to theta = 27.49°  99.7 %
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  3950 / 1 / 221
Goodness-of-fit on F²  1.034
Final R indices [I>2sigma(I)]  R1 = 0.0282, wR2 = 0.0671
R indices (all data)  R1 = 0.0324, wR2 = 0.0687
Absolute structure parameter  0.02(4)
Largest diff. peak and hole  0.544 and -0.381 e.Å⁻³

Table C.1. Crystallographic details for \([\textit{cis}-\text{Mo}_2(\text{mhp})_2(\text{CH}_3\text{CN})_4]^{2+}(\text{BF}_4)_2\) (1)
File: Chisholm 1449.
BIBLIOGRAPHY

Chapter One


Chapter Two


Chapter Three


[29] Frisch, Æ; Frisch, M.J.; Trucks, G.W. *Gaussian 03 User's Reference*; Gaussian Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 06492.


Chapter Four


Chapter Five


Appendix A

