Synthesis and reactions of phosphonito polymetallic complexes and halogen oxidation of cyclo-tetraphosphoxane molybdenum cage complexes

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Synthesis and reactions of phosphonito polymetallic complexes and halogen oxidation of cyclo-tetraphosphoxane molybdenum cage complexes

Valdez, Carmen, Ph.D.
University of New Hampshire, 1989
SYNTHESIS AND REACTIONS OF PHOSPHONITO POLYMETALLIC
COMPLEXES AND HALOGEN OXIDATION OF CYCLO-
TETRAPHOSPHOXANE MOLYBDENUM CAGE COMPLEXES

BY

CARMEN VALDEZ

B.S., Pontifical Catholic University of Peru, 1983

DISSERTATION

Submitted to the University of New Hampshire
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the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

May, 1989
This dissertation has been examined and approved.

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Mixed-valent tetrametallic complexes of the type
\[ \text{Mo}_2[\text{M(CO)}_4(\text{PhPO}_2)_2]_2^{4-} \] (M = Cr, Mo, W) were synthesized by the
nucleophilic attack of the phosphonito metallo-ligand cis-
\[ \text{M(CO)}_4(\text{PhPO}_2)_2^{4-} \] on dimolybdenum tetraacetate. These complexes were
characterized by elemental analyses and NMR, IR, and UV-Vis
spectroscopy. The x-ray crystal structure for the tetra-molybdenum
complex indicates a M-M bondlength of 2.186(2). Only weak
interactions were found with potential axial ligands such as amines,
phosphines and isonitriles. Oxidation with four equivalents of
iodine occurred at the Mo(0) sites yielding \[ \text{Mo}_2[\text{Mo(CO)}_3\text{I}_2(\text{PhPO}_2)_2]_2^{4-} \]
with new seven-coordinate Mo(II) sites. The phosphorous-31 NMR
spectrum of this complex exhibits temperature-dependent behavior
indicating rapid geometric isomerization in solution.

Phosphonito metallo-ligands were also used to assemble bimetallic
cage complexes of the adamantane type, \((\text{CO})_4^4 \text{M[PRPO]}_4 \text{M(CO)}_4^4\). The
reactivity of dimolybdenum cages (R = 1Pr2N, Ph) towards halogen
oxidation is dependent on the nature of the phosphorous substituent.
In a competitive iodination experiment, the phenyl cage reacted more
slowly than the isopropylamino cage. Both cages yield mixed-valent dihalo and tetrahalo complexes upon oxidation. Structural data suggests that the mixed-valent dihalo complexes of the isopropylamino cage are dimers in the solid state but monomers in solution. The tetrahalo complexes, \((\text{CO})_2X_2\text{Mo[RPO]}_4\text{Mo(CO)}_2X_2\), \((X = \text{Cl, Br, I})\) exhibit solubility behavior consistent with halogen-bridged polymeric units in the solid state.

In contrast, halogen oxidations of the phenyl cage yield the less stable, seven-coordinate mixed valent complexes \((\text{CO})_4\text{Mo[RPO]}_4\text{Mo(CO)}_3X_2\). These readily lose CO to give unidentified products. Limited data available for the tetrahalo phenyl cage complexes suggest that they exist as seven-coordinate monomers, \((\text{CO})_3X_2\text{Mo[RPO]}_4\text{Mo(CO)}_3X_2\).
This dissertation is dedicated to the memory of my parents
Leonardo and Julia

"Cuando se acerca el fin, escribió
Carthafílhus, ya no quedan imágenes
del recuerdo; solo quedan palabras.
Palabras, palabras desplazadas y
mutiladas, palabras de otros, fue
la pobre limosna que le dejaron
las horas y los siglos"

Jorge Luis Borges"
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Finally my deepest thanks go to my husband Thomas D. Gauthier (he was a saint while I was writing my dissertation), my brother Walter, my sister Julia and to Franklin and Helen Heald for their love, support, help and encouragement.
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INTRODUCTION
It is much easier to study chemical interactions in solution than in the solid state.\textsuperscript{1} Two reasons for this are: 1) the number of techniques amenable to the study of solutions greatly outnumbers the number of techniques amenable to the study of solids, and 2) in general solutions exist as homogeneous systems and are much easier to characterized compared to solids which in general exist as heterogeneous systems.\textsuperscript{2-3}

Many industrial processes such as the Fisher-Tropsch process involve solid state reactions. In the Fisher-Tropsch process heterogeneous solid catalysts are used in the transformation of a mixture of carbon monoxide and hydrogen into gasoline, diesel fuel, and other hydrocarbon derivatives.\textsuperscript{4} Because of the inherent difficulties in characterizing solid state reactions, the specifics of the catalytic process are still as of yet unknown although tremendous advances have been made in this area in the last 25 years. For example, in examining the Fisher-Tropsch process, it was found that the best catalysts are those made by the combination of electron-rich (e.g. cobalt, iron, ruthenium) and electron-poor (e.g. titanium, aluminum, silicon) metals.\textsuperscript{5}

The inherent difficulties in studying reactions involving metal surfaces have prompted researchers to seek alternative methods for studying these reactions. Polymetallic complexes consist of two or more metals held in close proximity by metal-metal bonds or by bridging ligands. Some researchers have suggested that the interaction of the metal centers in polymetallic complexes may mimic
metal-metal interactions taking place on solid surfaces. Furthermore, if the polymetallic complexes are constructed carefully then they incorporate metals with distinctive characteristics such as different oxidation state (high or low), position in the periodic table (early or late transition metals), and polarizability (hardness or softness). Thus, if the interaction of the metal centers held in close proximity in the polymetallic complex mimics the interaction of metal centers in a metal surface, then we may have a reasonable model in which to study these interactions.

In order to understand the synergistic effects that result from the combination of metals with different characteristics, we need to design a systematic synthesis of these polymetallic complexes. Ambidentate ligands containing two distinctive binding sites are possible candidates for the assembly of these complexes. One binding site needs to be a soft, pi-acceptor type for low-valent, electron-rich, late transition metals; while the other needs to be a hard donor site favoring high-valent, electrophilic, main group or early transition metals. Alkoxy alkyl phosphines \( \text{R}_2\text{CH}_2\text{OH} \), phosphinous acid \( \text{R}_2\text{POH} \) and phosphonous acid \( \text{RP(OH)}_2 \) derivatives are potential ambidentate ligands. In these species, the phosphorus acts as a soft donor ligand binding to a low-valent, electron-rich metal center while the oxygen anion is suitable for binding high-valent electrophilic metal cations.

The scope of this research is to use coordinated phosphonito ligands as entries for two type of complexes: polycyclic bimetallic cage complexes of the adamantane type structure; and tetrametallic complexes, where the phosphonito will act as a chelate ligand to bind
two metals. The reactivity of these two types of polymetallic complexes will also be investigated.

The first chapter will describe the synthesis of tetrametallic complexes, where a tetradentate metallo-ligand will chelate a metal dimer to form complexes of the type $M'[M(\text{PhPO}_2)_2]_2$, where $M$ are transition metal of the group 6 and $M'$ is molybdenum in different oxidation states. Furthermore, the reactivity of the tetrametallic complexes towards Lewis bases, Lewis acids and halogen oxidation will be investigated.

In the second chapter, the synthesis of polycyclic bimetallic cage complexes of the adamantane type structure $M[\text{PhPO}]_4,M$, where $M$ are transition metals of the group 6. The reactivity of the novel adamantane cage structures $\text{Mo}[\text{RPO}]_4\text{Mo}$ (R= Ph- or $^1\text{Pr}_2\text{N}$-) towards halogen oxidation will be investigated. The electronic and steric effect of the substituent on the phosphorus atom will be investigated. The products of the halogen oxidation are characterized by standard spectroscopic techniques. In addition to the characterization of the products of these common halogen oxidation reactions, this chapter will present an extensive study of the dynamic behavior of these complexes in solution on the NMR time scale.
SECTION I
SYNTHESIS AND REACTIONS OF COORDINATED PHOSPHONITO METALLO-LIGANDS.
INTRODUCTION

The combination of two types of metals in a complex can result in enhanced reactivity superior to that of either metal alone.\(^8\) This synergistic activation that results from the simultaneous action of the different metal sites on a substrate may result from their differences in oxidation states (high or low), position in the periodic table (main group, early or late transition metal), or polarizability (softness and hardness). As a result, there is currently much interest in the design of ligands capable of incorporating metals of different character.\(^5a,9\) Success in this area has been achieved using several different approaches. One approach is to use a heterodifunctional ligand possessing two possible coordination sites. Bullock and Casey were able to synthesize heterobimetallic complexes by using (diorganophosphino)cyclopentadienyl ligands.\(^6\) The cyclopentadienyl moiety is an ideal ligand for binding an early transition metal while the phosphine is an excellent ligand for binding a late transition metal.

![Diagram of early TM and late TM coordination sites](image-url)
The Mo-Mn complex shown in equation 1 was synthesized using this approach.

\[
\begin{align*}
\text{Mo(CO)}_6 + \text{[Mn(CO)}_4\text{Br]}_2 & \rightarrow \text{Mn(CO)}_4\text{PR}_2 \text{[Mn(CO)}_4\text{PR}_2]_2 \\
& \quad \text{(eq 1)}
\end{align*}
\]

However, in order to be successful with this approach, one has to be very selective in choosing a first metal that will combine to only one site of the heterodifunctional ligand, while preserving the other site for the second metal. As a result, the use of heterodifunctional ligands very often can lead to poor yields of the bimetallic complex. 6

Another group of potential ambidentate ligands are phosphinous and phosphonous acids, \(R_2\text{PO}^-\) and \((\text{RO})_2\text{PO}^-\). These ligands offer a second approach to the synthesis of polymetallic complexes. Deprotonation of these acids yield the phosphinito and phosphonito anions, \(R_2\text{PO}^-\) and \((\text{RO})_2\text{PO}^-\). In these species, the phosphorus, through its lone pair of electrons, can act as a soft donor ligand binding to low-valent, electron-rich metal centers. After deprotonation, the oxygen side is ideal for binding high-valent, electron-poor metal centers. The overall result is a ligand binding "soft" and "hard" metal centers without the problem encountered with the (diorganophosphido)cyclopentadienyl ligand. With the phosphonous and phosphinous acids there is only one site available to coordinate to
the metal (i.e. through the phosphorus atom). Once the phosphorus is coordinated to a metal, the hydrogen of the -OH moiety becomes very acidic, and can be easily removed by any weak base, leaving the oxygen with lone pairs of electrons available for coordination. \(^7\text{a}\)

Roundhill et al. used phosphonito ligands to first bind a \(d^8\) metal at the phosphorus site and then used these \(d^8\)-metal complexes of the type cis-\(\text{M} (\text{R}_2\text{PO})_2\) (where \(\text{M} = \text{Pd(II)}\) or \(\text{Pt(II)}\)) to chelate a second metal \(\text{M}'\) (where \(\text{M}' = \text{Cu(II)}, \text{UO}_2^{4+}, \text{Co(II)}\) or \(\text{VO}^{2+}\)) forming heterometallic complexes as shown below: \(^7\text{d},7\text{f},10\)

\[
\begin{align*}
\text{R}_1\text{P} & \quad \text{O} \quad \text{H} + \text{M}' \\
2\text{M} & \quad \text{R}_2\text{P} & \quad \text{O} \\
\end{align*}
\]

These metallo-ligands are analogous to the acetylacetonate complexes that are so important in classical coordination chemistry. In the pioneering work by Lewis and Oldham, a number of C-bonded 2,4-pentanedionato complexes of Pt(II) were prepared in which the second metal ion was inserted into the chelating site between the oxygens. \(^11\)

Scheme I shows the analogies between the Lewis and Roundhill complexes.
Scheme I: Analogies Between Lewis' Complex and Roundhill's Complex

Another approach to the synthesis of polymetallic complexes is through the use of coordinated chlorophosphines. The P-Cl bond in the chlorophosphines is very labile, therefore nucleophilic attack on this bond can lead to several P-E derivatives (where E = OH, SH, or NH₂), which are potential ambidentate ligands.

\[
M(R_2PCl) + EH \rightarrow M(R_2PE) + HCl \quad \text{(eq 2)}
\]

Kraihanzel and Bartish hydrolyzed dimethylchlorophosphine-(pentacarbonyl)molybdenum(0) and obtained the phosphinous acid derivative, which they later combined with \((\text{Me}_2\text{PCl})\text{Mo(CO)}_5\) in the presence of triethylamine to yield the diphosphoxane bridged bimetallic complex.\(^{12}\)

\[
\text{Me}_2\text{PCl} + \text{H}_2\text{O} \rightarrow \text{Me}_2\text{P-OH} \quad \text{(eq 3)}
\]
Gray et al.\textsuperscript{13} and Wong et al.\textsuperscript{14} also reported the nucleophilic displacement of chlorine from cis-

bis(diphenylchlorophosphine)tetracarbonylmolybdenum by base hydrolysis yielding a chelate product similar to the ones reported by Roundhill. This molybdenum chelate complex is a potential candidate for use in the synthesis of polymetallic complexes.

Another difunctional ligand that can be used in the synthesis of polymetallic complexes is the dichlorophosphine ($\text{RPCl}_2$). Interestingly, $\text{RPCl}_2$ has not been as widely used as $\text{R}_2\text{PCl}$ in the synthesis of polymetallic complexes. The use of coordinated organodichlorophosphine as a precursor in the synthesis of some heterocycles has been reported in the literature. For example, the reaction of ($\text{CO}$)$_5\text{Mo}($$\text{RPCl}_2$) with ethanediol leads to the synthesis of a five-membered ring heterocycle as shown in eq. 6.\textsuperscript{15}
Even more interesting is the synthesis of heterometallic complexes by the reaction of coordinated dichlorophenylphosphine with diironnonacarbonyl and similar complexes.\textsuperscript{16,17} In this synthesis the phosphorus acts as a phosphido ligand bridging two metals that are held together by a M-M bond, as well as coordinating a third.

\[
\text{PhPCl}_2 + \text{Fe}_2(\text{CO})_9 \rightarrow \begin{array}{c}
\text{(CO)}_4\text{Cr} \\
\text{Ph} \\
\end{array} \begin{array}{c}
\text{(CO)}_4\text{Fe} \\
\text{Fe(PO)}_4
\end{array}
\]  

(eq 7)

In our laboratory, Hutchinson used dichlorophenylphosphine in the synthesis of cis-\((\text{CO})_4\text{M(PhPCl)_2}_2\) (where M = Mo or Cr) and studied the hydrolysis of these complexes with the intent of assembling dimetallic-tetraphosphoxane cage complexes as shown in eq 8.\textsuperscript{18} Chapter II of this dissertation will elaborate on the reactions of these cage complexes.

\[
(\text{CO})_4\text{Mo(PhPCl)_2} + (\text{CO})_4\text{Mo(PhPO)}_2 \rightarrow 4 \text{Cl}^- + \begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{Ph}
\end{array} \\
\text{Mo(PO)}_4 \\
\text{Ph}
\]  

(eq 8)

The hydrolysis product of the dichlorophenylphosphine complex, cis-\([\text{CO})_4\text{Mo(PhPO)}_2}_2\text{H}_3\] \textsuperscript{-}, can also be deprotonated completely to give a highly nucleophilic array of four oxygens suitable for doubly-bridging of two metal centers. Formal analogues can be found in ligands like
pyrophosphate, methylene diphosphonate and dicarboxylates. In addition to the double bridging of metal dimers, the cis-(CO)₄Mo(PhPO₂)₂⁴⁻ may be able to react with two independent metals M' due to its flexibility. These two possible coordination modes are illustrated below.

Chapter I of this dissertation is concerned with the use of cis-(CO)₄M(PhPO₂)₂⁴⁻ in the formation of polymetallic complexes of the types illustrated above. The formation of type I complexes were attempted first since this was expected to be the easier of the two. Dimolybdenum tetraacetate was chosen as a suitable candidate to test the ability of the cis-(CO)₄Mo(PhPO₂)₂⁴⁻ to doubly bridge metal dimers. There are two main reasons for making this choice. First, the molybdenum dimer is easy to synthesize. This is prepared by
reaction of molybdenum hexacarbonyl and a mixture of acetic acid and acetic anhydride as shown below.

\[
\text{Mo(CO)}_6 + \text{CH}_3\text{COOH}/(\text{CH}_3\text{CO})_2\text{O } \rightarrow \text{Mo-Mo quadruple bond} \]

The complex is stable when stored in the dark under a nitrogen atmosphere. One major reason for this stability is the existence of a Mo-Mo quadruple bond. The other reason for choosing this dimer is that the chemistry of this species is well known and it is relatively easy to substitute other ligands for the acetate ligand.

An interesting aspect of the reaction of cis-(CO)₄M(PhPO₂)₂⁴⁻ with the molybdenum dimer is that the product should be a polymetallic complex having molybdenum in two different oxidation states, Mo(0) and Mo(II). Equation 10 shows this reaction.

\[
(\text{eq 10})
\]
Recently Cotton and co-workers reported the use of the anion ferrocenemonocarboxylic acid as a bridging ligand for \( \text{Mo}_2^{4+} \), however, in Cotton's complex the iron is far removed from the carboxylate unit and does not influence the characteristics of the dimolybdenum quadruple bond. 20

Since a great deal of research has already been devoted to the reaction chemistry of dimolybdenum tetraacetate, a broad base of information is available with which to compare similar reactions with \( \text{Mo}_2[(\text{CO})_4\text{M(PhPO}_2\text{)}_2]\_4^- \), hereafter referred as to \( \text{Mo}_2\text{M}_2 \). Three main types of reaction chemistry are encountered in the literature: (1) reactions in which the \( \text{Mo}_2(\text{O}_2\text{CR})_4 \) unit is preserved; (2) reactions in which substitution of some or all of the carboxylate groups occurs; and (3) reactions leading to complete disruption of the metal-metal bond. 21
Reactions in which the $\text{Mo}_2(\text{O}_2\text{CR})_4$ molecule remains intact include adduct formation of the type $\text{Mo}_2(\text{O}_2\text{CR})_4\text{L}_2$, and one-electron oxidation affording the $[\text{Mo}_2(\text{O}_2\text{CR})_4]^+$ cation. Ligands such as pyridine, diglyme, dimethylsulfoxide and halide, etc. have been reported to form adducts with the molybdenum(II) carboxylates.$^{22-24}$

$$\text{Mo}_2(\text{O}_2\text{CR})_4 + 2\text{L} \longrightarrow \quad (\text{eq 11})$$

Some of these adducts have been isolated and have been subjected to crystal-structure determination. However, many of them have only been observed in solution by Raman spectroscopy due to their instability. Raman spectroscopy provides an excellent probe to study the significance of Mo-L$_\text{ax}$ interactions by the reduction of the (Mo-Mo) Raman active mode upon complexation. The reaction of $\text{Mo}_2(\text{O}_2\text{CR})_4$ with iodine in dichloromethane leads to the one-electron oxidation of the dimer, $[\text{Mo}_2(\text{O}_2\text{CR})_4]^+$, which has been observed by EPR spectroscopy and by cyclic-voltammetry.$^{24}$

The reaction of molybdenum(II) carboxylates with bidentate ligands such as (dimethylphosphino)methane, (diphenylphosphido)ethane, several arsines derivatives and more recently the anion ferrocene monocarboxylic acid have led to the partial or complete substitution
of the carboxylates.\textsuperscript{20, 25} Also, reactions of molybdenum(II) carboxylate with phosphines that are good Lewis Bases and are sterically small give rise to partial substitution of acetates as shown in eq 12.\textsuperscript{26, 27}

\begin{equation}
\text{Mo}_2(\text{O}_2\text{CR})_4 + 2\text{L} \rightarrow \text{(eq 12)}
\end{equation}

Cleavage of multiple metal-metal bonds have been observed with ligands that are -acceptors such as carbon monoxide, nitriles, and isonitriles. The disruption of the multiple bond is believed to occur by the interaction of the HOMO of the M-M with the\textpi-orbitals of the ligand, thus weakening and eventually cleaving the multiple bond. For example, molybdenum(II) acetate, under mild reaction conditions, reacts with tert-butyl isonitrile (t-BuNC) to produce a yellow diamagnetic solid, \text{Mo(t-BuNC)}_5(\text{O}_2\text{CMe})_2.\textsuperscript{28}

In this study, reactions of these three main types of reagents with the \text{Mo}_2\text{M}_2 complex yielded significantly different results than those encountered with dimolybdenum tetraacetate.
RESULTS AND DISCUSSION

1. Synthesis and Characterization of cis-W(CO)$_4$(PhPCl$_2$)$_2$

Cis-W(CO)$_4$(PhPCl$_2$)$_2$ was synthesized using a method similar to the one reported by Hutchinson (Hutchinson, 1986) for the synthesis of cis-M(CO)$_4$(PhPCl$_2$)$_2$ (where M=Cr or Mo). The equations representing the preparation of these dichlorophenylphosphine complexes are shown below.

\[ \text{Cr(CO)}_4(\text{NBD}) + 2\text{PhPCl}_2 \rightarrow \text{cis/trans Cr(CO)}_4(\text{PhPCl}_2)_2 + \text{NBD} \]  

(eq 13)  

(1)  

(2)

\[ \text{Mo(CO)}_4(\text{NBD}) + 2\text{PhPCl}_2 \rightarrow \text{cis-Mo(CO)}_4(\text{PhPCl}_2)_2 + \text{NBD} \]  

(eq 14)  

(3)  

(4)

\[ \text{W(CO)}_4(\text{NBD}) + 2\text{PhPCl}_2 \rightarrow \text{cis-W(CO)}_4(\text{PhPCl}_2)_2 + \text{NBD} \]  

(eq 15)  

(5)  

(6)

NBD = Norbornadiene

The percent yields of complexes 2, 4, and 6 in the reactions above were 65, 90 and 70% respectively. Substitution of norbornadiene for dichlorophenylphosphine in complexes 4 and 6
proceeded smoothly at room temperature. Complete substitution of norbornadiene in complex 4 was achieved in thirty minutes; however, three hours was necessary for complete substitution in complex 6 and sixteen hours under reflux conditions were required for complex 2. As indicated in equation 12, the product of the reaction, complex 2, is actually a combination of cis and trans isomers. The cis and trans isomers are easily separated and are formed in a 2:1 ratio. The apparent difficulty in the substitution of norbornadiene for dichlorophenylphosphine in complex 1 can be explained by its increased stability due to better overlap of the norbornadiene $\pi$-orbitals with the chromium d-orbitals. This is not the case with the softer molybdenum or tungsten where there is a better overlap of the metal d-orbitals with the phosphorus d-orbitals of the chlorophosphine.

Each of the complexes were characterized by phosphorus-31 NMR and IR. In addition, complex 6 was further characterized by carbon-13 and proton NMR. The phosphorus-31 NMR spectra for complexes 2, 4, and 6 each exhibited a single resonance. The chemical shifts with respect to $^{85}\%$ H$_3$PO$_4$ are given in Table I.

Phosphorus-31 NMR was used heavily in the characterization of reaction mixtures and products of metal-phosphine complexes and proved to be an excellent tool for monitoring reactions. This is due to the fact that phosphorus-31 has 100% natural abundance, a nuclear spin of
Table I. Phosphorus-31 NMR Spectral Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-(CO)$_4$M(PhPCl$_2$)$_2$ $^a$</td>
<td></td>
</tr>
<tr>
<td>M = Cr (2)</td>
<td>203.0</td>
</tr>
<tr>
<td>M = Mo (4)</td>
<td>171.1</td>
</tr>
<tr>
<td>M = W (6)</td>
<td>131.5 ($^1J(P,W)$=171 Hz)</td>
</tr>
<tr>
<td>cis-[(CO)$_4$M(PhPO$_2$)$_2$H$_3$]TBA$^b$</td>
<td></td>
</tr>
<tr>
<td>M = Cr (7)</td>
<td>170.0</td>
</tr>
<tr>
<td>M = Mo (8)</td>
<td>145.5</td>
</tr>
<tr>
<td>M = W (9)</td>
<td>120.5 ($^1J(P,W)$=141 Hz)</td>
</tr>
<tr>
<td>(Mo$_2$[(CO)$_4$M(PhPO$_2$)$_2$])TBA$_2$Na$_2$</td>
<td></td>
</tr>
<tr>
<td>M = Cr (10)$^c$</td>
<td>237.6</td>
</tr>
<tr>
<td>M = Mo (11)$^d$</td>
<td>217.3</td>
</tr>
<tr>
<td>M = W (12)$^d$</td>
<td>196.5 ($^1J(P,W)$=134 Hz)</td>
</tr>
</tbody>
</table>

$^a$ recorded in methylene chloride solution, using C$_6$D$_6$ as lock solvent.

$^b$ recorded in THF solution, using C$_6$D$_6$ as lock solvent, TBA = tert-butylammonium

$^c$ recorded in acetone-d$_6$

$^d$ recorded in DMSO-d$_6$
one-half (I=1/2), a relative sensitivity of 6.6% compared to the proton (at constant field) and a wide range of chemical shift (> 600 ppm). Another interesting aspect of phosphorus-31 NMR is when the phosphorus atom is coordinated to a metal, the "coordination shift" can be correlated to the characteristics of the metal center. For example, for complexes 2, 4 and 6, a high-field shift of the phosphorus-31 NMR resonance was observed upon descending group 6 of the Periodic Table.

Also reported in Table I are the one-bond coupling constants between phosphorus and tungsten for each of the tungsten complexes $^1J(P,W)$. Tungsten exists as a combination of two isotopes, $^{183}W$ and $^{185}W$. The $^{183}W$ isotope is NMR-active and has a nuclear spin of one-half and a natural abundance of 14.3%. Several groups have reported $^1J(P,W)$ values for the complexes $W(CO)_5(PR_3)$ and cis and trans-$W(CO)_4(PR_3)_2$. These values span the range from 112 to 526 Hz. The $^1J(P,W)$ for complex 6 falls in this range. It has been suggested that the magnitude of the $^1J(P,W)$ for the cis and trans-$W(CO)_4(PR_3)_2$ depends on the extent of the metal-phosphorus d-$\pi$-back bonding; however, this remains under debate.

The infrared spectra of cis-$M(CO)_4(PhPCl_2)_2$ ($M=Cr$, Mo, and W) show a very characteristic stretching frequency in the carbonyl region of the spectra indicating $C_{2v}$ symmetry. Table II shows the carbonyl stretching frequency for the
Table II. Infrared Data of the Carbonyl Region in cm\(^{-1}\) for Chlorophenylphosphine Complexes and their Precursors (a).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_{\text{CO}}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al(trans)</td>
</tr>
<tr>
<td>cis-(CO(_4)M(NBD)</td>
<td></td>
</tr>
<tr>
<td>M = Cr (1)</td>
<td>2014</td>
</tr>
<tr>
<td>M = Mo (3)</td>
<td>2025</td>
</tr>
<tr>
<td>M = W (5)</td>
<td>2025</td>
</tr>
<tr>
<td>cis-(CO(_4)M(PhPCl(_2))(_2)</td>
<td></td>
</tr>
<tr>
<td>M = Cr (2)</td>
<td>2037</td>
</tr>
<tr>
<td>M = Mo (4)</td>
<td>2044</td>
</tr>
<tr>
<td>M = W (6)</td>
<td>2038</td>
</tr>
</tbody>
</table>

(a) KBr pellet
(b) Bands strong and broad. The \(B_1\), \(A_1\) (cis) and \(B_2\) are not resolved.
$A_1^{\text{trans}}$ band for complexes 1, 2, 3, 4, 5 and 6 as well as for the $B_1$, $A_1^{\text{cis}}$ and $B_2$, although these bands are not well resolved. These stretching frequencies lie in the region of terminal CO.

For CO containing complexes having $C_{2v}$ symmetry, four bands are expected to be observed in the CO region of the infrared spectrum. These bands are attributed to the four possible CO vibrations illustrated in Figure 1.

![Figure 1. CO Vibrations for cis-(CO)$_4$ML$_2$.](image)

The band centered about 2000 cm$^{-1}$ is due to the $A_1^{\text{trans}}$ vibration mode. The bands attributed to the $B_1$, $A_1^{\text{cis}}$ and $B_2$ modes are found below 2000 cm$^{-1}$. The $A_1^{\text{cis}}$ vibration falls between $B_1$ and $B_2$ and is difficult to resolve. In complexes 2, 4 and 6 the $B_1$, $B_2$ and $A_1^{\text{cis}}$ bands were not resolved because the complexes decomposed rapidly in air and also because these bands are difficult to resolve in a KBr matrix.
As indicated in Table II, the $A_1$ band in the chlorophosphine product shifts to higher energy compared to the starting materials for each of the metal complexes. The reason for this is that chlorophenylphosphine is a better -acceptor than NBD; therefore, there is less electron density at the metal center. This results in a weaker back-bonding with the $\pi^*$ orbitals of the carbonyl and a stronger C=O bond.

2. Hydrolysis of cis-$(\text{CO})_4W(\text{PhPCl}_2)_2$

Complex 6 was hydrolyzed to its phosphonous acid derivative using the procedure reported by Hutchinson in the hydrolysis of chromium and molybdenum analogues. Complex 6 was hydrolyzed in aqueous THF solution in the presence of sodium hydroxide, and the hydrolysis product was isolated as a tetrabutylammonium salt.

\[
(\text{CO})_4M(\text{PhPCl}_2)_2 + \text{NaOH(aq)} \rightarrow [(\text{CO})_4 M(\text{PhPO}_2)_2H_3]^-(\text{eq 16})
\]

- $M=\text{Cr} (7) (65 \%)$
- $M=\text{Mo} (8) (85 \%)$
- $M=W (9) (62 \%)$

Phosphorus-31 NMR was used to monitor the hydrolysis reaction and indicated that one hour was necessary to complete the reaction. The addition of tetrabutylammonium bromide was necessary to precipitate the products. Complexes 7, 8, and 9 in the above reactions were isolated in 65, 85 and 62 percent yield respectively. These complexes
are white solids and stable if stored in a nitrogen atmosphere. By contrast, the tetraprotonated hydrolysis product M(CO)₄(PhPO₂)ₓH₄, an oil, decomposes rapidly.

The single resonance peak found in the phosphorus-3¹ NMR of complexes 2, 4 and 6 is shifted upfield upon hydrolysis. The magnitude of this shift ranges from 11 ppm for the tungsten analogue to 40 ppm for the chromium complex. This upfield shift can be rationalized by an overall increase in electron density in the complex due to the net negative charge. Upon hydrolysis, the \( ^1J(P,W) \) decreases from 171 Hz to 141 Hz in the chlorophosphine tungsten complex. Since, the first order coupling constant is a qualitative measure of the bond strength between P-W, the decrease in the coupling constant indicates a weakening of the P-W bond. The reason for this is the substitution of chlorine by oxygen, a better electron-withdrawing ligand, effectively decreasing the electron density around the phosphorus, lessening its ability to donate electrons to the metal and weakening that bond.

In Table III, the C-O and P-O stretching frequencies for complexes 7, 8 and 9 are listed. The \( A_1 \) band in complexes 7, 8, and 9 are shifted to lower values (14-50 cm⁻¹) compared to those of the precursors, cis-M(CO)₄(PhPCl₂)₂, again indicating an increase in electronic density around the metal, due to the overall negative charge.

Complexes 7, 8, and 9 can be deprotonated completely with a strong base such as sodium hydride to generate a highly nucleophilic complex as shown in eq 17. This complex can be used as a starting material in the synthesis of polymetallic complexes.
Table III: Infrared Absorption of the Stretching Frequencies of the CO and P-O Region in cm$^{-1}$ (a)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{CO}$ A$_1$</th>
<th>$\nu_{CO}$ B$_1$</th>
<th>$\nu_{CO}$ B$_2$</th>
<th>$\nu_{P-O}$ A$_1$ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[[CO]$_4$M(PhPO$_2$)$_2$]$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M = Cr (7)</td>
<td>1998</td>
<td>1891</td>
<td>1867</td>
<td>826</td>
</tr>
<tr>
<td>M = Mo (8)</td>
<td>2000</td>
<td>1914</td>
<td>1876</td>
<td>825</td>
</tr>
<tr>
<td>M = W (9)</td>
<td>2000</td>
<td>1905</td>
<td>1869</td>
<td>826</td>
</tr>
<tr>
<td>[Mo$_2$[[CO]$_4$M(PhPO$_2$)$_2$]$_2$]$^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M = Cr (10)</td>
<td>1998</td>
<td>1886</td>
<td>1842</td>
<td>835</td>
</tr>
<tr>
<td>M = Mo (11)</td>
<td>1999</td>
<td>1880</td>
<td>1849</td>
<td>839</td>
</tr>
<tr>
<td>M = W (12)</td>
<td>1998</td>
<td>1875</td>
<td>1840</td>
<td>839</td>
</tr>
</tbody>
</table>

(a) KBr pellet
(b) Bands below 2000 cm$^{-1}$ not well resolved.
(CO)₄M(PhPO₂)₂H₃ + NaH → MoP₂O₂⁻ + H₂ (eq 17)

The sodium salt of complexes 7, 8 and 9 is used in situ and no attempt to isolate the salt was made. This procedure has been used by Wong et al. in the synthesis of coordinated phosphoxanes via coordinated dichlorophenylphosphinous acid.³⁴

3. Synthesis and Characterization of

\{Mo₂[(CO)₄M(PhPO₂)₂]₂\}_₂TBA₂Na₂ (M=Cr, Mo, or W)

The method used to prepare Mo₂[(CO)₄M(PhPO₂)₂]₂, involves substitution of acetate in the molybdenum dimer, Mo₂(CH₃COO)₄. This method has been used widely in the synthesis of complexes where the
Mo$_2^{+4}$ core remains intact. For example, many of the carboxylate derivatives of the dimolybdenum acetate have been prepared by the reaction of Mo$_2$(CH$_3$COO)$_4$ with the desired carboxylic acids.$^{24}$ Burk et al. used Mo$_2$(CH$_3$COO)$_4$ as starting material in the synthesis of several Mo$_2$(R$_2$PX$_2$)$_4$ ($X_2=O_2$, S$_2$, or OS).$^{35}$ In this case, the reaction of Mo$_2$(CH$_3$COO)$_4$ with cis-[(CO)$_4$M(PhPO$_2$)$_2$H$_3$]$^{-1}$ did not proceed as expected in eq 20.

\[
\text{Mo}_2(\text{CH}_3\text{COO})_4 + 2\text{cis-[(CO)$_4$M(PhPO$_2$)$_2$H$_3$]$^{-1}$} \rightarrow
\]

\[
\text{Mo}_2[(\text{CO})_4\text{M(PhPO$_2$)$_2$H$_3$}]_2^{-2} + 4\text{CH}_3\text{COOH}
\] (eq 20)

It is reasonable that the cis-[(CO)$_4$M(PhPO$_2$)$_2$H$_3$]$^{-1}$ is not a sufficiently strong nucleophile to labilize the Mo-O bond in the molybdenum dimer. In order to enhance its nucleophilicity, deprotonation of the hydrolysis product, cis-[(CO)$_4$M(PhPO$_2$)$_2$H$_3$]$^{-1}$, with sodium hydride was necessary. The reaction involved in the formation of the Mo$_2$M$_2$ complex is shown in eq 21.

\[
\begin{align*}
\text{Mo}_2(\text{OAc})_4 & \quad \text{R} \quad \text{R} \\
\text{M} & \quad \text{P} \quad \text{O}^- \\
\text{R} & \quad \text{P} \quad \text{O}^- \\
\text{R} & \quad \text{P} \quad \text{O}^- \\
\text{M} & \quad \text{P} \quad \text{O}^- \\
\text{M} & \quad \text{P} \quad \text{O}^- \\
\end{align*}
\]

\[
\text{eq 21}
\]

\[
\begin{align*}
\text{M} & = \text{Cr} \quad (10) \\
\text{M} & = \text{Mo} \quad (11) \\
\text{M} & = \text{W} \quad (12)
\end{align*}
\]
Subsequent reaction of deprotonated hydrolysis product with the molybdenum dimer was monitored by phosphorus-31 NMR. One hour was required for the substitution of the acetate by the chromium hydrolysis product; however, 24 hours was required for the molybdenum and tungsten analogues. The difference in the reaction time between Cr and Mo or W can be rationalized in terms of the nucleophilicity of the cis-(CO)$_4$M(PhPO$_2$)$_2$$^{4-}$. These results suggest that the Cr complex is the best nucleophile of the triad.

An intermediate species formed during substitution of the acetate for the -PO$_2$ moiety was detected in the phosphorus-31 NMR for the molybdenum reaction but not the chromium. Substitution of the acetates perhaps occurs in two steps as shown in Scheme II.

\[
\text{Mo}_2(\text{OAc})_4 + \text{Mo}_2(\text{OAc})_4 \rightarrow 2\text{AcO}^- + \left[\text{Mo}_2(\text{CO})_4(\text{PhPO}_2)_2\right]^{4-}
\]

\[
-2\text{AcO}^- \downarrow \rightarrow \left[\text{Mo}_2(\text{CO})_4(\text{PhPO}_2)_2\right]^{4-} + \text{Mo}_2(\text{CO})_4(\text{PhPO}_2)_2
\]

Scheme II: Possible Pathway for Acetate Substitution by the cis-(CO)$_4$M(PhPO$_2$)$_2$$^{4-}$ at the Mo$_2$$^{4+}$ Core.

This is supported by the observation of three single resonances in the spectrum of the reaction mixture of the molybdenum hydrolysis product with the molybdenum dimer. The chemical shifts of these peaks appear at 217.3, 197.4 and 142.9 ppm. The peak at 217.3 is assigned to complex 11, the peak at 197.4 is assigned to the partially
substituted molybdenum dimer and the peak at 142.9 is due to the molybdenum hydrolysis product.

Complexes 10, 11 and 12 are orange-red solids, very soluble in polar organic solvents such as THF, DMSO, acetone and acetonitrile, and moderately soluble in methylene chloride. They can be recrystallized from THF/ether or acetone/ether. These tetrametallic complexes were isolated in 53, 65 and 37 percent yields respectively. They are air-stable in the solid state and are the first examples of molybdenum phosphonites that replace the carboxylates in Mo₂(OAc)₄. Previously, reaction of phosphonates (O₂PR₂⁻, where R= Ph- or Oct-) with Mo₄⁴⁺ produced only polymeric species.

Phosphorus-3¹ NMR spectrum of complexes 10, 11 and 12 each revealed a single resonance which shifted considerably, almost uniformly (Δδ = 67-76 ppm), downfield from their precursors to 237.6, 217.3, and 196.5 ppm respectively. Since the phosphorus experiences a substantial deshielding due to the effect of the diamagnetic anisotropy of the quadruple bond, the deshielding will affect the nucleus at a position near the horizontal plane intersecting the center of the primary axis (ie Mo(II)-Mo(II)). This phosphorus-3¹ chemical shift was also affected by the type of solvent used. For example, complex 11 gave a single resonance at 224.7 ppm when dissolved in acetone or acetonitrile. In THF or DMSO the resonance shifted to 217.3 ppm, and in pyridine the singlet appeared at 214.7 ppm. Thus, a decrease in chemical shift was observed as the donor ability of the solvent increased. This is explained in terms of the ability of the solvent lone pair to form a weak sigma bond in the axial positions of the Mo-Mo complex, thereby reducing the diamagnetic anisotropy of the quadruple bond.
From the proton NMR spectra of complexes 10, 11 and 12 it was determined that these complexes exist as disodium and ditetraethylammonium salts. From the area integration of the protons in the phenyl ring versus the methylene proton bounded to the nitrogen, it was determined that the ratio \( \text{Mo}_2[(\text{CO})_4\text{M(PhPO}_2)_2]_2)/\text{TBA} \) was 1/2.

Carbon-13 NMR confirmed the structure assigned in eq. 20. For example, the carbon-13 NMR spectrum of complex 11 reveals four singlets at 13.9, 20.2, 24.3, and 59.1 ppm due to the carbons in the tetrabutylammonium salt. The aromatic region of the spectrum shows typical peaks for phenyl-carbons in the region of 127-130.5 ppm. Carbon-13 NMR of the carbonyl groups bound to the Mo(0) show two distinctive groups of resonances. At lower frequency there is an apparent triplet at 211.8 ppm \( (^2\text{J}_{\text{PC}} = 13 \text{ Hz}) \) which is assigned to the carbonyls in the axial positions. The higher frequency resonance is a multiplet at 223.9 ppm assigned to the carbonyls in the equatorial positions. The high chemical shift observed for the equatorial carbonyls is in agreement with the anisotropy effect experienced by the phosphorus due to the quadruple bond. The carbonyl and P=O stretching frequencies of complexes 10, 11 and 12 are shown in Table III. The carbonyl stretching frequencies lie below 2000 cm\(^{-1}\) and have not shifted with respect to the precursors. However, P=O stretching frequency has shifted to higher energy by 13 to 15 cm\(^{-1}\) compared to the precursor (8, 9 and 10), indicative of the reduction of electron density in the P=O moiety due to complexation to the Mo\(_2^+\) electrophile.
Table IV. Electronic Absorptions of Mo₂M₂ and Mo₂(OAc)₄ Complexes in Ethanol

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>Abs</th>
<th>M(molL⁻¹)</th>
<th>$\varepsilon$(cm⁻¹M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₂(OAc)₄</td>
<td>294.6</td>
<td>0.7698</td>
<td>3.3x10⁴⁻</td>
<td>2330</td>
</tr>
<tr>
<td>Mo₂Cr₂</td>
<td>337.8</td>
<td>0.4383</td>
<td>9.9x10⁵⁻</td>
<td>4430</td>
</tr>
<tr>
<td>Mo₂Mo₂</td>
<td>351.3</td>
<td>0.8158</td>
<td>8.5x10⁵⁻</td>
<td>9590</td>
</tr>
<tr>
<td>Mo₂W₂</td>
<td>340.8</td>
<td>0.4583</td>
<td>8.5x10⁷⁻</td>
<td>5390</td>
</tr>
</tbody>
</table>
Figure 2. Electronic Spectra for Mo₂(OAc)₄ and Complex 11
The electronic data of complexes 10, 11, 12 and \( \text{Mo}_2(\text{CH}_3\text{COO})_4 \) are listed in Table IV. Figure 2 illustrates a typical spectrum of \( \text{Mo}_2\text{M}_2 \) and the molybdenum acetate complex. All of these complexes exhibit a single band at 337.8, 351.3, 340.9 and 294.6 nm respectively in ethanol, with extinction coefficients \( \varepsilon \) of 4430, 9590, 5390 and 2330 cm\(^{-1}\)M\(^{-1}\) respectively. Burtlitch and co-workers have also observed an absorption at 334 nm \( \varepsilon = 6400 \text{ cm}^{-1}\text{M}^{-1} \) for \( \text{Mo}_2(\text{S}_2\text{PET}_2)_4 \).\(^{35} \) The band at 294.6 nm has been assigned to a transition of the MLCT (metal-ligand charge transfer) type. Proposed assignment of this band \( ^1\text{A}_{1g} \rightarrow ^1\text{E}_{\text{u}} (\delta \rightarrow \pi^* \text{CO (eu)}) \) is based on an \( \chi\alpha \) calculation.\(^{37-38} \) As previously discussed by Trogler and Gray, assignments of these bands are uncertain in the absence of polarized spectra.\(^{39} \)

A single crystal X-ray structure was determined for complex 11, where the sodium cations were exchanged for protons in the process of crystallization. Selected bond angles and bond lengths are shown in Table V. An ORTEP diagram of the anion of complex 11 is shown in Figure 3.

The overall symmetry of the molecule is \( C_1 \) and the crystals belong to the \( \text{Pbca} \) space group. An inversion center relates the two \( \text{Mo(II)} \) centers, \( \text{Mo(1)} \) and \( \text{Mo(1)a} \), as well as the two \( \text{Mo(CO)}_4 \) moieties, \( \text{Mo(2)} \) and \( \text{Mo(2)a} \). At the \( \text{Mo(0)} \) centers, the average axial \( \text{Mo-CO} \) distances are considerably larger at 2.02(3) Å compared to the equatorial average of 1.92(2) Å. The \( \text{Mo-P} \) bondlengths average 2.518(4) Å which is normal for \( \text{Mo(0)}-\text{P} \) single bonded. The \( \text{Mo(II)}-\text{Mo(II)} \) bondlength falls in the range of bond distances reported for quadruply bond dimolybdenum derivatives. The shortest bondlength reported is 2.037(3) Å for \( \text{Mo}_2[\text{PyN(0)CH}_3]_4 \) and the longest reported is
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<th>Bond Distance/Angle</th>
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<td>Mo(1)-Mo(1a)</td>
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<tr>
<td>Mo(1)-O(5)</td>
<td>1.988(7)</td>
</tr>
<tr>
<td>Mo(1)-O(6)</td>
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<td>O(5)-P(2)-C(11)</td>
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<tr>
<td>O(7a)-P(2)-C(11)</td>
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<td>Mo(2)-C(3)-O(3)</td>
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<td>Mo(2)-C(4)-O(4)</td>
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Table V. Selected Bond Distances (Å) and Bond Angles (°) For Complex 11
Figure 3. ORTEP Diagram of the Anion

\[ \text{Mo}_2\{\text{(CO)}_4\text{Mo(PhPO}_2\text{)}_2\}^4^- \]
The Mo(II)-Mo(II) bond length in complex 11 is longer than that in any other Mo$_2$Mo complex spanned by four bridging ligands. For example, Mo$_2$(SO$_4$)$_4$$^{4-}$ at 2.111(1) Å$^{40}$, Mo$_2$(S$_2$PEt$_2$)$_4$ at 2.133(1) Å$^{35}$, and Mo$_2$(OAc)$_4$ at 2.0934(8) Å$^{41}$ The Mo-Mo bond length of complex 11 can be compared to the Mo-Mo bond length of Mo$_2$[O$_2$P(OEt)$_2$]$_4$·2THF with a bond order of 3.5, which has a similar separation of 2.191(1) Å$^{42}$ By comparison Mo$_2$(HPO$_4$)$_4$ contains a triple bond at a separation of 2.223(2) Å$^{43}$ A listing of pertinent parameters for molybdenum dimers is given in Table VI.

A striking difference between complex 11 and other Mo$_2$$^{4+}$ complexes is the average Mo(II)-O bond length at 1.989(6) Å. This is shorter than those in Mo$_2$(OAc)$_4$ (2.115(3) Å$^{44}$, Mo$_2$(SO$_4$)$_4$$^{4-}$ (2.251(2) Å), Mo$_2$(S$_2$PEt$_2$)$_4$ (2.148(29) Å), and Mo$_2$[O$_2$P(OEt)$_2$]$_4$ (2.15 Å); and is at least as short as the 2.030(2) Å found in (Mo$_3$Mo) Mo$_2$(OCH$_2$-t-Bu)$_4$PMe$_3$ and the 2.012(3) Å found in (Mo$_3$Mo) Mo$_2$(HPO$_4$)$_4$.$^{45}$ Qualitatively, the shortening of the Mo(II)-O bond and the lengthening of the Mo(II)-Mo(II) bond in complex 11 may be understood in terms of the mutual influence of the -PO$_2$ π-donor ability and the Mo-Mo quadruple bond. In (Mo$_4$Mo)$^{4+}$ there are formally no vacant Mo d-orbitals to form bonds with the O of the -PO$_2$ moiety of the organometallic ligand. That is, four d-orbitals are used to form the Mo-Mo quadruple bond, $\sigma$, $\pi$, $\delta$ (d$_{z^2}$, d$_{xz}$, d$_{yz}$ and d$_{xy}$), and one d$_{x^2-y^2}$ with the s and p orbitals involved in the formation of Mo-O bonds.$^{44}$ The filled p orbitals of the oxygen will have to mix with the empty antibonding MO's, $\pi^*$ and $\delta^*$, of the Mo-Mo bond, thereby
Table VI. Comparison of Mo-Mo and Mo-O Bond Distances in Some Complexes with M-M Quadruple Bond.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M-M, Å</th>
<th>M-O, Å (average)</th>
<th>O-O Å (bite dist)</th>
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<tr>
<td>Mo₂(CH₃COO)₄</td>
<td>2.0934(8)</td>
<td>2.115(3)</td>
<td>2.24(3)</td>
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<tr>
<td>Mo₂(SO₄)₄⁻</td>
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<td>2.251(2)</td>
<td>2.42(2)</td>
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<tr>
<td>Mo₂(S₂PET₂)₄</td>
<td>2.133(1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo₂(OSPET₂)₄</td>
<td>2.128(2)</td>
<td>2.148(29)</td>
<td>-</td>
</tr>
<tr>
<td>*Mo₂(HPO₄)₄⁻</td>
<td>2.223(2)</td>
<td>2.012(3)</td>
<td>2.49(3)</td>
</tr>
<tr>
<td>Mo₂[(CO)₄Mo(PhPO₂)₂]₄⁻</td>
<td>2.186(2)</td>
<td>1.989(6)</td>
<td>2.48(6)</td>
</tr>
<tr>
<td>**Mo₂[O₂P(OEt)₂]₄.2THF</td>
<td>2.191(1)</td>
<td>2.15</td>
<td>-</td>
</tr>
<tr>
<td>Mo₂(OCH₂-t-B)₄(PMe₃)₄</td>
<td>2.209(1)</td>
<td>2.030(2)</td>
<td>-</td>
</tr>
<tr>
<td>Mo₂Cl₈⁻</td>
<td>2.139(4)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* A triply-bonded molybdenum dimer.
** Molybdenum dimer with a bond order of 3.5.
weakening and lengthening the Mo-Mo bond and shortening the Mo(II)-O bonds. A similar effect is observed for the complex Mo$_2$(OCH$_2$-t-Bu)$_4$(PMe$_3$)$_4$.

The average O-O bite distance for each PhPO$_2$ is 2.48(6) Å. This value is considerably larger than the average bite distance of the bridging carboxylate (2.24(3) Å). Likewise, the O-O bite distance for Mo$_2$(SO$_4$)$_4$ is 2.42(3) Å and for the phosphato complex (Mo$_3$MO), 2.49(3) Å. The O-O bite distance correlates with the Mo-Mo bondlength; the greater the O-O bite distance, the longer the Mo-Mo.

Attempts to extend the synthesis of tetrametallic complexes using the organometallic ligand cis-(CO)$_4$M(PhPO$_2$)$_2$ with metal dimers other than molybdenum were carried out using Cr$_2$ and Rh$_2$. Cr$_2$(CH$_3$COO)$_4$L$_2$ (where L = H$_2$O or MeOH) and Rh$_2$(CH$_3$COO)$_4$L$_2$ (where L = MeOH or THF) were used as starting materials. These chromium and rhodium dimers have ligands (L) coordinated in the M-M axial positions.

The reaction of Cr$_2$(CH$_3$COO)$_4$L$_2$ with cis-(CO)$_4$M(PhPO$_2$)$_2$ (where M = Cr or Mo) did not give the desired product, Cr$_2$[(CO)$_4$M(PhPO$_2$)$_2$]$_2$ even under vigorous reaction conditions. The cis-(CO)$_4$M(PhPO$_2$)$_2$ was recovered after 48 hours of reaction time. There are two possible reasons for the unreactivity of the deprotonated complex 8 towards Cr$_2$(OAc)$_4$. One could be the high negative charge in the deprotonated hydrolysis product, which is a very electron rich complex. No Cr$_2$X$_8$ ion or Cr$_2$(SO$_4$)$_4$ or analogues of those formed by molybdenum have yet been synthesized. Reaction of the chromium acetate dimer with halide or sulfates only produced blue complexes indicative of high spin d$^4$ Cr(II) mononuclear complexes. The lone
pairs of the halide or oxygens of the sulfates may interact with the metal atom, disrupting the Cr–Cr bond. The other reason for the failure in substituting the acetates at the chromium dimer may be that the \(-\text{PO}_2\) moiety can not bridge the Cr–Cr bond length. This is less likely since bondlengths in Cr\(_2^{4+}\) can span a wide range, from 1.828(2) in Cr\(_2(2\text{-MeO}-5\text{MeC}_6\text{H}_3)_4\) to 2.451(1) in Cr\(_2(O_2\text{CH})_2\text{CHO}_2\text{H}\), a wider range than for Mo\(_2^{4+}\).\(^{24}\) The reaction of Rh\(_2(CH_3\text{COO})_4\text{I}_2\) with cis-\((\text{CO})_4\text{Mo(PhPO}_2)_2\)\(^{-}\) was more encouraging. A clear color change from green to red was observed upon mixing of the reagents. However, the phosphorus-31 NMR spectrum of the reaction mixture revealed only a broad peak at 140 ppm, which may be assigned to unreacted hydrolysis product. Interestingly no other resonance in the \(^{31}\text{P-NMR}\) spectrum was observed. However, the infrared spectrum of an aliquot of the reaction mixture showed that the stretching frequencies of the carbonyl region have shifted to higher energies at 2013, 1921, and 1907 cm\(^{-1}\). The stretching frequencies of the carboxylates were observed at 1546 and 1498 cm\(^{-1}\); and were of comparable intensity to the carbonyl peaks. More importantly the P–O stretching frequency has shifted from 825 cm\(^{-1}\) in the starting material to 885 cm\(^{-1}\). This shift may be due to the coordination of the \(-\text{PO}_2\) moiety to an electron-withdrawing group such as Rh\(_2^{4+}\). Unfortunately attempts to isolate the product were unsuccessful due to the reversible nature of the reaction. Based upon the IR evidence it is believed that the following equilibrium was established.
Substitution of only two acetate ligands on Rh₂(OAc)₄L₂ is well documented. Kinetic studies of acetate substitution in Rh₂(CH₃COO)₄L₂ showed that the rate constants for the first, second, third and fourth replacement of CH₃CO₂ for CF₃CO₂ are in the ratio of 1 : 2 : 0.1 : 0.025. There is clearly a preference for the formation of Rh₂(CH₃COO)₂(CF₃COO)₂ over the tetrasubstituted species, but it too has yet to be isolated.

Preliminary work in the use of deprotonated complex 8 as a nucleophile towards electrophiles such as R₂M'Cl₂ (M' = Sn or Si; R = Me or Benzyl), PhPCl₂, Me₃SiCl, Cl₂PN(Me)PCl₂, cis-(Ph₃P)₂PtCl₂ and Pd₃(AcO)₆ was investigated with the hope of forming polycyclic complexes such as the ones illustrated below.
Results with the main group reagents indicated that some reaction had occurred; however, these reactions did not go to completion. In most cases, the expected product sodium chloride was isolated. The products were very air sensitive and attempts at isolation by means of column chromatography or solvent extraction were unsuccessful yielding in most cases oily samples with very complicated phosphorus-31 NMR spectra. The IR spectra showed unresolved peaks especially in the carbonyl region. One possible way to isolate some of the products may be by using a Chromatotron. In the Chromatotron the sample is in contact with the support phase for only a short period of time and the separation can be carried out under an inert gas atmosphere.

Reaction of the deprotonated hydrolysis product with the platinum complex was unsuccessful. The platinum complex was recovered in quantitative yields. A possible reason for the unreactivity might be that the Pt-Cl bonds are too strong. The reaction of the deprotonated hydrolysis product with the palladium complex yielded a black metallic precipitate indicating reduction of Pd(II) to Pd(0).

\[
2(\text{Ph}_3\text{P})_2\text{PtCl}_2 + (\text{CO})_4\text{Mo(PhPO}_2)_2^4 \rightarrow \]

\[
(\text{CO})_4\text{Mo}(\text{PhPO}_2)_2^4
\]
4. Reactivity Studies of \( \text{Mo}_2[(\text{CO})_4\text{Mo}(\text{PhPO}_2)_2]_2\) \(\text{TBA}_2\text{Na}_2\),

Complex 11

4.1 Adduct Formation

Like its precursor, \( \text{Mo}_2(\text{AcO})_4 \), complex 11 appears to have little tendency to form stable axial adducts with hard donors such as triethylamine (Et\(_3\)N), pyridine (py). Only the strong donor 4,4'-dimethylaminopyridine (DMAP) afforded an isolable 2:1 adduct. Most of the highly negative charged molybdenum quadruply-bonded compounds are known to form very stable adducts with \( \pi \)-donors such as \( \text{H}_2\text{O} \), amines, etc. For example, \( \text{Mo}_2\text{Cl}_8 \) is isolated with two molecules of water coordinated in the axial position; \(^{24}\) even the sulfate complex is isolated with two molecules of water. It is reasonable to believe that complex 11 should react with \( \sigma \)-donors and form stable solvent adducts as shown in equation 23. However, the X-ray structure reveals the absence of solvent coordinated in the axial position.

\[
\text{Mo}_2[(\text{CO})_4\text{Mo}(\text{PhPO}_2)_2]_2^{4-} + 2L \rightarrow \text{Mo}_2[(\text{CO})_4\text{Mo}(\text{PhPO}_2)_2]_2^{4-} \quad (\text{eq 23})
\]
Reaction of complex 11 with pyridine afforded a weakly bonded adduct and its isolation was unsuccessful. Stephensen and others reported evidence for the pyridine adduct of the Mo₂(CH₃COO)₄ but they were also unable to characterize the adduct because it readily lost the bound pyridine. Our adduct was only identified by phosphorus-31 NMR: a shift in the phosphorus-31 NMR spectrum from 224.7 to 214.8 ppm was observed upon addition of pyridine to complex 11.

The reaction of complex 11 with 4,4'-dimethylaminopyridine (DMAP) afforded the desired adduct, complex 13, isolated as an orange solid. It is soluble in acetone and quite stable in the solid state. Its phosphorus-31 NMR spectrum revealed a single resonance at 219.6 ppm in acetone (complex 11 in acetone showed a singlet at 224.7 ppm). Its proton-NMR spectrum exhibited the characteristic peaks for the phenyl ring protons at 7.4 and 7.2 ppm; two set of peaks at 6.4 and 6.3 ppm can be assigned to the pyridine ring protons, and a singlet at 2.9 ppm to the methyl protons of the -N(CH₃)₂ moiety. The infrared spectrum of complex 13 closely resembles the spectrum of complex 11 in the carbonyl and P-O region. Carbonyl stretching frequencies were observed at 1997, 1984 and 1831 cm⁻¹. The P-O stretching frequency is increased by 23 cm⁻¹ to 848 cm⁻¹. The increase in the P-O stretching frequency can be attributed to a back-donation between the lone pair of electrons of the oxygens with some of the empty orbitals of the phosphorus. By forming a stable axial adduct with DMAP, complex 11 does not require the use of extra oxygen lone pairs, therefore leaving sufficient electron density in the oxygens for the multiple bonding to phosphorus.
Based upon these results, the adduct formation is greatly favored by ligands that are strong $\sigma$-donors. $\text{Et}_3\text{N}$ ($pK_a = 10.64$) has the least $\sigma$-donor ability of the three ligands investigated. DMAP ($pK_a = 9.70$) is a stronger base than pyridine ($pK_a = 5.29$) and forms the most stable adduct.

Adduct formation was also investigated with ligands having $\pi$-acceptor abilities such as $\text{PPh}_3$ and tert-butylisonitrile. In addition to simple adduct formation, isonitriles are known to form complexes known as class 2 complexes, as illustrated in scheme III:

Scheme III: Two Classes of Complexes Formed upon Reaction of $\text{Mo}_2(\text{O}_2\text{CR})_4$ with $\pi$-Accepter Ligands.

Isonitriles are also known to disrupt the $\text{Mo}_2^{4+}$ core as shown in eq 24.

$$\text{Mo}_2(\text{CH}_3\text{COO})_4 + \text{t-BuNC} \rightarrow [\text{Mo}(\text{t-BuNC})_6(\text{CH}_3\text{COO})]^+ \quad (\text{eq 24})$$

In contrast to $\text{Mo}_2(\text{AcO})_4$ neither triphenylphosphine nor tert-butylisonitrile gave any reaction with complex 11 even in the presence of excess ligand or at refluxing temperatures. For example, the starting material was recovered in quantitative yields after refluxing with triphenylphosphine or isonitrile for three days. Since no
obvious steric factors can be deduced from its molecular structure for complex 11, the Mo(II)'s must have sufficient multiple bonding from their electron rich oxo-ligands to have little need for further complexation.

4.2 Halogen Oxidation

The iodine oxidation of complex 11 occurred at the Mo(0) sites, resulting in a stereochemically non-rigid seven-coordinate Mo(II) complex.

\[
\text{Mo}_2[\text{(CO)}_4\text{Mo(PhP}_2\text{O}_2)_2]^4 \rightarrow 2\text{I}_2 \rightarrow \text{Mo}_2[\text{(CO)}_3\text{I}_2\text{Mo(PhP}_2\text{O}_2)_2]^4 + 2\text{CO}
\]

(eq 25)

Addition of iodine to a THF solution containing complex 11 resulted in CO evolution. The reaction was complete in one hour. An orange powder was collected from the reaction mixture in 68% percent yield. Elemental analysis and spectroscopic data are consistent with the identification of the product as \(\text{Mo}_2[\text{(CO)}_3\text{I}_2\text{Mo(PhP}_2\text{O}_2)_2]^4\text{(THF)}_2\text{TBA}_2\text{Na}_2\). Complex 14 was found to be very unstable.
In contrast to complex 11, this complex readily crystallizes with two molecules of THF, presumably in the axial positions. This is observed in the proton NMR spectrum of complex 14 recorded in acetone-$d_6$ which shows the two characteristic multiplets of THF. This can be explained since oxidation of the Mo(0) to Mo(II) decreases electron density at the Mo$_2$ dimer.

In air the orange solid turned to a black insoluble powder insoluble in common organic solvents. Slow diffusion of iodine into a THF solution containing complex 11 afforded bright orange crystals of complex 14, however, these too lost CO readily upon removal from the mother liquor.

Carbon monoxide loss in complex 14 can be monitored by infrared spectroscopy. Figure 4 illustrates the change in the infrared spectra over a 24 hour period. Initially, the carbonyl region of the IR spectrum shows three distinctive bands at 2002, 1941 and 1881 cm$^{-1}$. These bands can be
Figure 4. IR Spectra of Complex 14 over a 24 Hour Period (a) Time 0, (b) 1 Hour, and (c) 24 Hours.
assigned to the three carbonyls in the seven-coordinate Mo(II). The P-O stretching frequency has shifted from 839 cm\(^{-1}\) in complex 11 to 881 cm\(^{-1}\) in complex 14. After one hour, the three carbonyl bands have broadened and the sharp P-O peak has also broadened and increased in intensity. After twenty-four hours, almost all the carbonyl bands are gone and the main absorption is the P-O stretching frequency. The results from the infrared spectra indicated the decarbonylation of complex 14 and perhaps the formation of a polymeric structure bridged by iodide and P-O.

Elemental analyses (C, H and N) of the decomposition product indicated a lost in C.

Phosphorus-31 NMR of complex 14 reveals a single broad peak at 198 ppm with a half-width of 113 Hz. The broadness of the peak can be attributed to the fluxional behavior of the seven-coordinate Mo(II) sites. Besides the broad peak at 198 ppm, another singlet at 72 ppm was also observed. This is believed to be some unidentified decomposition product. This was confirmed when a phosphorus-31 NMR spectrum of an in-situ reaction of Mo\(_2\)Mo\(_2\) and I\(_2\) did not show this peak. After one hour, however, the broad peak at 198 ppm changed dramatically as shown in Figure 5.

Seven-coordinated complexes often show stereochemical nonrigidity on the NMR time scale. Variable-temperature NMR studies were done on complex 14 with the hope of obtaining a limiting spectrum. An in-situ NMR experiment would give us a better understanding of the product of the iodination.
Figure 5. Phosphorus-31 NMR of Complex 14 in Acetone-d₆ (a) Initially, and (b) After One Hour.
Figure 6. Variable Temperature Phosphorus-31 NMR of the In-situ Reaction of Complex 11 with Four Equivalents of Iodine.
The reaction was done in a 10 mm NMR tube at 14 °C in acetone-d$_6$. Figure 6 shows the variable temperature NMR spectra.

At 14 °C the phosphorus-31 NMR spectrum reveals a broad peak at 198 ppm with a half-width of 112 Hz. The limiting spectrum is reached at -45 °C and consists of a major singlet at 195.1 ppm as well as an AB pattern ($\delta_A = 202.2$ (d), $\delta_B = 190.9$ (d) and J=83 Hz) and a small doublet at 181.8 ppm with J=63 Hz. The observed temperature dependence in the NMR of complex 14 is consistent with stereochemically non-rigid seven-coordinate complexes.

While a full structural assignment cannot be made based solely on the IR and NMR data, a prediction of possible structures can be made based on the Kepert model. There are at least three reasonable geometries including the pentagonal bipyramid, the capped trigonal prism and the capped octahedron. Kepert used the ligand's normalized bite, b, to predict which of these geometries is preferred. This is defined as $b=2\sin \alpha/2$; where, $\alpha$ is the angle formed by $P_1$-$Mo_2$-$P_2$ in complex 11. From the X-ray structure of complex 11, b was calculated to be 1.27. According to the Kepert model, complexes with this ligand's normalized bite should have the capped trigonal prism or the capped octahedron structure. This suggests possible structures as A, B, C and D shown in Figure 7. Structure A and C should give rise to an AB spectrum in the NMR while structure B and D will give rise to a singlet. The observed NMR spectra most likely indicates an equilibrium between several of these structures.
Figure 7. Possible Dynamic Structures around the Mo(CO)$_3$I$_2$ Sites.
CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

Conclusion

Complexes 10, 11, and 12 are the first examples of complexes containing a dimolybdenum quadruple bond spanned by two cis-(CO)$_4$M(PhPO$_2$)$_2$$^{4-}$ metallo-ligands. Complex 11 has a center of symmetry and features a long Mo-Mo bond length of 2.186(2) Å and very short Mo(II)-O bond lengths comparable to those in some alkoxides metal dimers. Only weak interactions are found between complex 11 and potential axial ligands like amines, pyridine and phosphines. It is inert towards Mo-Mo bond rupture by $\pi$-acceptor ligands such as tert-butylisonitrile and phosphines. The lack of reactivity may be due to the rigidity of the Mo$_2$(O$_2$PPh)$_4$ core supported by strong Mo-O bonds, or to the fact that the Mo$_2$ dimer has sufficient multiple bonding from the electron-rich cis-(CO)$_4$Mo(PhPO$_2$)$_2$$^{4-}$ ligands to have little need for further complexation. Reactivity toward iodine oxidation reveals clearly that the reaction occurred at the Mo(0) sites with loss of CO to form an unstable Mo(II)$_4$ complex, 14. In contrast to complex 11, complex 14 readily crystallizes with two molecules of THF, presumably in the axial positions. This difference can be attributed to the loss of electron density following oxidation of the metallo-ligands.

Suggestions For Future Work
Synthesis of other tetraradical complexes with metal dimers having triple, double or single bonds should be of interest, since these have some resemblance to the chemistry of organic compounds having multiple bonds. The oxygens of the phosphonites can be replaced by NH or S to give cis-(CO)$_4$M(RPX$_2$)$_4$ (X = NH or S) by simple reaction of the coordinated di-chlorophosphines. Preliminary work has been done using liquid ammonia for amminolysis of cis-(CO)$_4$Mo(PhPCl$_2$)$_2$ to give cis-(CO)$_4$Mo(PhP(NH$_2$)$_2$)$_2$ which can also presumably be used as an organometallic-ligand in the synthesis of polymetallic complexes. Most interesting will be the synthesis of the sulfur analogues, since $R_2$PS$_2$ is known to have two different modes of coordination, bridging or chelating.

Extension of the use of cis-(CO)$_4$Mo(PhPO$_2$)$_2$ as a nucleophile towards main group electrophiles has been tested in preliminary work. Although we were unable to isolate the products, the results were encouraging. Future success of these metallo-ligands as nucleophiles will depend on the selection of electrophile. This must have labile leaving groups in the proper orientation to interact with the rectangular array of four oxygens. Optimization of the reaction with main group reagents like Me$_3$SiCl, Me$_2$SiCl$_2$, Cl$_2$P(O)YP(O)Cl$_2$ (Y = NR, CHR, etc.) should give very interesting polycyclic products.

The use of transition or late transition metal electrophiles with high metal oxidation states, or late transition metals should be investigated. Complexes similar to the ones obtained by Roundhill's coordinated R$_2$PO$^-$ ligands should be investigated first. The appropriate reagents are Cu(acac)$_2$, Pt(acac)$_2$, and VO$_2$(acac). Other complexes that have been used in the synthesis of polymetallic
complexes include \([\text{Cu(CH}_3\text{CN)}_4]\text{BPh}_4\), \(\text{cis-Pt(R}_2\text{P-(CH}_2\text{)}_n\text{PR}_2\)(L}_2\) (\(L = \text{halide}\)), \(\text{MoO}_2\text{Cl}_2\), etc. Polymetallic complexes that can result from the nucleophilic attack of \(\text{cis-}(\text{CO})_4\text{M(PhPO}_2\text{)}_2\) \(4^-\) metallo-ligand on these may have unique reactivities that are promising for the activation of small molecules like \(\text{CO}\) and \(\text{CO}_2\).
EXPERIMENTAL

All operations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under nitrogen. \( \text{M(CO)}_6 \) (M=Cr, Mo, and W) was purchased from Alfa Chemicals and used without further purification. PhPCl\(_2\) was purchased from Strem Chemicals and vacuum-distilled under nitrogen prior to use. Norbornadiene (NBD), tert-butyl isocyanide (t-BuNC) and 4-dimethylamino pyridine (DMAP) were purchased from Aldrich Chemical Co. and used without further purification. \( [(\text{CO})_4\text{M(PhPO}_2\text{)}_2\text{H}_3\text{TBA}] \) (M=Cr, and Mo) was prepared as described by Hutchinson.\(^{18}\) W(CO)\(_4\)(NBD) was prepared according to the literature.\(^{19}\) Mo\(_2\)(CH\(_3\)COO)\(_4\) was prepared according to previously reported methods.\(^{20}\)

NMR spectra were recorded on a Bruker AM-360, JEOL FX90Q or a Varian 360A. IR spectra were recorded on a Perkin Elmer 283B instrument. UV-VIS spectra were recorded on a CARY 219 spectrometer. Elemental analysis were performed at the University of New Hampshire Instrumentation facility with a Perkin Elmer 240 B Elemental Analyzer.

X-ray crystal structure determinations were carried out by Dr. Eric J. Gabe, Chemistry Division, National Research Council of Canada, Ottawa K1A OR9 (Canada).

Synthesis of \( \text{cis-(PhPCl}_2\text{)}_2\text{W(CO)}_4\), Complex (6). \( \text{(CO)}_4\text{W(NBD)} \) (1.4000 g, 3.6 mmol) was dissolved in methylene chloride (8 mL) with stirring. PhPCl\(_2\) (1.0 mL, 7.5 mmol) was added via syringe and stirring was
maintained for an additional 4 h. The solvent was then removed under-vacuum, and silica gel (1 g) was added to the yellow residue along with hexane (10 mL). The hexane was removed under-vacuum and a 1:1 mixture of methylene chloride:hexane (10 mL) was added to the remaining yellow solid. Schlenk filtration followed by washing with CH$_2$Cl$_2$:hexane and removal of excess solvent under-vacuum left a yellow semi-solid. Hexane (10 mL) was then added to the yellow semi-solid and the insolubles were removed by Schlenk filtration. The filtrate was placed in a dry-ice/acetone bath for 1 h. The solvent was removed by syringe and the remaining solid was dried under-vacuum to give the desired product (1.65 g, 70% yield). Phosphorus-31 NMR 132 ppm (singlet), $^1$J(P,W)=170Hz; IR (KBr) U/CO 2038, 1942, 1916 cm$^{-1}$.

Synthesis of [(CO)$_4$W(PhPO$_2$)$_2$H$_3$]TBA, Complex (9). (CO)$_4$W(PhPCl$_2$)$_2$ (1.63 g, 2.5 mmol) was dissolved in THF (15 mL) with stirring. NaOH (20 mL, 0.60 M) was added dropwise and stirring was maintained for 1 h. The initial bright yellow solution turned brown after ca 5 min. THF was removed under-vacuum and distilled water (20 mL) was added to the reaction mixture. The pH was then brought to 7 with a dilute solution of HCl. At this time a brown precipitate was removed by Schlenk filtration. Tetrabutylammonium bromide (4.83 g, 15 mmol) was added to the filtrate and the pH was dropped to ca 7 to ensure complete precipitation of the [(CO)$_4$W(PhPO$_2$)$_2$H$_3$]TBA. A white solid was filtered and dried under-vacuum to give the desired product (1.15 g, 62% yield). Anal. Calcd. for WP$_2$N$_8$C$_{32}$H$_{49}$: C, 46.78; H, 5.97; N, 1.70. Found: C, 45.92; H, 5.93, N, 1.64. Phosphorus-31 NMR 120.5 ppm (singlet), $^1$J(P,W)= 141 Hz; Proton-NMR 7.8 ppm (phenyl ring protons in
in the para positions); 7.2 ppm (phenyl ring protons in the ortho and meta positions); 9.1 ppm (broad, P-OH); IR (KBr) $\nu_{\text{CO}}$ 2000, 1905, 1827, $\nu_{\text{PO}}$ 826 cm$^{-1}$.

**Synthesis of $\{\text{Mo}_2[(\text{CO})_4\text{Cr(PhPO}_2^2\text{)}_2\text{]}_2\}\text{TBA}_2\text{Na}_2$, Complex (10).**

$[(\text{CO})_4\text{Cr(PhPO}_2^2\text{)}_2\text{H}_3\text{]}\text{TBA} (1.4524$ g, $2.1$ mmol) was dissolved in THF (25 mL) with stirring. NaH (ca 1 g) was added to the solution and stirred until no more effervescence was observed. The excess NaH was removed by Schlenk filtration. Mo$_2$(CH$_3$COO)$_4$ (0.2256 g, 0.5 mmol) was then added to the filtrate, the solution changed color from brown to red upon contact with the molybdenum dimer. After 3 h a white solid which was later identified as sodium acetate, was removed by filtration. Toluene (5 mL) was added dropwise to the filtrate via syringe to give a brown solid. The brown solid was dried under-vacuum recrystallized from THF/ether to give brown rectangular crystals of the desired product (0.39 g, 53% yield). Anal. calcd. for Mo$_2$Cr$_2$Na$_2$N$_2$P$_2$O$_4$C$_{16}$H$_{92}$: C, 47.70; H, 5.71; N, 1.74. Found: C, 48.05, H, 6.25; N, 1.69.

Phosphorus-31 NMR 237.6 ppm (singlet). Proton-NMR: $\delta$, 7.7 ppm (phenyl ring protons in the para position); $\delta$, 7.2 ppm (phenyl ring protons in the ortho and meta positions); $m$, 3.3 ppm (NCH$_2$C); $m$, 1.4 ppm (CCH$_2$CH$_2$C); $t$, 0.9 ppm (CCH$_3$) acetone-$d_6$. Absorption spectra in EtOH ($9.9\times10^{-5}$ M), $\lambda_{\text{max}} = 337.8$ nm, $\varepsilon = 4.4\times10^3$ M$^{-1}$cm$^{-1}$. IR (KBr) $\nu_{\text{CO}}$ 1987, 1886, 1842, $\nu_{\text{PO}}$ 838 cm$^{-1}$.

**Synthesis of $\{\text{Mo}_2[(\text{CO})_4\text{Mo(PhPO}_2^2\text{)}_2\text{]}_2\}\text{TBA}_2\text{Na}_2$, Complex (11).**

$[(\text{CO})_4\text{Mo(PhPO}_2^2\text{)}_2\text{H}_3\text{]}\text{TBA} (1.7841$ g, $2.44$ mmol) was dissolved in THF (30 mL) with stirring. NaH (ca 1 g) was added and the solution stirred
until no more effervescence was observed. The excess NaH was removed by filtration. \( \text{Mo}_2(\text{CH}_3\text{COO})_4 \) (0.2606 g, 0.609 mmol) was added to the filtrate and stirring was maintained for 24 h. The solution changed from light-brown to deep red upon contact with the molybdenum dimer. Sodium acetate was removed by filtration, and toluene (5 mL) was added dropwise to the filtrate and stirred for 1 h. A brown solid was collected by filtration and recrystallize from THF/Ether to give orange micro-crystals of the desired product (0.6743 g, 65% yield).

Anal. calcd. for \( \text{Mo}_4\text{Na}_2\text{N}_2\text{P}_4\text{O}_{16}\text{C}_6\text{H}_{92} \): C, 45.20; H, 5.40; N, 1.65. Found: C, 45.25; H, 5.89; N, 1.73. Phosphorus-31 NMR 217.3 ppm (singlet). Proton-NMR: \( \delta \), 7.7 ppm (phenyl ring proton in the para position); \( \delta \), 7.2 ppm (phenyl protons in the ortho and meta positions); \( \delta \), 3.3 ppm (NCH\(_2\)C); \( \delta \), 1.4 ppm (CCH\(_2\)CH\(_2\)C); \( \delta \), 0.9 ppm (CCH\(_3\)) acetone-\( \delta \)\(_6\). Carbon-13 NMR: \( \delta \), 223.9 ppm (CO in the equatorial position); \( \delta \), 212.7 ppm (\( J \text{PC} = 13 \text{ Hz} \), CO in the axial positions); \( \delta \), 150.4 ppm (\( J \text{PC} = 19 \text{ Hz} \), C\(_2\)C-P); \( \delta \), 129.3 ppm (\( J \text{PC} = 7 \text{ Hz} \), carbons in the ortho positions); \( \delta \), 128.8 ppm (\( J \text{PC} = 6 \text{ Hz} \), carbons in the meta positions); \( \delta \), 127.8 ppm (carbon in the para position); \( \delta \), 58.8 ppm (NCH\(_2\)C); \( \delta \), 23.9 ppm (CCH\(_2\)C); \( \delta \), 19.8 ppm (CH\(_3\)CH\(_2\)C); \( \delta \), 13.5 ppm (CH\(_3\)C). Absorption spectra in EtOH (8.5x10\(^{-5}\) M), \( \lambda \text{max} = 351.3\text{nm}, \varepsilon = 9.59\times10^3 \text{ M}^{-1}\text{cm}^{-1} \). IR (KBr) \( \nu/\text{CO} 1999, 1881, 1849, \nu/\text{PO} 839 \text{ cm}^{-1} \).

Crystals suitable for x-ray were obtained by slow diffusion of hexane into a methylene chloride solution of \( \text{Mo}_4 \).

Synthesis of \( \{\text{Mo}_2[(\text{CO})_4\text{W(PhPO}_2\text{)}_2\text{]}_2\}\text{TBA}_2\text{Na}_2 \), Complex (12). 
\( [(\text{CO})_4\text{W(PhPO}_2\text{)}_2\text{H}_3] \text{TBA} \) (0.6119 g, 0.73 mmol) was dissolved in THF (15 mL) with stirring. NaH (ca 0.5 g) was added to the solution and
stirred vigorously until no more effervescence was observed. Schlenk filtration removed the excess NaH. \( \text{Mo}_2(\text{CH}_3\text{COO})_4 \) (0.0781 g, 0.18 mmol) was added to the filtrate and stirring was maintained for 24 h. Sodium acetate was removed by filtration and toluene (5 mL) was added to the filtrate and stirred for an additional 15 min. Schlenk filtration followed by washing with ether and drying under-vacuum gave the desired product (0.067 g, 37% yield). Anal. calcd. for \( \text{Mo}_2\text{W}_2\text{Na}_2\text{N}_2\text{P}_4\text{O}_{16}\text{C}_6\text{H}_{92} \): C, 41.12; H, 4.92; N, 1.50. Found: C, 40.88; H, 5.32; N, 1.37. Phosphorus-31 NMR 196.5 ppm (singlet), \( ^1J(P,W)=134 \) Hz. Proton-NMR: \( \delta \) 7.7 ppm (phenyl ring protons in the para position); \( \delta \) 7.2 ppm (phenyl ring protons in the ortho and meta positions); \( \delta \), 3.3 ppm (NCH\(_2\)C); \( \delta \), 1.4 ppm (CCH\(_2\)CH\(_2\)C); \( \delta \), 0.9 ppm (CCH\(_3\)) acetone-d\(_6\). Absorption spectra in EtOH (8.5\( \times \)10\(^{-5}\)M), \( \lambda_{max} = 340.8 \text{ nm, } \epsilon = 5.39\text{M}^{-1}\text{cm}^{-1} \). IR (KBr) \( \nu \text{CO} = 1998, 1875, 1840, \nu \text{PO} = 839 \text{ cm}^{-1} \).

Synthesis of \( \{\text{Mo}_2[(\text{CO})_4\text{Mo(PhPO}_2)_2]\}_2\cdot2\text{DMAP}\}\text{TBA}_2\text{Na}_2\), Complex (13).

\[ \text{Mo}_4(\text{CO})_8(\text{PhPO}_2)_4 \text{TBA}_2\text{Na}_2 \] (0.2090 g, 0.125 mmol) was dissolved in THF (10 mL) with stirring. DMAP (0.0316 g, 0.258 mmol) was added to the solution and stirring was maintained for 1 h. After ca 30 min. the solution turned cloudy and an orange precipitate started to fall out. The precipitate was removed by Schlenk filtration and the excess solvent removed under-vacuum to give the desired product (0.1653 g, 68% yield). Anal. calcd. for \( \text{Mo}_4\text{Na}_2\text{N}_6\text{O}_6\text{C}_{78}\text{H}_{112} \): C, 48.22; H, 5.76; N, 4.32. Found C, 47.69; H, 5.94; N, 4.23. Phosphorus-31 NMR 219.7 ppm (singlet). Proton-NMR: \( \delta \), 8.1 ppm (phenyl ring proton in the para position); \( \delta \), 7.3 ppm (phenyl ring protons in the ortho and meta
positions); m, 6.3 ppm (pyridine ring protons); s, 2.8 (CH$_3$N). IR (KBr)$\nu$CO 1997, 1884, 1870, 1831, $\nu$PO 848 cm$^{-1}$.

**Synthesis of [Mo$_2$[(CO)$_3$I$_2$Mo(PhPO$_2$)$_2$]$_2$.2THF]$\text{TBA}_2\text{Na}_2$, Complex (14).**

[Mo$_4$(CO)$_4$(PhPO$_2$)$_4$]$\text{TBA}_2\text{Na}_2$ (0.1632 g, 0.09 mmol) was dissolved in THF (10 mL) with stirring. Iodine (0.0488 g, 0.19 mmol) was added to the solution and stirred for an additional 2 h. The solution turned dark red after ca 5 min. and gas evolution was observed. Schlenk filtration, followed by washing with THF and removal of excess solvent under-vacuum gave the desired product (0.1362 g, 70% yield). Anal. calcd. for Mo$_4$I$_2$N$_2$Na$_2$P$_4$O$_8$: C, 36.63; H, 4.71; N, 1.22. Found: C, 36.29; H, 4.71; 4.71; N, 1.20. Phosphorus-31 NMR, b, 208ppm. IR (KBr)$\nu$CO 2002, 1941, 1881, $\nu$PO 881 cm$^{-1}$.

Bright-orange crystals were obtained by slow diffusion of iodine solution into a [Mo$_4$(CO)$_8$(PhPO$_2$)$_4$]$\text{TBA}_2\text{Na}_2$ solution in THF over 7 days.
SECTION II

GROUP 6 TRANSITION METAL PHENYL CAGE COMPLEXES AND

HALOGEN OXIDATION OF MOYBDENUM CAGE COMPLEXES:

\((\text{CO})_4\text{Mo}[\text{RPO}]_4\text{Mo(\text{CO})}_4\) (\(\text{R} = \text{Pr}_2\text{N}\) and \(\text{Ph}\))
INTRODUCTION

The serendipitous formation of an adamantane-type bimetallic cage complex of the unknown cyclo-tetraphosphoxane \([RPO]_4\) from the thermal reaction of \(\text{Mo(CO)}_6\) with bis-diisopropylaminophosphine oxide led to the investigation of molybdenum complexes of cyclo-phosphoxane ligands. \(^{49}\)

\[2 \text{Mo(CO)}_6 + 4(\text{Pr}_3\text{N})_2\text{P(O)}\text{H} \rightarrow 4 \text{CO} + 4\text{Pr}_2\text{NH}_2 + (\text{eq} \ 1)\]

Cyclo-phosphoxane ligands or cyclic anhydrides of phosphorus (III), \([RPO]_n\), are rare. By contrast, numerous examples of cyclic condensed metaphosphates and thiophosphates of phosphorus (V) have long been known. The first report of the synthesis of a cyclo-phosphoxane ring \([RPO]_3\) (where \(R = \text{OEt, Et}_2\text{N and Pr}_2\text{N}\)) was in 1967. However, these compounds were not fully characterized. It was only in 1980 that Niecke isolated and fully characterized the cyclic trimer of diisopropylaminophosphinic acid anhydride, \([\text{Pr}_2\text{NPO}]_3\) \(^{50}\). More
recently, Chasar and co-workers reported the synthesis of \([\text{RPO}]_3\) and \([\text{RPO}]_2\) \(\text{where } R = 2,6\text{-di-tert-butyl-4-methyl-phenoxy}\).

The coordination chemistry of these potential polydentate ligands has yet to be investigated. Recently, in an attempt to elucidate the mechanism of formation of the novel adamantane dimolybdenum cage, Wong was able to isolate the first complex of \([\text{^P^NPO}]\) which was fully characterized as \((\text{CO})_5\text{Mo[RPO]}_3\).\(^{52}\)

Cyclo-tetraphosphoxanes, \([\text{RPO}]_4\), are only known in the complexed form. In contrast, the sulfur and nitrogen analogues of cyclo-tetraphosphoxanes (\([\text{RPS}]_4\) and \([\text{RPNR’}]_4\) \(\text{where } R = \text{mesistyl and } R’ = \text{Me}\)) are known in the complexed and uncomplexed forms. For example, \([\text{RPNR’}]_4\) is known to react with \(\text{Mo(CO)}_6\) to form \((\text{CO})_3\text{Mo[RPNR’]}_4\).\(^{53}\) In this case, the cyclo-tetraphosphazane adopts a crown conformation which enables it to act as a tridentate ligand. By contrast, the cyclo-tetraphosphoxane, \([\text{^P^2NPO}]_4\), adopts a boat-boat conformation,
and serves as a tetradeptate ligand chelating two metals as shown in eq 26. The geometrical constraints of the cyclo-tetraphosphoxane orients the two metal coordination spheres orthogonally to each other.

\[
\text{[MeNPMel}_4\text{Mo(CO)}_3
\]

The near quantitative yield of complex 15, which will be referred to as the isopropylamino cage, indicates that its formation is highly favored. Analogues to \((^1\text{Pr}_2\text{N})_2\text{P(O)H}\) such as \((\text{Cy}_2\text{N})_2\text{P(O)H}\), \([(\text{PhCH}_2)_2\text{N}]_2\text{P(O)H}\) and \((\text{Et}_2\text{N})_2\text{P(O)H}\) have been used in attempted syntheses of related bimetallic adamantane cage complexes. Only phosphine oxides with cone angles similar to \((^1\text{Pr}_2\text{N})_2\text{P(O)H}\) such as \((\text{Cy}_2\text{N})_2\text{P(O)H}\) led to the formation of the cage complex. The benzyl and ethylamino phosphine oxide yielded only traces of the corresponding cage.\(^{54}\) In order to extend the synthesis of bimetallic cage complexes to other phosphine derivatives, an alternate route was developed. Hutchinson reported the synthesis of di-molybdenum phenylcage complex by the nucleophilic attack of \([([\text{CO})_4\text{Mo(PhPO}_2)_2])_4^-\) on cis-\((\text{CO})_4\text{Mo(PhPCl}_2)_2\) affording the corresponding adamantane-type bimetallic cage shown below.\(^{18}\)
This synthetic approach is more general than the thermal reaction, eq 1, since it allows the preparation of hetero- as well as homo-bimetallic cages. Thus far, only the Cr and Mo homo-bimetallic phenyl cages have been synthesized. In order to complete the synthesis of phenyl-cages of group 6, the tungsten analogue was synthesized by a similar procedure. A comparison of spectroscopic and analytical data of the Cr, Mo and W phenyl-cages will be presented later in this chapter.

**Halogen Oxidation of Molybdenum Cages**

Halogen oxidation of molybdenum carbonyl complexes is well documented. This type of reaction is believed to be one of the key steps in catalytic processes. For example, Mo(II) substituted halocarbonyls, \([\text{MoX}_2(\text{CO})_3\text{L}_2]\) (L= phosphine or arsine; \(X= \text{Cl and Br}\)), are currently under investigation as catalysts for the ring-opening polymerization of norbornene.

Molybdenum-substituted halocarbonyls have been known for almost two decades. There are two synthetic routes to their synthesis as illustrated below:
\[ \text{Mo(CO)}_6 + 2L \rightarrow \text{Mo(CO)}_4L_2 \xrightarrow{X_2} \text{Mo(CO)}_3X_2L_2 \quad \text{(eq 2)} \]

or

\[ \text{Mo(CO)}_6 + X_2 \rightarrow \text{Mo(CO)}_4X_2 \xrightarrow{2L} \text{Mo(CO)}_3X_2L_2 \quad \text{(eq 3)} \]

If one assumes that the effective atomic number rule applies then complexes with seven-coordination number are expected. Seven-coordinate complexes are interesting in their own right because no regular polyhedral structure exists for seven ligands. There are at least 104 possible geometries; however, not all of them have favorable energies. Kepert has performed energy repulsion calculations for seven-coordinated complexes and found that there are three possible geometries with lowest energies: the pentagonal bipyramid, the capped octahedron and the capped trigonal prism. According to the calculations, these three geometries have similar energies and lead to complexes that often have non-rigid solution stereochemistry. Kepert also introduced a parameter to characterized seven-coordinated complexes with chelating ligands. This parameter is the normalized bite angle, \( b \) (\( b = \frac{2\sin \alpha}{2} \)), shown in Figure 1.

![Figure 1: Normalized Bite Angle in Chelate Complexes](image-url)
Numerous seven-coordinate complexes follow Kepert's prediction on structural preference. For complexes with $M(\text{bidentate})(\text{unidentate})_5$, Kepert predicted that a capped trigonal prism (A) or a pentagonal bipyramid (B) should be favored when $b < 1.1$. For seven coordinate complexes with $b > 1.2$, there are four stereochemistries of comparable energies that are favored including capped octahedron (C). These structures are illustrated in Figure 2.

Lippard and Colton reported the crystal structure of several seven-coordinated complexes, among them is $\text{Mo(CO)}_3\text{I}_2(\text{dpmp})$, which has $b = 1.33$ and a capped trigonal prism geometry. Most of the $M(\text{bidentate})(\text{unidentate})_5$ contain $R_2Y(\text{CH}_2)_nYR_2$ (where $Y = \text{P}$ or $\text{As}$). Very few complexes with bidentate ligands, such as $R_2\text{P}OPR_2$, have been reported in the literature. Bradley et al. were the first to report the synthesis and crystal structure of $\text{Mo(CO)}_3\text{I}_2(R_2\text{POPR}_2)$ ($R = \text{Ph}$ or tolyl; and $X = \text{I}$ or $\text{Br}$). In both cases the normalized bite angle was less than 1.1 and Kepert's calculations accurately predicted the structures to be pentagonal bipyramidal.

\[
\text{Mo(CO)}_3\text{I}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2) \quad \text{Mo(CO)}_3\text{I}_2(\text{Ph}_2\text{POPPPh}_2)
\]
Seven-coordinate complexes often exhibit non-rigid solution stereochemistry, leading to dynamic NMR. Proton and carbon-13 NMR have been used extensively to investigate molecules that exhibit fluxional behavior on the NMR time scale. Although phosphorus-31 NMR has not been widely used, Bradley et al. reported dynamic phosphorus-31 NMR results in the investigation of Mo(CO)$_3X_2$(R$_2$POPR$_2$) complexes and found that at least two isomers with seven-coordinate geometry exist in solution. The isomer that is in greater amount is the pentagonal bipyramid which is found in the solid-state x-ray structure.

Halogen oxidation of molybdenum cage complexes, 15 and 16, was investigated for several reasons. One reason is that the metal centers are separated by fixed distances which could make these complexes candidates for the investigation of charge transfer. There are many reports in the literature of charge transfer in systems where the metal centers are separated by fixed distances. The molybdenum atoms in cage complexes are so situated due to constraint of the cyclo-tetraphosphoxane cage structure. As a result, mixed-valent cage complexes could be synthesized which could give valuable information concerning metal-metal interactions. Another reason to investigate halogen oxidation of the cage complexes arises from the different phosphorous substituents of the two cages: isopropylamino vs phenyl. The steric and electronic effects of the substituents can play an important role in the nature of the halogen oxidation products.
Figure 2. Stereochemistry for \([M(\text{bidentate})(\text{unidentate})_3]\)
RESULTS AND DISCUSSION

1. Group 6 Transition Metal Phenyl Cage Complexes

Group 6 transition metal phenyl cage complexes were synthesized by the nucleophilic attack of \([(\text{CO})_4M(\text{PhPO}_2)_2]^{-4}\) on cis-(\text{CO})_4M(\text{PhCl}_2)_2 to afford the bimetallic cages shown below:

\[
(\text{CO})_4M(\text{PhPCl}_2)_2 + (\text{CO})_4M(\text{PhPO}_2)_2^{-4} \rightarrow (\text{CO})_4M[\text{PhP}O]_4M(\text{CO})_4 + 4 \text{Cl}^- \quad (\text{eq 4})
\]

M = Mo, 16
Cr, 17
W, 18

Complexes 16, 17 and 18 are all stable white solids that decompose slowly in solution. The molybdenum and tungsten phenyl cages were isolated in 33-50 % yield while the yield of chromium phenyl cage was only 15 % yield. The low to moderate percent yields are due to the fact that the coordinated chlorophenylphosphine complexes can adopt at least three possible orientations, only one of which is ideal for the assembly of the adamantanoid cage. The chromium phenyl cage was isolated in lower yields than the molybdenum and tungsten analogues because \((\text{CO})_4\text{Cr(PhPCl}_2)_2\) exists as a cis/trans equilibrium mixture in solution.

A phosphorus-31 NMR spectrum of the reaction mixture for the synthesis of complex 18 showed several peaks at 129.5, 147.2 and 156.8
ppm. The peak at 156.8 ppm is a clear singlet and is attributed to the tungsten phenyl cage. The two other peaks appear as doublets with $J_{pp} = 59$ Hz. The tungsten reaction is the only reaction that does not show any decomposition products as indicated by signals due to uncoordinated phosphines around 0 ppm. Thin-layer chromatography of the reaction mixture suggests the presence of at least four complexes, including complex 18. Attempts to isolate the other three by solvent extraction and column chromatography were unsuccessful. These other species are presumably partially formed cage complexes.

The analytical and spectroscopic data for complex 18 are consistent with data obtained for the molybdenum and chromium analogues originally synthesized by Hutchinson. Infrared and NMR data for complexes 16, 17 and 18 are shown in Tables I and II. Complex 18 exhibits carbonyl stretching frequencies characteristic of $C_{2v}$ symmetry at 2022, 1948 and 1912 cm$^{-1}$. The POP stretching frequency appears at 881 cm$^{-1}$. Phosphorus-31 NMR shows a singlet at 158.6 ppm with satellites due to $^{31}P-^{183}W$ coupling ($J_{PW} = 162$ Hz). Proton NMR spectrum reveals two broad peaks at 7.6 and 7.9 ppm due to the phenyl protons. In the carbon-13 NMR spectrum, the carbonyl region consists of two sets of apparent triplets at 203.9 ($J_{PC} = 15$ Hz) and 199.9 ($J_{PC} = 9$ Hz) ppm assigned to the carbonyls that are in the equatorial and axial positions respectively. The aromatic region has four peaks at 138.5 ($J_{PC} = 15$ Hz), 133.6, 129.4 and 129.2 ppm.
Table I. Infrared and Phosphorus-31 NMR of Group 6 Transition Metal Phenyl Cage Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>IR(KBr, cm⁻¹)</th>
<th>νCO</th>
<th>νPOP</th>
<th>Phosphorus-31 NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2024, 1955, 1927</td>
<td>882</td>
<td></td>
<td>185.2</td>
</tr>
<tr>
<td>17</td>
<td>2014, 1970, 1930</td>
<td>880</td>
<td></td>
<td>211.6</td>
</tr>
<tr>
<td>18</td>
<td>2022, 1948, 1912</td>
<td>881</td>
<td></td>
<td>158.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(J_PW=162Hz)</td>
</tr>
</tbody>
</table>
Table II. Carbon-13 NMR of Group 6 Transition Metal Phenyl Cage Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Aryl (ppm)</th>
<th>Carbonyl (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>143.3, 137.7, 133.5</td>
<td>217.3 (t, $J_{PC} = 6$ Hz)</td>
</tr>
<tr>
<td></td>
<td>114.3</td>
<td>212.0 (t, $J_{PC} = 11$ Hz)</td>
</tr>
<tr>
<td>17</td>
<td>139.1 (t, $J_{PC} = 15$ Hz)</td>
<td>223.8 (t, $J_{PC} = 16$ Hz)</td>
</tr>
<tr>
<td></td>
<td>133.2, 129.4</td>
<td>217.8 (t, $J_{PC} = 9$ Hz)</td>
</tr>
<tr>
<td>18</td>
<td>138.5 (t, $J_{PC} = 29$ Hz)</td>
<td>203.9 (t, $J_{PC} = 15$ Hz)</td>
</tr>
<tr>
<td></td>
<td>133.6</td>
<td>199.9 (t, $J_{PC} = 9$ Hz)</td>
</tr>
<tr>
<td></td>
<td>129.4 (t, $J_{PC} = 10$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>129.2 (t, $J_{PC} = 6$ Hz)</td>
<td></td>
</tr>
</tbody>
</table>
2. Halogen Oxidation of Dimolybdenum Cages of the Cyclo-
tetraphosphoxane Ligand, \([\text{RP}O]_4(R = ^1\text{Pr}_2\text{N or Ph}),\)

Complexes 15 and 16

It is useful to compare the cage structures of complexes 15 and 16 before discussing their reactivity towards halogen oxidation. Significant x-ray data for complexes 15 and 16 are presented in Table III. As shown in Table III, the \(P_4O_4\) ring of the cages are similar with average P-O bond lengths varying slightly at 1.640-1.646 Å. The average O-P-O bond angles differ by only 3° and the average P-O-P bond angles are also similar at 127.8-131°.

The effect of the phosphorus substituent (\(^1\text{Pr}_2\text{N-P vs Ph-P}\)) is most clearly observed in the molybdenum coordination spheres. Severe distortion of the axial carbonyls in the molybdenum coordination sphere is observed for complex 15 but not for complex 16. These are bent by 13° from linearity in complex 15. Similarly, the carbonyls in the equatorial position are closed up from the ideal 90°, by almost 5° in complex 15 while in complex 16 they are at 88.1°. The M-C-0 bond angles are bent from linearity by 8° in complex 15. P-Mo-P bond angles are at 76.0° and 77.7° for complexes 15 and 16 respectively and the normalized bite angles, \(b\), are 1.23 and 1.25 respectively. Complex 15 also has longer Mo-P bond lengths, 2.5 Å compared to 2.435 Å for complex 16. Most relevant is the metal-metal separation which decreases from 6.0 Å in complex 15 to 4.53 Å in complex 16. These results indicate a more congested steric environment around the metal centers of complex 15 compared 16. These differences will be
Table III. Comparison X-ray Data of Isopropylaminocage and Phenyl Cage.

<table>
<thead>
<tr>
<th></th>
<th>Isopropylaminocage</th>
<th>Phenylcage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-P</td>
<td>2.501(2) Å</td>
<td>2.435(2) Å</td>
</tr>
<tr>
<td>Mo-C</td>
<td>1.986(6) Å</td>
<td>2.040(8) Å</td>
</tr>
<tr>
<td>Mo-C\text{ax}</td>
<td>2.139(6) Å</td>
<td>2.023(7) Å</td>
</tr>
<tr>
<td>P-0\text{eq}</td>
<td>1.642(4) Å</td>
<td>1.646(1) Å</td>
</tr>
<tr>
<td>Mo-Mo\text{(separation)}</td>
<td>6.001(1) Å</td>
<td>4.531(1) Å</td>
</tr>
<tr>
<td>P-Mo-P</td>
<td>76.0(1)°</td>
<td>77.74(6)°</td>
</tr>
<tr>
<td>C-Mo-C</td>
<td>167.3(2)°</td>
<td>179.2(3)°</td>
</tr>
<tr>
<td>C-Mo-C\text{ax}</td>
<td>85.3(2)°</td>
<td>88.1(3)°</td>
</tr>
<tr>
<td>Mo-C-O\text{eq}</td>
<td>172.1(1)°</td>
<td></td>
</tr>
<tr>
<td>P-O-P</td>
<td>131.0(2)°</td>
<td>127.8(4)°</td>
</tr>
<tr>
<td>O-P-O</td>
<td>99.0°</td>
<td>102.0°</td>
</tr>
<tr>
<td>bite angle, b</td>
<td>1.23°</td>
<td>1.25°</td>
</tr>
</tbody>
</table>
Figure 3: Ortep Diagrams for Complexes 15 and 16
significant in influencing the halogen oxidation products of these cage complexes.

2.1. **Halogen Oxidation of the Isopropylamino Cage.**

**Complex 15**

2.1.1 **Mixed-valent dihalo-complexes of 15.** The reaction of isopropylamino cage with two equivalents of iodine or sulfuryl chloride afforded the mixed-valent isopropylamino cage-I$_2$ and isopropylamino cage-Cl$_2$. However, reaction of complex 15 with two equivalents of bromine yielded only complex 15 and the isopropylamino cage-Br$_4$; that is, both metal centers were oxidized to the +2 oxidation state. In order to synthesize the mixed-valent isopropylamino cage-Br$_2$, a halide exchange reaction of isopropylamino cage-I$_2$ with two equivalents of tetraethylammonium bromide was successfully carried out.

\[
\text{(CO)}_4\text{Mo}[\text{Pr}_3\text{NPO}_4\text{Mo}(\text{CO})_4 + \text{I}_2 \xrightarrow{\text{SO}_2\text{Cl}_2} \text{(eq 5)}] \\
\text{(CO)}_4\text{Mo}[\text{Pr}_3\text{NPO}_4\text{Mo}(\text{CO})_4 \text{I}_2 + 2\text{Et}_4\text{NBr}]
\]

\[X = \text{I} \quad (19)\]

\[\text{Br} \quad (20)\]

\[\text{Cl} \quad (21)\]
An in-situ reaction of complex 15 with two equivalents of iodine was carried out in methylene chloride at 0°C. A phosphorus-31 NMR spectrum recorded at this temperature showed fluxional behavior. The spectra at different temperatures are shown in Figure 4. A peak due to the isolated product (19) is observed among peaks due to the formation of a seven-coordinate mixed-valent intermediate. This indicates that the halogen oxidation of complex 15 initially yields a seven-coordinate mixed-valent intermediate, 

$$(\text{CO})_4\text{Mo}^{[\text{Pr}_2\text{NPO}]}_4\text{Mo}^{\text{CO}}_3\text{I}_2$$

which readily loses CO to give the final product.

Complexes 19, 20 and 21 are obtained in good yields (75-85%) and are relatively stable in the solid state when stored under nitrogen. Complex 21 is the most stable while complex 19 is the least.

Elemental analyses of complexes 19, 20 and 21 were consistent with the formula $\text{Mo}_2^{\text{CO}}_6\text{X}_2^{[\text{Pr}_2\text{NPO}]}_4$. Molecular weight determinations by vapor pressure osmometry indicate that these complexes exist as monomers in solution. Interestingly, complex 19 gave the best agreement between the calculated and experimental molecular weight and complex 21 gave the worst.

Infrared spectroscopy is a valuable tool in the identification of these metal carbonyl complexes. Two regions were examined closely. These two regions are where the carbonyl and the POP stretching frequencies are observed. The $A_1$ band of the carbonyl region was used as a probe to monitor the oxidation state of the metal center. Complexes 19, 20 and 21 exhibited an $A_1$ band at 2024 cm$^{-1}$. This band has shifted by 10 cm$^{-1}$ to higher energy upon oxidation of the parent complex indicating a decrease in electronic density at the Mo(0).
Figure 4. Variable Temperature Phosphorus-31 Spectra of In-situ Reaction of Complex 19 with Two Equivalents of Iodine
This constituted one of the major evidences that charge transfer exist between the Mo(0) and Mo(II) sites. Below 2000 cm\(^{-1}\) there are at least three transitions which can be assigned to the \(B_1\), \(A_1\) and \(B_2\) bands of the carbonyls bound to the Mo(0) and to the carbonyls bound to the Mo(II). A shift to higher energy is observed in the POP stretching frequency in the mixed-valent complexes. This shift is approximately 10-19 cm\(^{-1}\).

Such a shift has been correlated with a decreased in the P-O-P angle for complexes having POP as chelating ligands.\(^6\) Bradley reported a shift to higher energy in the POP stretching frequency upon oxidation of \((\text{CO})_4\text{Mo}[\text{Ar}_2\text{POPOAr}_2]\) to \((\text{CO})_3\text{I}_2\text{Mo}[\text{Ar}_2\text{POPOAr}_2]\) in agreement with the decrease in POP angle from 63.82 to 61.9.\(^5\) These results suggest that the P-O-P bond angle in the isopropylamino cage decreases upon oxidation, a result that will be borne out by structural work.

Infrared data of the carbonyl and POP stretching frequencies are presented in Table IV.

Proton-NMR spectra of complexes 19, 20 and 21 consist of two sets of septets in a 1:3 ratio at 5.3 and 4.1 ppm and an apparent doublet of triplets at 1.35 ppm. The former are attributed to the methine protons of the diisopropylamino group and the doublet of triplets is assigned to the methyl protons of the isopropylamino group. Carbon-13 NMR spectra of complexes 19, 20 and 21 in the alkyl region are complex when compared to the spectrum recorded for complex 15. Complex 15 has a single methyl peak at 24.1 ppm and a doublet at 47.0 ppm (\(^2J_{PC} = 6\) Hz) assignable to the methine carbons.\(^6\) The spectra of the mixed-valent complexes reveal three peaks at 23.0-24.9 ppm due to three types of methyl groups and apparent doublets and triplets at 47.5-
Table IV: IR Data of the C=O and POP Stretching Frequencies of Isopropylamino Cage Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>νC=O</th>
<th>νPOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylamino cage</td>
<td>2015, 1923, 1906, 1887</td>
<td>875(m,d)*</td>
</tr>
<tr>
<td>Isopropylamino Cage-(X_2)</td>
<td>2024, 1979, 1915</td>
<td>885(m,d)*</td>
</tr>
<tr>
<td>(X = I) (19)</td>
<td>2027, 1983, 1948(sh), 1933</td>
<td>892,</td>
</tr>
<tr>
<td>(X = Br) (20)</td>
<td>2024, 1979, 1953, 1909</td>
<td>887(sh),</td>
</tr>
<tr>
<td>(X = Cl) (21)</td>
<td>2027, 1983, 1947(sh), 1932</td>
<td>894**,</td>
</tr>
<tr>
<td>Isopropylamino Cage-(X_4)</td>
<td>2025, 1975, 1960, 1920</td>
<td>889(m,d)*</td>
</tr>
<tr>
<td>(X = I) (22)</td>
<td>2030, 1984, 1950(sh), 1934</td>
<td>895,</td>
</tr>
<tr>
<td>(X = Br) (23)</td>
<td>1977, 1921</td>
<td>885*</td>
</tr>
<tr>
<td>(X = Cl) (24)</td>
<td>1978, 1923</td>
<td>890*</td>
</tr>
<tr>
<td></td>
<td>1979, 1929</td>
<td>897*</td>
</tr>
</tbody>
</table>

(m) medium, (sh) shoulder, (d) doublet.
* KBr matrix
** CHCl₃
Table V: Carbon-13 NMR for the Isopropyl Region of the Isopropylamino Cage Complexes in CDCl₃

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₃</th>
<th>CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylaminocage</td>
<td>24.1(s)</td>
<td>47.0(J_p_C=6Hz)</td>
</tr>
<tr>
<td>Isopropylamino Cage-X₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = I (19)</td>
<td>23.2(s)</td>
<td>47.5(s); 48.0(s)</td>
</tr>
<tr>
<td></td>
<td>24.0(d) (J_p_C= 2Hz)</td>
<td>48.3(d) (J_p_C= 8Hz)</td>
</tr>
<tr>
<td></td>
<td>24.5(d) (J_p_C=2 Hz)</td>
<td>49.0(t) (J_p_C=4 Hz)</td>
</tr>
<tr>
<td>X = Br (20)</td>
<td>23.4(t) (J_p_C=4 Hz)</td>
<td>48.0(d) (J_p_C= 4Hz)</td>
</tr>
<tr>
<td></td>
<td>24.1(s); 24.6(s)</td>
<td>48.5(s); 48.7(s); 49.9(s)</td>
</tr>
<tr>
<td>X = Cl (21)</td>
<td>23.3(s); 24.0(s)</td>
<td>47.7 (s)</td>
</tr>
<tr>
<td></td>
<td>24.5(s); 24.7(s)</td>
<td>48.0(d) (J_p_C= 7Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.5(t) (J_p_C= 12Hz)</td>
</tr>
</tbody>
</table>
Table VI. Carbon-13 NMR of the CO Region of Isopropylamino Cage Complexes in CDCl₃

<table>
<thead>
<tr>
<th>Complex</th>
<th>CO at Mo(II)</th>
<th>CO at Mo(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylamino Cage</td>
<td>213.0(t) (²J_{PC}=15Hz)</td>
<td>213.0(d of d)</td>
</tr>
<tr>
<td></td>
<td>207.3(t) (²J_{PC}=12Hz)</td>
<td></td>
</tr>
<tr>
<td>Isopropylamino Cage-X₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = I (19)</td>
<td>233.4(t) (²J_{PC}=27Hz)</td>
<td>213.0(d of d)</td>
</tr>
<tr>
<td></td>
<td>(²J_{PC}=10Hz,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>²J_{PC}=4Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>211.0(t) (²J_{PC}=15Hz)</td>
<td>206.2(t) (²J_{PC}=12Hz)</td>
</tr>
<tr>
<td>X = Br (20)</td>
<td>236.0(t) (²J_{PC}=31Hz)</td>
<td>212.8(d of d)</td>
</tr>
<tr>
<td></td>
<td>(²J_{PC}=13Hz, ²J_{PC}=4Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>212.2(t) (²J_{PC}=13Hz)</td>
<td>206.3(t) (²J_{PC}=12Hz)</td>
</tr>
<tr>
<td>X = Cl (21)</td>
<td>239.5(t) (²J_{PC}=27Hz)</td>
<td>212.8(t) (²J_{PC}=9Hz)</td>
</tr>
<tr>
<td></td>
<td>212.1(t) (²J_{PC}=12Hz)</td>
<td>206.9(t) (²J_{PC}=11Hz)</td>
</tr>
</tbody>
</table>
49.7 ppm in the methine region. Carbon-13 NMR data of the isopropylamino groups are listed in Table V.

Results of the carbon-13 NMR in the carbonyl region are presented in Table VI. Four groups of peaks are observed including two apparent triplets at 206 ppm ($^2J_{PC}$= 12 Hz) and 212 ppm ($^2J_{PC}$= 10-13 Hz) and a doublet of doublets at 213 ppm ($^2J_{PC}$=12Hz, $^2J_{PC}$= 4 Hz). The triplet at 206 ppm is assigned to the axial carbonyls and the peaks at 212 and 213 ppm are assigned to the carbonyls in the equatorial positions that are bound to the Mo(0). The two carbonyls bound to the Mo(II) are equivalent and appear as an apparent triplet at 233.4-239.5 ppm with $^2J_{PC}$ constants in the 27-33 Hz range.

Phosphorus-31 NMR spectra of complexes 19 and 21 in chlorocarbon solvents such as CH$_2$Cl$_2$ and CHCl$_3$ are typical of AMX$_2$ spin systems. The AM peaks of the spectrum are at $^1J_A = 161.8-162.9$ ppm and $^2J_M = 157.2-157.5$ ppm ($^2J_{AM} = 40$Hz). The chemical shift for X$_2$ ($^1J_X$) varies with the halide and is 132.6 ppm for the iodo complex (19) and 153.1 ppm for the chloro complex (21) ($^1J_{AX} = J_{MX} = 12-15$ Hz). This confirms our assignment of peaks at high field (X) to the phosphorus atoms bound to Mo(II) while the other two sets of peaks (AM) are assignable to the two phosphoruses on Mo(0). The bromide complex (20) shows a slightly different spectral behavior. In pure chlorocarbon solvents the X$_2$ portion of the spectrum is not resolved but appears as a broad peak. This peak shows solvent chemical shift dependence. For example, it appears at 137 ppm in CHCl$_3$ and shifts to 140 ppm in CH$_2$Cl$_2$. This peak is resolved into a doublet in a 1:1 mixture of CH$_2$Cl$_2$/acetonitrile with X now at 147.1 ppm ($^1J_{AX} = J_{MX} = 15$Hz). It should be noted that the dark red-brown coloration of complex 20 in
CH₂Cl₂ turned bright yellow with addition of CH₃CN indicative of a major change in the Mo(II)'s primary coordination sphere. Phosphorus-31 NMR data for these mixed-valent complexes are listed in Table VII. Figure 5 illustrates the solvent dependence of the phosphorus-31 NMR spectra of complex 20.

A single-crystal x-ray study of complex 20 was completed (Figure 6). Its molecular geometry consists of two adamantane cages doubly bridged by bromides. The crystal belongs to the space group P2₁/c. The coordination sphere around each Mo(0) is a distorted octahedron. P-Mo(0)-P angles have opened up slightly to 77.7° from 76.1° in the parent complex. Carbonyls in the axial position are distorted from linearity with C-Mo(0)-C at 171.4°. Metal-carbon bond lengths are at 1.94(6) Å and 2.00(3) Å for carbonyls trans and cis to phosphines respectively.

The oxidized metal center has a capped trigonal prismatic structure as predicted by the Kepert energy repulsion calculations (b > 1.1). Figure 7 illustrates the coordination geometry around Mo(II). A bromide anion is in a unique capping position (Mo-Br bond length is 2.528(8) Å). The quadrilateral face contains two cis-phosphoruses (Mo-P bond length at 2.466(6) Å) and two cis-bromides (Mo-Br bond length average is 2.572(3) Å) which bridge the other cage's Mo(II) center. Two carbonyls make up the remaining edge (Mo-C bond length average is 1.93(4) Å). The C-Mo(II)-C bond angle is very small at 54°.

The Mo-P bond lengths for Mo(0) and Mo(II) are similar at 2.47 Å and 2.466 Å. This is considerably less than the value predicted for the sum of single bond radii (2.71 Å),
Table VII. Phosphorus-31 NMR Data of the Isopropylamino Cage Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Shift (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylamino Cage</td>
<td>150.3 (s)</td>
<td>CDCl$_3$</td>
</tr>
<tr>
<td>Isopropylamino Cage-X$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>CH$_2$Cl$_2$/</td>
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<tr>
<td></td>
<td>$^2$J $AM$ = 40, $AX$ = 15, $MX$ = 15 Hz</td>
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<td>CDCl$_3$</td>
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<td></td>
<td>$^2$J $AM$ = 39, $AX$ = 15, $MX$ = 15 Hz</td>
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<tr>
<td>Isopropylamino Cage-X$_4$</td>
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<tr>
<td>X = I (22)</td>
<td>137.2(A'); 144.7(B')</td>
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<tr>
<td>X = Br (23)</td>
<td>157.9(A'); 145.1 (B')</td>
<td>CD$_3$CN</td>
</tr>
</tbody>
</table>

(a) Chemical shift referred to 85% H$_3$PO$_4$. 
Figure 5. Phosphorus-31 NMR Spectra of complex 20 in (a) CDCl$_3$ and (b) CD$_3$CN/CH$_2$Cl$_2$. 
Figure 6. Ortep Diagram for the X-ray Structure of Complex 20
Figure 7. Structure around each Mo(II) end of
\[(\text{CO})_4\text{Mo}[^{1}\text{Pr}_2\text{NPO}]_4\text{Mo(CO)}_2\text{Br}_2\}_2\]
indicating that these bonds have some double bond character through back donation from the metal (d → d). Within the cage itself the P-O bond lengths are at 1.623-1.644 Å and the P-O-P bond angle is at 129.8°. This angle has indeed decreased by 1.2° with respect to the parent cage, a fact reflected in the increased POP stretching frequency in the IR. The two cages share a common edge of the capped quadrilateral face and are related by an inversion center of symmetry. A list of relevant bond lengths and bond angles is presented in Table VIII.

Dimeric complexes of molybdenum with a capped trigonal prism structure are rare. There are only five such structures reported in the literature with this geometry. 63

Molybdenum(III) dimer with 1,4,2 capped trigonal prism environment
Table VIII. Important Bond-lengths and Bond-angles for Isopropylamino Cage-Br₂.

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<thead>
<tr>
<th></th>
<th>Bond-length (Å)</th>
<th>Bond-angle (°)</th>
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<tr>
<td>C(41)-N(4)</td>
<td>124(4)</td>
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By inference from their similar IR data, complexes 19, 20, and 21 all presumably exist as dimers in the solid state. As a result each of the metal centers obeys the eighteen electron rule. However, in solution their halide bridges are disrupted by the solvent and they apparently exist as monomers. Furthermore, the NMR evidence would only be consistent with a trigonal prismatic structure, a very unusual structure for six-coordinate metal centers with monodentate ligands. In addition, the broadness of the high field peak in the solution phosphorus-31 NMR spectrum of complex 20 remains to be explained.

There are several possible explanations for this. One possible explanation is a short spin-lattice relaxation time ($T_1$) if the quadrupolar effect of the bromines shortens the $T_1$ of phosphoruses trans to them. An alternate explanation is that if the solution geometry is derived from the solid-state dimeric structure, an equilibrium may exist between the dimer and monomer which is near coalescence, thus causing the broad signal. A third possibility would be the presence of a halide dissociation equilibrium as shown in eq 6:

\[(\text{CO})_4\text{Mo}[\text{RPO}]_4\text{Mo(CO)}_2\text{Br}_2 + S \rightarrow (eq \ 6) \]

\[[((\text{CO})_4\text{Mo}[\text{RPO}]_4\text{Mo(CO)}_2\text{BrS})^+ + \text{Br}^-]

(S = Solvent)

This can also broaden the phosphorus signals at the Mo(II) sites. A final explanation may be that an equilibration exists between two or more closely-related isomeric geometries, broadening the high-field signal.
In order to test the first hypotheses, $T_1$ measurements were conducted by using the inversion-recovery method. The pulse sequence used was $[180°-t-90°]^n$. In our case the $180°$ pulse was 52 μs and the number of acquisitions, $n$, was 100. Since the relaxation process is exponential with a time constant of $(T_1)^{-1}$, a plot of $\ln[(I_0-I)/2I_0]$ vs $t$, where $I$ is the intensity of the peak, will have a slope of $1/T_1$. $T_1$ values for the three types of phosphoruses were all in the range 4.4-10.9 sec. The broad peak has a $T_1$ value of 5.9 sec which is clearly inconsistent with the first hypothesis.

If an equilibrium exists between monomer and dimer in solution, then concentration should have a significant effect. At low concentrations the equilibrium should favor the monomer. This effect was studied by taking phosphorus-31 NMR spectra at different complex concentrations. Results were not definitive due to solubility constraints and the limited range of concentrations available (0.012-0.006 M). Spectra at lower concentrations were not obtainable since the number of scans for a given signal/noise (S/N) ratio is proportional to the square of the concentration. We calculated that a concentration of 0.0006 M will require four days for a reasonable S/N ratio. As the mixed-valent complex is barely stable in solution overnight this experiment could not be carried out.

Another way to investigate the monomer and dimer equilibrium is as a function of solvent polarity. Polar solvents should disrupt the bromide bridges and discourage dimerization. Figure 5 shows two spectra of complex 20; spectrum (a) was taken in chloroform and spectrum (b) was taken in a mixture of methylene chloride/acetonitrile (complex 20 is not very soluble in pure acetonitrile). In (b) the
broad peak at high field has been resolved into a doublet with $J_{pp} = 14$ Hz, and has also shifted to lower field by 7 ppm. Though the other two sets of peaks have also shifted to lower fields, these are much less dramatic: $\delta_A = 1$ ppm and $\delta_M = 2$ ppm. A plot of $\delta_X$ vs dielectric constant ($\varepsilon$) of the solvent is almost linear as shown in Figure 8. This suggests that there may indeed be an equilibrium between monomer and dimer. It should be noted that the molecular weight determination of complex 20 (Table IX) indicates that it exists primarily as the monomer in chloroform. Furthermore, polar solvents such as acetonitrile can also encourage halide dissociation.

In order to determine if there is halide dissociation in complex 20, conductivity measurements were made. The conductivities for the mixed-valent cages in acetonitrile are listed in Table IX. These indicate that the iodo complex, 19, dissociates more than the bromo complex, 20. From studies on a large number of compounds it is known that the molecular conductivity of a $10^{-3}$ M solution of a univalent (1:1) electrolyte in acetonitrile is around 120-160 ohm$^{-1}$, whereas for a unibivalent (1:2) electrolyte the conductivity is near 260 ohm$^{-1}$. Neither of our complexes have conductivities in these ranges. The values for complexes 19 and 20 are only 71 and 51 ohm$^{-1}$ respectively. Most importantly, a graph of molar conductivity vs (concentration)$^{1/2}$ indicates that these complexes behave as weak electrolytes in solution (Figure 9).
Table IX: Molecular Weight Determination and Conductivity Measurements of Isopropylamino Cage Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular Weight (CHCl₃)</th>
<th>Molar Conductivity (ohm mol⁻¹ dm²⁻¹)ᵃ</th>
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<tr>
<td></td>
<td>Theory</td>
<td>Exp</td>
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<tr>
<td>Isopropylamino Cage-X₂</td>
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<td>X = I (16)</td>
<td>1201.7</td>
<td>1234±7</td>
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<td>X = Br (17)</td>
<td>1107.8</td>
<td>1169±110</td>
</tr>
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<td>X = Cl (18)</td>
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<td>1010±60</td>
</tr>
<tr>
<td>Isopropylamino Cage-X₄</td>
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<tr>
<td>X = I (19)</td>
<td>1399.5</td>
<td>1198±27</td>
</tr>
<tr>
<td>X = Br (20)</td>
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<td>-</td>
</tr>
</tbody>
</table>

ᵃ Solvent acetonitrile, concentration 10⁻³ M
Figure 9. Plot of Conductivities for Complex 19 and 20
The effect of varying [Br\(^-\)] was also investigated next by phosphorus-31 NMR titration of complex 20. Results are shown in Figure 10. After addition of one-half equivalent of Br\(^-\) to a solution containing complex 20 in CDCl\(_3\) a +3.3 ppm chemical shift of the high-field Mo(II) peak \(\delta_X\) was observed. This peak also sharpened considerably. A smaller 0.2-0.4 ppm shift was observed for the other peaks. After 8 equivalents of Br\(^-\) were added, \(\delta_X\) shifted to 144.5 ppm with further sharpening of the doublet. Thus, it is apparent that bromide concentration plays a significant role in the broadening of this high-field peak. However, the other two possibilities; monomer/dimer equilibrium and the presence of several isomers, cannot be ruled out.

Since variable-temperature NMR studies often yield useful information on structural dynamics, variable temperature phosphorus-31 NMR spectra of complexes 20 and 19 in CH\(_2\)Cl\(_2\) were recorded. Although the results were inconclusive since the coalescence temperatures were not reached with the instrumentation available, some preliminary conclusions can be drawn. Figure 11 shows the variable temperature data for complex 20 in CH\(_2\)Cl\(_2\). The AMX\(_2\) spin system spectrum consists of a doublet at low-field \((A)\), a doublet of triplets \((M)\) and an area-two doublet at high-field \((X)\). At 0°C \((A)\) at 163.2 ppm and \((M)\) at 158.8 ppm are well resolved, while \((X)\) at the highest field is still very broad. The spectrum at -23°C shows significant changes. The doublet \((A)\) has broadened and shifted to lower field \((\Delta \delta = 2\) ppm\). The \((M)\) signals also broaden, shifting very slightly to higher field. Most interesting is the resolution of \((X)\) into two broad peaks at 144 ppm and 134 ppm. At -46°C, all peaks have broadened. The doublet \((A)\) has broadened
Figure 10. The Effect of [Br−] on the Phosphorus-31 NMR of Complex 20. (a) [Br−]/[20] = 0, (b) [Br−]/[20] = 0.5, (c) [Br−]/[20] = 1, and (d) [Br−]/[20] = 8
Figure 11. Variable Temperature Phosphorus-31 NMR of Complex 20
into the base-line and shifted further to lower field ($\Delta \delta = 3.7$ ppm).

By contrast, the two high-field peaks (144 ppm and 134 ppm) have sharpened and have shifted to lower and higher fields respectively. Finally, at the lowest temperature attained, $-90^\circ$C, the lowest-field peak has almost resolved into a doublet at 167.1 ppm. The region between 165 and 140 ppm still shows overlapping, broad peaks making meaningful assignments impossible. Clearly a limiting spectrum is not reached.

Since the results from the variable temperature phosphorus-31 NMR of complex 20 were inconclusive, a study of the dynamic NMR of complex 19 was undertaken. A simpler set of spectra was anticipated because complex 19 has a well-resolved phosphorus-31 NMR spectrum at room temperature. The results are shown in Figure 20. At $-23$ C the spectrum of complex 19 closely resembles that of 20. The doublet (A) at lowest field (163.5 ppm) has broadened. In addition, the other two set of peaks ($MX_2$) have begun to lose fine structure. When the temperature reaches $-46$ C, the doublet (A) coalesces while (M) appears as a broad peak almost in the base-line. The original doublet at 134.0 ppm ($X_2$) has lost almost all its fine structure and shifts very slightly to higher field. At $-90^\circ$C peak (A) has re-emerged as a doublet at lower field ($\Delta \delta = 4$ ppm).

At this temperature (M) has grown from the base-line but is still unresolved and the original doublet ($X_2$) at 134 ppm now appears as a broad singlet at higher field ($\Delta \delta = 0.5$ ppm). Again a limiting spectrum is not achieved.

In summary, the variable temperature spectra of both complexes 19 and 20 show conclusively that neither is static at room temperature.
Figure 12. Variable Temperature Phosphorus-31 NMR of Complex 19
Their apparent AMX₂ spectra therefore result from the rapid equilibration between two or more solution species.

Of the three possible hypotheses; monomer-dimer equilibrium, bromide dissociation, and isomeric equilibration, the second can be discarded for the following reasons. (1) Addition of Br⁻ to complex 20 in CHCl₃ gave a similar spectrum to that of 20 in CH₃CN. If the second hypothesis was correct, the former should inhibit Br⁻ dissociation while the latter should encourage it. (2) Conductivity measurements in CH₃CN clearly show that Br⁻ dissociation is not extensive even in this polar solvent.

Both monomer-dimer (eq 6a) and isomeric equilibrations (eq 6b) can account for all the present experimental results. These include molecular weight data, phosphorus-31 NMR spectra in CHCl₃, CH₂Cl₂, and CH₃CN/CH₂Cl₂, variable temperature NMR data, conductivity studies, bromide dependence, color change in CH₃CN, and precedence of suggested structures.

(S = Solvent)
In the absence of limiting spectral data, we cannot choose one hypothesis over the other. It is also possible that both processes are actually involved. In either case the rapid dynamic process(es) at ambient temperature results in an $AMX_2$ phosphorus-31 NMR average spectrum.

2.1.2 Tetrahalo-Complexes of Isopropylamino Cage.

**Complex 15.** Reaction of four equivalents of iodine, bromine or sulfuryl chloride with the isopropylamino-cage afforded the tetrahalide complex according to the following reaction:

\[
\begin{align*}
2 \text{I}_2 & \quad 15 + 2 \text{Br}_2 & \quad \rightarrow \\
2 \text{SO}_2\text{Cl}_2 & \quad 2 \text{I}_2 \text{S}0_2\text{Cl}_2 \\
\end{align*}
\]

\[X = \text{I}, 22\]
\[\text{Br}, 23\]
\[\text{Cl}, 24\]

Elemental analyses are consistent with the formation of $\text{Mo(CO)}_2X_2[\text{RPO}]_4\text{Mo(CO)}_2X_2$. Complex 22 is a dark red solid, obtained in 91% yield. Complexes 23 and 24 are orange and yellow solids respectively and are obtained in quantitative yields. Due to solubility problems, the characterization of these complexes has relied on elemental analysis and IR. Complex 22 is soluble in
moderately polar solvents such as methylene chloride or chloroform.
Complex 23 is only soluble in acetonitrile and decomposes in methanol and DMSO. Complex 24 is insoluble in most organic solvents. It decomposes immediately in DMSO, yielding a green-blue solution, indicative of oxidation of Mo(II). Attempts to identify the decomposition product were unsuccessful. Solubility of these tetrahalo cages decreases in the following order: 22 > 23 > 24.

The best evidence to suggest that the cage structure is retained and that there are only two carbonyls left on each molybdenum is given by the IR spectra (Table VI). Two carbonyl stretches of similar intensities appear below 2000 cm\(^{-1}\) for all three complexes. They can be assigned to the symmetric and asymmetric stretches for the cis-Mo(CO)\(_2\) unit. POP stretching frequencies appear at 885, 870 and 897 cm\(^{-1}\) for complexes 22, 23 and 24 respectively.

\[ Ra_{sym} = 2r\cos \alpha \quad Ra_{asym} = 2r\sin \alpha \]

In preliminary work on these reactions, Turnbull also suggested that the cage structure is maintained upon oxidation.\(^6\) Phosphorus-31 NMR of complexes 22 and 23 are reported in Table VII and are typical of AA'BB' spin systems (Figure 13). These suggest that each metal's two phosphorus atoms are magnetically non-equivalent. The carbon-13 NMR of complex 22 shows eight lines corresponding to two carbonyls on each molybdenum.
Molecular weight determination of complex 22 in CHCl₃ revealed that it is monomeric (Table IX). Conductivity measurements of complexes 22 and 23 in acetonitrile revealed that although both are weak electrolytes, 23 dissociates to a lesser extent than 22. These data suggest that both complexes 22 and 23 exist as monomers in solution.

All attempts to grow crystals for x-ray structure determination in the solid state were unsuccessful. In the absence of such data, geometrical information can be derived from the IR data. Bond angles (α) between two CO's can be determined to a good approximation by the relative intensities of different CO stretching modes. By Cotton's method each CO oscillator is treated as a dipole and the total dipole vector for the entire vibrational mode is taken to be the sum of these individual vectors. Since observed intensities are proportional to
the squares of the dipole vectors, the following relationship between
the intensities and the angles between the CO's can be established:

\[
\frac{I_{\text{sym}}}{I_{\text{asym}}} = \frac{R_{\text{sym}}^2}{R_{\text{asym}}^2} = \left( \frac{2r \cos \theta}{2r \sin \phi} \right)^2
\]

(eq 8)

\( r = \) dipole vector of individual CO

\( R = \) dipole vector for the symmetric and antisymmetric
vibrational modes of a \( \text{M(CO)}_2 \) moiety.

Here \( I_{\text{sym}} \) and \( I_{\text{asym}} \) are the intensities of the symmetric and
asymmetric vibrational mode of the CO's respectively.

Using Cotton's method we were able to estimate the angle between
the two carbonyl ligands in tetrahalo cage complexes. The intensity
ratios \( (I_{\text{sym}} / I_{\text{asym}}) \) were 1.13, 1.15 and 1.23 for complexes 22, 23
and 24 respectively. Solving eq 8, the CO-M-CO angle were calculated
to be 86.5°, 86° and 84° respectively. When compared to the x-ray
data of the mixed-valent isopropylamino cage-\( \text{Br}_2 \), complex 20, the
tetrahalo-complexes should not have a similar capped trigonal prism
geometry around their Mo(II) because the CO-M-CO angles are
significantly larger than CO-M-CO angle (54°) found in complex 20.
Based on Kepert's geometrical prediction using the bite angle and
calculated CO-M-CO angles, the alternative geometry should be the
capped octahedron; where each cage unit will be bridged to another by
halide anions as illustrated in Figure 14. Several molybdenum (II)
and tungsten (II) complexes are known to have this geometry. For
example, Cotton determined the single x-ray structure for \([W(CO)_{4}Br_{2}]_{2}\) and found this geometry with an average CO-M-CO angle of 73. \(^{67}\)

Therefore the three tetrahalo complexes are most likely polymeric in the solid state with cages linked by halide-bridges. Such a chain structure is consistent with the observed solubility trend since the iodide should form the weakest bridge and chloride the strongest.

2.2 **Halogen Oxidation of Molybdenum Phenyl Cage, 16**

2.2.1 **Mixed Valent Dihalo Complexes of Phenyl Cage.** Reaction of molybdenum phenyl cage with two equivalents of iodine or sulfuryl chloride at 0°C afforded the mixed-valent, stereochemically non-rigid phenyl cage–I\(_2\) (25) and phenyl cage–Cl\(_2\) (26) containing seven-coordinate Mo(II)'s (eq 9).

\[
(\text{CO})_{6}\text{Mo[PhPO]_{4}Mo(CO)_{4}} + I_{2} + \text{SO}_{2}\text{Cl}_{2} \rightarrow (\text{CO})_{4}\text{Mo} - \text{P}^{\text{X}}(\text{CO})_{3}X_{2}
\]

\(X = \text{I} \ (25)\)

\(\text{Cl} \ (26)\)
Figure 14. Capped Octahedra Bridged by Halides (X)
The oxidation needs to be carried out at 0°C because these products readily lose CO. Infrared spectroscopy of the carbonyl region was used to monitor progress of the reaction. It was found that the halogen oxidation of one of the Mo(0) was complete within half an hour. Complex 25 lost CO faster than complex 26. This is accompanied by its color change from yellow to a dark-red, poorly soluble and ill-characterized solid.

Figure 15 shows a variable-temperature phosphorus-31 NMR of the in-situ reaction of phenyl cage complex with I₂ upon warming from -70°C. In addition to the ABX₂ pattern, the singlet around 168 ppm is due to the tetraiodo-cage formed at higher temperatures. The small signals are presumably due to some intermediates in the formation of the mixed-valent complex.

Complexes 25 and 26 are non rigid in solution as shown by their variable-temperature phosphorus-31 NMR spectra. These spectra are typical of ABX₂ spin systems. The AB portion of each is assignable to the phosphorus atoms bound to the Mo(0) while the X₂ triplet is assignable to those bound to Mo(II). Chemical shifts and coupling constants for the spectrum at -40°C are listed in Table X. The AB peaks are shifted downfield from the original value and the X₂ triplet is shifted to higher field.

In complex 25 there are apparently two distinct dynamic processes one of which causes broadening of the low-field peaks at 0°C. The second concerns the X₂ triplet though the coalescence temperature was not reached due to the limits of the variable-temperature unit of the spectrometer, though it is clear that at -70°C this has started to broaden. Again either the capped trigonal prismatic or capped
Figure 15. Variable Temperature Phosphorus-31 NMR of Phenyl Cage-$I_2$ (25)
octahedral geometries may be assigned. Figure 16 shows two possible geometries for the Mo(II) site that may account for the dynamic NMR.

![Figure 16. Two Possible Geometries for the Seven-coordinate Mo(II) centers](image)

Similar results are observed for complex 26. This reaction is much slower and the presence of starting material signal was observed. Figure 17 shows the variable temperature NMR for complex 26.

In order to isolate the iodine reaction product it was necessary to add acetonitrile to the reaction mixture in the last step of the workup. The mixed-valent complex then precipitated out of solution as a yellow microcrystalline solid. Elemental analyses were consistent with the formula \((\text{CO})_4\text{Mo[RP]_4Mo(CO)_2I}_2(\text{CH}_3\text{CN}) \) (25a). This was isolated in 60-80% yield. Its infrared spectrum in the carbonyl region shows five bands. As expected for a decreased metal electron density, the \(A_1\) band has shifted considerably to higher energy with respect to the starting material, appearing at 2034 cm\(^{-1}\). The POP stretching frequency has also shifted to higher energy by 20 cm\(^{-1}\).
Table X. Infrared and Phosphorus-31 NMR Data of Phenyl Cage Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>IR (KBr, cm⁻¹)</th>
<th>Phosphorus-31 NMR* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl Cage</td>
<td>2024, 1953, 1925</td>
<td>882</td>
</tr>
<tr>
<td>Phenyl Cage-X₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = I (25)</td>
<td>2040, 1988, 1976</td>
<td>902</td>
</tr>
<tr>
<td></td>
<td>1976</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = Cl (26)</td>
<td>2035, 1978, 1917</td>
<td>897</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl Cage-X₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = I (27)</td>
<td>1992, 1927, 1886</td>
<td>911</td>
</tr>
<tr>
<td>X = Br (28)</td>
<td>1988, 1931, 1883</td>
<td>900</td>
</tr>
<tr>
<td>X = Cl (29)</td>
<td>1978, 1917</td>
<td>902</td>
</tr>
</tbody>
</table>

* data collected at -40°C, except for the phenyl cage that was collected at room temperature.
which indicates that the P-O-P bond angle has been compressed.

Proton NMR spectrum of complex 25a shows a broad peak at 7.5 ppm due to protons bound to the phenyl rings and another broad peak at 1.9 ppm due to the methylene proton of the acetonitrile. Phosphorus-31 NMR spectra of complex 25a is very complex. This could mean that there are several structural isomers depending on the site of acetonitrile substitution. Binding of acetonitrile to the mixed-valent cage was found to be reversible. Bubbling of CO gas into a solution containing complex 25a at -40°C yielded the phosphorus-31 NMR spectra of complex 25 (Figure 18).

Complex 26a was isolated from methylene chloride/hexane as a yellow solid slightly soluble in methylene chloride. Its infrared data are shown in Table 15. Proton NMR of complex 26a shows a broad peak at 7.5 ppm due to the phenyl protons. Phosphorus-31 NMR shows multiplets around 202 and 178 ppm. Both complexes 25a and 26a are very unstable and attempts to grow crystals for x-ray structure were unsuccessful as they lose CO and solvent of crystallization when removed from the mother liquor.

Based on these results, phenyl-cage oxidations yield complexes 25 and 26, (CO)$_4$Mo[PhPO]$_4$Mo(CO)$_3$I$_2$. These reversibly lost CO upon workup in acetonitrile to give 25a and 26a, (CO)$_4$Mo[PhPO]$_4$Mo(CO)$_2$X$_2$(CH$_3$CN). In either case, seven-coordinate Mo(II) centers are formed.
Figure 17. Variable Temperature Phosphorus-31 NMR of Phenyl Cage-Cl₂ (26)
Figure 18. Phosphorus-31 NMR of Phenyl Cage-I. (a) Before Passing CO. (b) After Passing CO.
2.2.2 Tetrahalo-Complexes of Phenyl Cage, 16. Reaction of phenyl cage with four equivalents of iodine, bromine or sulfuryl chloride were carried out in methylene chloride at 0°C as shown in eq 10.

\[
\begin{align*}
16 + 2\text{I}_2 & \quad \rightarrow \quad \text{X}_2(\text{CO})_3\text{Mo} - \text{P} \quad (\text{eq} \ 10) \\
16 + 2\text{Br}_2 & \\
16 + 2\text{SO}_2\text{Cl}_2 & \\
\end{align*}
\]

\( X = \text{I} \) (27)

\( \text{Br} \) (28)

\( \text{Cl} \) (29)

Complexes 27 and 28 are orange solids while complex 29 was isolated as a yellow solid. Elemental analyses are consistent with the formula \( \text{Mo}(\text{CO})_3\text{X}_2[\text{RPO}]_4\text{Mo}(\text{CO})_3\text{X}_2 \). Once isolated the tetrahalide complexes are insoluble in chlorocarbon solvents and only slightly soluble in acetone in which they rapidly decompose to give dark-red, paramagnetic solutions. Infrared data are presented in Table X. Carbonyl regions of complexes 27 and 28 consist of three bands below 2000 \( \text{cm}^{-1} \) in the 1883–1992 \( \text{cm}^{-1} \) range. The carbonyl region of complex 29, on the other hand, shows two broad bands at 1978 and 1917 \( \text{cm}^{-1} \).

For metal carbonyl complexes with very low symmetry the number of CO bands depends on the number of carbonyls present. There are few reports in the literature concerning IR data of the carbonyl region of seven-coordinate complexes. Bradley reported IR data on two complexes
(CO)$_3$MoX$_2$[Ar$_2$PPOAr$_2$], where X = I or Br. Both complexes have a pentagonal bipyramid structure giving rise to three IR active bands; however, the spectra varied considerably depending on the nature of the solvent of crystallization or the IR matrix. The POP stretching frequencies also vary with the nature of the halogen. In the three complexes reported here, these have shifted to higher energy from the parent phenyl cage. The POP stretching frequency for complex 27 shifted by approximately 30 cm$^{-1}$ and for complexes 28 and 29 by approximately 18 cm$^{-1}$. These results again indicate that the P-O-P bond angles in these complexes are compressed upon halogenation.

Phosphorus-31 NMR of an in-situ reaction of phenyl cage with four equivalents of iodine shows a product with dynamic behavior on the NMR time scale. Over a temperature range of 0°C to -70°C these show a broad singlet at 164 ppm with a half-width of 37 Hz. Interestingly the halogen oxidation is slow enough to show complex 25 slowly converting to complex 27. The coalescence temperature was not reached even at -70°C. This is consistent with complexes 27, 28 and 29 being highly fluxional seven-coordinate species.

3. Comparison of the Reactivity of Isopropylamino Cage, 15 and Phenyl Cage, 16.

Competitive iodination between isopropylamino (15) and phenyl (16) cages was carried out by using a solution of one equivalent of each cage in methylene chloride and adding two equivalents of iodine at 0°C. Progress of the reaction was monitored by phosphorus-31 NMR. Results indicate that the isopropylamino cage reacts much faster than
the phenyl cage which agrees with infrared spectra data indicating that the molybdenums in the former are more electron rich. This is reflected in the position of the carbonyl absorption bands. The $A_1$ band for the isopropylamino cage appears at $2014 \text{ cm}^{-1}$ while for the phenyl cage is at $2024 \text{ cm}^{-1}$. Consistent with this, cyclic voltammetric data recorded in methylene chloride show two irreversible one-electron oxidation waves at 1.15 and 1.52 V (vs. Ag/AgCl) for cage (15), and 1.3 and 1.57 V for cage (16). The more electron rich metal environment in 15 is probably due to lone-pair donation from the amino-nitrogens into the cage phosphorus atoms.$^{54}$

In both cases, in-situ NMR evidence indicate initial formation of $(\text{CO})_4\text{Mo[RPO]}_4\text{Mo(CO)}_3X_2$. For the isopropylamino cage product, this intermediate rapidly loses one CO to give isolated products containing Mo(CO)$_2X_2$ centers. By contrast, the phenyl-cage product remains Mo(CO)$_3X_2$ where one CO can be reversibly displaced by good donors like acetonitrile. Overall, the isopropylamino cage halogenation products are considerably more stable in storage.
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Conclusions

Bimetallic cage complexes of the group 6 transition metal can be synthesized by the nucleophilic attack of \((\text{CO})_4\text{M(PhPO}_2\text{)}_2^{4-}\) on a cis-\((\text{CO})_4\text{M(PhPCl}_2\text{)}_2\) complex \((\text{M} = \text{Mo, Cr, and W}).\) The steric and electronic effects of the phosphorus, substituents in the ligand influence the reactivity and nature of a metal's halogen oxidation. Halogen oxidation of bimetallic molybdenum cages yield two types of complexes: mixed-valent dihalo complexes and tetrahalo cage complexes.

Mixed-valent cage complexes exist as monomers in solution. Isopropyl-amino cage complexes apparently exist as \((\text{CO})_4\text{Mo}^{1\text{Pr}}_2\text{NPO})_4\text{Mo(CO)}_2\text{X}_2\text{S} (X = \text{I, Br or Cl; } S = \text{solvent})\) while the phenyl cage complexes exist as \((\text{CO})_4\text{Mo[PhPO}]_4\text{Mo(CO)}_2\text{X}_2 (X = \text{I or Cl}).\) In the solid state mixed-valent isopropylamino cage bromide exists as a dimer, while the phenyl cage complexes apparently exist as monomers. A single-crystal x-ray structure of the dibromo complex showed that two cage units are joined by double halide bridges. The coordination geometry around the Mo(II) center is a capped trigonal prism which is unusual for dimeric Mo(II) complexes.

Phosphorus-31 NMR spectra recorded at RT showed an averaged AMX$_2$ spin system for the mixed-valent isopropyl-cage complexes, suggestive of a rapid equilibrium between monomer and dimer or the existence of two or more isomeric geometries. Similarly, the phenyl cage complexes showed fluxional behavior on the NMR time scale at RT. At
temperatures below 0 C the phosphorus-31 NMR spectrum is characteristic of an \( \text{ABX}_2 \) spin system, which suggests a rapid equilibrium of two or more isomeric geometries.

Reaction of cage complexes with four equivalents of halide afforded the tetrahalo complexes. Spectroscopic and analytical data indicate that the tetrahalo-isopropylamino cage complexes have two carbonyls bound to each Mo(II) center. A reasonable solid-state structure is a polymeric chain where each cage unit is bridged at both ends to others by halides. Infrared and elemental analysis data of the tetrahalo-phenyl cage complexes suggest that they exist as seven-coordinate Mo(II) monomers with three carbonyls bound to each metal center.

Finally, a competitive halogen oxidation reaction of the two cages supports the hypothesis that the P-substituents exert a major influence on cage reactivity. The isopropyl-amino cage is more electron rich due to its dialkylamino substituents and yields Mo(CO)\(_2\)X\(_2\) centers as a result of oxidation while phenyl cage yields Mo(CO)\(_3\)X\(_2\) centers. Products of the halogen oxidation of isopropyl-amino cage are also more stable than those of phenyl cage. The latter readily loses CO to give unidentified products.

**Suggestions for Future Work**

Future work in this area might involve studies of the formation of these phenyl cage complexes and their intermediates. A good candidate for this study should be the tungsten cage. One possible way to isolate the intermediates is through the use of a Chromatotron,
since, the reaction mixture will not be in prolonged contact with the stationary phase.

As amminolysis of \((\text{CO})_4M(\text{PhPCl}_2)_2\) yields \((\text{CO})_4M[\text{PhP(NH}_2)_2]_2\), this will extend the synthesis of Group Six transition metal cages to analogues of the cyclo-tetraphosphoxane ring such as \([\text{RP(NH)}]_4\). This may be used in a similar way to yield \((\text{CO})_4M[\text{RP(NH)}]_4M(\text{CO})_4\). The reactivity of the tungsten phenyl cage should be investigated since tungsten is known to readily undergo oxidation to higher oxidation states. This could lead to interesting high-valent complexes different from the products of molybdenum phenyl cage.

Halogen oxidation products of cage 15 could be used in further reactions such as substitution at the P-sites. In attempts to get crystals of complexes 19, 21 and 22, di-isopropylammonium halides were isolated from their solutions. This indicates that the P-N bond is easily cleaved by traces of hydrogen halide. Thus the possibility of using hydrogen halides to yield complexes such as \((\text{CO})_4\text{Mo}[\text{RPO}]_2[\text{XPO}]_2\text{Mo(2CO)}_2\text{X}_2\) and \((\text{CO})_2\text{X}_2\text{Mo[XPO]}_4\text{Mo(2CO)}_2\text{X}_2\) exists. It is well documented that P-X bonds are reactive, hence these will serve as useful precursors to a variety of novel functionalized cage complexes.

Since coalescence temperatures were not reached for complexes 19 and 20 due to instrumental limitations, a high-field NMR instrument along with a solvent-mixture with a freezing point below -100 C is needed. A higher magnetic field will effectively raise the coalescence temperature, allowing slow-exchange spectra to be obtained. Complex 19 should be investigated first since its solution
behavior appears less complicated. This should be followed by full analysis and simulations of the dynamic process(es).
EXPERIMENTAL

Isopropylamino cage-I₄ (22) and Isopropylamino cage-Br₄ (23) were prepared according to the procedure reported by Turnbull.  

Synthesis of [(CO)₄W(PhPO)₄W(CO)₄], Complex(18) [W(CO)₄(PhPO₂)₂H₃]TBA (0.95 g, 1.16 mmol) was dissolved in THF (15 mL) with stirring. NaH (50% oil dispersion, ca 0.5g) which was previously washed with hexane, was added to the THF solution which caused strong effervescence. The reaction mixture was vigorously stirred until no more effervescence was observed. The excess NaH was removed by Schlenk filtration to give a light-brown solution. (PhPCl₂)₂W(CO)₄ (0.76 g, 1.16 mol) was dissolved in THF(10 mL) and transferred via syringe into the light-brown solution. The light-brown solution turned purple, then black after ca 2 min, and finally turned to yellow after ca 5 min. After 24 h, a white solid was collected by Schlenk filtration. This was placed in a Schlenk flask and methylene chloride (10 mL) was added with stirring. Schlenk filtration followed by addition of hexane to the filtrate and removal of excess solvent under-vacuum gave the desired product (0.37 g, 37% yield). Anal. Calc. for W₂P₄O₁₂C₃₂H₂₀: C, 35.30; and H, 1.84. Found: C, 34.11 ; and H, 2.36. Phosphorus-31 NMR: s, 158.6 ppm (J_PW = 162Hz); IR (KBr) ¯CO 2022, 1980, 1948, 1912, ¯POPO 881.
Synthesis of Isopropylamino Cage-I$_2$, Complex (19) Isopropylamino cage (0.4952 g, 0.493 mmol) was dissolved in methylene chloride (10 mL). Iodine (4.8 mL, 0.54 mmol) was added dropwise via syringe with vigorous stirring, producing abundant gas. The solution changed color from yellow to burgundy. The mixture was stirred for one hour to insure completion. The solvent was removed under-vacuum and the burgundy precipitate was washed with acetonitrile (5 mL). A burgundy solid was filtrated and dried under-vacuum to yield the desired product (0.50 g, 85% yield). Anal. Calc. for Mo$_2$I$_2$P$_4$N$_4$O$_{10}$C$_{10}$H$_{56}$: C, 29.97; H, 4.69; and N, 4.66. Found: C, 29.84; H, 4.83; and N, 4.83. Phosphorus-31 NMR in CHCl$_3$: d, 161.8 ppm ($^2$J$_{pp}$ = 40 Hz); d of d, 157.2 ppm ($^2$J$_{pp}$ = 40 Hz and $^2$J$_{pp}$ = 12 Hz); d, 132.6 ppm ($^2$J$_{pp}$ = 12 Hz). IR (KBr) $\nu$CO 2024, 1979, 1915 cm$^{-1}$ and $\nu$POP 885 cm$^{-1}$. Molecular weight in CHCl$_3$: calc, 1201.68 g/mol; found, 1234.6 g/mol.

Synthesis of Isopropylamino Cage-Br$_2$, Complex (20) Isopropylamino cage-I$_2$ (0.1891 g, 0.157 mmol) was dissolved in a 2:1 mixture of methylene chloride/acetonitrile (6 mL/3 mL). Tetraethylammonium bromide (0.0662 g, 0.314 mmol) was added then to the solution. The mixture was stirred for one hour and the solvent removed under-vacuum. Toluene (5 mL) was added and stirred vigorously for five minutes. A white precipitate of NEt$_4$I was removed by filtration. The filtrate was evaporate to dryness in vacuo to yield an orange solid. This solid was washed with hexane (5 mL) and dried under-vacuum to yield the desired complex (0.13 g, 76%). Anal. Calc. for Mo$_2$Br$_2$P$_4$N$_4$O$_{10}$C$_{10}$H$_{56}$: C, 34.13; H, 5.76; and N, 5.00. Found: C, 34.33; H, 5.50; and N, 5.50. Phosphorus-31 NMR in CD$_3$CN/CH$_2$Cl$_2$: d, 162.9 ppm
(\textsuperscript{2}J_{pp} = 40 \text{ Hz}); \text{ d}\text{ of t}, 157.5 \text{ ppm} (\textsuperscript{2}J_{pp} = 40 \text{ Hz}, \textsuperscript{2}J_{pp} = 15 \text{ Hz}); \text{ d}, 147.1 \text{ ppm} (\textsuperscript{2}J_{pp} = 15 \text{ Hz}). IR (KBr) \nu_{CO} 2024, 1979, 1953, 1909 \text{ cm}\textsuperscript{-1} and \nu_{POP} 887 \text{ cm}\textsuperscript{-1}. Molecular weight in CHCl\textsubscript{3}: calc., 1107.88 g/mol; found, 1169.44 g/mol.

Crystals suitable for single x-ray structure were obtained by slow evaporation of methylene chloride from a 2:1 methylene chloride/acetonitrile ratio.

Synthesis of Isopropylamino Cage-Cl\textsubscript{2}, Complex 21. Isopropylamino cage (0.310 g, 0.309 mmoles) was dissolved in methylene chloride (5 mL). Sulfuryl chloride (0.8 mL, 0.309 mmoles) was added via syringe with vigorous stirring, producing CO gas. After one hour, a yellow precipitate of isopropylamino cage-Cl\textsubscript{2} was formed. The precipitate was removed by filtration using a medium fret. Very slowly to the filtrate, hexane (3mL) was added via syringe, stirred vigorously and filtered to yield 0.27g (85\%) of a bright yellow solid. Anal. Calcd. for Mo\textsubscript{2}Cl\textsubscript{2}P,N,O, H\textsubscript{2}C\textsubscript{30}: C, 34.13; H, 5.76; and N, 5.00. Found: C, 34.33; H, 5.50; and N, 5.50. Phosphorus-31 NMR in CDCl\textsubscript{3}: \text{ d}, 162.9 ppm (\textsuperscript{2}J_{pp} = 39 \text{ Hz}), \text{ d}\text{ of t}, 157.5 \text{ ppm} (\textsuperscript{2}J_{pp} = 39 \text{ Hz} and \textsuperscript{2}J_{pp} = 15 \text{ Hz}); \text{ d}, 152.0 \text{ ppm} (\textsuperscript{2}J_{pp} = 15 \text{ Hz}). IR (KBr) \nu_{CO} 2025, 1975, 1960, 1920 \text{ cm}\textsuperscript{-1} and \nu_{POP} 885 \text{ cm}\textsuperscript{-1}. Molecular weight in CHCl\textsubscript{3}: calc., 1018.88 g/mol; found, 1157.69 g/mol.

Synthesis of Isopropylamino Cage-Cl\textsubscript{4}, Complex 24. Isopropylamino cage (0.270 g, 0.268 mmol) was dissolved in methylene chloride (10 mL). Sulfuryl chloride (1.5 mL, 0.565 mmol) was added dropwise via syringe with vigorous stirring, producing a yellow solution and abundant gas.
After one hour, a yellow solid was collected by filtration using a medium frit. The solid was dried under-vacuum to yield 0.29 g (100%) of a bright yellow solid. Anal. Calcd. for Mo$_2$Cl$_4$P$_4$N$_4$O$_8$H$_{56}$C$_{28}$: C, 32.50; H, 5.73; and N, 5.52. Found: C, 32.96; H, 5.42; and N, 5.42. IR (KBr) CO 1979, 1929 cm$^{-1}$ and POP 897 cm$^{-1}$.

Synthesis of Phenyl Cage-I$_2$, Complex 25a. Phenyl cage (0.2673 g, 0.2930 mmol) was dissolved in methylene chloride (10 mL). The solution was cooled down to approximately 0°C and wait five minutes to ensure that the temperature of the solution was around 0°C. Iodine (0.0744 g, 0.2930 mmol) was then added with vigorous stirring and the reaction mixture was cooled down to -10°C. The progress of the reaction was followed by observing the carbonyl bands in the IR. After half an hour, the carbonyl bands due to the starting material, phenyl cage were gone. The solvent was removed under-vacuum and the residue was washed with cold acetonitrile (4 mL). The solvent was removed by filtration using a medium frit; the precipitate was dried under-vacuum to yield 0.2210 g (64% yield) of a microcrystalline yellow solid. Anal. Calcd. for Mo$_2$I$_4$P$_4$NO$_{10}$H$_{23}$C$_{33}$: C, 33.59; H, 1.95; and N, 1.18. Found: C, 33.64; H, 2.07; and N, 1.23. IR (KBr) νCO 2040, 1998, 1936, 1916 cm$^{-1}$ and νPOP 902 cm$^{-1}$.

Synthesis of Phenyl Cage-Cl$_2$, Complex 26a. Phenyl cage (0.1551 g, 0.170 mmol) was dissolved in methylene chloride (5 mL). The solution was cooled down to -5°C. Sulfuryl chloride (0.41 mL, 0.170 mmol) was added dropwise via syringe with vigorous stirring, producing and orange solution and abundant gas evolution. The progress of the
reaction was monitored by IR. After half an hour, a yellow solid of phenyl cage-Cl$_4$ was removed by filtration; cold hexane (1 mL) was added dropwise via syringe and the temperature dropped to -40°C. A yellow powder was collected by filtration and dried under-vacuum to yield 0.1250 g (77% yield). IR (KBr) $\nu$CO 2035, 1973, 1936 cm$^{-1}$; $\nu$POP 897 cm$^{-1}$.

**Synthesis of Phenyl Cage-I$_4$, Complex 27.** Phenyl cage (0.3465 g, 0.38 mmol) was dissolved in methylene chloride (10 mL). The solution was cooled down to 0°C. Iodine (0.1929 g, 0.76 mmol) was then added under vigorous stirring. The temperature of the reaction mixture was dropped to -10°C. After half an hour, the solvent was removed under-vacuum and the residue was washed with cold hexane (10 mL). The solid was removed by filtration and dried under-vacuum to yield 0.330 g (78% yield) of an orange solid. Anal. Calc. for Mo$_2$I$_4$P$_4$O$_{10}$C$_{30}$H$_{20}$: C, 25.70; and H, 1.53. IR (KBr) $\nu$CO 1992, 1931, 1883 cm$^{-1}$; POP $\nu$ 911 cm$^{-1}$.

**Synthesis of Phenyl Cage-Br$_4$, Complex 28.** Phenyl cage (0.3210 g, 0.3520 mmol) was dissolved in methylene chloride (5 mL). Bromine (1.4 mL, 0.739 mmol) was added dropwise via syringe with vigorous stirring, producing an orange solution an abundant gas evolution. After one hour, an orange precipitate was filtered from the solution and dried under-vacuum. To the filtrate cold hexane (3 mL) was added dropwise via syringe and an orange solid precipitated out. The solid was collected by filtration and dried under-vacuum. Elemental analysis revealed the two solids to be of identical composition. The
combination of both solids yield 0.2931 g (70% yield). Anal. Calc. for \( \text{Mo}_2\text{Br}_4\text{P}_4\text{O}_{10}\text{C}_{30}\text{H}_{20} \): C, 30.61; and H, 1.79. Found C, 30.61; and H, 1.96. IR (KBr) \( \nu \text{CO} 1988, 1931, 1883 \text{ cm}^{-1} \); \( \nu \text{POP} 900 \text{ cm}^{-1} \)

Synthesis of Phenyl Cage–\( \text{Cl}_4 \), Complex 29. Phenyl cage (0.1676 g, 0.184 mmol) was dissolved in methylene chloride (5 mL). Sulfuryl chloride (0.9 mL, 0.368 mmol) was added very slowly via syringe with vigorous stirring, producing an orange solution with abundant gas evolution. The reaction mixture was placed in an ice-salt bath at \(-5\) C for one hour. After one hour, half of the solvent was removed in vacuo, cold hexane (2 mL) was added very slowly via syringe, filtered and dried under-vacuum to yield 0.1290 g (70% yield) of a yellow solid. IR (KBr) \( \nu \text{CO} 1978, 1917 \text{ cm}^{-1} \); \( \nu \text{POP} 902 \text{ cm}^{-1} \)

Spin Lattice Relaxation Time Measurements, (\( T_1 \)), for Complex 20

\( T_1 \) measurements were made using the inversion recovery method (ref). The 90° pulse was determined before the \( T_1 \) measurement and found to be 26 \( \mu \text{s} \). The phase error detection method was used on the sample to be measured. The phase error detection method requires that the phasing first be set using a normal single pulse acquisition with a pulse width less than 90°. Then, a \( (180° - t - 90°) \) sequence is applied, using a very short \( t \) (10\( \mu \text{sec} \)) while varying the pulse width for the 180° and 90° pulses. When the test value is the true 90° pulse, the spectrum will be completely inverted and properly phased.

The inversion recovery method for \( T_1 \) determination involves the following pulse sequence: \([180° - t - 90° - A_t - D]^n\), where \( t \) is the pulse interval between the 180° and 90° pulses, \( A_t \) is the acquisition
time, and D is the time between the end of the acquisition time and
the beginning of the next pulse. The D value was chosen such \( (A_t + D) > 5T_1 \)
and values for \( t \) were chosen to span the range from
approximately 0.4 \( T_1 \) to 1.2 \( T_1 \). The variable \( n \) is the number of scans
used for the FID. The value of \( n \) was chosen to be \( n = 100 \) and so a
satisfactory signal was obtained.

The appropriate equation for the \( T_1 \) measurement is:

\[
I_t = I [1 - 2\exp(-t/T_1)]
\]

where \( I \) is the signal height measured at \( t = 0 \), i.e. \( t \) is greater
than 5-10 \( T_1 \)'s and \( I_t \) is the signal height at time \( t \). All spectra
were stored on floppy disc using the automatic STACK pattern.
Analysis of the data for \( T_1 \) measurement was done on the computer
attached to the spectrometer, using the JEOL packaged program, except
the \( T_1 \) determination for the broad peak was done by measuring the
height of the peak and plotting \( \ln I_t/I \) vs \( t \), from the slope the \( T_1 \)
was determined.

**Molecular Weight Determination**

A Michrolab V/P/O Model 301A vapor pressure osmometer was used to
determine the molecular weight of complexes 19, 20, 21, and 22.
Molecular weight determination were made in chloroform. Naphthalene
was used to construct a calibration curve.


(42b) Nocera, D.G.; Michigan State University, private communication.


(56a) Archer, R.D. Inorg. Chem. (1979), 18, 48-51


