TERMINAL LIGAND SUBSTITUTION TRENDS OF ALKYLIDYNE-CAPPED TRINUCLEAR MOLYBDENUM CLUSTERS

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Richard Cannan Brookins

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TERMINAL LIGAND SUBSTITUTION TRENDS OF ALKYLIDYNE-CAPPED TRINUCLEAR MOLYBDENUM CLUSTERS

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Abstract

of

TERMINAL LIGAND SUBSTITUTION TRENDS OF ALKYLIDYNE-CAPPED
TRINUCLEAR MOLYBDENUM CLUSTERS

by

Richard Cannan Brookins

Alkylidyne-capped molybdenum (IV) clusters have shown applications in metal-organic reactions as heterogeneous catalysts. A series of alkylidyne-capped clusters have been synthesized and characterized using spectroscopic techniques. The inductive ability of the alkyl group on the bridging carboxylates was varied to analyze the effect on rates of terminal ligand substitution. The rate data for the first substitution step was collected using variable-temperature $^1$H NMR. Trends in reactivity for the first substitution step are supported using Hammett constants. A new trinuclear molybdenum cluster with bridging dichloroacetates has been crystallized and fully characterized. As a byproduct of this cluster under basic conditions, a new polyoxomolybdate cluster (Mo$_{10}$) was discovered. Lastly, a chloroacetate bridged trinuclear molybdenum (IV) cluster was synthesized to support the trend in reactivity that showed the rate of terminal methanol substitution increases with decreasing electron-withdrawing alkyl group character. The magnitudes of
the activation parameters reported herein for four Mo$_3^+$ clusters all indicate a D or I$_d$
reaction mechanism for terminal ligand substitution.

______________________________, Committee Chair
Jacqueline R. Houston, Ph.D

______________________________
Date
DEDICATION

I would like to dedicate this thesis to my wife Victoria, who during this experience blessed our family with two beautiful girls, Abigail Grace and Margaret Elizabeth. You all have been my inspiration and motivation, thank you for your love, support and patience.

I would also like to dedicate this thesis to my parents, June and Craig, who have always believed in me and continue to support my dreams and goals. I am forever grateful that you have taught me the value of hard work and what it brings to our lives. Thank you and I love you both very much. I would like to thank my grandparents, Gary and June Miller, for the many years of support and the great example they have set for me in my life. I love you very much and cherish the times we have together. Lastly, I would like to dedicate this thesis to a close friend and colleague, Roman Ishchuk, that I think about and miss each day. Thank you for your incredible insight my friend.

To my dog Izzy, you were the most soft-spoken and gentle dog in the world. You will be deeply missed by your family. I think about you everyday and the many times you brought me comfort during these times. I was very blessed to have you and only wish to be the man you think I am. Love you Izzy dog.
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continuing our relationships both personally and professionally. Thank you for your support.
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LIST OF ABBREVIATIONS

$\text{Mo}_3^+$ = generic alkylidyne-capped trinuclear molybdenum (IV) cluster

$\text{Mo}_3^{2+}$ = generic bi-oxo capped trinuclear molybdenum (IV) cluster

$\text{M}_3^+$ = parent trinuclear molecular ion

TLS = turnover-limiting step

$\mu_3$ = three-coordinate capping ligand or three-coordinate ligand (general)

$\mu_4$ = four-coordinate ligand

L = terminal ligand

LFSE = ligand field stabilization energies

en = ethylenediamine

Å = angstrom(s)

A = associative mechanism

D = dissociative mechanism

I = interchange mechanism

$I_d$ = interchange dissociative mechanism

$I_a$ = interchange associative mechanism

RDS = rate-determining step

$k$ = rate constant

$k_{\text{obsd}}$ = observed rate constant

$k_{\text{exp}}$ = experimental rate constant
$k_{\text{avg}} = \text{average rate constant}$

$\Delta H_{\text{obsd}}^\ddagger = \text{observed activation enthalpy}$

$\Delta S_{\text{obsd}}^\ddagger = \text{observed activation entropy}$

DMA = dimethylacetamide

MeOD-$d_4 = \text{deuterated methanol}$

NMR = nuclear magnetic resonance

VT-NMR = variable-temperature nuclear magnetic resonance

acetic acid-$d_4 = \text{deuterated acetic acid}$

$\text{CD}_3\text{NO}_2-d_3 = \text{deuterated nitromethane}$

py = pyridine

pyridine-$d_5 (\text{py-d}_5) = \text{deuterated pyridine}$

$I = \text{NMR signal intensity}$

TMS = trimethylsilyl; tetramethylsilane

TSP = 2,2,3,3-$d(4)-3-(\text{trimethylsilyl})\text{propionic acid sodium salt}$

$t_{1/2} = \text{half-life}$

$\sigma_m = \text{Hammett value at the meta-position of benzoic acid}$

$\sigma_p = \text{Hammett value at the para-position of benzoic acid}$

R = alkyl group

Mo$_{10}$ = polyoxomolybdate cluster

$^\circ \text{C} = \text{degrees Celsius}$

Anal. = combustion elemental analysis
calcd = calculated

CIF = crystallographic information file

\( \text{cm}^{-1} = \text{wavenumber(s)} \)

\( \delta = \text{chemical shift reference in parts per million} \)

\( S_{N1} = \text{unimolecular nucleophilic substitution} \)

\( S_{N2} = \text{bimolecular nucleophilic substitution} \)

\( \text{eq} = \text{equation} \)

\( \text{FT} = \text{Fourier transform} \)

\( \text{h} = \text{hour(s)} \)

\( \text{IR} = \text{infrared} \)

\( \text{Me} = \text{methyl} \)

\( \text{MHz} = \text{megahertz} \)

\( \text{min} = \text{minute(s); minimum} \)

\( \text{mM} = \text{millimolar (millimoles per liter)} \)

\( \text{ppm} = \text{part(s) per million} \)

\( \text{obsd} = \text{observed} \)

\( \text{rel} = \text{relative} \)

\( \text{rt} = \text{room temperature} \)

\( \text{q} = \text{quartet (spectral)} \)

\( s = \text{singlet (spectral); second(s); strong (spectral)} \)

\( t = \text{triplet (spectral)} \)
m = multiplet (spectral); milli

\( t \) = time; temperature in units of degrees Celsius (°C)

T = absolute temperature in units of kelvins (K)

temp = temperature

TS = transition state

UV = ultraviolet

vis = visible

unsub = un-substituted trinuclear species

mono-sub = mono-substituted trinuclear species

di-sub = di-substituted trinuclear species

tri-sub = tri-substituted trinuclear species (fully substituted)

BDE = bond dissociation energy

br = broad (spectral)

vw = very weak (spectral)

m = medium (spectral)

vs = very strong (spectral)

w = weak (spectral)

sh = shoulder (spectral)
Chapter 1

INTRODUCTION

1.1 Applications, scientific impact, and research objective

Trinuclear alkylidyne-capped molybdenum clusters with generic formula $[\text{Mo}_3(\mu_3-\text{O})(\mu_3-\text{CR})(\mu_2\text{O}_2\text{CR})_6(L)_3]^+$ (Figure 1) (abbreviated as $\text{Mo}_3^+$), have found many applications in inorganic chemistry including heterogeneous organometallic catalysis. In the work conducted by Zama et al., the $\text{Mo}_3^+$ cluster $[\text{Mo}_3(\mu_3-\text{O})(\mu_3-\text{CCH}_3)(\mu_2\text{O}_2\text{CCH}_3)_6(\text{CH}_3\text{OH})_3]\text{Cl}$ was grafted onto oxide supports and used in propene metathesis.\(^1\) It was found that the $\mu_3$-$\text{CCH}_3$ ligand dissociates at high temperatures to form 2-butene and ethene. In addition, Bino\(^2\), Bogoslavsky\(^3\) and Bunz\(^4\) have shown that $\text{Mo}_3^+$ clusters produce various organics in aqueous solution via metathesis reactions, and these organic products can be used in the total synthesis of vitamin E and material science. Although these clusters may seem reactive, they are relatively stable at temperatures above 100 °C.\(^5-7\)

Trinuclear $\text{M}_3^+$ clusters ($\text{M}=$Mo or W) are stable in a variety of solutions such as aqueous media, acids and in the presence of oxygen.\(^8\) The stability of $\text{M}_3^+$ clusters is related to the coordination environment. All nine valence orbitals on the metal ion (five d, one s and three p atomic orbitals) participate in bonding to yield a coordination number of nine. In the generic formula above, the terminal ligands (L) are most labile followed by the bridging carboxylates ($\mu_2\text{O}_2\text{CR}$), which are bidentate. It appears that the three-
coordinate capping ligands ($\mu_3$-O, $\mu_3$-CR) are most stable although the $\mu_3$-CR ligand has been shown to dissociate.\textsuperscript{1} It is important to quantify rates of ligand substitution to better understand the turnover-limiting step (TLS) in a catalytic reaction. By quantifying rates of ligand substitution for trinuclear metal catalysts, a model can be developed for predicting rates of ligand substitution based on structure. Understanding rates of ligand substitution and mechanistic pathways will help guide the processes of optimizing large-scale organic reactions and understanding the role of molybdenum as a catalyst in chemical reactions.\textsuperscript{8,9}

**Figure 1.** The structure of [Mo\textsubscript{3}(\mu\textsubscript{3}-O)(\mu\textsubscript{3}-CR)(\mu-O\textsubscript{2}CR)\textsubscript{6}(L)\textsubscript{3}]\textsuperscript{+}, where L is a neutral ligand and R is an alkyl group.
Although structural data for Mo$_3^{+}$ clusters is well published in the literature, there has been only one study that reported kinetic data for ligand substitution$^{10}$ and few reports that suggest how the clusters behave in solution.$^{11-13}$ Investigating chemical kinetics is particularly important because ligand substitution is critical to understanding the function of alkylidyne-capped clusters as organometallic catalysts. It is important to be able to predict rates of ligand substitution for catalytic turnover and reaction efficiency. Equally important is the mechanism associated with ligand substitution reactions. This study aims to develop reactivity trends by quantifying rates of terminal ligand substitution for alkylidyne-capped Mo$_3^{+}$ clusters.

This work will provide insight into how structure dictates reactivity for ligand substitution reactions. The techniques and methodologies described herein can be applied to many trinuclear molybdenum (IV) clusters. By varying the inductive ability of the carboxylates a trend in reactivity can be developed based on structure. Rates of ligand substitution for a series of alkylidyne-capped Mo$_3^{+}$ clusters with different bridging groups and terminal ligands are analyzed in detail.

1.2 Structure of alkylidyne-capped trinuclear Mo$_3^{+}$ clusters

Alkylidyne-capped Mo$_3^{+}$ clusters have unique structural characteristics such as metal-metal bonding, coordination numbers larger than six, and highly symmetrical coordination environments. The alkylidyne-capped clusters are assigned the point group C$_{3v}$, which contains a C$_3$ principal rotational axis and three vertical mirror planes. Alkylidyne-capped Mo$_3^{+}$ clusters consist of three Mo ions, each in the +4 oxidation state,
connected through metal-metal bonding to form the trinuclear core. Each molybdenum (IV) ion is a d\(^2\) metal and contains two valence electrons in the d-subshell. The equal sharing of the d-electrons allows for metal-metal bonding between adjacent metal ions that are bridged by carboxylates through the oxygen atoms. The bridging carboxylates span the edges of the trinuclear core; three bridging carboxylates extend above and three extend below the plane that contains the metal core. Also located above and below this plane are the three-coordinate alkylidyne cap (µ\(_3\)-CR) and oxygen cap (µ\(_3\)-O). The overall charge for alkylidyne-capped Mo\(_3\)\(^+\) clusters is +1, which depends on the oxidation states of the metal ions and the charge of the bound ligands. Lastly, terminal ligands (L) coordinate at the three vertices of the trinuclear core to complete the cluster (Figure 1). Synthesis, crystallographic data and NMR spectra for a limited number of alkylidyne-capped Mo\(_3\)\(^+\) clusters have been previously reported in the literature.\(^{11-14}\) Consequently, knowledge is lacking with regards to how these clusters behave in solution and function as catalysts.

1.3 Trends that influence rates of ligand substitution

The number of studies on ligand substitution has vastly grown over the past few decades and these studies have primarily focused on mononuclear transition metal centers. Trends that influence terminal ligand substitution of trinuclear metal clusters have been established. They show substitution can be influenced indirectly by neighboring electron donating or electron withdrawing groups. The coordination number, ionic radius, electron configuration and the type of metal ion can influence rates of ligand substitution. The electronic effects, ligand field stabilization energies (LFSE), steric
hindrance and the energies associated with specific ligand binding modes also influence ligand substitution.\textsuperscript{9,15,16} Subtle changes in structure, such as altering the inductive ability of bound ligands, can also affect ligand substitution. Although these effects do not change the bonding interaction between the metal and dissociating ligands, they do have an indirect influence on the rate of ligand substitution through inductive effects.

Water exchange and substitution rates for mononuclear metal complexes that contain early and late transition metals, as well as alkali and alkaline earth metals, have been extensively described by Merbach and Richens.\textsuperscript{15,16} According to these reviews one of the most reactive aqueous metal ions is cesium (Cs\textsuperscript{+}). A water molecule bound to the aqua form of Cs\textsuperscript{+} has an estimated average residence time of nearly $10^{-10}$ seconds. The estimated average residence time for a water molecule bound to a Li\textsuperscript{+} ion is roughly one order of magnitude longer than Cs\textsuperscript{+} at $10^{-9}$ seconds. Both average lifetimes for bound water ligands were estimated indirectly from ligand substitution experiments. The difference in rates is an excellent example of how the size of metal ions can influence rates of ligand substitution. Due to the large ionic radius of a Cs\textsuperscript{+} ion (1.67-1.81 Å), the distance between the water and metal ion is considered long. This results in fast rates of substitution compared to a lithium ion (Li\textsuperscript{+}), which has a much smaller ionic radius (0.59-0.92 Å).\textsuperscript{15-18}

Structural characteristics other than the ionic radius of the metal also affect ligand substitution reactions. The metal-cluster type and the coordination environment that surrounds the metal complex can influence ligand substitution. A classic example of steric influence on metal-cluster ligand dissociation utilizes octahedral cobalt (III)
clusters. For example, the generic formula of the clusters is trans-[Co(L)$_2$Cl$_2$]$^+$ with
different substituted ethylenediamine (en) ligands (L). The degree of substitution on the
en ligands causes a crowded steric environment. The steric hindrance accelerates the rate-
determining step (RDS) in a dissociative (D) reaction, which is bond breakage. The rate
constants for acid hydrolysis ranged from 3.2 x 10$^{-5}$ s$^{-1}$ (ethylenediamine) to 1.5 x 10$^{-4}$ s$^{-1}$
(D-, L-2,3-butanediamine) spanning nearly one order of magnitude.$^{15,19,20}$

When rates of ligand substitution are being compared, ligand field effects need to
be considered in addition to size and sterics. The d-orbitals on a metal ion lose
degeneracy when placed into a ligand environment. For a metal complex with octahedral
geometry the d-orbitals split into $e_g$ and $t_{2g}$ sets of atomic orbitals due to electrostatic
repulsions between the d-electrons and the electron pairs on the ligands. Because the $d_{x^2}$
and $d_{y^2}$ orbitals extend in the direction of approaching ligands, the $e_g$ set is raised in
energy. In the presence of a new incoming ligand the d-electrons on the metal tend to
occupy the lower energy orbitals resulting in a net gain in stability. The energy that is
released is referred to as the ligand field stabilization energy (LFSE).$^{21}$ The LFSE for an
octahedral complex can be calculated using Equation 1, where $n$ is the number of
electrons.

$$LFSE = n_{upper} \frac{3}{2} \Delta_o + n_{lower} - \frac{2}{5} \Delta_o$$  \hspace{1cm} (1)$$

As characterized by the spectrochemical series, ligands are classified as strong or
weak depending on the electron-donor atoms in the ligand. To illustrate LFSE and how it
can influence ligand substitution reactions the following two aqueous metal clusters have
been chosen, [Fe(H$_2$O)$_6$]$^{3+}$ and [Cr(H$_2$O)$_6$]$^{3+}$. Both complexes are high-spin but iron (III)
has a d⁵ and chromium (III) a d³ metal electron configuration. The LFSE for a high-spin d⁵ complex is zero because all valence d-orbitals are equally populated. An equal distribution of electrons in d-orbitals results in no net gain in energy stabilization as the incoming ligand approaches. This explains why [Fe(H₂O)₆]³⁺ is more reactive towards water exchange (k₂⁹₈K=1.6 x 10² s⁻¹).¹⁵ The LFSE for the d³ complex [Cr(H₂O)₆]³⁺ is -6/5Δ₀ resulting in a net gain in stability with respect to energy and therefore more inert behavior toward water exchange (k₂⁹₈K=3.4 x 10⁻⁶ s⁻¹).¹⁵ Thus LFSE influence rates of ligand substitution and can be used to predict reaction rates.

1.3.1 Mechanisms of ligand substitution

Ligand substitution reactions can be characterized as associative (A), dissociative (D) or interchange (Iₐ or Iₐ). In an A mechanism bond formation precedes bond cleavage and the intermediate species has a higher coordination number then the starting complex. The rate-determining step (RDS) is bond formation, so the exiting ligand has only a minor influence on the rate of ligand substitution. Upon the formation of the intermediate complex, the rotational, translational and vibrational degrees of freedom decrease and the overall activation entropy decreases. An A pathway is illustrated in Scheme 1.²

\[
\begin{align*}
L_nM - X + Y & \xrightarrow{k_1, k_{-1}} L_nM - X + Y \\
& \xrightarrow{k_2, -X} L_nM - Y \\
\end{align*}
\]

**Scheme 1.** Associative ligand substitution reaction.
An A mechanism follows a second order rate law that depends on the concentration of starting metal complex \([L_nM—X]\) and the incoming ligand \([Y]\).

\[
Rate = k_{obsd}[L_nM - X][Y]
\]  

(2)

The observed rate constant \(k_{obsd}\) becomes a summation of the rate constant for the solvent assisted pathway \(k_1\), which has no dependence on the starting material concentration \([L_nM—X]\), and the rate constant that is dependent on the concentration of the incoming ligand \([Y]\) \(k_2\).\(^9\)

\[
k_{obsd} = k_2[Y] + k_1
\]

(3)

As the concentration of starting material and incoming ligand \([Y]\) increase the observed rate constant \(k_{obsd}\) also increases proportionally. The data can be fit to a linear equation where the slope is equal to \(k_2\) and the y-intercept equal to the rate constant associated with solvent substitution \(k_1\). In many ligand substitution reactions the incoming ligand is the solvent molecule and simplifies \textbf{Equation 3} to

\[
k_{obsd} = k_1
\]

(4)

\textbf{Equation 2} can also be simplified to \textbf{Equation 4} by assuming the change in concentration of the incoming ligand is negligible due to its presence in large excess.
This leads to an overall second order rate equation that is first-order in the concentration of the starting metal complex $[L_nM—X]$ and $[Y]$, as shown in Equation 2. When solvent is the incoming ligand the reaction follows a pseudo first-order rate law where the rate is first-order in the concentration of starting metal complex $[L_nM—X]$ and first-order overall.

$$Rate = k_{obsd}[L_nM - X]$$  \hspace{1cm} (5)

The second substitution pathway to consider is dissociative (D) in which bond cleavage precedes bond formation of the approaching ligand (Scheme 2). This results in a more disordered environment with increased degrees of freedom. The intermediate complex is of lower coordination number than the starting complex due to bond breakage. The rate-determining step is bond cleavage and the overall activation entropy is positive as result of this step.

$$L_nM — X \xrightleftharpoons[k_{-1}]{k_1} \text{L}_nM^+ + X \xrightarrow{k_2, +Y} L_nM — Y$$

**Scheme 2.** Dissociative ligand substitution reaction.

A purely dissociative reaction has no dependence on the concentration of the entering ligand $[Y]$ and is zero order for that reactant. The rate law for a dissociative process can be depicted as
\[ \text{Rate} = - \frac{d[L_nM^-X]}{dt} = k_2[L_nM^+][Y] \quad (6) \]

By assuming the lifetime of the intermediate species \((L_nM^+)\) is short, the steady state approximation can be used and the concentration of intermediate metal species \([L_nM^+]\) becomes

\[ [L_nM^+] = \frac{k_1[L_nM^-X]}{k_{-1}[X]+k_2[Y]} \quad (7) \]

By inserting the algebraic simplification of the steady state approximation \((7)\) into \((6)\) for \([L_nM^+]\) the following rate equation is obtained for the decrease in the concentration of starting material \(([L_nM-X])\) with respect to time.\(^{19}\)

\[ \text{Rate} = - \frac{d[L_nM^-X]}{dt} = \frac{k_1k_2[L_nM^-X][Y]}{k_{-1}[X]+k_2[Y]} \quad (8) \]

If the forward reaction dominates \((k_2 >> k_{-1})\), then the summation of the denominator is approximately equal to the \(k_2[Y]\) term and the overall rate equation simplifies to what is most commonly seen for a dissociative ligand substitution reaction \((\text{Scheme 2})\) as seen in \textbf{Equation 9}.

\[ \text{Rate} = k_1[L_nM-X] \quad (9) \]

The rate is first-order overall and first-order in the concentration of the starting metal complex. The bonding interactions between metal and departing ligand play a crucial role in the rate of a dissociative reaction.\(^9\)

Lastly, a substitution reaction can follow a pathway that is not purely D or A, but is an intermediate reaction mechanism called an interchange (I). If bond dissociation dominates the mechanism is interchange dissociative \((I_d)\) and mimics that of an organic
S_{N}1 reaction. If bond association dominates the mechanism is interchange associative (I_{a}) and mimics the S_{N}2 backside-attack reaction in which the leaving group departs almost simultaneously.

\[
L_{n}M \xrightarrow{k_1} \quad \left[ \begin{array}{c} \text{L}_{n}M \xrightarrow{X} \text{L}_{n}M \xrightarrow{Y} \end{array} \right] \xrightarrow{k_2} \quad L_{n}M \xrightarrow{Y}
\]

**Scheme 3.** Interchange (I) mechanism (I_{a} or I_{d}).

An interchange mechanism (I_{a} or I_{d}) is a concerted two-step reaction with the formation of several possible transition state complexes that result from simultaneous bond formation and cleavage. The bond dissociation energy (BDE) for the existing metal-ligand bond (M—X) varies depending on the reaction mechanism (I_{a} or I_{d}).^{9,22}

### 1.4 Rates and activation parameters for ligand substitution at trinuclear clusters

There have been several studies that report on ligand substitution reactions for trinuclear metal clusters in which the first substitution step is monitored.\(^{10,23-28}\) A ligand substitution reaction for a trinuclear metal complex is illustrated in **Scheme 4** below. In this reaction a water molecule is substituted by ligand (L). The starting complex is fully ligated with water molecules and is referred to as the un-substituted species. The complex in which a single water molecule is replaced by ligand (L) is referred to as the mono-substituted species. Subsequent ligand substitution steps give the di- and tri-substituted...
trinuclear species. The reactions are monitored using different spectroscopic techniques such as NMR, IR and UV-Vis spectroscopy. The signal decay (area or intensity) that corresponds to the starting material (the un-substituted species) is typically the target.

**Scheme 4.** Dissociative ligand substitution reaction for the first substitution step (L = neutral ligand).

1.4.1 First-order reactions and Eyring equations

Many dissociative ligand substitution reactions for trinuclear metal compounds follow first-order reaction kinetics which correspond to the rate law shown in **Equation 10** where \([M_3^+]\) is the concentration of the un-substituted metal complex, \(t\) is time and \(k_{obsd}\) is the observed rate constant in units of \(s^{-1}\).

\[
Rate = -\frac{d[M_3^+]}{dt} = k_{obsd}[M_3^+] \quad (10)
\]
If Equation 10 is integrated with respect to time the rate law becomes Equation 11, which is referred to as the integrated rate law.

\[ [M_3^+]_t = [M_3^+]_0 e^{-kt} \]  

(11)

Taking the natural log of both sides of Equation 11 yields the following linear relationship shown in Equation 12, which is known as the linear form of the integrated rate law.

\[ ln[M_3^+]_t = -k_{obsd}t + ln[M_3^+]_0 \]  

(12)

By plotting \( ln[M_3^+] \) versus time (\( t \)) a straight line is observed where the slope (\( m \)) is equal to the rate constant (\( -k_{obsd} \)). At some time (\( t \)) during the reaction, equilibrium is reached between the substituted metal-ligand complex (M-L) and the free incoming ligand (L).

The linear relationship illustrated in Equation 12 may not be the most accurate representation of the data, although it is most commonly utilized.\(^{29}\) Over time, Equation 12 will result in concentration values that approach zero; this can be an issue if equilibrium is reached.

A more rigorous approach is to fit the data to an exponential equation. The area or intensity of the signal that corresponds to the decay in concentration of the un-substituted species [\( M_3^+ \)] can be monitored with respect to time and fit to the following exponential equation:

\[ y = a + be^{ct} \]  

(13)

In this equation “\( y \)” is the area or intensity of the signal, “\( a \)” is an asymptote, “\( b \)” is a scalar, “\( c \)” is the rate constant (\( k_{obsd} \)) and “\( t \)” is time. Rate constants can be accurately measured for the first substitution step of a trinuclear metal cluster using (13).
The relationship between the rate of ligand substitution and temperature is described by the Eyring equation developed by Henry Eyring in 1935. The Eyring equation is as follows

\[ k_{\text{exp.}} = \frac{k_B T}{h} e^{-\frac{(\Delta H^{\ddagger} + \Delta S^{\ddagger})}{R}} \]  

(14)

and can be written in the linearized form shown below (15).

\[ \ln \left( \frac{k_{\text{exp.}}}{T} \right) = -\frac{\Delta H^{\ddagger}}{R} + \left( \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^{\ddagger}}{R} \right) \]  

(15)

For the linearized form of the Eyring equation (15), \( \Delta H_{\text{obsd}}^{\ddagger} \) is the activation enthalpy (kJ mol\(^{-1}\)) and \( \Delta S_{\text{obsd}}^{\ddagger} \) is the activation entropy (J mol\(^{-1}\) K\(^{-1}\)), \( h \) is Planck’s constant (J s), \( R \) is the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)) and \( k_B \) is Boltzmann’s constant (J K\(^{-1}\)). By plotting \( \ln(k_{\text{obsd}}/T) \) against \( 1/T \) a straight line is observed. The data can be fit to a linear equation (15) with the slope (m) equal to \( -\Delta H_{\text{obsd}}^{\ddagger}/R \) and y-intercept equal to \( \ln(k_B/h) + \Delta S_{\text{obsd}}^{\ddagger}/R \). From the slope and y-intercept the magnitude of the activation parameters (\( \Delta H^{\ddagger} \) and \( \Delta S^{\ddagger} \)) can be calculated to suggest either a D or A ligand substitution reaction. It is common to see large error associated with extrapolation of \( \Delta S_{\text{obsd}}^{\ddagger} \) from the y-axis but this error is not more significant than the error associated with \( \Delta H_{\text{obsd}}^{\ddagger} \). The difference in error for the activation parameters has been deemed a misconception by Lente who showed using algebra that (15) can be manipulated to yield \( \Delta H_{\text{obsd}}^{\ddagger} \) by extrapolation to the y-axis instead of \( \Delta S_{\text{obsd}}^{\ddagger} \). The lack of precision for a \( \Delta S_{\text{obsd}}^{\ddagger} \) value is significant for two reasons: the units for entropy (J mol\(^{-1}\) K\(^{-1}\)) are influenced by temperature, and the slightest change in the slope has a large effect on the extrapolation to the y-axis, which yields \( \Delta S_{\text{obsd}}^{\ddagger} \). The precision of the intercept data depends heavily on temperature. The Eyring equation has
aided scientists in their ability to understand steps associated with ligand substitution mechanisms.\textsuperscript{18,31}

1.4.2 Insight into the reaction mechanism

For a D mechanism the activation parameters will show a large activation enthalpy ($\Delta H_{\text{obsd}}^{\dagger}$) and positive activation entropy ($\Delta S_{\text{obsd}}^{\dagger}$). The large $\Delta H_{\text{obsd}}^{\dagger}$ is explained due to the bond dissociation energy (BDE) required in the bond breakage step to form the intermediate of lower coordination number. The positive $\Delta S_{\text{obsd}}^{\dagger}$ is due to the bond breakage step (a more disordered coordination sphere) and an increase in the number of degrees of freedom during the formation of the transition state complex. An interchange dissociative mechanism ($I_D$) would have a noticeably smaller $\Delta H_{\text{obsd}}^{\dagger}$ and less positive $\Delta S_{\text{obsd}}^{\dagger}$ indicating the incoming ligand must have an influence on the reaction (Figure 2). The closer the incoming ligand in proximity to the metal and departing ligand, the more associative the activation parameters become.

For an A mechanism the activation parameters will show a small activation enthalpy $\Delta H_{\text{obsd}}^{\dagger}$ and negative $\Delta S_{\text{obsd}}^{\dagger}$. The small $\Delta H_{\text{obsd}}^{\dagger}$ is explained by assistance from the incoming ligand, which lowers the activation energy required to form the intermediate. The intermediate is a more ordered species of higher coordination number resulting in a negative $\Delta S_{\text{obsd}}^{\dagger}$. For an interchange associative mechanism ($I_A$) the $\Delta H_{\text{obsd}}^{\dagger}$ will be slightly larger then expected and the $\Delta S_{\text{obsd}}^{\dagger}$ slightly less negative indicating that bond breakage is competing in the reaction. Activation parameters can be determined from the temperature dependence on the rate to gain insight into the mechanistic pathway but they have to be interpreted with caution. Without sufficient data that covers a wide
temperature range the extrapolation of the activation entropy $\Delta S_{\text{obsd}}^\ddagger$ (y-intercept) and the activation enthalpy $\Delta H_{\text{obsd}}^\ddagger$ (slope, m) can come with significant error. It can be challenging to distinguish between a purely D (or A) pathway and the corresponding interchange (I) mechanism by considering only the activation enthalpy and entropy ($\Delta H^\ddagger$, $\Delta S^\ddagger$).

![Reaction coordinate diagram](image)

**Figure 2.** Reaction coordinate diagram for interchange mechanism ($I_d$ or $I_a$).

1.5 Previous research

Previous studies on trinuclear metal complexes such as Mo$_3^+$ and other trinuclear clusters [ie. W$_3^+$, Cr$_3^+$, Rh$_3^+$, Ru$_3^+$ and Fe$_3^+$] have shown that ligand type$^{10,32}$, inductive abilities,$^{23,24}$ metal ions,$^{28,33}$ and steric$^{10,34}$ influence rates of substitution. These clusters share many structural commonalities. For example, the Fe$_3^+$, Ru$_3^+$, Rh$_3^+$ and Cr$_3^+$ clusters are o xo-centered clusters in which the three-coordinate oxygen ($\mu_3$-O, -2 charge) is centrally located in the horizontal plane that contains the trinuclear core. Additionally,
these trinuclear metal complexes have two sets of three bridging carboxylates (µ-O₂CR, -1 charge) that extend above and below the trinuclear plane. These clusters also have terminal ligands (L) bound to each metal ion.

However, alkylidyne-capped trinuclear metal clusters such as Mo₃⁺ and W₃⁺ differ slightly from other trinuclear structures because the three-coordinate capping ligands (μ₃-O and μ₃-CR) extend above and below the trinuclear plane. The terminal ligands (typically waters) are bound to each of the three metal vertices (Figure 3).

![Figure 3. Cr³⁺ (left) and W³⁺ (right) where R = alkyl groups.](image)

1.5.1 Studies on oxo-centered chromium (III), rhodium (III), ruthenium (III) clusters and a molybdenum (IV) bi-oxo capped cluster

In a study conducted by Fujihara et al., it was found that the bridging carboxylates affect ligand substitution for a series of oxo-centered trinuclear chromium (III)
complexes, [Cr$_3$(μ$_3$-O)(μ-O$_2$CR)$_6$(H$_2$O)$_3$]NO$_3$, where R =CH$_3$, CH$_2$CH$_3$, CH$_2$Cl, CHCl$_3$, CH$_3$OCH$_2$, (CH$_3$)$_3$C, CH$_2$ClCH$_2$,(CH$_3$CH$_2$)$_2$CH.$^{23}$ The substitution of the terminal water ligands by dimethylacetamide (DMA) (Scheme 5) was monitored by plotting the intensity of the d—d absorption band using UV-Vis spectroscopy at temperatures ranging from 273-298 K with respect to time. The rate of water substitution by DMA was found to be first-order. From the data presented by Fujihara et al., $\Delta H_{\text{obsd}}^{\dagger}$ values ranged from 98-123 ±2-4 kJ mol$^{-1}$, and $\Delta S_{\text{obsd}}^{\dagger}$ values ranged from 29-81 ±3-13 J mol$^{-1}$ K$^{-1}$, which suggests a dissociative mechanism (D or I$_d$) and is consistent with other trinuclear metal species of Ru$_3^+$, Rh$_3^+$ and Mo$_3^+$.10,24-26,28 Fujihara found the activation parameters to be virtually unchanged and suggested a dissociative pathway (D or I$_d$) for all nine Cr$_3^+$ clusters examined in this study. However, the reaction rates were influenced by the presence of either electron donating or electron withdrawing alkyl groups on the bridging carboxylates. The kinetic data suggested the following trend in reactivity for water substitution by DMA (R=(CH$_3$)$_3$C > CH$_2$CH$_3$ > CH$_3$ > (CH$_3$CH$_2$)$_2$CH > CH$_2$ClCH$_2$ > CH$_3$OCH$_2$ > H > CH$_2$Cl > CHCl$_2$. As the inductive ability increased on the alkyl group the rate of ligand substitution slowed.
Scheme 5. H$_2$O substitution for dimethylacetamide (DMA) in 

$$[\text{Cr}_3(\mu_3-O)(\mu-O_2\text{CR})_6(\text{H}_2\text{O})_3]\text{NO}_3.$$ 

Sasaki and coworkers$^{28}$ took a different approach and studied oxo-centered trinuclear Rh$_3^+$ and Ru$_3^+$ clusters both with bridging acetate ligands. Examined was the substitution reaction of terminal water ligands by methanol-d$_4$ (MeOD-d$_4$) for oxo-centered trinuclear rhodium (III), ruthenium (III) and a mixed metal trinuclear species that contains two ruthenium (III) and one rhodium (III) ion, [Ru$_2$Rh($\mu_3$-O)(\mu-O$_2$CCH$_3$)(H$_2$O)$_3$]$^+$. All three of these complexes contain six bridging acetates which allowed Sasaki to draw conclusions in regard to the reactivity of the terminal water ligands based on the differences in the metal ions that make up the trinuclear core. The rates for all three metal clusters were found to be first-order and the relatively constant activation parameters suggested dissociative (D or I$_d$) mechanisms ($\Delta H^\ddagger = 102$-109 kJ mol$^{-1}$; $\Delta S^\ddagger = 22$-42 J mol$^{-1}$ K$^{-1}$). However, the reaction rates varied depending on the metal species. Sasaki et al. found the rates of water substitution for the mixed metal cluster to be an order of magnitude slower than both homo-trinuclear metal clusters. In addition, the trinuclear Ru$_3^+$ complex was found to be only slightly more inert towards water
substitution then the Rh\textsubscript{3}\textsuperscript{+}. As result Sasaki et al. suggested that the slower substitution rates were due to the electronic configuration of the metal ions and LFSE. As result, the overlap of (metal-d\pi)-(oxygen-p\pi) orbitals influences the rate of water substitution.\textsuperscript{28} The studies on Rh\textsubscript{3}\textsuperscript{+} clusters continued with the work of Houston and coworkers.

In another study, Houston et al. examined the oxo-centered trinuclear rhodium (III) cluster, [Rh\textsubscript{3}(\mu\textsubscript{3}-O)(\mu-O\textsubscript{2}CCH\textsubscript{3})\textsubscript{6}(OH\textsubscript{2})\textsubscript{3}]ClO\textsubscript{4}, and the rates of water exchange were monitored by high-pressure \textsuperscript{17}O NMR.\textsuperscript{26} The temperature dependence on the rates showed a large activation enthalpy (\Delta H\textsuperscript{‡} = 99 \pm 3 kJ mol\textsuperscript{-1}) and positive activation entropy (\Delta S\textsuperscript{‡} = 43 \pm 10 J mol\textsuperscript{-1} K\textsuperscript{-1}), indicative of a D pathway. The increase in the reactivity of the terminal water ligands of [Rh\textsubscript{3}(\mu\textsubscript{3}-O)(\mu-O\textsubscript{2}CCH\textsubscript{3})\textsubscript{6}(OH\textsubscript{2})\textsubscript{3}]ClO\textsubscript{4}, compared to Rh(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+}, was most likely due to the central oxide ion (\mu\textsubscript{3}-O, 2- charge). This has been described as a trans-effect, which weakens the Rh-H\textsubscript{2}O bond trans to the \mu\textsubscript{3}-O ligand.\textsuperscript{26} This work is consistent with Fujihara et al. and Sasaki et al. who proposed that water substitution for \mu\textsubscript{3}-O trinuclear Cr\textsubscript{3}\textsuperscript{+}, Rh\textsubscript{3}\textsuperscript{+} and Ru\textsubscript{3}\textsuperscript{+} follows a D pathway based on highly positive activation parameters.\textsuperscript{23,28}

In an additional Rh\textsubscript{3}\textsuperscript{+} study conducted by Houston et al. the alkyl groups on the bridging carboxylates were varied (R=CH\textsubscript{3}, CH\textsubscript{2}CH\textsubscript{3}, CH\textsubscript{2}CH\textsubscript{2}Cl, CH\textsubscript{2}Cl, CHCl\textsubscript{2}) to study the inductive effects on terminal water substitution.\textsuperscript{24} The terminal water ligands were substituted by MeOD-d\textsubscript{4} and the reactions again followed a D pathway. Although the activation enthalpy and entropy here remained practically unchanged (\Delta H\textsuperscript{‡} = 99-115 kJ mol\textsuperscript{-1}; \Delta S\textsuperscript{‡} = 48-52 J mol\textsuperscript{-1} K\textsuperscript{-1}), the rates of ligand substitution were heavily influenced by the electron donating or electron withdrawing ability of the alkyl group on
the bridging carboxylates; the measured rate constants span nearly three orders of magnitude. As the inductive ability of the alkyl groups increases, the rates of water substitution by MeOD-d$_4$ decrease. In contrast, rates increase as the electron donating ability of the alkyl group increases. The following trend was established to illustrate the difference in ligand substitution rates for five Rh$_3^+$ clusters: R = CH$_2$CH$_3$ > CH$_3$ > CH$_2$CH$_2$Cl > CH$_2$Cl > CHCl$_2$. This trend is consistent with the trend established by Fujihara for oxo-centered Cr$_3^+$ clusters. This work established a methodology for estimating rates of water exchange for other Rh$_3^+$ clusters using $^{103}$Rh NMR spectroscopy.

Also published by Houston et al. is a kinetic study on the acetate-bridged bi-oxo capped trinuclear molybdenum (IV) anion [Mo$_3$(µ$_3$-O)$_2$(µ-O$_2$CCH$_3$)$_6$(O$_2$CCH$_3$)$_3$] that contains terminal acetate ligands. The terminal acetates were substituted by D$_2$O, MeOD-d$_4$ and acetic acid-d$_4$ ligands. The substitution and exchange rates were determined by monitoring the disappearance of the terminal acetate signal on the $^1$H NMR spectra over time. Using variable-temperature $^1$H NMR (VT-$^1$H NMR), rates were measured at temperatures ranging from 25-52 °C. The large values for the activation enthalpy ($\Delta H^\ddagger = 115$-$126$ kJ mol$^{-1}$) and positive values for the activation entropy ($\Delta S^\ddagger = 52$-$80$ J mol$^{-1}$ K$^{-1}$) suggest a dissociative mechanism (D or I$_d$) for terminal acetate substitution by D$_2$O and MeOD-d$_4$. The activation parameters for the substitution of terminal acetate ligands by acetic acid-d$_4$ (or acetate-d$_4$) pointed to an associative mechanism (A or I$_a$) ($\Delta H^\ddagger = 63$ kJ mol$^{-1}$, $\Delta S^\ddagger = -97$ J mol$^{-1}$ K$^{-1}$) indicating that bond
formation was preferred over bond breakage. The ligand substitution reaction was described as a multistep reaction that involved complex aqueous solution chemistry.\textsuperscript{32}

1.5.2 Trinuclear molybdenum (IV) clusters

Along with Cr\textsuperscript{3+}, Rh\textsuperscript{3+} and Ru\textsuperscript{3+} trinuclear metal clusters, Mo\textsuperscript{3+} clusters have been studied as well; however, there are fewer reports on these structures. Cotton et al. studied the reaction of Mo(CO)\textsubscript{6} with acetic acid and acetic anhydride used to synthesize trinuclear molybdenum clusters.\textsuperscript{35} The reaction was originally used in the formation of dimolybdenum tetraacetate, Mo\textsubscript{2}(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{4}, a compound that contains a Mo-Mo quadruple bond.\textsuperscript{36} However, the yield of the yellow crystalline material was low. This led Cotton and coworkers to believe the supernatant contained additional Mo products that remained in solution. There are three forms (two prominent forms) that can be isolated from this reaction (Figure 4); the Mo\textsubscript{3}\textsuperscript{2+} bi-oxo capped cluster, [Mo\textsubscript{3}(μ\textsubscript{3}-O)\textsubscript{2}(μ-O\textsubscript{2}CR)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}]\textsuperscript{2+}, the single alkylidyne-capped (μ\textsubscript{3}-O and μ\textsubscript{3}-CR) Mo\textsubscript{3}\textsuperscript{+} cluster, [Mo\textsubscript{3}(μ\textsubscript{3}-O)(μ\textsubscript{3}-CR)(μ-O\textsubscript{2}CR)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}]\textsuperscript{+}, and the bi-alkylidyne-capped cluster, Mo\textsubscript{3}(μ\textsubscript{3}-CR)\textsubscript{2}(μ-O\textsubscript{2}CR)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}.\textsuperscript{37}
Figure 4. Additional reaction products proposed by Cotton et al. (single alkylidyne-capped (top); bi-oxo capped (bottom left); bi alkylidyne-capped (bottom right) trinuclear molybdenum (IV) clusters.}

In 1976, Bino et al. reported the first Mo$_3^+$ structure, [Mo$_3$(μ$_3$-OCH$_2$CH$_3$)$_2$(μ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$](CF$_3$SO$_3$)$_2$, but only a crystal structure was reported. The crystal structure was later believed to be partially incorrect, in that the two capping μ$_3$-OCH$_2$CH$_3$ ligands were misidentified. A few years later in 1980 the crystal structure was revised and characterized correctly as [Mo$_3$(μ$_3$-CCH$_3$)$_2$(μ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]SbF$_6$. In this report Bino et al. crystallized a series of [Mo$_3$(μ$_3$-Y)(μ$_3$-R)(μ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]X clusters with
varying three-coordinate capping ligands (Y=R=O, Y=O and R=CCH₃ and Y=R=CCH₃) and counter ions (X= SbF₆⁻, Br⁻, CF₃SO₃⁻, BF₄⁻, C₇H₇SO₃⁻). A year later in 1981, the crystal structure of one of these clusters previously examined by Bino et al., [Mo₃(µ₃-O)(µ₃-CCH₃)(µ-O₂CCH₃)₆(H₂O)₃]BF₄, was reported again but with additional \(^1\)H, \(^{13}\)C NMR and UV-Vis data. The spectroscopy experiments gave insight into the initial stability of [Mo₃(µ₃-O)(µ₃-CCH₃)(µ-O₂CCH₃)₆(H₂O)₃]BF₄ in aqueous solution.\(^3,4,39\)

Once the alkylidyne-capped and bi-alkylidyne-capped Mo₃⁺ clusters were isolated, the dissociation of the alkylidyne cap was examined by Bogoslavsky\(^3\) and Bino\(^2\) in which they propose a radical de-coupling reaction to generate the bi-oxo capped cluster (Scheme 6). It was hypothesize that the dissociation of the alkylidyne cap creates a free radical (a carbyne) in solution that can couple to other carbynes to generate alkynes and other organics in minor yields. However, the proposed mechanism and the origins of certain reaction products are debatable. The main product that results from the dissociation of the three-coordinate capping ligand (µ₃-CCH₃) is acetic acid generated by the reaction of a methyl carbyne radical with water as reported by Bogoslavsky et al.\(^3\) The ethylidyne-capped Mo₃⁺ cluster contains six bridging acetates that could account for the detection of acetic acid in aqueous solution if the bridging ligands dissociate from the trinuclear core.\(^2,4,13,39\)
Scheme 6. The dissociation of $\mu_3$-CY ligands to form 2-butyne or 3-hexyne in water.

1.5.3 Bridging carboxylates of trinuclear molybdenum (IV) clusters

In a report by Nakata and coworkers, the following cluster was crystallized:

$[\text{Mo}_3(\mu_3-O)(\mu_3-\text{CCH}_3)(\mu_2-\text{O}_2\text{CC}_6\text{H}_5)_6(\text{CH}_3\text{OH})_3]\text{Cl}$. This was the first publication to report that the bridging carboxylate ligands undergo substitution. This paper was also the first to report a Mo$_3^+$ cluster that had a capping three-coordinate alkylidyne ligand different from the alkyl group on the bridging carboxylates. This cluster was synthesized by reacting the ethylidyne-capped cluster with bridging acetates in the presence of benzoic acid, triethylamine, methanol and acetonitrile. The six bridging acetate ligands were substituted by benzoates and the terminal water ligands substituted by methanol to give the cluster in the form of a chloride salt.
In a similar finding, Bino et al. initially reported the crystal structure of \([\text{Mo}_3(\mu_3-O)(\mu_3-C\text{CH}_2\text{CH}_3)(\mu_2\text{O}_2\text{C}\text{CH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3](\text{Zn}_2\text{Br}_4)_{1/2}\), in which the bridging carboxylates are propionates and \(\mu_3\text{-CR}\) is a propylydine capping ligand.\(^{14}\) This reaction was run in propionic acid and propionic anhydride in the presence of molybdenum hexacarbonyl, suggesting substitution of the bridging ligands was not the synthetic objective. Although this structure is very interesting, only crystallography data supported this finding. Nearly thirty years later in 2012, Pineda et al. isolated the mixed-crystal, \([\text{Mo}_3(\mu_3-O)(\mu_3\text{-CR})(\mu_2\text{O}_2\text{C}\text{CH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]\text{Br}, R=\text{CH}_3\text{ and CH}_2\text{CH}_3\), which had both ethyldyne and propylydine capping ligands (50:50 or 40:60 ratio) with bridging propionates.\(^{12}\) Crystallography data as well as DEPT-135, \(^1\)H, \(^{13}\)C NMR were reported.

1.5.4 Kinetic studies on ethyldyne-capped clusters with terminal pyridine and methanol ligands

Although the solution chemistry of \(\text{Mo}_3^+\) is not well understood, Nakata et al. synthesized a trinuclear \(\text{Mo}_3^+\) cluster in pyridine to form, \([\text{Mo}_3(\mu_3-O)(\mu_3\text{-CCH}_3)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_6(\text{py})_3]\text{BF}_4\).\(^{10}\) This was accomplished by dissolving the aqua form, \([\text{Mo}_3(\mu_3-O)(\mu_3\text{-CCH}_3)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]\text{BF}_4\), in pyridine and precipitating it out with diethyl ether as the \(\text{Mo}_3^+\) cluster with ligated pyridines. Nakata monitored the exchange of ligated pyridine with bulk pyridine-d\(_5\) (Scheme 7) in nitromethane-d\(_3\) (CD\(_3\)NO\(_2\)-d\(_3\)) by variable-temperature \(^1\)H NMR (VT-\(^1\)H NMR) but over a temperature range that included a few low temperatures with room temperatures and above (273, 282, 293, 308 K). The measured rate constants were from an average rate of pyridine exchange for any of the three-coordination sites on the \(\text{Mo}_3^+\) cluster.
Scheme 7. Ligated pyridine exchange with pyridine-d$_5$ via a dissociative mechanism.

From the kinetic data, a large $\Delta H_{\text{obsd}}^\ddagger$ (112 ±1 kJ mol$^{-1}$) and positive $\Delta S_{\text{obsd}}^\ddagger$ (77 ±5 J mol$^{-1}$ K$^{-1}$) were determined suggesting the mechanism was D. The rate constants were found to be virtually independent of the pyridine-d$_5$ concentration and dependent on the nature of leaving ligands (pyridine). This indicated that the metal-pyridine bond breaks prior to association of the incoming pyridine-d$_5$ molecule and that the reaction was first-order. For the cluster first reported by Bino, [Mo$_3$(μ$_3$-O)(μ$_3$-CCH$_3$)(μ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]BF$_4$, Nakata also studied the substitution of terminal water ligands by MeOD-d$_4$ and found the rate to be first-order and the mechanism to be D. It was proposed that the alkylidyne (μ$_3$-CR) and three-coordinate oxygen (μ$_3$-O) ligands enhance the reactivity of the terminal ligands through the trans labilization effect although they are not technically trans to the dissociating ligands.$^{10}$

1.6 Thesis research

This study aims to build on the work of Nakata by synthesizing ethylidyne-capped Mo$_3^+$ clusters with different alkyl groups (R groups) in order to understand how electronic
structure affects ligand substitution. Kinetic experiments have been performed to determine the rate of terminal ligand substitution or exchange for the first substitution step using VT-$^1$H NMR spectroscopy. For each complex an Eyring plot has been generated to assign a mechanism.

Each cluster in this study contains similar structural characteristics such as a trinuclear molybdenum (IV) core with three-coordinate capping $\mu_3$-O and $\mu_3$-CR ligands. The R groups on the bridging carboxylates and terminal ligands are different. The generic form of the clusters are $[\text{Mo}_3(\mu_3$-O)$)(\mu_3$-CY)$(\mu$-O$_2$CR)$_6$($\text{L}$)$_3$]$X$ ($Y$=$\text{CH}_3$, CH$_3$ and CH$_2$CH$_3$ (mixed-crystal); R=CH$_3$, CH$_2$CH$_3$, CH$_2$Cl, CHCl$_2$; $L$=pyridine or MeOH and $X$=Br$^-$, BF$_4^-$, ClO$_4^-$). The decay in the $^1$H NMR signal(s) that corresponds to the un-substituted Mo$_3^+$ cluster were monitored by $^1$H NMR with respect to time at different temperatures. Rate constants were determined at temperatures approximately greater than or equal to 25 °C. The activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) were calculated from an Eyring plot to draw conclusions about the mechanistic pathway based on the magnitude of the parameters. It was expected that substitution reactions for Mo$_3^+$ clusters would follow a D pathway based on previous reports in the literature.$^{10}$

Although the activation parameters for each Mo$_3^+$ cluster were expected to indicate a D or I$_d$ mechanism, the reaction rates can vary depending on the terminal and incoming ligands as well as the alkyl group on the bridging carboxylates. The goal is to improve the understanding of mechanistic pathways and ultimately reaction rates associated with organic reactions that utilize Mo$_3^+$ as a catalyst. One limitation is that trends in reactivity have only been developed for two trinuclear metal clusters, Cr$_3^+$ and
Rh$_3^+$. To date, only one ligand substitution study has been published in the literature for Mo$_3^+$ clusters that could contribute to the development of a trend.$^{10}$ It is important to continue with kinetic studies on Mo$_3^+$ clusters to develop reactivity trends to better understand how these clusters perform as catalysts.
2.1 Establishing a methodology

The first step of this study was to establish a viable methodology to investigate terminal ligand substitution of alkylidyne-capped trinuclear molybdenum (IV) clusters. The trinuclear molybdenum (IV) cluster \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\text{BF}_4\cdot\text{9H}_2\text{O} \) (Figure 5) was first characterized by Bino et al.\(^1\) The cluster contains molybdenum ions in the +4 oxidation state with one set of bridging acetates that extend into the plane and another that extend away. The cluster has water ligands terminally bound to each molybdenum ion of the trinuclear cluster. The overall charge on the complex is +1, which is balanced by a tetrafluoroborate counter ion (\(\text{BF}_4^-\)).
Nakata et al. dissolved [\(\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\)BF\(_4\)\(^-\) in pyridine to form the tri-substituted species [\(\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{py})_3\)]BF\(_4\)\(^-\)0.5py shown in Scheme 6, via a water substitution reaction.\(^{10}\) Using VT-\(^1\)H NMR Nakata et al. studied the pyridine exchange of ligated pyridine for bulk pyridine-d\(_5\) at temperatures ranging from -0.3 °C to 34.6 °C. The reported rate constants span over two orders of magnitude (2.3 \(\times\) 10\(^{-5}\) -7.43 \(\times\) 10\(^{-3}\) s\(^{-1}\)). From the kinetic data, a large \(\Delta H_{\text{obsd}}\)\(^{\ddagger}\) (112 \(\pm\) 1 kJ mol\(^{-1}\)) and positive \(\Delta S_{\text{obsd}}\)\(^{\ddagger}\) (77 \(\pm\) 5 J mol\(^{-1}\) K\(^{-1}\)) were determined, suggesting the mechanism was D.

To establish a methodology, the Nakata experiment\(^{10}\) was repeated for the complex [\(\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{py})_3\)]BF\(_4\) at temperatures ranging from 25 - 35 °C (\(\pm\)0.01 °C / °C) [298 K (in duplicate), 303 K and 308 K]. The reaction rates and
activation parameters were found to be consistent with the work done by Nakata et al. as reported in Table 1 and Table 2.

**Table 1.** Comparison of activation parameters for methodology establishment

<table>
<thead>
<tr>
<th></th>
<th>[Mo₃(µ₁-CCH₃)(µ₁-O)(µ-O₂CCH₃)₆(py)₃]BF₄ (This work)</th>
<th>[Mo₃(µ₁-CCH₃)(µ₁-O)(µ-O₂CCH₃)₆(py)₃]BF₄ (Nakata)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHᵢ</td>
<td>129 (±4) kJ mol⁻¹</td>
<td>112 (±1) kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔSᵢ</td>
<td>125 (±13) J mol⁻¹ K⁻¹</td>
<td>77 (±5) J mol⁻¹ K⁻¹</td>
</tr>
</tbody>
</table>

**Table 2.** Rate constant comparison for methodology establishment

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>[py-d₅]/M</th>
<th>Rate const. k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nakata</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>0.52</td>
<td>1.21 x 10⁻⁴</td>
</tr>
<tr>
<td>294</td>
<td>0.52</td>
<td>7.95 x 10⁻⁴</td>
</tr>
<tr>
<td>308</td>
<td>0.52</td>
<td>6.71 x 10⁻³</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>297.6</td>
<td>1.16</td>
<td>4.90 ±0.06 x 10⁻⁴</td>
</tr>
<tr>
<td>303</td>
<td>1.16</td>
<td>1.27 ±0.01 x 10⁻³</td>
</tr>
<tr>
<td>308</td>
<td>1.16</td>
<td>2.93 ±0.02 x 10⁻³</td>
</tr>
</tbody>
</table>

Nakata monitored the intensity of the signals that corresponds to the 2,6-protons for ligated pyridine. The following linear McKay-type equation (Equation 16) was used to plot the change in signal intensity with respect to time.

\[
\ln \left( \frac{I_t - I_\infty}{I_0 - I_\infty} \right) = - \left( \frac{3m+n}{3mn} \right) R t + \text{constant} \quad (16)
\]
Here $m$ and $n$ are the initial concentrations of $[\text{Mo}_3^+]$ and $[\text{py-d}_5]$. For the signal intensity ($I$) the following equation was used, $I = p/(p + q)$ where $p$ and $q$ are the relative integrated intensities of ligated and free pyridine. By plotting the left-hand side of Equation 16 versus time a straight line is observed in which the slope $R (=k_{\text{exp}}/m)$ yields a rate constant. Nakata et al. suggested the rate was virtually independent of the pyridine-d$_5$ concentration $[\text{py-d}_5]$ and followed first-order reaction kinetics.$^{10}$

2.2 Studies on $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{py})_3]\text{BF}_4$

The structure of $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{py})_3]\text{BF}_4$ (Figure 6) has been synthesized previously by Nakata in 1991$^{10}$ and the synthesis and characterization was reproduced in this study. The ethylidyne-capped cluster with terminal water ligands was dissolved in neat pyridine and heated at 40 °C for approximately 15 hours. Precipitation upon the addition of diethyl ether at room temperature yielded an orange solid. The acetate-bridged trinuclear $\text{Mo}_3^+$ cluster has $C_{3v}$ symmetry. Each molybdenum ion is in the +4 oxidation state and is bridged to an adjacent molybdenum (IV) ion through bidentate acetate ligands. Terminal pyridine ligands are bound to each molybdenum ion. The complex has an overall charge of +1 and was precipitated as a tetrafluoroborate salt. Nakata characterized the $\text{Mo}_3^+$ cluster using the following spectroscopic techniques: $^1\text{H}$, $^{13}\text{C}$ and $^{95}\text{Mo}$ NMR, FT-IR and UV-Vis spectroscopy. VT $^1\text{H}$-NMR experiments were repeated at temperatures at and above room temperature to study the rate of pyridine exchange.
2.2.1 Deducing rate constants

The rate constants for each kinetic experiment were determined by integrating the area under the $^1$H NMR signals at $\delta = 9.23$ (Figure 9), which correspond to the 2,6-protons on bound pyridine ligands. The peak areas are directly proportional to the concentration of the un-substituted Mo$_3^+$ species and were normalized relative to tetramethyldisilane (TMS). Plots for the decay in area count of the signals at $\delta = 9.23$ versus time (in seconds) are shown in Figures 7A-D and Figure 8 for 25 °C and above (±0.01 °C / °C). A three variable exponential (Equation 13) is used to deduce rate constants ($k_{\text{obsd}}$). Table 2 and Table 3 summarize the rate constants at different temperatures and the concentrations of pyridine. Duplicate experiments were conducted at room temperature to verify the data was reproducible. The reaction progress was
monitored via $^{1}$H NMR for a period of time greater than three half-lives. This is to ensure a sufficient number of data points were collected to accurately measure the rate constants.

**Figure 7A.** 297.6 K

\[ y = 0.008 + 0.243e^{(-0.00049t)} \]

\[ R^2 = 0.9999116 \]

**Figure 7B.** 297.4 K

\[ y = 0.011 + 0.758e^{(-0.00047t)} \]

\[ R^2 = 0.9999772 \]
Figure 7A-D. Decay in the area of signals corresponding to the 2,6-protons of bound pyridine with time at various temperatures: 297.6 (A), 297.4 (B), 303 (C) and 308 K (D).
Figure 8A. 297.6 K

Figure 8B. 303 K
Figure 8A-C. The decay in the area count of the signals corresponding to the 2,6-protons of bound pyridine with time at various temperatures: 297.6 K (8A), 303 K (8B) and 308 K (8C).

2.2.2 Activation parameters, rate constants and temperature

The $^1$H NMR spectra of [Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCH$_3$)$_6$(py)$_3$]BF$_4$ have unique features due to the C$_{3v}$ symmetry of the fully substituted Mo$_3^+$ complex (Figure 6). The protons on the alkylidyne ligand and bridging carboxylates gave well-resolved and distinct signals that can be assigned (see Appendix A). Upon the addition of pyridine-d$_5$, the three unique overlapping sets of signals that correspond to the protons of
bound pyridine decrease over time ($\delta = 9.25, 8.13, 7.69$) and the three sets of signals that correspond to bulk pyridine ($\delta = 8.55, 7.73, 7.32$) increase respectively until equilibrium is reached (Figure 9).

![297.4 K NMR spectra illustrating pyridine exchange for [Mo₅(µ₃-O)(µ₃-CCH₃)(µ-O₂CCH₃)₆(py)₃]BF₄ at 297.4 K in CD₃NO₂-d₃ (t=0 min, t=35 min, t=58 min, t=81 min).](image)

**Figure 9.** $^1$H NMR spectra illustrating pyridine exchange for [Mo₅(µ₃-O)(µ₃-CCH₃)(µ-O₂CCH₃)₆(py)₃]BF₄ at 297.4 K in CD₃NO₂-d₃ (t=0 min, t=35 min, t=58 min, t=81 min).

Substitution of the pyridine ligands of Mo₅(µ₃-O)(µ₃-CCH₃)(µ-O₂CCH₃)₆(py)₃]BF₄ happens quickly ($t_{1/2} = 24.6$ minutes at 298 K). Upon substitution,
splitting is observed in the $^1$H NMR signals that correspond to the inequivalent 2,6-protons on the pyridine ligands. This is due to a loss in symmetry during the process of terminal ligand substitution. The un-substituted and tri-substituted species have $C_{3v}$ symmetry and the mono- and di-substituted species have lower symmetry (Scheme 8).

Scheme 8. Pyridine exchange reaction to show substitution steps.

From the rate data (Figures 7A-D), the activation parameters $\Delta H_{\text{obsd}}^{\dagger} = 129 \pm 4$ kJ mol$^{-1}$ and $\Delta S_{\text{obsd}}^{\dagger} = 125 \pm 13$ J mol$^{-1}$ K$^{-1}$ indicate a D mechanism due to the magnitude of the activation parameters (large $\Delta H_{\text{obsd}}^{\dagger}$; positive $\Delta S_{\text{obsd}}^{\dagger}$) obtained from the Eyring plot (Figure 10). The $\Delta H_{\text{obsd}}^{\dagger}$ is large (129 ± 4 kJ mol$^{-1}$) indicating the amount of energy required to reach the intermediate complex is significant and there is no assistance by the incoming ligand. The positive $\Delta S_{\text{obsd}}^{\dagger}$ value (125 ± 13 J mol$^{-1}$ K$^{-1}$) suggests an increase in the vibrational, translational and rotational degrees of freedom upon formation of the intermediate complex. This suggests a D pathway for the pyridine exchange reaction.
2.3 Studies on [Mo$_3$(µ$_3$-CY)(µ$_3$-O)(µ-O$_2$CCH$_2$CH$_3$)$_6$(py)$_3$]Br, (Y=CH$_3$ & CH$_2$CH$_3$)

The structure of [Mo$_3$(µ$_3$-CY)(µ$_3$-O)(µ-O$_2$CCH$_2$CH$_3$)$_6$(py)$_3$]Br, (Y=CH$_3$ and CH$_2$CH$_3$) has not been previously reported or studied kinetically. The synthesis utilized the same workup as Nakata$^{10}$ which dissolved the aqua form of Mo$_3^+$ in neat pyridine and heated to 40 °C resulting in the substitution of terminal water ligands by pyridine. The propanoate-bridged trinuclear Mo$_3^+$ cluster has C$_{3v}$ symmetry and each molybdenum ion is in the +4 oxidation state. Bridging propanoates span the edges of the trinuclear cluster. Three bridging propanoates extend out of the plane toward the three-coordinate capping ligands µ$_3$-CCH$_3$ or µ$_3$-CCH$_2$CH$_3$ and the other three extend into the plane toward the

**Figure 10.** Eyring plot for the pyridine exchange of

Mo$_3$(µ$_3$-O)(µ$_3$-CCH$_3$)(µ-O$_2$CCH$_3$)$_6$(py)$_3$]BF$_4$.
other capping ligand $\mu_3$-O. Bound to each molybdenum ion are terminal pyridines. The compound has an overall charge of +1 and was precipitated as a bromide salt (Figure 11). VT $^1$H-NMR experiments were performed to measure the rate of pyridine exchange for the binary mixture of clusters that differ only in the three-coordinate capping ligand, $\mu_3$-CCH$_2$CH$_3$ or $\mu_3$-CCH$_3$ (Figure 11). This cluster was also characterized by a variety of spectroscopy techniques: $^1$H NMR, FT-IR, UV-Vis and elemental analysis.

2.3.1 Deducing rate constants

Using $^1$H NMR, it was difficult to distinguish the rate of pyridine exchange for each individual Mo$_3^+$ cluster in the mixed alkylidyne-capped Mo$_3^+$ system. As a result, an average rate constant ($k_{\text{avg}}$) was measured for the decay of both un-substituted species (Figures 12A-E and Figure 13). The decay in area was again fit to a three variable
exponential equation (Equation 13). Duplicate room temperature kinetic experiments were performed to assure the data was reproducible. The reaction was monitored for a period of time greater than three half-lives to assure enough data points were collected to accurately determine the rate constants. The decay in area of the $^1$H NMR signals corresponding to the 2,6-potons of bound pyridine ligands was monitored with respect to time at varying temperatures [25 °C and above (±0.01 °C)]. The rate of decay increased with increasing temperature.

\[ y = 0.057 + 0.777e^{-0.00085t} \]

\[ R^2 = 0.999645 \]

Figure 12A. 297.7 K
Figure 12B. 297.8 K

\[ y = 0.081 + 0.960e^{(-0.00083t)} \]

\[ R^2 = 0.998249 \]

Figure 12C. 303 K

\[ y = 0.023 + 0.350e^{(-0.00195t)} \]

\[ R^2 = 0.999136 \]
Figure 12D. 306 K

\[ y = 0.020 + 0.237e^{-0.00267t} \]

\[ R^2 = 0.999729 \]

Figure 12E. 308 K

\[ y = 0.078 + 0.874e^{-0.00377t} \]

\[ R^2 = 0.999122 \]

Figure 12A-E. The decay in $^1$H NMR signals corresponding to the 2,6-protons of bound pyridine with time at varying temperatures: 297.7 (A), 297.8 (B), 303 (C), 306 (D) and 308 K (E).
Figure 13A. 297.7 K

Figure 13B. 303 K
Figure 13C. 306 K

Figure 13D. 308 K
Figure 13A-D. The decay in area count of the signals corresponding to the 2,6-protons of bound pyridine ligands with time at varying temperatures: 297.7 K (13A), 303 K (13B), 306 K (13C) and 308 K (13D).

2.3.2 Variable-temperature $^1$H NMR and activation parameters

In an attempt to try and resolve the rates of ligand substitution for both the ethylidyne capped and propylidyne capped clusters, $[\text{Mo}_3(\mu_3\text{-CY})(\mu_3\text{-O})(\mu_2\text{O}_2\text{CCH}_2\text{CH}_3)_3(py)_3]\text{Br}$, (Y=CH$_3$ and CH$_2$CH$_3$), the $^1$H NMR signals from the three-coordinate alkylidyne-capping ligands were considered. The protons on the alkylidyne capping ligands ($\mu_3\text{-CCH}_3$ and $\mu_3\text{-CCH}_2\text{CH}_3$) give unique $^1$H NMR signals. Unfortunately, the $\mu_3\text{-CCH}_3$ signal ($\delta=2.43$) overlaps with the signals that correspond to the methylene protons ($\mu\text{-O}_2\text{CCH}_2\text{CH}_3$) on the bridging propionates ($\delta=2.41-2.47$) that share space near the $\mu_3\text{-O}$ ligand. The signal overlap was significant enough that the signals could not be resolved (See Appendix B). The furthest downfield signals at $\delta=9.33$ (Figure 14) were again selected to represent the decay of the un-substituted Mo$_3^+$ species. The signals are an overlapping doublet of doublets due not only to the splitting that occurs in the formation of the mono-substituted species, but also the presence of two Mo$_3^+$ species in solution with differing alkylidyne ligands which give rise to inequivalent proton signals that are indistinguishable. The un-substituted Mo$_3^+$ species with terminal pyridine ligands undergoes pyridine exchange with py-d$_5$ allowing the decay in the un-substituted form to be monitored by $^1$H NMR. The first substitution step is the primary
focus of this study and all other forms of substituted Mo$_3^{+}$ species were omitted from this study.

Figure 14. $^1$H NMR spectra of Mo$_3$(µ$_3$-O)(µ$_3$-CY)(µ-O$_2$CCH$_2$CH$_3$)$_6$(py)$_3$]Br, Y = CH$_3$ and CH$_2$CH$_3$ at 303 K in CD$_3$NO$_2$ (t=0 min, t=12 min, t=27 min, t=38 min).

The pyridine exchange reaction for the mixed-crystal Mo$_3$(µ$_3$-O)(µ$_3$-CY)(µ-O$_2$CCH$_2$CH$_3$)$_6$(py)$_3$]Br, Y = CH$_3$ and CH$_2$CH$_3$ (Figure 14) happens quickly ($t_{1/2} = 13.6$ minutes at 298 K) compared to the ethylidyne-capped cluster with bridging acetate ligands ($t_{1/2} = 24.6$ minutes at 298 K). The $\Delta H_{\text{obsd}}^\ddagger = 108 \pm 5$ kJ mol$^{-1}$ and $\Delta S_{\text{obsd}}^\ddagger = 59 \pm 17$ J mol$^{-1}$ K$^{-1}$ indicate a D mechanism (Figure 15). The smaller $\Delta H_{\text{obsd}}^\ddagger$ for the mixed cluster system indicates the activation energy required to reach the intermediate complex
is slightly lower than the ethylidyne-capped cluster. The significantly lower $\Delta S_{\text{obsd}}^\ddagger$ suggests a decrease in entropy upon the formation of the intermediate. Steric hindrance caused by the bridging propionates ($R=\text{CH}_2\text{CH}_3$) may contribute to the smaller $\Delta S_{\text{obsd}}^\ddagger$ value. The incoming py-$d_5$ ligand gets closer in proximity (compared to the ethylidyne-capped Mo$_3^+$ cluster with bridging acetate ligands; $R=\text{CH}_3$) to the site of ligand exchange before dissociation of the outgoing ligand (py) occurs. The longer alkyl group ($R=\text{CH}_2\text{CH}_3$) on the bridging carboxylates could hinder the ability of the outgoing pyridine ligand to dissociate. More data over an extended temperature range is needed to accurately determine the $\Delta H_{\text{obsd}}^\ddagger$ and $\Delta S_{\text{obsd}}^\ddagger$ values. However, the magnitudes of the activation parameters suggest a D mechanism. The activation parameters for both alkylidyne-capped Mo$_3^+$ clusters are in good agreement with Nakata et al.$^{10}$ Although the activation parameters are similar for Mo$_3^+$ $R=\text{CH}_3$ and $R=\text{CH}_2\text{CH}_3$ mixed-crystal, there are differences in the rates.
Figure 15. Eyring plot for the pyridine exchange of $\text{Mo}_3(\mu_3-\text{O})(\mu_3-\text{CY})(\mu-$

$\text{O}_2\text{CCH}_2\text{CH}_3)_6(\text{py})_3]\text{Br}$, $Y = \text{CH}_3$ and $\text{CH}_2\text{CH}_3$ mixed-crystal.

The rate of exchange for the mixed alkylidyne-capped cluster is faster than the ethylidyne-capped cluster due to the enhanced electron donating ability of the $R$ group on the bridging carboxylates [$t_{1/2}$ at 298K ($R=\text{CH}_2\text{CH}_3$) $= 13.6$ minutes, $t_{1/2}$ at 298K ($R=\text{CH}_3$) $= 24.6$ minutes] as shown in Table 3.
Table 3. Temperatures, rate constants and half-lives for both clusters \([\text{Mo}_3(\mu_3-\text{CY})(\mu_3-\text{O})(\mu-\text{O}_2\text{CR})_6(\text{py})_3]X\), (Y=CH₃ or both CH₃ and CH₂CH₃, R=CH₃ or CH₂CH₃, X=Br⁻, BF₄⁻)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>R=CH₃</th>
<th>R=CH₂CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate const. (k (s^{-1}))</td>
<td>(t_{1/2} \text{ (min)})</td>
</tr>
<tr>
<td>298 (25 °C)</td>
<td>4.90 ±0.06 x 10⁻⁴</td>
<td>23.58</td>
</tr>
<tr>
<td>298 (25 °C)</td>
<td>4.69 ±0.04 x 10⁻⁴</td>
<td>24.63</td>
</tr>
<tr>
<td>303 (30 °C)</td>
<td>1.27 ±0.01 x 10⁻³</td>
<td>9.10</td>
</tr>
<tr>
<td>306 (33 °C)</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>308 (35 °C)</td>
<td>2.93 ±0.02 x 10⁻³</td>
<td>3.94</td>
</tr>
</tbody>
</table>

The electron donating or withdrawing ability of different R groups can be estimated using Hammett constants that are derived from the Hammett equation. Although the Hammett equation is a linear Gibbs Free energy relationship between structure and reactivity based on ionization of benzoic acids in water at 25 °C, one can still utilize the constants to rank the electron donating and withdrawing abilities of different ligands. The Hammett constants for the following alkyl groups are as follows: R=CH₃ (\(\sigma_m = -0.06, \sigma_p = -0.14\)), R=CH₂CH₃ (\(\sigma_m = -0.08, \sigma_p = -0.13\)), R=CH₂Cl (\(\sigma_m = 0.11, \sigma_p = 0.12\)) R=CHCl₂ (\(\sigma_m = 0.31, \sigma_p = 0.32\)), where the \(\sigma\) values represent the electronic effects of the substituent at the meta- (\(\sigma_m\)) and para- (\(\sigma_p\)) positions of benzoic acid.⁴⁰⁻⁴³ Although the inductive effects of R=CH₃ and R=CH₂CH₃ are similar, there is a difference in the rates consistent with the increase in electron donating ability of the alkyl groups (R=CH₂CH₃ > CH₃). As the electron donating ability increases so does the rate. This is consistent with work done by Fujihara and Houston on Cr³⁺ and Rh₃⁺ clusters.²³,²⁴
In addition to studying pyridine kinetics water substitution kinetics were also examined for Mo$_3$(µ$_3$-O)(µ$_3$-CCH$_3$)(µ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]BF$_4$ and Mo$_3$(µ$_3$-O)(µ$_3$-CY)(µ-O$_2$CCH$_2$CH$_3$)$_6$(H$_2$O)$_3$]Br, Y=CH$_3$ and CH$_2$CH$_3$. The substitution kinetics in water are complicated and non-conducive to VT-$^1$H NMR due to poor solubility. The dissolution of Mo$_3^+$ in D$_2$O showed slow dissociation of the bridging carboxylates. The stability of both clusters was monitored over time in D$_2$O. The aqueous solution chemistry of both Mo$_3^+$ clusters is complex and precipitation occurs readily. This complicates studying ligand substitution by NMR due to non-homogeneous solutions.

2.4 Studies on [Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCHCl)$_6$(CH$_3$OH)$_3$]O$_2$CCHCl$_2$

The dichloroacetate-bridged cluster was synthesized using the acetate bridged ethylidyne capped Mo$_3^+$ cluster [Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]Br as the starting material. The ethylidyne capped Mo$_3^+$ cluster was dissolved in neat dichloroacetic acid and heated at 115 °C for 4 hours. Deionized water was then added to the solution resulting in an orange-colored precipitate. The clean and dry precipitate was dissolved in methanol and after several days in the refrigerator at 10 °C slow evaporation of methanol yields red, block-shaped crystals. The X-ray crystallography data (Figure 17A) showed the cluster has structural characteristics consistent with the other Mo$_3^+$ clusters reported herein. There are four Mo$_3^+$ clusters per unit cell arranged in a cubic crystal system of the space group P2$_1$3 (Figure 17B). From the crystallography data, bond lengths and angles were established (Table 4 and Table 5). This is the first reported finding of this cluster in the literature. The trinuclear core is capped with three-coordinate ethylidyne (µ$_3$-CCH$_3$) and oxygen (µ$_3$-O) ligands. Six bridging dichloroacetates are
bound through the oxygen atoms to adjacent molybdenum ions and the terminal ligands are methanol. The cluster has $C_{3v}$ symmetry and an overall charge of $+1$. The charge was balanced by a free dichloroacetate anion (Figure 16).

**Figure 16.** Structure of $[\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3] \text{O}_2\text{CCHCl}_2$. 
Figure 17A. The thermal ellipsoid plot of $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-$
$\text{O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]^+$. 

Figure 17B. The unit cell for $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-$
$\text{O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]^+$. 
Figure 17A-B. Thermal ellipsoid plot (17A) and the unit cell (17B) of [Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCHCl₂)₆(CH₃OH)₃]⁺ (Hydrogen atoms omitted for clarity). The green atoms refer to chloride, the red atoms represent oxygen ions and the blue atoms represent molybdenum (IV) ions.

Table 4. Select bond lengths for [Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCHCl₂)₆(CH₃OH)₃]⁺

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Mo</td>
<td>2.7751(6) Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-O(µ₃-O)</td>
<td>1.968(3) Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-O(µ-O₂CCHCl₂)</td>
<td>2.106(3)-2.131(3) Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-O(CH₃OH)</td>
<td>2.145(3) Å</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Select bond angles for [Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCHCl₂)₆(CH₃OH)₃]⁺

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Mo-Mo</td>
<td>60.00(1)°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-O(µ₃-O)-Mo</td>
<td>89.7(1)°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-C(µ₃-CCH₃)-Mo</td>
<td>83.1(3)°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(µ-O₂CCHCl₂)-Mo-O(µ-O₂CCHCl₂)</td>
<td>73.2(1)-76.7(1)°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(µ-O₂CCHCl₂)-Mo-O(µ-O₂CCHCl₂)</td>
<td>87.6(1)-91.7(1)°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dichloroacetate Mo₃⁺ cluster was characterized by elemental analysis, ¹H, ¹³C NMR, FT-IR and UV-Vis spectroscopy. The ¹³C and ¹H NMR spectra were collected in dry MeOD-d₄ and chemical shifts are relative to TMS. The ¹H NMR signal that corresponds to the ethylidyne cap (µ₃-CCH₃) is observed at δ = 2.71 and the two sets of bridging dichloroacetates (µ-O₂CCHCl₂) are observed at δ = 6.51 and 6.58. The protons on the bridging dichloroacetates appear downfield due to neighboring chlorine atoms, which deshield them. Also observed in the ¹H NMR is the counter ion dichloroacetate (O₂CCHCl₂) at δ = 5.98. The ¹³C NMR spectrum shows two signals at δ = 65.54 and 65.31 for the alkyl carbons (µ-O₂CCHCl₂) and δ = 176.61 and 176.36 for the carbonyl
carbons (µ-O$_2$CCHCl$_2$) on the bidentate dichloroacetates. The signals that correspond to the ethylidyne cap are δ = 31.20 (µ$_3$-CCH$_3$) and 303.71 for the three-coordinate carbon cap (µ$_3$-CCH$_3$). The spectroscopic data can be found in Appendix C and a detailed synthesis in the experimental section of Chapter 4.

2.4.1 Attempt at ligating terminal pyridines via the Nakata method and the formation of Mo$_{10}$

When the acetate-bridged ethylidyne capped structure was dissolved in neat pyridine and heated overnight the terminal water ligands were substituted by pyridine. This procedure was initially described by Nakata et al.$^{10}$ When the dichloroacetate bridged Mo$_3^+$ cluster was dissolved in neat pyridine and gently heated, red arrowhead-shaped crystals formed. The structure was determined by X-ray crystallography to be [Mo$_{10}$O$_{10}$($\mu$$_3$-O)$_8$($\mu$-O)$_8$(py)$_8$](py)$_2$ (abbreviated Mo$_{10}$, Figure 18).

The Mo$_{10}$ structure has a cube-like polyoxomolybdate core with edge-bridging and terminal oxygen ligands, as well as terminal pyridine ligands. The cluster has two asymmetric faces opposite of one another that contain molybdenum (VI) ions (atom shown as Mo(3) in Figure 18) that extend away from each face elongating the cube shape. Connected to the asymmetric molybdenum (VI) ions are three types of unique Mo-O bonds (µ-O, µ$_3$-O, and Mo=O). The asymmetric molybdenum ions are bound through metal-metal bonding to adjacent molybdenum (V) ions located at the vertices of the cube. The oxidation states of the ten molybdenum ions that form the elongated cube-like structure are +5 (8 Mo) and +6 (2 Mo), indicating that oxidation of molybdenum
occurred in the formation of Mo$_{10}$. From the crystallography data (Figure 18) bond lengths and angles were established (Tables 6-8).

Figure 18. Thermal ellipsoid plot of the Mo$_{10}$O$_{10}$($\mu_3$-O)$_8$($\mu$-O)$_8$(py)$_8$ cluster (Hydrogen atoms omitted and carbon atoms not labeled for clarity).

Table 6. Select bond lengths for the polyoxomolybdate Mo$_{10}$ core

<table>
<thead>
<tr>
<th>Mo-Mo (edge)</th>
<th>Mo-Mo (asymmetric)</th>
<th>Mo-O($\mu_3$-O)</th>
<th>Mo-O($\mu$-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5662(6)-2.6061 Å</td>
<td>3.0137(6) Å</td>
<td>1.963(2)-2.285(3) Å</td>
<td>1.817(3)-2.059(2) Å</td>
</tr>
</tbody>
</table>
Table 7. Select bond lengths for the terminal ligands of Mo$_{10}$

<table>
<thead>
<tr>
<th></th>
<th>Mo=O</th>
<th>Mo-py</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.688(3)-1.696(3)Å</td>
<td>2.208(3)-2.231(3)Å</td>
</tr>
</tbody>
</table>

Table 8. Select bond angles for the Mo$_{10}$ cluster

<table>
<thead>
<tr>
<th>Mo-Mo-Mo</th>
<th>Mo-O(μ$_3$-O)-Mo</th>
<th>Mo-O(μ-O)-Mo</th>
<th>O(μ$_3$-O)-Mo-O(μ-O) (cube vertex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.86(1)$^\circ$</td>
<td>90.39(9)$^\circ$</td>
<td>82.79(9)-100.3(1)$^\circ$</td>
<td>155.5(1)-164.9(1)$^\circ$</td>
</tr>
</tbody>
</table>

Although X-ray crystallography and far-IR data for a nearly identical cluster has been previously reported, the synthetic approach differs significantly from what is reported herein. Modec et al. synthesized the complex [Mo$_{10}$O$_{28}$Py$_8$]•7Py by reacting (PyH)$_2$[MoOCl$_5$] in a mixture of pyridine and methanol.$^{44}$ The molybdenum starting material used is mononuclear and undergoes oxidation from Mo(IV) to Mo(VI). The trinuclear Mo$_3^+$ starting material that this study used to synthesize Mo$_{10}$ is also oxidized, but from Mo(IV) to Mo(V) and then to Mo(VI).

Modec et al. reported an X-ray structure of Mo$_{10}$ with two μ$_4$-O ligands. The additional bonds are between an asymmetric molybdenum ion and the nearest oxygen that is part of one symmetric cubic face. This additional molybdenum-oxygen bond was reported to be 2.620(3) Å$^{44}$ and is nearly 0.3 Å longer than the longest molybdenum-oxygen bond reported in Table 6 above. In Figure 18, three-coordinate oxygen ligands (μ$_3$-O) are the highest coordination of oxygen species reported herein. Using FT-IR spectroscopy Modec et al. reported several molybdenum-oxygen vibrational frequencies
for \([\text{Mo}_{10}\text{O}_{28}\text{Py}_8]\cdot7\text{Py}\). However, due to the similarity in bond bending and stretching frequencies for higher coordinate molybdenum-oxygen bonding modes (\(\mu\)-O, \(\mu_3\)-O, \(\mu_4\)-O) it was challenging to assign the signals due to overlap. The molybdenum-oxygen stretching frequencies reported herein for \(\text{Mo}_{10}\) are consistent with those reported by Modec et al. (see Appendix D or Chapter 4). The cluster was found to be insoluble in a variety of protic and aprotic solvents and therefore it was not conducive for NMR analysis.

2.4.2 Kinetic experiments by variable-temperature \(^1\)H NMR for \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2\)

VT-\(^1\)H NMR experiments were performed in a dual-solvent system (MeOD-d\(_4\)/CD\(_3\)NO\(_2\)-d\(_3\)) where the ligated methanol ligands were substituted by incoming pyridine ligands (Figure 19). The \(^1\)H NMR signals that correspond to the ethylidyne protons (\(\mu_3\text{-CCH}_3\)) are well resolved for each substitution product observed. The decrease in signal intensity that corresponds to the protons on the ethylidyne capping ligand (\(\mu_3\text{-CCH}_3\), \(\delta = 2.66\)) of the un-substituted species, \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]^+\), was the target signal monitored via \(^1\)H NMR. The growth and decay of the \(\mu_3\text{-CCH}_3\) protons that correspond to the mono-substituted species \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_2(\text{py})]^+\) are observed as a product of the first substitution step (growth) and as a reactant for the second substitution step (decay). The growth of the di-substituted species \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})(\text{py})_2]^+\) is also observed however there is no decay of this species. The tri-substituted complex, \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCHCl}_2)_6(\text{py})_3]^+\), is not observed in the \(^1\)H NMR data.
Figure 19. Shifted overlay of the $\mu_3$-CCH$_3$ signals that correspond to the un-, mono- and di-substituted Mo$_3^+$ species in 1.1 M pyridine.

A series of kinetic experiments were performed at room temperature and above using two different pyridine concentrations (1.1 M, 0.1 M). The first set of kinetic experiments used a 1.1 M pyridine concentration and measured rate constants at five temperatures with room temperature runs repeated in triplicate [25 °C (x3), 28 °C, 30 °C, 33 °C, 35 °C (±0.01 °C / °C)]. Data for the first substitution step was collected continuously for at least three half-lives and fit to a three variable exponential equation. The rate constants nearly span one order of magnitude (1.575-8.010 x 10$^{-3}$ s$^{-1}$). The rate is first-order in the concentration of the metal complex, [Mo$_3^+$], and first-order overall.
Figure 20A. 296.9 K

\[ y = 0.014 + 0.198e^{(-0.00158t)} \]

\[ R^2 = 0.999228 \]

Figure 20B. 297.2 K

\[ y = 0.005 + 0.111e^{(-0.00158t)} \]

\[ R^2 = 0.999762 \]
**Figure 20C. 297.4 K**

- **Equation:**
  
  \[ y = 0.009 + 0.254e^{(-0.00186t)} \]

- **R²:** 0.999705

**Figure 20D. 301 K**

- **Equation:**
  
  \[ y = 0.004 + 0.066e^{(-0.00318t)} \]

- **R²:** 0.999999
Figure 20E. 303 K

Normalized Area (2.6 ppm)

\[ y = 0.003 + 0.063e^{(-0.00338t)} \]

\[ R^2 = 0.999900 \]

Figure 20F. 305 K

Normalized Area (2.6 ppm)

\[ y = 0.013 + 0.262e^{(-0.00605t)} \]

\[ R^2 = 0.999575 \]
Figure 20A-G. The decay in area count of the signal corresponding to the protons on the μ₃-CCH₃ ligand at 296.9 K (A), 297.2 K (B), 297.4 K (C), 301 K (D), 303 K (E), 305 K (F) and 308 K (G) for the dichloroacetate-bridged cluster in 1.1 M pyridine.

By using the temperature dependence on the rate, an Eyring plot was generated (Figure 21) to calculate the activation parameters associated with the first substitution step. The activation parameters were determined to be $\Delta H_{\text{obsd}}^{\ddag} = 109 \pm 8 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{obsd}}^{\ddag} = 70 \pm 28 \text{ J mol}^{-1} \text{ K}^{-1}$. The magnitudes of the activation parameters indicate a D mechanism. The large activation enthalpy ($\Delta H_{\text{obsd}}^{\ddag}$) is related to the energy required in the bond breakage step to reach the intermediate species. The activation entropy ($\Delta S_{\text{obsd}}^{\ddag}$) is positive which suggests an increase in degrees of freedom. However, the $\Delta S_{\text{obsd}}^{\ddag}$ value is not very large indicating the incoming pyridine ligands could be in close proximity to the Mo—O(CH₃OH) site before dissociation. The activation parameters reported herein
are consistent with work reported by Nakata et al. for pyridine-pyridine-d₅ exchange and water substitution by methanol-d₄ for the Mo₃⁺ cluster with bridging acetate ligands. In the Nakata study, the pyridine concentration was varied and was shown to have a minor influence on the exchange rate.

![Eyring plot](image)

**Figure 21.** Eyring plot for the first methanol substitution step of the dichloroacetate-bridged cluster in 1.1 M pyridine.

In **Figure 19**, additional signals labeled as Mo₁₀ precursor are observed and shifted slightly downfield from each un- and mono-substituted Mo₃⁺ species. These signals are not very intense but appear in the ¹H NMR spectra at each temperature. These
signals were assigned to a Mo$_3^+$ precursor complex in the formation of the Mo$_{10}$ cluster. This study found that the Mo$_{10}$ forms under highly basic conditions (See Chapter 4). The ethylidyne-capped Mo$_3^+$ cluster with bridging dichloroacetate ligands was dissolved in neat py to form Mo$_{10}$, so a Mo$_3^+$ precursor complex is no surprise when the pyridine concentration is approximately 1.1 M. With the addition of pyridine, the precursor complex forms immediately and the reaction will reach equilibrium. By comparing the area under the ethylidyne cap signal ($\mu_3$-CCH$_3$) for the fully substituted Mo$_3^+$ species in MeOD-d$_4$ with the area of each substituted species after the addition of CD$_3$NO$_2$-d$_3$ and pyridine, it was confirmed that the Mo$_{10}$ precursor originated from the Mo$_3^+$ cluster (See Table in Appendix D). The precursor complex undergoes ligand substitution similar to Mo$_3^+$ suggesting the complex still contains a trinuclear core and surrounding ligands.

There is no evidence in the $^1$H NMR spectra of bridging dichloroacetate dissociation, as the corresponding signal for free dichloroacetate has been assigned and the area monitored over time. The slight deshielding of the protons that correspond to the ethylidyne cap ($\mu_3$-CCH$_3$) of the Mo$_{10}$ precursor can be explained if one of the molybdenum (IV) ions is oxidized to molybdenum (V). Oxidation of molybdenum from +5 to +6 does occur in the Mo$_{10}$ synthesis reported by Modec et al.$^{44}$ Because the Mo$_{10}$ precursor immediately forms and reaches equilibrium it does not affect the kinetics concerning ligand substitution for the targeted Mo$_3^+$ complex.

To reduce the formation of the Mo$_3^+$ precursor, the concentration of pyridine was lowered to approximately 0.1 M and the kinetic experiments repeated at temperatures ranging from 25–37 °C (±0.01 °C / °C). The decay in the ethylidyne cap signal ($\mu_3$-
CCH$_3$) of the un-substituted species, [Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-0$_2$CCHCl$_2$)$_6$(CH$_3$OH)$_3$]$^+$, was monitored over time at 297 K (x2), 301 K, 305 K and 310 K (Figure 22A-E). The data was fit to a three variable exponential (Equation 13) to deduce the rate constants. By lowering the pyridine concentration, the formation of the Mo$_{10}$ precursor was not observed (Figure 23).

![Figure 22A. 297.0 K](image)
Figure 22B. 296.9 K

\[ y = 0.187 + 0.556e^{-0.000158t} \]
\[ R^2 = 0.9995939 \]

Figure 22C. 301 K

\[ y = 0.160 + 0.550e^{-0.000346t} \]
\[ R^2 = 0.9998104 \]
Figure 22A-E. The decay in the area count of the signal corresponding to the protons on the $\mu_3$-CCH$_3$ ligand at 297.0 (A), 296.9 (B), 301 (C), 305 (D), 310 K (E) for the dichloroacetate-bridged cluster in 0.1 M pyridine.
Figure 23. Overlay of the $^1$H NMR signals corresponding to the $\mu_3$-CCH$_3$ ligand of the un-, mono- and di-substituted Mo$_3^+$ species in 0.1 M pyridine.

An Eyring plot was generated to calculate the activation parameters associated with the first substitution step to further evaluate the mechanistic pathway (Figure 24). The activation parameters were determined to be $\Delta H_{\text{obsd}}^{\dagger} = 116 \pm 7$ kJ mol$^{-1}$ and $\Delta S_{\text{obsd}}^{\dagger} = 74 \pm 23$ J mol$^{-1}$ K$^{-1}$. Based on the magnitudes of both parameters the assigned mechanistic pathway is D. The activation parameters are consistent with those determined for the 1.1 M pyridine concentration ($\Delta H_{\text{obsd}}^{\dagger} = 109 \pm 8$ kJ mol$^{-1}$, $\Delta S_{\text{obsd}}^{\dagger} = 70 \pm 28$ J mol$^{-1}$ K$^{-1}$).
Although the activation parameters are virtually unchanged, an obvious difference in the rate is observed for both pyridine concentrations.

![Eyring plot for the first methanol substitution step of the dichloroacetate-bridged cluster in 0.1 M pyridine.](image)

**Figure 24.** Eyring plot for the first methanol substitution step of the dichloroacetate-bridged cluster in 0.1 M pyridine.

A summary of the rate data at both pyridine concentrations was established in **Table 9** below. The rate constants for the 0.1 M pyridine span nearly one order of magnitude and are slower than those measured for the 1.1 M pyridine concentration. The rate data suggests a slight dependence on the concentration of pyridine for the first substitution step. For both concentrations the reaction followed first-order kinetics (**Table 9**).
Table 9. Kinetic data for \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2\) in 1.1 M and 0.1 M pyridine

<table>
<thead>
<tr>
<th>T (K)</th>
<th>[Mo$_3^+$] (mM)</th>
<th>[py] (M)</th>
<th>t$_{1/2}$ (min)</th>
<th>Rate const. k (s$^{-1}$)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.9</td>
<td>3.77</td>
<td>1.1</td>
<td>7.31</td>
<td>1.58 ±0.06 x 10$^{-3}$</td>
<td>5.933 x 10$^{-6}$</td>
</tr>
<tr>
<td>297.2</td>
<td>4.32</td>
<td>1.1</td>
<td>6.21</td>
<td>1.86 ±0.07 x 10$^{-3}$</td>
<td>8.023 x 10$^{-6}$</td>
</tr>
<tr>
<td>297.4</td>
<td>4.37</td>
<td>1.1</td>
<td>7.31</td>
<td>1.58 ±0.03 x 10$^{-3}$</td>
<td>6.893 x 10$^{-6}$</td>
</tr>
<tr>
<td>301</td>
<td>3.67</td>
<td>1.1</td>
<td>3.63</td>
<td>3.18 ±0.01 x 10$^{-3}$</td>
<td>1.168 x 10$^{-5}$</td>
</tr>
<tr>
<td>303</td>
<td>4.31</td>
<td>1.1</td>
<td>3.42</td>
<td>3.38 ±0.07 x 10$^{-3}$</td>
<td>1.457 x 10$^{-5}$</td>
</tr>
<tr>
<td>305</td>
<td>4.37</td>
<td>1.1</td>
<td>1.91</td>
<td>6.05 ±0.20 x 10$^{-3}$</td>
<td>2.644 x 10$^{-5}$</td>
</tr>
<tr>
<td>308</td>
<td>3.49</td>
<td>1.1</td>
<td>1.44</td>
<td>8.01 ±1.50 x 10$^{-3}$</td>
<td>2.797 x 10$^{-5}$</td>
</tr>
<tr>
<td>297</td>
<td>4.98</td>
<td>0.1</td>
<td>70.44</td>
<td>1.64 ±0.06 x 10$^{-3}$</td>
<td>8.161 x 10$^{-7}$</td>
</tr>
<tr>
<td>296.9</td>
<td>4.2</td>
<td>0.1</td>
<td>73.12</td>
<td>1.58 ±0.02 x 10$^{-3}$</td>
<td>6.639 x 10$^{-7}$</td>
</tr>
<tr>
<td>301</td>
<td>4.42</td>
<td>0.1</td>
<td>33.39</td>
<td>3.46 ±0.04 x 10$^{-3}$</td>
<td>1.530 x 10$^{-6}$</td>
</tr>
<tr>
<td>305</td>
<td>4.53</td>
<td>0.1</td>
<td>22.70</td>
<td>5.09 ±0.20 x 10$^{-3}$</td>
<td>2.308 x 10$^{-6}$</td>
</tr>
<tr>
<td>310</td>
<td>4.64</td>
<td>0.1</td>
<td>8.96</td>
<td>1.29 ±0.02 x 10$^{-3}$</td>
<td>6.001 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

2.5 Studies on \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4\)

In order to develop a trend in reactivity based on structure for ligand substitution, the following cluster was synthesized by dissolving \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{Br}\) into neat chloroacetic acid. The mixture was gently refluxed at 85 °C for approximately twelve hours followed by the addition of water. Allowing the water to slowly evaporate yielded red-orange hexagonal-shaped crystals, while fast water reduction via rotary evaporation yielded an orange-colored microcrystalline. Although the red hexagonal-shaped crystals were not conducive for single crystal X-ray crystallography analysis, they were soluble in MeOD-d$_4$ and able to be analyzed via
NMR spectroscopy. The NMR data showed the red crystals to be consistent in structure with the orange-colored microcrystal in solution. UV-Vis and FT-IR spectroscopy were also performed to characterize this compound (see Appendix E).

2.5.1 Characterization of \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4\) by NMR spectroscopy

Following the dissolution of \([\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4\) in MeOD-\(d_4\) the terminal water ligands are substituted by MeOD-\(d_4\) ligands. This reaction happens quickly at room temperature. After just minutes the ligand substitution reaction has reached equilibrium as shown in the \(^1\text{H}\) NMR spectrum (Figure 25).
Figure 25. $^1$H NMR spectrum of $[\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu_2\text{O}=\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4$ in MeOD-d$_4$ / TMS.

The protons on each set of three chemically equivalent bridging chloroacetates ($\mu_2\text{O}=\text{CCH}_2\text{Cl}$, 6H) correspond to the signals downfield at $\delta = 4.28$ and 4.34 respectively. These signals appear downfield because of the chlorine atom on the alkyl group of the bridging chloroacetates. Also present is the three-coordinate ethylidyne capping ligand ($\mu_3\text{-CCH}_3$, 3H) at $\delta = 2.47$. This signal is resolved, although small quantities of additional Mo$_3^+$ species at equilibrium exist at equilibrium in solution. The protons on the ethylidyne cap ($\mu_3\text{-CCH}_3$, 3H) of the other Mo$_3^+$ species are observed at $\delta = 2.45$ and 2.44 respectively. These two species originate from the equilibrium of the water-methanol substitution reaction that occurs with the addition of MeOD-d$_4$. This ligand substitution
reaction reaches equilibrium quickly but small quantities of \( \text{Mo}_3^+ \) species with terminal water ligands remaining in solution. Also present in minute quantities is unreacted starting material, \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\)\(\text{Br}\). The \( ^1\text{H} \) NMR spectrum in Figure 25 above shows signals at \( \delta = 2.26 \) and 2.19 for the bridging acetates (\(\mu-\text{O}_2\text{CCH}_3, 9\text{H}\)) and at \( \delta = 1.99 \) for free acetate (\(\text{O}_2\text{CCH}_3, 3\text{H}\)). The protons on the ethylidyne ligand \(\mu_3-\text{CCH}_3\) are not observed because the concentration is too low.

2.5.1 Kinetic studies on \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\)\(\text{ClO}_4\) by variable-temperature \( ^1\text{H} \) NMR spectroscopy

Upon the addition of CD\(_3\text{NO}_2\)-d\(_3\) and pyridine to \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{MeOD}-\text{d}_4)_3]^+\), the terminal MeOD-d\(_4\) ligands are substituted by pyridine. All substituted \( \text{Mo}_3^+ \) species (mono-, di- and tri-substituted) are observed on the \( ^1\text{H} \) NMR spectra depending on the reaction conditions. The decay in area of the signal that corresponds to the protons on the ethylidyne capping ligand (\(\mu_3-\text{CCH}_3, \delta = 2.4980\)) of the un-substituted species was monitored with respect to time (Figure 26). Kinetic data was collected at temperatures ranging from 24-37 °C (±0.01 °C / °C) [297 K (x2), 301K, 305 K and 310 K] (Figures 27A-E). The data was fit to an exponential equation (Equation 13) to deduce a rate constant for the first methanol substitution step. The other substituted forms of \( \text{Mo}_3^+ \) (-mono, -di, -tri) were not the focus of this study.
**Figure 26.** Overlay of the $^1$H NMR signal corresponding to the $\mu_3$-CCH$_3$ ligand of the un-, mono- and di-substituted Mo$_3$$^+$ species in 0.1 M pyridine at 296.7 K (tri-substituted species not present at this pyridine concentration).

**Figure 27A.** 296.7 K
Figure 27B. 296.3 K

\[ y = 0.061 + 0.250e^{-0.001034t} \]

\[ R^2 = 0.9996716 \]

Figure 27C. 301 K

\[ y = 0.063 + 0.298e^{-0.001412t} \]

\[ R^2 = 0.9996571 \]
Figure 27A-E. The decay in the 1H NMR signal corresponding to the \( \mu_3\text{-CCH}_3 \) ligand with time at varying temperatures: 296.7 (A), 296.3 (B), 301 (C), 305 (D), 310 K (E) for the chloroacetate-bridged cluster.
2.5.2 Kinetic data for \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4\) terminal methanol substitution by pyridine

For the first substitution step the rate constants ranged from \(1.121 \times 10^{-3}\) s\(^{-1}\) and the reaction followed first-order kinetics as shown in Table 10. The rate data showed that methanol substitution by pyridine for \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{MeOD-d}_4)_3]\text{ClO}_4\) is faster (\(t_{1/2} = 10.31\) minutes at 296.7 K) compared to \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2\) (\(t_{1/2} = 73.12\) minutes at 296.9 K). This is consistent with trends already published in the literature for trinuclear \(\text{Cr}_3^+\) and \(\text{Rh}_3^+\) clusters.\(^{23,24}\) The trend is also consistent with the kinetic data reported herein for pyridine exchange of the two alkylidyne-capped clusters with bridging acetates and propanoates (\(R=\text{CH}_2\text{CH}_3 > \text{CH}_3\)), which was explained using Hammett constants.

Table 10. Kinetic data for \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4\) in 0.1 M pyridine

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>[\text{Mo}_3^+] (mM)</th>
<th>(t_{1/2}) (min)</th>
<th>Rate const. (k) (s(^{-1}))</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.7</td>
<td>1.64</td>
<td>10.31</td>
<td>1.12 ±0.03 x 10(^{-3})</td>
<td>1.842 x 10(^{-6})</td>
</tr>
<tr>
<td>296.3</td>
<td>2.90</td>
<td>11.22</td>
<td>1.03 ±0.03 x 10(^{-3})</td>
<td>3.006 x 10(^{-6})</td>
</tr>
<tr>
<td>301</td>
<td>2.90</td>
<td>8.19</td>
<td>1.41 ±0.05 x 10(^{-5})</td>
<td>4.104 x 10(^{-6})</td>
</tr>
<tr>
<td>305</td>
<td>1.52</td>
<td>4.81</td>
<td>2.40 ±0.10 x 10(^{-3})</td>
<td>3.634 x 10(^{-6})</td>
</tr>
<tr>
<td>310</td>
<td>2.32</td>
<td>2.28</td>
<td>5.07 ±0.02 x 10(^{-5})</td>
<td>1.178 x 10(^{-5})</td>
</tr>
</tbody>
</table>
2.5.3 Mechanism and activation parameters for $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-$O$_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4$

The rate data was used to formulate an Eyring plot to deduce a mechanistic pathway based on the magnitude of the activation parameters (Figure 28). The activation parameters for the first substitution step of MeOD-d$_4$ by pyridine for the $[\text{Mo}_3(\mu_3-$CCH$_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{MeOD-d}_4)_3]\text{ClO}_4$ were determined to be $\Delta H_{\text{obsd}}^{\ddagger} = 83 \pm 10$ kJ mol$^{-1}$ and $\Delta S_{\text{obsd}}^{\ddagger} = -23 \pm 32$ J mol$^{-1}$ K$^{-1}$. Although the activation entropy ($\Delta S^{\ddagger}$) is negative and suggests an A mechanism, the reaction mechanism still follows a D pathway. The narrow temperature range (25-37 °C) at which the ligand substitution reaction was monitored limits the accuracy of the extrapolation to the y-axis that yields the $\Delta S_{\text{obsd}}^{\ddagger}$ value. Each molybdenum (IV) center is nine-coordinate and sterically hindered creating little space for the attack of an approaching ligand. A D mechanism is consistent with most trinuclear clusters published in the literature, with the exception of W$_3^{+2}$ and Nb$_3^{+4}$.$^{15}$ The large activation enthalpy ($\Delta H_{\text{obsd}}^{\ddagger} = 83 \pm 10$ kJ mol$^{-1}$) is approximately equal to the energy required in the bond breakage step. The large $\Delta H_{\text{obsd}}^{\ddagger}$ is consistent with a D mechanism. The magnitude of $\Delta H_{\text{obsd}}^{\ddagger}$ does not suggest assistance from the incoming ligand, which would lower $\Delta H_{\text{obsd}}^{\ddagger}$ significantly. This suggests a D mechanism for ligand substitution is most likely.
Figure 28. Eyring plot for the first methanol substitution step of the chloroacetate-bridged cluster in 0.1 M pyridine.

2.6 Trends in reactivity for terminal ligand substitution

As previously discussed in chapter 1, Fujihara and Houston have established trends in reactivity for trinuclear Cr$_3^+$ and Rh$_3^+$ clusters that are influenced by structure. One of the key differences in structure is the centrally located three-coordinate oxygen ligand that is bound directly to the M$_3^+$ core (M = Cr or Rh). Although it has previously been proposed that the three-coordinate ligands influence terminal ligand substitution, this was not the focus of this study. However, varying the alkyl group on the bridging carboxylate ligands has an effect on the rate of terminal ligand substitution. Alkyl groups were selected with varying electron donating and withdrawing abilities to observe the
electronic effect on terminal ligand substitution. It was found for trinuclear molybdenum (IV) clusters that the rate of terminal ligand substitution was dependent on the electronic structure of the alkyl group on the bridging carboxylates. Trinuclear Mo$_3^+$ clusters showed activation parameters consistent with a D or I$_d$ mechanism as expected for a nine coordinate cluster.

2.6.1 Comparison of rates for trinuclear metal clusters with bridging chloro- and dichloroacetates

The oxo-centered Cr$_3^+$ and Rh$_3^+$ structures have a coordination number of six compared to the Mo$_3^+$ clusters, which are nine-coordinate. High coordination environments cause steric hindrance, which promotes bond dissociation. The rates of ligand substitution are fast for the higher coordinate Mo$_3^+$ clusters with bridging chloro- and dichloroacetates indicating sterics and the metal d-orbitals influence ligand substitution. There are differences in the central or capping ligands of the clusters illustrated in Table 11 that also influence rates of ligand substitution. The positions of the bridging carboxylates and three-coordinate ligands relative to the terminal ligands are important in interpreting rates of ligand substitution. In addition to the number of ligands that surround a metal center, the inductive effects of those ligands also influence rates of ligand substitution.
Table 11. A comparison of rate constants \( (k_{298K}) \) for trinuclear metal clusters with bridging dichloro- and chloroacetate ligands

<table>
<thead>
<tr>
<th>Cluster</th>
<th>R group</th>
<th>Rate constant ( (s^{-1}) )</th>
<th>Substitution Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cr}_3^+ )</td>
<td>( \text{CH}_2\text{Cl} )</td>
<td>( 1.80(4) \times 10^{-5} )</td>
<td>( \text{H}_2\text{O} \rightarrow \text{DMA} )</td>
</tr>
<tr>
<td>( \text{Cr}_3^{+ , a} )</td>
<td>( \text{CHCl}_2 )</td>
<td>( 1.2(5) \times 10^{-5} )</td>
<td>( \text{H}_2\text{O} \rightarrow \text{DMA} )</td>
</tr>
<tr>
<td>( \text{Rh}_3^+ )</td>
<td>( \text{CH}_2\text{Cl} )</td>
<td>( 5.0 \times 10^{-4} )</td>
<td>( \text{H}_2\text{O} \rightarrow \text{MeOD-d}_4 )</td>
</tr>
<tr>
<td>( \text{Rh}_3^+ )</td>
<td>( \text{CHCl}_2 )</td>
<td>( 2.3 \times 10^{-5} )</td>
<td>( \text{H}_2\text{O} \rightarrow \text{MeOD-d}_4 )</td>
</tr>
<tr>
<td>( \text{Mo}_3^+ )</td>
<td>( \text{CH}_2\text{Cl} )</td>
<td>( 1.121 \times 10^{-3} )</td>
<td>( \text{MeOD-d}_4 \rightarrow \text{py} )</td>
</tr>
<tr>
<td>( \text{Mo}_3^+ )</td>
<td>( \text{CHCl}_2 )</td>
<td>( 1.640 \times 10^{-4} )</td>
<td>( \text{MeOH} \rightarrow \text{py} )</td>
</tr>
</tbody>
</table>

\( a \) rate constant determined at 308 K

The inductive effect from the alkyl \( (R) \) group on the bridging carboxylates influence rates of ligand substitution. As the electron donating ability of the \( R \) group increases so does the rate. The rate increase results from longer bonds between the molybdenum (IV) ions and terminal ligands. As the electron withdrawing ability of the \( R \) group increases the rate decreases. This is due to shorter bonds between molybdenum (IV) ions and terminal ligands \((\text{Mo—L})\). This trend is illustrated in Table 11 for three trinuclear clusters. The electron donating or withdrawing ability of different \( R \) groups can be estimated using Hammett constants. For \( R=\text{CH}_2\text{Cl} \) \((\sigma_m = 0.11, \sigma_p = 0.12)\) and \( R=\text{CHCl}_2 \) \((\sigma_m = 0.31, \sigma_p = 0.32)\), where \( \sigma \) values represent different electronic effects at the meta- \((\sigma_m)\) and para- \((\sigma_p)\) positions on benzoic acid.\(^42\) Dichloroacetic acid \((R=\text{CHCl}_2)\) is the stronger acid and has the more positive Hammett constants compared to chloroacetic acid \((R=\text{CH}_2\text{Cl})\). This relates to the \( R \) groups ability to donate electrons into the ring of benzoic acid, which is inhibited by strong electron withdrawing atoms. As electron density is donated into the trinuclear system surrounding bonds weaken and rates
of dissociation increase. Electron withdrawing atoms pull electron density away from the system causing bonds to strengthen and rates of ligand substitution to slow. This is consistent with the trend in reactivity found for methanol substitution of Mo$_3^+$ clusters with bridging chloro- and dichloroacetate ligands reported herein (R = CH$_2$Cl > CHCl$_2$).

2.6.2 Comparison of activation parameters for trinuclear molybdenum (IV) clusters

Methanol substitution and pyridine exchange reactions for a series of trinuclear Mo$_3^+$ clusters with varying alkyl groups were performed to develop trends in reactivity based on structure for Mo$_3^+$ clusters. The substitution reactions studied here correlate well with work published by Nakata et al.$^{10}$ All substitution reactions for Mo$_3^+$ clusters reported in Table 12 follow a D mechanism.
Table 12. Comparison of activation parameters for substitution and exchange reactions of Mo$^+$ clusters

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substitution-type</th>
<th>$\Delta H^\dagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\dagger$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CCH_3)(\mu-O_2CCH_3)_6(py)_3]BF_4^b$</td>
<td>py $\rightarrow$ py-d$_5$</td>
<td>112 ± 1</td>
<td>77 ± 5</td>
</tr>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CCH_3)(\mu-O_2CCH_3)_6(py)_3]BF_4^a$</td>
<td>py $\rightarrow$ py-d$_5$</td>
<td>129 ± 4</td>
<td>125 ± 13</td>
</tr>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CY)(\mu-O_2CCH_2CH_3)_6(py)_3]Br$, Y = CH$_3$ &amp; CH$_2$CH$_3^a$</td>
<td>py $\rightarrow$ py-d$_5$</td>
<td>108 ± 5</td>
<td>59 ± 17</td>
</tr>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CCH_3)(\mu-O_2CCH_3)_6(H_2O)_3]BF_4^b$</td>
<td>H$_2$O $\rightarrow$ MeOD-d$_4$</td>
<td>93 ± 11</td>
<td>49 ± 47</td>
</tr>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CCH_3)(\mu-O_2CCHCl)_6(CH_3OH)_3]O_2CCHCl_2^a$</td>
<td>MeOH $\rightarrow$ py</td>
<td>116 ± 7</td>
<td>74 ± 23</td>
</tr>
<tr>
<td>$[\text{Mo}_3(\mu_3-O)(\mu_3-CCH_3)(\mu-O_2CCH_2Cl)_6(CH_3OH)_3]^+^a$</td>
<td>MeOD-d$_4$ $\rightarrow$ py</td>
<td>83 ± 10</td>
<td>-23 ± 32</td>
</tr>
</tbody>
</table>

$^a$ This work

$^b$ Ref. [10]

The activation parameters associated with the first ligand substitution step for alkylidyne-capped Mo$^+$ clusters indicate a D mechanism (Table 12). The activation enthalpy ($\Delta H^\dagger$) values range from 83-132 kJ mol$^{-1}$. The magnitude of $\Delta H^\dagger$ is consistent with other trinuclear metal clusters that follow D mechanisms. The activation entropy ($\Delta S^\dagger$) values range from 135-(-23) J mol$^{-1}$ K$^{-1}$, with all but one cluster having values that are positive. If the temperature range is not broad enough, extrapolation to the y-axis ($\Delta S^\dagger$) can easily be inaccurate. This is the case for the Mo$^+$ cluster with bridging chloroacetate ligands (R=CH$_2$Cl), which showed -23 J mol$^{-1}$ K$^{-1}$ for $\Delta S_{\text{obsd}}^\dagger$. The reaction is clearly not associative with a large $\Delta H_{\text{obsd}}^\dagger$ value (83 kJ mol$^{-1}$) and a coordination number of nine that allows little space for an approaching ligand. Assigning an A
mechanism would not be consistent with what has previously been reported in the literature or with the observations made in this study.
Chapter 3

CONCLUSIONS AND FUTURE WORK

3.1 Concluding remarks and future work

The alkyl groups on the bridging carboxylates were varied to observe the influence on terminal ligand substitution for a series of alkylidyne-capped trinuclear molybdenum (IV) clusters. Kinetic experiments were performed on all reported Mo$_3^+$ clusters to examine rates of terminal ligand substitution or exchange. The rate data was obtained using VT-$^1$H NMR and Eyring plots were generated to gain insight into mechanistic pathways. The activation parameters for each Mo$_3^+$ cluster analyzed suggest a D mechanism for terminal ligand substitution. Although the activation parameters only vary slightly between clusters, there is an obvious difference in the rates. With the support of Hammett constants, two trends were established which show that as the electron donating ability of the alkyl group increases (R=CH$_3$ < CH$_2$CH$_3$) so does the rate of terminal ligand substitution. In contrary, as the electron withdrawing ability of the alkyl group increases (R=CH$_2$Cl < CHCl$_2$) the rate decreases.

The ethylidyne-capped cluster with bridging dichloroacetates is a new structure that has not been previously published in the literature. The X-ray structure is just one of three published findings in the literature to date that contain an alkyl group on the alkylidyne-capping ligand different from the alkyl group on the bridging carboxylates. Under basic conditions the Mo$_{10}$ cluster forms as a byproduct of the dichloroacetate-
bridged ethylidyne-capped Mo$_3^+$ cluster. Although a similar X-ray structure for Mo$_{10}$ has been previously reported, this is the first reported polyoxomolybdate formed as a byproduct of a Mo$_3^+$ reaction. The X-ray structure reported herein for Mo$_{10}$ is unique in that it does not contain four-coordinate oxygen species. An ethylidyne-capped cluster with bridging chloroacetates was also isolated, characterized and crystallized. Unfortunately, the crystals were not suitable for single crystal X-ray crystallography. Characterization of the chloroacetate-bridged ethylidyne-capped cluster was performed using spectroscopic techniques.

Future work will focus on developing new Mo$_3^+$ clusters with bridging carboxylates that differ in the alkyl (R) groups. By varying the alkyl character of the bridging carboxylates, the reactivity of other ligands can be influenced. With the addition of new Mo$_3^+$ structures, organic chemists can begin to choose from a bank of potential molybdenum catalysts. The alkylidyne-capping ligand has been previously discussed and remains a top research interest moving forward due to its applications as a reactive carbyne radical once dissociated from Mo$_3^+$. Although it has been postulated that the ethylidyne-capping ligand dissociates under mild aqueous conditions, this study found the ligand to be stable through the process of substituting the bridging carboxylates to form new clusters. In addition, the formation of new polyoxomolybdates using Mo$_3^+$ clusters as a starting material also has the potential for future success.
Chapter 4

EXPERIMENTAL SECTION

The following chemicals were purchased for synthesis and spectroscopy experiments: Mo(CO)$_6$ (Acros Organics, 98%), acetic acid (Macron Chemicals), acetic anhydride, propionic acid, propionic anhydride (Fisher Scientific), triethylamine (Spectrum Chemical Mfg. Corp.), chloroacetic acid (Mallinckrodt Chemical Works), dichloroacetic acid, 2,2,3,3-$d$(4)-3-(trimethylsilyl)propionic acid sodium salt or TSP (Alfa Aesar), potassium tetrafluoroborate, tetramethylsilane or TMS (Sigma Aldrich), sodium bromide, sodium perchlorate, methanol, diethyl ether (Fisher Scientific), pyridine (EMD Chemicals Inc.), deuterated water (Cambridge Isotope Laboratories Inc.), CD$_3$NO$_2$-d$_3$, MeOD-d$_4$, py-d$_5$ (Acros Organics). $^1$H NMR and $^{13}$C NMR spectra were collected at 500 MHz and 125 MHz using a Bruker Avance III spectrometer. All chemical shifts reported are in ppm relative to TSP, TMS, or the residual solvent signal (MeOD-d$_4$, CD$_3$NO$_2$-d$_3$, HOD) on the $\delta$ (ppm) scale. Peak multiplicity is denoted by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). FT-IR data was collected using a Thermo Scientific Nicolet iS50 instrument with a Smart iTR or generic sample holder with baseplate. All signals are reported in cm$^{-1}$ and bands are denoted as broad (br), very strong (vs), strong (s), medium (m), weak (w), very weak (vw) and shoulder (sh). UV-Vis spectra were collected using a Shimadzu UV-2401 spectrophotometer with 1.0 cm path length quartz cuvettes. Single crystal X-ray diffraction experiments were performed in
collaboration with the University of California Davis and the diffraction data was collected using a Bruker SMART1000 CCD system at T = 90 K with approximately 30,000-46,000 reflections collected depending on the structure reported.

$[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]X, \ X=\text{BF}_4^- \text{ or Br}^-$

To a 250 mL 3-neck round bottom flask was added Mo(CO)$_6$ (2.0g), acetic acid (20 mL), acetic anhydride (10 mL) and triethylamine (1.5 mL). The mixture was gently refluxed for 24 hours. The solution was cooled to room temperature, filtered and left in the fume hood overnight. An orange precipitate was collected, washed with diethyl ether and dried under vacuum. The precipitate was diluted with deionized water before loading onto a DOWEX 50WX-2 cation-exchange column prepared in water using a peristaltic pump. The compound was eluted with 0.2 M NaBr (aq) or KBF$_4$ (aq) solution. Two well resolved bands were observed. The orange band was collected and concentrated via rotary evaporation then placed into a 10-15 °C fridge for slow evaporation and crystallization. The red/orange crystals are collected, washed with diethyl ether and dried under vacuum before using them to synthesize other clusters (0.4215 g, 7 % yield).

$^1$H NMR data were collected using 16 scans, 90° pulse width of 11.50 μs and a relaxation delay of 1.0 s. $^1$H NMR spectra were collected in D$_2$O and chemical shifts set relative to TSP. $^1$H NMR (500 MHz, D$_2$O/TSP): δ 2.40 ppm (s, 3H, μ$_3$-CCH$_3$); δ 2.18 ppm (s, 9H, μ-Ο$_2$CCH$_3$); δ 2.11 ppm (s, 9H, μ-Ο$_2$CCH$_3$). Far-IR (CsI) cm$^{-1}$: 583(w), 518(m), 467(w), 379(vs), 328(vs), 314(sh), 305(sh), 290(w), 280(w), 267(w), 254(w), 247(w), 227(s), 203(m).
[Mo₃(µ₃-CY)(µ₃-O)(µ-O₂CCH₂CH₃)₆(H₂O)₃]Br, (Y=CH₃ and CH₂CH₃)

To a three-neck 250 mL round bottom flask was added Mo(CO)₆ (6.0 g), propionic acid (18 mL) and propionic anhydride (72 mL). The reaction mixture was gently refluxed for 4 hours. The mixture was cooled, filtered and diluted with 1200 mL of deionized water. The water was then removed via rotary evaporation to near dryness. The brown precipitate was diluted again with 300 mL deionized water and loaded onto a DOWEX 50WX-2 cation-exchange column prepared in water. The product was eluted with 0.2 M NaBr. Two well resolved bands were observed. The orange band was collected and the solution volume reduced using rotary evaporation. The product was placed in the refrigerator and after several days orange crystals formed (0.0294 g, 0.5 % yield).

¹H NMR data were collected with 16 scans, 90° pulse width of 11.50 µs and a relaxation delay of 1.0 s. ¹³C NMR data were collected with a pulse width of 9.25 µs and a relaxation delay of 2.0 s. NMR spectra were collected in D₂O and chemical shifts are reported relative to TSP. ¹H NMR (500 MHz, D₂O/TSP): δ 3.13-3.17 ppm (q, 2H, µ₃-CCH₂CH₃); δ 2.47 – 2.43 ppm (q, 12H, µ-O₂CCH₂CH₃); δ 2.41 ppm (s, 3H, µ₃-CCH₃); δ 2.42 – 2.36 ppm (q, 12H, µ-O₂CCH₂CH₃); δ 1.12 - 1.06 ppm (m (four t sets overlapping), 36H, µ-O₂CCH₂CH₃); δ 0.95-0.92 ppm (t, 3H, µ₃-CCH₂CH₃). ¹³C NMR (125 MHz, D₂O/TSP): δ 304.15 ppm, µ₃-CCH₂CH₃; δ 299.09 ppm, µ₃-CCH₃; δ 190.59, 190.49, 190.46, 190.16 ppm, µ-O₂CCH₂CH₃; δ 43.85 ppm, µ₃-CCH₂CH₃; δ 33.52 ppm, µ₃-CCH₃;
δ 32.76, 32.54, 32.51 ppm, µ-O₂CCH₂CH₃; δ 17.44 ppm, µ₃-CCH₂CH₃; δ 12.69, 12.44, 12.37, 12.32 ppm, µ-O₂CCH₂CH₃.

[Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCH₃)_6(py)_3]Br

To a 10 mL vial was added red-orange crystals of [Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCH₃)_6(H₂O)_3]Br (0.02 g) and pyridine (3 mL) then the vial capped. The vial was placed into a 40 °C bath for 12 hours. The reaction mixture is allowed to cool to room temperature. Upon the addition of diethyl ether (O(CH₂CH₃)₂) an orange precipitate was observed. The precipitate was collected, washed with diethyl ether and dried under vacuum. ¹H NMR spectra were collected in deuterated nitromethane-d₃ (CD₃NO₂) and chemical shifts are reported relative to TMS. ¹H NMR (500 MHz, CD₃NO₂/TMS): δ 9.26 – 9.23 ppm (d, 6H); δ 8.16 – 8.11 ppm (2 sets of t, overlap, 3H); δ 7.72 – 7.68 ppm (t, overlap with bulk pyridine signal, 6H); δ 2.61 ppm (s, 3H, µ₃-CCH₃); δ 2.22 ppm (s, 9H, µ-O₂CCH₃); δ 2.11 ppm (s, 9H, µ-O₂CCH₃); δ 2.86 ppm (s, H₂O residual); δ 3.44-3.40 ppm (q, O(CH₂CH₃)₂ residual); δ 1.14-1.11 ppm (t, O(CH₂CH₃)₂ residual). IR (cm⁻¹): 3124(w), 3086(w), 2934(w), 1638(w), 1607(m), 1560(s), 1448(m), 1442(vs), 1359(w), 1222(s), 1046(s), 1033(sh), 1013(sh), 874(w), 765(m), 697(m), 675(s).

[Mo₃(µ₃-CY)(µ₃-O)(µ-O₂CCH₂CH₃)_6(py)_3]Br, (Y=CH₃ and CH₂CH₃)

To a 10 mL vial was added red-orange crystals of [Mo₃(µ₃-CY)(µ₃-O)(µ-O₂CCH₂CH₃)_6(H₂O)_3]Br, (Y=CH₃ and CH₂CH₃) (0.02 g) and pyridine (3 mL). The vial was capped and placed into a 40 °C bath for 12 hours. The reaction mixture was
allowed to cool to room temperature. Upon the addition of diethyl ether an orange precipitate was observed. The precipitate was collected, washed with diethyl ether and dried under vacuum. NMR spectra were collected in nitromethane-d$_3$ (CD$_3$NO$_2$) and chemical shifts are reported relative to TMS. $^1$H NMR (500 MHz, CD$_3$NO$_2$/TMS): δ 9.36 – 9.32 ppm (d-d, overlap, 12H); δ 8.15 – 8.10 ppm (m, overlap, 6H); δ 7.71 – 7.70 ppm (t-t, overlap with bulk pyridine signal, 12H); δ 3.47 – 3.40 ppm (q, 2H, µ$_3$-C(CH$_3$)$_2$CH$_3$); δ 2.68 ppm (s, 3H, µ$_3$-C(CH$_3$)$_3$); δ 2.51 – 2.45 ppm (qd, 12H, µ-O$_2$C(CH$_2$)$_3$CH$_3$); δ 2.42 – 2.36 ppm (qd, 12H, µ-O$_2$C(CH$_2$)$_3$CH$_3$); δ 1.19 – 1.15 ppm (t, 3H, µ$_3$-C(CH$_2$)$_3$H$_3$); δ 1.07 – 1.04 ppm (t, 9H, µ-O$_2$C(CH$_2$)$_3$CH$_3$); δ 1.03 – 0.98 ppm (m three overlapping t sets), 27H, µ-O$_2$C(CH$_2$)$_3$CH$_3$); δ 2.86 ppm (s, H$_2$O residual); δ 3.29-3.24 ppm (q, O(CH$_2$CH$_3$)$_2$ residual); δ 1.14-1.11 ppm (t, O(CH$_2$CH$_3$)$_2$ residual). IR (cm$^{-1}$): 3667(w), 3301(w), 2976(w), 2940(w), 1737(w), 1606(m), 1552(vs), 1463(sh), 1436(vs), 1376(w), 1304(s), 1219(m), 1065(w), 1044(w), 1014(w), 900(w), 809(w), 767(m), 696(m).

$[\text{Mo}_3(\mu_3\text{-C(CH$_3$)$_3}$)(µ-Ô)(µ-O$_2$C(CH$_2$)$_3$)$_6$(CH$_3$OH)$_3$]O$_2$CCHCl$_2$

To a 100 mL three-neck round bottom flask was added $[\text{Mo}_3(\mu_3\text{-C(CH$_3$)$_3}$)(µ-Ô)(µ-O$_2$C(CH$_2$)$_3$)$_6$(H$_2$O)$_3$]Br$ (0.44 g) and dichloroacetic acid (11 mL). The reaction mixture was gently heated to 114 °C for 4 hours. The reaction was allowed to cool to room temperature. Upon dissolution with 50 mL deionized water an orange precipitate was observed. The reaction mixture was heated a second time to 80 °C for 1 hour. After the reaction cooled to room temperature the orange precipitate was collected and dried under vacuum (0.48 g, 100 % yield). The precipitate (0.1389 g) was dissolved in methanol (5
mL) and placed into a refrigerator for slow evaporation to yield red block shaped crystals (0.0683 g, 51 % yield).

$^1$H NMR data were collected with 16 scans, 90° pulse width of 11.50 µs and a relaxation delay of 1.0 s. $^{13}$C NMR spectra were collected with a pulse width of 9.25 µs and a relaxation delay of 4.0 s. NMR spectra were collected in MeOD-d$_4$ and chemical shifts are reported relative to TMS or the MeOD-d$_4$ residual solvent peak. $^1$H NMR (500 MHz, MeOD-d$_4$/TMS): δ 6.56 ppm (s, 3H, µ-O$_2$CCHCl$_2$); δ 6.48 ppm (s, 3H, µ-O$_2$CCHCl$_2$); δ 5.98 ppm (s, 1H, free-O$_2$CCHCl$_2$); δ 2.68 ppm (s, 3H, µ$_3$-CCH$_3$). $^{13}$C NMR (125 MHz, MeOD-d$_4$): δ 303.71 ppm, µ$_3$-CCH$_3$; δ 176.76, 176.53 ppm, µ-O$_2$CCHCl$_2$; δ 170.24 ppm, free-O$_2$CCHCl$_2$; δ 69.93 ppm, free-O$_2$CCHCl$_2$, δ 65.63, 65.41 ppm, µ-O$_2$CCHCl$_2$; δ 31.30 ppm, µ$_3$-CCH$_3$. IR (diamond, CsI; cm$^{-1}$): 3068(w), 3006(w), 2966(w), 1609(s), 1486(m), 1447(w), 1417(s), 1378(sh), 1227(m), 1149(w), 1128(w), 1071(w), 1045(w), 987(m), 937(w), 890(w), 817(m), 777(w), 726(m), 674(m), 569(w), 530(s), 503(w), 466(w), 431(s), 412(sh), 398(sh), 375(w), 351(w), 336(s), 303(m), 279(m), 254(m), 247(m), 227(w), 203(w). UV (CH$_3$OH): λ$_{max}$ = 259 nm (ε = 12961 M$^{-1}$ cm$^{-1}$); λ$_{max}$ = 394 nm (ε = 5112 M$^{-1}$ cm$^{-1}$). Anal. Calcd for C$_{19}$H$_{22}$Cl$_{14}$Mo$_{10}$O$_{18}$: C, 17.26; H, 1.68; Cl, 37.53; Mo, 21.76. Found: C, 17.30; H, 1.50; Cl, 37.38, Mo, 21.1.

$[\text{Mo}_{10}\text{O}_{10}(\mu-\text{O})_{8}(\mu-\text{O})_{3}(\text{py})_{8}]^{+}(\text{py})_{2}$

To a 5 mL vial was added $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2$ (0.0699 g) and 1 mL pyridine. The vial was then capped and placed into a 40 °C water bath for 12 hours to give red/orange arrowhead
shaped crystals. The crystals were collected, washed with diethyl ether and dried (0.0110 g, 16 % yield). IR (diamond, CsI; cm⁻¹): 3112(w), 3074(w), 3048(w), 1630(s), 1606(m), 1572(w), 1486 (w), 1447(s), 1359(w), 1218(s), 1154(w), 1067(s), 1045(s), 945(vs), 891(m), 844(vs), 795(s), 733(vs), 642(vs), 609(vs), 553(m), 518(sh), 493(vs), 456(w), 441(w), 395(w), 373(m), 339(m), 324(w), 308(sh), 304(w), 279(w), 262(sh), 254(w), 227(w), 203(w). Anal. Calcd for C₅₀H₅₀Mo₁₀N₁₀O₂₆: C, 27.72; H, 2.33; Mo, 44.29; N, 6.47. Found: C, 24.07; H, 2.34; Mo, 41.4; N, 5.19. The material is hydroscopic resulting in lower percentages for Mo, C and N.

\[ \text{[Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \]

To a 100 mL three-neck round bottom flask was added \([\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\text{Br} \) (0.4377 g) and monochloroacetic acid (10 g) gently heated to 50-60 °C. The reaction mixture was gently heated to 100 °C for 4 hours. The reaction was allowed to cool to room temperature. To the mixture 50 mL deionized water was added and the reaction gently heated again at 75 °C for 1 hour. At room temperature the reaction mixture was loaded onto a Dowex 50WX-2 cation-exchange column prepared in water. The compound was eluted with 0.2 M NaClO₄ aqueous solution. One red/orange band was collected and concentrated using rotary evaporation until an orange precipitate was observed (0.2 g, 43 % yield).

\(^1\)H NMR data were collected with 16 scans, 90° pulse width of 11.50 μs and a relaxation delay of 1.0 s. \(^{13}\)C NMR data were collected with a pulse width of 9.25 μs and relaxation delay of 2.0 s. NMR spectra were collected in MeOD-d₄ and D₂O. Chemical
shifts are reported relative to TMS, a residual solvent peak or TSP. $^1$H NMR (500 MHz, MeOD-d$_4$/TMS): $\delta$ 4.34 ppm (s, 6H, $\mu$-O$_2$CCH$_2$Cl), $\delta$ 4.27 ppm (s, 6H, $\mu$-O$_2$CCH$_2$Cl), $\delta$ 2.49 ppm (s, 3H, $\mu_3$-CCH$_3$); $\delta$ 2.469 ppm (s, 3H, $\mu_3$-CCH$_3$ equilibrium species); $\delta$ 2.467 ppm (s, 3H, $\mu_3$-CCH$_3$ equilibrium species); $\delta$ 2.25 ppm (s, 9H, $\mu$-O$_2$CCH$_3$ residual species); $\delta$ 2.18 ppm (s, 9H, $\mu_3$-CCH$_3$ residual species); $\delta$ 1.98 ppm (s, 3H, free-$\mu$-O$_2$CCH$_3$ residual species). $^1$H NMR (500 MHz, D$_2$O/TSP): $\delta$ 4.31 ppm (s, 6H, $\mu$-O$_2$CCH$_2$Cl); $\delta$ 4.25 ppm (s, 6H, $\mu$-O$_2$CCH$_2$Cl); $\delta$ 4.05 ppm (s, 2H, free-$\mu$-O$_2$CCH$_2$Cl); $\delta$ 2.50 ppm (s, 3H, $\mu_3$-CCH$_3$); $\delta$ 2.24 ppm (s, 9H, $\mu$-O$_2$CCH$_3$ residual); $\delta$ 2.17 ppm (s, 9H, $\mu$-O$_2$CCH$_3$ residual); $\delta$ 1.95 ppm (s, 3H, free-$\mu$-O$_2$CCH$_3$ residual). $^{13}$C NMR (125 MHz, D$_2$O): $\delta$ 301.38 ppm, $\mu_3$-CCH$_3$; $\delta$ 179.46, 178.95 ppm, $\mu$-O$_2$CCHCl$_2$; $\delta$ 41.78, 41.72 ppm, $\mu$-O$_2$CCHCl$_2$; $\delta$ 30.51 ppm, $\mu_3$-CCH$_3$. IR (diamond, CsI; cm$^{-1}$): 3593(w), 3519(w), 3298(w), 3142(w), 3014(w), 2955(w), 2954(sh), 2921(w), 1576(s), 1434(vs), 1401(sh), 1269(s), 1191(w), 1066(s), 966(w), 929(w), 793(s), 705(w), 684(w), 548(m), 539(sh), 467(w), 458(w), 452(w), 418(sh), 399(s), 375(m), 352(m), 327(m), 315(w), 303(m), 290(w), 279(s), 254(m), 247(m), 227(s), 208(m), 203(m). UV (CH$_3$OH): $\lambda_{\text{max}} = 254$ nm ($\varepsilon = 13508$ M$^{-1}$ cm$^{-1}$); $\lambda_{\text{max}} = 391$ nm ($\varepsilon = 4428$ M$^{-1}$ cm$^{-1}$). Anal. Calced for C$_{16}$H$_{23}$Cl$_7$Mo$_3$O$_{18}$: C, 18.49; H, 2.23; Cl, 23.88; Mo, 27.69. Anal. Calced for C$_{14}$H$_{21}$Cl$_7$Mo$_3$O$_{20}$: C, 16.09; H, 2.02; Mo, 27.54; Cl, 23.74. Found: C, 15.48; H, 2.39; Mo, 23.4; Cl, 23.37. The material is hydrated resulting in lower percentages for Mo and C.
Appendix A

Spectra of $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu_2-\text{CCH}_3)_b(\text{L})_3]X$, $X=\text{Br}^-$, $\text{BF}_4^-$, $\text{L}=\text{H}_2\text{O}$ or pyridine
[Mo$_3$(μ$_3$-CCH$_3$)(μ$_3$-O)(μ-O$_2$CCH$_3$)$_6$(H$_2$O)$_3$]BF$_4$ ($^1$H NMR, D$_2$O, 500 MHz, 1.99-2.49 ppm)
[Mo₃(µ₃-CCH₃)(µ₃-O)(µ-Ο₂CCH₃)₆(H₂O)₃]BF₄ (¹H NMR, D₂O, 500 MHz, 1.95-2.52 ppm)
$[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu_2\text{CCH}_3)_6(\text{py})_3]\text{BF}_4$ ($^1\text{H NMR, 500 MHz, CD}_3\text{NO}_2-\text{d}_3, 0.99-3.61 \text{ ppm})$
[\text{Mo}_3(\mu_3-CCH_3)(\mu_3-O)(\mu-O_2CCH_3)_6(py)_3]\text{BF}_4 (^1\text{H NMR, 500 MHz, CD}_3\text{NO}_2-d_3, 1.00-3.60 \text{ ppm})
[Mo₃(μ₃-CCH₃)(μ₃-O)(μ-O₂CCH₃)₆(py)₃]BF₄: FT-IR (neat, ATR diamond)
[Mo$_3$(μ$_3$-CCH$_3$)(μ$_3$-O)(μ-Ο$_2$CCH$_3$)$_6$(H$_2$O)$_3$]Br: Far-IR (neat, CsI)
Appendix B

Spectra of \([\text{Mo}_3(\mu_3-\text{CY})(\mu_3-\text{O})(\mu_2\text{CCH}_2\text{CH}_3)_6(L)_3]\text{Br}, (L=\text{H}_2\text{O, py}; Y=\text{CH}_3 \text{ and CH}_2\text{CH}_3)\)
[\text{Mo}_3(\mu_3\text{-CY})(\mu_3\text{-O})(\mu_2\text{CCH}_2\text{CH}_3)_6(\text{H}_2\text{O})_3]\text{Br}, (Y=\text{CH}_3 \text{ and CH}_2\text{CH}_3) \left( ^1\text{H NMR, 500 MHz, D}_2\text{O, 0.73-3.36 ppm} \right)
[Mo$_3$(µ$_3$-CY)(µ$_3$-O)(µ-O$_2$CCH$_2$CH$_3$)$_6$(H$_2$O)$_3$]Br, (Y=CH$_3$ and CH$_2$CH$_3$) (¹H NMR, 500 MHz, D$_2$O, 0.80-3.30 ppm)
[Mo$_3$(μ$_3$-CY)(μ$_3$-O)(μ-CH$_2$CCH$_2$CH$_3$)$_6$(H$_2$O)$_3$]Br, (Y=CH$_3$ and CH$_2$CH$_3$) ($^{13}$C NMR, 125 MHz, D$_2$O)
$[\text{Mo}_3(\mu_3-\text{CY})(\mu_3-\text{O})(\mu-\text{O}_2\text{CCH}_2\text{CH}_3)_6(\text{py})_3]\text{Br}$, ($Y$=CH$_3$ and CH$_2$CH$_3$) ($^1$H NMR, 500 MHz, CD$_3$NO$_2$-d$_3$, 0.63-3.66 ppm)
\[ \text{[Mo}_3(\mu_3-\text{CY})(\mu_3-\text{O})(\mu_2\text{CCH}_2\text{CH}_3)_6(\text{py})_3]Br}, \text{ (Y=CH}_3 \text{ and CH}_2\text{CH}_3) \ (^{1}H \text{ NMR, 500 MHz, CD}_3\text{NO}_2\text{-d}_3, -0.10-4.50 \text{ ppm}) \]
[Mo₃(µ₃-CY)(µ₃-O)(µ-O₂CCH₂CH₃)₆(py)₃]Br, (Y=CH₃ and CH₂CH₃): FT-IR (neat, ATR diamond)
Appendix C

Spectra of $[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]_2\text{CCHCl}_2$
[Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCHCl₂)₆(CH₃OH)₃]O₂CCHCl₂ (¹³C NMR, 125 MHz, MeOD-d₄)
$[\text{Mo}_3(\mu_3-\text{CCH}_3)(\mu_3-\text{O})(\mu_2\text{O}_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2$ ($^1\text{H}$ NMR, 500 MHz, MeOD-d$_4$, -0.28-6.87 ppm)
\([\text{Mo}_3(\mu_3-C\text{CH}_3)(\mu_3-O)(\mu-O_2C\text{CHCl}_2)_2(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2\) (\(^1\text{H NMR, 500 MHz, MeOD-}d_4, \text{-0.50-7.00 ppm}\))
[Mo₃(μ₃-CCH₃)(μ₃-O)(μ-O₂CCHCl₂)₆(CH₃OH)₃]O₂CCHCl₂ spiked with NaO₂CCHCl₂

(^1H NMR, 500 MHz, MeOD-d₄, 5.45-7.04 ppm)
Expanded $^1$H NMR (500 MHz, MeOD-d$_4$, 6.36-6.61 ppm) of the $\mu$-O$_2$CCCHCl$_2$ signals following the substitution of methanol by pyridine.
[Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCHCl₂)₆(CH₃OH)₃]O₂CCHCl₂: FT-IR (neat, ATR diamond)

Wavenumber (cm⁻¹)

% Transmittance
[Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCHCl$_2$)$_6$(CH$_3$OH)$_3$]O$_2$CCHCl$_2$: Far-IR (neat, CsI)
$[\text{Mo}_3(\mu_3\text{-CCH}_3)(\mu_3\text{-O})(\mu_2\text{CCHCl}_2)_6(\text{CH}_3\text{OH})_3]\text{O}_2\text{CCHCl}_2$: UV (CH$_3$OH): $\lambda_{\text{max}} = 259$ nm ($\varepsilon = 12961$ M$^{-1}$ cm$^{-1}$); $\lambda_{\text{max}} = 394$ nm ($\varepsilon = 5112$ M$^{-1}$ cm$^{-1}$)
Appendix D

Spectra of $[\text{Mo}_{10}\text{O}_{10}(\mu-\text{O})_8(\mu_3-\text{O})_8(\text{py})_8](\text{py})_2$
$[\text{Mo}_{10}\text{O}_{10}(\mu-\text{O})_8(\mu_3-\text{O})_8(\text{py})_8](\text{py})_2$: FT-IR (neat, ATR diamond)
[Mo_{10}O_{10}(\mu-O)_8(\mu_3-O)_8(py)_8](py)_2: Far-IR (neat, CsI)
NMR integration data at 298K that supports the origin of the Mo$_{10}$ precursor complex is Mo$_3^+$ and undergoes substitution (* are the integrations associated with the substituted species of the Mo$_{10}$ precursor complex).
Appendix E

Spectra of $[\text{Mo}_3(\mu_3-C\text{CH}_3)(\mu_3-\text{O})(\mu_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4$
[Mo₃(μ₃-CCH₃)(μ₃-O)(μ-O₂CCH₂Cl)₆(H₂O)₃]ClO₄ (¹H NMR, 500 MHz, D₂O, 1.89-5.09 ppm)
[Mo$_3$(μ$_3$-CCH$_3$)(μ$_3$-O)(μ-O$_2$CCH$_2$Cl)$_6$(H$_2$O)$_3$]ClO$_4$ ($^1$H NMR, 500 MHz, D$_2$O, -0.10-5.00 ppm)
\[ \text{[Mo}_3(\mu_3-C\text{CH}_3)(\mu_3-O)(\mu-O_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \quad (^{13}\text{C NMR, 125 MHz, D}_2\text{O}) \]
[Mo₃(µ₃-CCH₃)(µ₃-O)(µ-O₂CCH₂Cl)₆(H₂O)₃]ClO₄ (¹H NMR, 500 MHz, MeOD-d₄, 0.12-5.01 ppm)
[Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCH$_2$Cl)$_6$(H$_2$O)$_3$]ClO$_4$ (H NMR, 500 MHz, MeOD-d$_4$, -0.12-5.01 ppm)
[Mo₃(μ₃-CCH₃)(μ₃-O)(μ-O₂CCH₂Cl)₆(H₂O)₃]ClO₄: FT-IR (neat, ATR diamond)
[Mo$_3$(µ$_3$-CCH$_3$)(µ$_3$-O)(µ-O$_2$CCH$_2$Cl)$_6$(H$_2$O)$_3$]ClO$_4$: Far-IR (neat, CsI)
[Mo$_3$(μ$_3$-CCH$_3$)(μ$_3$-O)(μ-O$_2$CCH$_2$Cl)$_6$(H$_2$O)$_3$]ClO$_4$: UV (CH$_3$OH): $\lambda_{\text{max}} = 254$ nm ($\varepsilon = 13508$ M$^{-1}$ cm$^{-1}$); $\lambda_{\text{max}} = 391$ nm ($\varepsilon = 4428$ M$^{-1}$ cm$^{-1}$)
REFERENCES


