BINUCLEAR AND TRINUCLEAR COMPOUNDS CONTAINING OSMIUM AND GROUP 6 METAL ATOMS.

by

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B.Sc., Simon Fraser University, 1979
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Binuclear and Trinuclear Compounds Containing Osmium and Group 6 Metal Atoms

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ABSTRACT

New 18-electron bis-substituted osmium complexes Os(CO)$_3$LL$'$ (L = PMe$_3$; L$'$ = PMe$_3$, PPh$_3$, P(o-tol)$_3$) have been synthesized. One of these, Os(CO)$_3$(PMe$_3$)$_2$ undergoes oxidative addition reactions with CH$_2$Cl$_2$, S$_8$, and O$_2$ to form Os(CO)$_2$(PMe$_3$)$_2$(Cl)$_2$, Os(CO)$_2$(PMe$_3$)$_2$(S)$_2$, and Os(CO)$_2$(PMe$_3$)$_2$(CO)$_3$, respectively.

The Os(CO)$_4$(PR$_3$) and Os(CO)$_3$LL$'$ complexes react with M(CO)$_5$ (M = Cr, Mo, W) fragments to form complexes with unbridged dative metal-metal bonds, e.g., (L)(OC)$_4$OsM(CO)$_5$ and LL$'$(OC)$_3$OsM(CO)$_5$. Intramolecular CO site exchange between the two metal centers is facile, and with the exception of [(o-tolO)$_3$P](Me$_3$P)(OC)$_3$OsW(CO)$_5$, the complexes exist as an equilibrium mixture of two isomers in solution at room temperature. A comparison of the "$\sigma \rightarrow \sigma^*$" transition in the UV/VIS spectra of several of the mono- and bis-substituted bimetallic complexes indicates that the metal-metal bond is weakest in the (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$ complex and strongest in the [(MeO)$_3$P](OC)$_4$OsM(CO)$_5$ complexes.

An unprecedented bonding arrangement has been discovered in the complexes (Pc)(OC)$_4$OsOs(CO)$_3$(Pc)W(CO)$_5$ and (Pc)$_2$(OC)$_3$Os- Os(CO)$_4$W(CO)$_5$ (Pc = P(OCH$_2$)$_3$CCH$_3$) formed in the preparation of (Pc)(OC)$_4$OsW(CO)$_5$ and from the reaction of Os(CO)$_5$(Pc) with (Pc)(OC)$_4$OsW(CO)$_5$, respectively. These complexes are believed to contain two unbridged dative metal-metal bonds in tandem (i.e., Os$\rightarrow$Os$\rightarrow$W). The structure in solution is the same as that in
the solid state.

The heterotrimetallic clusters \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PR}_3)]_2\) (\(\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{OMe}; \text{R}_3 = (\text{OCCH}_2)_3\text{CMe}\)) have been prepared by photolysis of the \((\text{L})(\text{OC})_4\text{OsM(CO)}_5\) complexes in \(\text{C}_6\text{F}_6\). The chromium derivatives represent the first examples of clusters containing osmium and chromium. In all cases the metals are in a triangular arrangement with no bridging carbonyls. Low temperature \(^{13}\text{C}\) NMR studies indicate that there is unrestricted rotation of the \(\text{M(CO)}_5\) fragment in these clusters at 151 K. The barrier to rotation is estimated to be significantly less than 29 kJ mol\(^{-1}\). The \(^{13}\text{C}\) NMR studies indicate that there is a low energy CO site-exchange process in the equatorial plane, and a higher energy process that involves only the axial carbonyls. A fourth exchange process that is slow on the NMR time scale has been observed in the \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PMe}_3)]_2\) (\(\text{M} = \text{Cr}, \text{W}\)) clusters; it is consistent with a trigonal twist at the Os centers. Reaction of \((\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PR}_3)]_2\) (3) with \(\text{H}_2\) under mild conditions yielded \((\mu-\text{H})_2(\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\) (4). The \(^{31}\text{P}\{'\text{H}\}\) and \(^{1}\text{H}\) NMR spectra of 4 indicates that each hydrogen bridges a separate Os-W bond; furthermore, the \(^{13}\text{C}\) NMR spectrum shows that the complex is rigid at room temperature with respect to CO site exchange. Reaction of 3 with \(\text{P(OMe)}_3\), gave \([(\text{MeO})_3\text{P}](\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\) in which the axial CO on the \(\text{W(CO)}_5\) fragment was substituted by \(\text{P(OMe)}_3\). The CO site-exchange processes in this cluster were completely blocked by the \(\text{P(OMe)}_3\) ligand.
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DEDICATION

To My Parents

Richard Tuthill Davis
and
Jane Gray Bennett Davis
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CHAPTER 1
INTRODUCTION

The field of organometallic chemistry attained a position of prominence amongst the chemical community with the Nobel Prize award to Wilkinson and Fischer in 1973. Since that time, the field has expanded tremendously. Major achievements in the use of organometallic complexes as homogeneous catalysts have been realized; this accomplishment alone has taken organometallic chemistry beyond the realm of pure curiosity and elevated it to a position of fundamental importance and intense interest with respect to commercial applications. Thus, a large amount of attention at both the academic and industrial levels has been focused on the use of organometallic species to accomplish specific reactions in synthetic organic chemistry.

While the advances in the use of organometallic complexes have been significant, the field of organometallic chemistry is still relatively immature compared to organic chemistry and coordination chemistry. Thus, much of the research in organometallic chemistry is motivated by a curiosity to understand and characterize the fundamentals of the field. These efforts have led to the discovery of new areas in organometallic chemistry; these have provided new insights into the rich structural and chemical diversity that has come to be characteristic of organometallic complexes. Some examples include the activation of C-H bonds in hydrocarbons by electron rich organotransition metal complexes,¹ and the rapidly expanding study of metal
Another major advance in the field of organometallic chemistry culminated with the award of the Nobel Prize in Chemistry to Hoffmann in 1981. In his Nobel Lecture entitled "Building Bridges Between Inorganic and Organic Chemistry", Hoffmann described how organic and inorganic fragments could be related by the frontier orbitals associated with each fragment. He defined this as the isolobal analogy. The greatest impact of the isolobal concept is that it allows the inorganic chemist to think of transition metal compounds (with all the associated electrons and orbitals) in terms of much more easily understood organic analogues. Thus, the isolobal concept has helped to remove a boundary between inorganic and organic chemistry and enabled specialists in each of these fields of chemistry to have a greater appreciation for the other.

It was curiosity that led Pomeroy and Rushman in 1983 to the discovery of the first example of a complex in which a dative bond between two transition metals could be unambiguously assigned. Prior to that time there was no clear precedent for an 18-electron transition metal complex to act as a two electron donor to a coordinatively unsaturated 16-electron transition
metal fragment. The X-ray crystal structure of one of the early examples of these complexes is shown in Figure 1.1. The lack of any bridging groups across the metal-metal bond is in contrast to the complexes that had been previously reported to contain a dative metal-metal bond between transition metal fragments. Thus, the metal-metal bonding in complexes like (Me,P)(OC)₄OsW(CO)₅ is analogous to that found in main group Lewis base Lewis acid complexes such as H₃NBF₄.

In order to study a previously unexplored area, a strategy needs to be developed to meet particular objectives. Those objectives pertinent to the study of the dative metal-metal bonding interaction are precisely those that have been established for dative bonds between main group elements, and those established for single covalent bonds between transition metals. Thus, the primary focus of our studies was to determine what effect the electronic nature of the donor and acceptor species would have on the metal-metal bond. Another focus of fundamental importance was to compare the thermal and photochemical reactivity of the dative metal-metal bond with that of a covalent

![Figure 1.1. Molecular Structure of (Me,P)(OC)₄OsW(CO)₅.](image)
metal-metal bond.

Since a dative bond is formed by the combination of a Lewis base (donor fragment) and a Lewis acid (acceptor fragment), it is reasonable to expect that a change in the HOMO-LUMO interaction of the base and acid would have an effect on the strength and stability of the metal-metal bond. Thus, to meet the first objective, we proposed to make a series of Os(CO)$_4$(L) complexes (where L is a phosphorus ligand) to act as the donor complex to a coordinatively unsaturated M(CO)$_5$ ($M = Cr, Mo, W$) fragment. A precedent for the use of Os(CO)$_4$(L) complexes as a ligand had already been established in 1984 with the preparation of (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (see Figure 1.1) by Pomeroy and Rushman. The preparation of the Os(CO)$_4$(L) complexes has been described previously by Pomeroy and coworkers. We also proposed to make several Os(CO)$_3$(L)$_2$ complexes in which both the substituted groups are phosphorus ligands. It was anticipated that the increased electron density on the Os atom in the Os(CO)$_3$(L)$_2$ compounds would make these complexes better $\sigma$ donors towards an M(CO)$_5$ fragment. In terms of a Lewis base Lewis acid interaction, we believed that this would result in a stronger dative metal-metal bond. The preparation and characterization of the Os(CO)$_4$(L) and Os(CO)$_3$(L)$_2$ complexes is described in Chapter 2.

Although there was originally no intention to study the chemistry of any of the mononuclear osmium complexes, the presence of the Os(II) complexes Os(CO)$_{2-n}$(PMe$_3$)$_{2+n}$(X)$_2$ ($X = Cl$, 

4
n = 0; $X_2 = \text{CO}_3^{2-}$, $n = 0, 1$) that formed as by-products in the preparations of Os(CO)$_n$(PMe$_3$) and Os(CO)$_3$(PMe$_3$)$_2$ suggested that Os(CO)$_3$(PMe$_3$)$_2$ was particularly susceptible to oxidative addition reactions. A small number of reactions of Os(CO)$_3$(PMe$_3$)$_2$ with electrophiles have been investigated. A discussion of these reactions is given in Chapter 2.

The synthetic route to the preparation of bimetallic complexes by the reaction of an 18-electron pentacoordinate osmium complex with $\text{M(CO)}_5$(THF) ($\text{M} = \text{Cr, Mo, W}$) was established with the preparation of $(\text{Me}_3\text{P})(\text{OC})_6\text{OsW(CO)}_5$. Thus, the 18-electron osmium complex functions as a two electron donor ligand to W(CO)$_5$ in the same way as, for example, PPh$_3$ acts as a two electron donor ligand. Work which preceded that described in this thesis showed that this synthetic route was general for the preparation of numerous $(\text{L})(\text{OC})_4\text{OsM(CO)}_5$ complexes, and also for the preparation of $(\text{OC})_5\text{OsCr(CO)}_5$. Thus, the same procedure was employed to prepare new $(\text{L})(\text{OC})_4\text{OsM(CO)}_5$ and $(\text{L})_2(\text{OC})_3\text{OsM(CO)}_5$ complexes. (The use of 18-electron complexes as ligands that can displace MeCN and cyclooctene (COE) from Os$_3$(CO)$_{11}$(MeCN) and Os$_3$(CO)$_{10}$(COE)$_2$, respectively, has recently been employed for the syntheses of tetranuclear clusters of osmium.)

The new bimetallic complexes share some common features with those prepared previously in that they all contain unbridged metal-metal bonds, are fluxional with respect to carbonyl site exchange, and (with only one exception) exist as a mixture of two isomers that are in equilibrium in solution. An X-ray
crystal structure of \((\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5\) confirmed the donor-acceptor nature of the metal-metal bond. Some novel and unexpected features that relate to the strength of the metal-metal bond and the isomer ratios are evident from these studies. Details about these complexes are presented in Chapter 3. A description of the first complex that contains dative metal-metal bonds in tandem is also included in Chapter 3.

A question that often arises is, what is the difference between a dative metal-metal bond and a covalent metal-metal bond? Both types of bonding interactions involve two electrons that are shared between two atoms. Our experimental evidence (e.g., lack of solubility of the complexes in nonpolar solvents) indicates that the electron density in the dative metal-metal bond is not shared equally between the two metal atoms. This leads to another question; that is, what distinguishes a dative bond from a polar covalent bond? Detailed studies to address these questions have not yet been carried out, but experimental evidence gained so far about the thermal and photochemical reactivity does illustrate some differences between complexes with dative metal-metal bonds and complexes with covalent metal-metal bonds.

Bimetallic complexes with covalent metal-metal bonds have been studied extensively, and the bonding interaction between the two 17-electron fragments is well understood.\textsuperscript{11} The thermal reactivity of these complexes, for example, typically involves loss of a ligand from one of the metal centers. Early studies on \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) showed that the dative metal-metal bond was
cleaved heterolytically with subsequent substitution by a two electron donor ligand (e.g., PPh₃) under thermal conditions. Thus, the thermal reactivity of complexes with dative metal-metal bonds is distinctly different from that of complexes with covalent metal-metal bonds.

The photochemistry of the complexes with dative metal-metal bonds had, however, not been explored. The photochemistry of complexes with covalent metal-metal single bonds is firmly established. With few exceptions, the primary photoprocess in these complexes (in solution at ambient temperature) involves homolytic cleavage of the metal-metal bond to give two radical fragments. The products of these reactions are simply those that are generated from the recombination of the radical fragments. In contrast, photolysis of complexes with dative metal-metal bonds produces heterotrimetallic clusters. The formation of metal clusters by photolysis of bimetallic complexes was unprecedented until this time. Some aspects of the photoreactivity of complexes with dative metal-metal bonds are discussed in Chapters 3 and 4.

One of the goals of chemists involved with metal cluster synthesis is to develop synthetic routes that will allow clusters of a desired size and composition to be prepared. Some noteworthy successes in this area have been achieved by Stone, Werner, and Vahrenkamp. As previously mentioned, work in our laboratory has shown that metal clusters of a desired composition can be prepared by the addition of an
18-electron complex (as a donor ligand) to a preexisting cluster. However, most clusters have been prepared by either thermolysis reactions of small clusters to make larger ones, or by simple ligand modification of stable precursor clusters.

Heterometallic clusters are of particular interest due to the chemical diversity imparted to the cluster by the presence of two (or more) different metal centers. The presence of two different metals provides the cluster with two potentially different sites of reactivity. As noted above, the photolysis of bimetallic complexes with dative metal-metal bonds yields heterotrimetallic clusters. Further studies have shown that this is a general route for the preparation of \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PR}_3)]_2\) \((\text{M} = \text{Cr, Mo, W})\) clusters. Thus, a number of heterometallic clusters can be prepared that contain osmium, a preselected group 6 metal, and preselected phosphorus ligands. The \((\text{OC})_5\text{Cr-[Os(CO)}_3(\text{PMe}_3)]_2\) complex, prepared in this way, represents the first example of a heterometallic cluster that contains both osmium and chromium. The synthesis and characterization of \(\text{Os}_2\text{M}\) \((\text{M} = \text{Cr, Mo, W})\) cluster compounds is described in Chapter 4.

Aside from the unique synthetic route used to prepare the metal clusters described above, the cluster complexes exhibit fluxional behavior that is unique amongst metal clusters. Variable temperature \(^{13}\text{C}\) NMR spectroscopy has allowed organometallic chemists to examine in some detail the mechanisms by which ligands, and in particular carbonyl ligands, undergo site exchange over several metal centers. The use of complexes labeled with
$^{13}$CO offers a substantial improvement in the signal to noise ratio compared to spectra obtained for complexes in which $^{13}$C is at natural abundance levels. Thus, small amounts of minor isomers and, in some cases, coupling to spin 1/2 nuclei that are very low in natural abundance can be observed. Both of these factors, along with coupling to spin 1/2 nuclei that are both abundant and of high sensitivity (e.g., $^{31}$P, $^1$H) aid in the assignment of the $^{13}$C NMR resonances to specific carbonyl ligands. The difference in the chemical shift regions of carbonyl ligands attached to different metal centers, and in different positions on the metal centers (e.g., axial or equatorial positions) also provides important information to make the assignments.

The $(OC)_5M[Os(CO)_3(PR_3)]_2$ complexes are perfectly suited for such studies since the chemical shifts of $^{13}$C NMR resonances for carbonyl ligands attached to osmium are significantly different from those for carbonyl ligands attached to a group 6 metal. The phosphorus nuclei of the substituent ligands provide a useful "tag" for the carbonyl ligands attached to the same osmium atom since $^{31}$P-$^{13}$C coupling is usually easily detected. Where the group 6 metal is tungsten, there is another "tag" provided by the $^{183}$W nucleus (spin 1/2, 14.3% natural abundance). The variable temperature $^{13}$C and $^{31}$P NMR spectra of many of these cluster complexes have now been examined in detail. These studies indicate that there are four separate carbonyl exchange mechanisms in these clusters. Each of the exchange processes
occurs with a different activation energy. In all of the complexes, one of the exchange processes remains fast on the NMR time scale even at 150 K. The \((OC)_5Cr[Os(CO)_3(PMe_3)]_2\) complex exhibits all four exchange processes; this is believed to be the first example of a cluster in which this many distinct carbonyl site exchange processes have been observed. The fluxional behavior of the \((OC)_5M[Os(CO)_3(PR_3)]_2\) clusters is discussed in Chapter 5.

In summary, this thesis describes the synthesis and characterization of some new monomeric osmium complexes, bimetallic complexes with dative metal-metal bonds, and heterotrimetallic clusters. The monomeric complexes of osmium described in Chapter 2 form the building blocks for the preparation of the bimetallic complexes with dative metal-metal bonds described in Chapter 3. The bimetallic complexes then form the precursors for the preparation of heterotrimetallic clusters described in Chapter 4. The extraordinary fluxional behavior of some of the cluster complexes is described in Chapter 5.

In an interview after he was awarded the Priestley Medal by the American Chemical Society in 1985, Henry Taube (also the recipient of the Nobel Prize in Chemistry in 1983) commented that one of the most valuable lessons he was taught as a graduate student was "to slow down and observe carefully; to make capital not only out of what happens [in a chemical system], but what doesn't happen". In other words, take the time to be curious. It can be said that much of the work described in this
thesis was the direct result of curiosity. The syntheses of the heterometallic clusters, the investigation of the fluxional properties of the clusters, and the isolation, preparation, and characterization of the first compound that contains dative bonds in tandem provided challenges along the way. It was challenges like these that provided the stimulus to be curious.
CHAPTER 2

PREPARATION AND REACTIVITY OF COMPLEXES OF THE GENERAL FORMULA

\[ Os(CO)_{5-n}(L)_n \ (n = 1, 2) \]

2.1 Introduction.

The chemistry of many monomeric organometallic complexes is well understood. Some of these complexes have a well-established reputation as reagents and catalysts in organic synthesis.\(^9\) Cornerstone examples include \( \text{Rh(Cl)}(\text{PPh}_3)_3 \) (Wilkinson's catalyst\(^20\)) for the hydrogenation of unconjugated olefins and acetylenes at ambient temperature and low pressure, \( \text{Na}_2\text{Fe(CO)}_4 \) (Collman's reagent\(^21\)) for the conversion of alkyl halides to acyl halides (among other uses), and \( \text{HCo(CO)}_4 \) believed to be the active species in the oxo reaction.\(^22\) Areas of currently intense research interest include oxidative addition and reductive elimination reactions\(^23\) since these reactions are implicated in many catalytic cycles,\(^24\) and metal alkylidene and alkylidyne chemistry\(^25\) since these complexes are obligatory intermediates in the mechanisms proposed for olefin and acetylene metathesis reactions.\(^26\) In addition, mononuclear complexes that are chiral at the metal center have proven to be effective reagents for stereoselective addition of nucleophilic substrates to coordinated aldehyde,\(^27\) olefin,\(^28\) alkylidene\(^29\) and allyl\(^30\) ligands.

A survey of the recent literature also reveals an intense interest in the synthesis, characterization, and use of metal
complexes that have oxygen bound directly to the metal atom.\textsuperscript{31} The complexes, in the forms of oxo or peroxo species, are believed to be important in selective catalytic oxidation processes.\textsuperscript{32} Some of these complexes may also serve as models for understanding the mode of action of biological oxygen carriers.\textsuperscript{33}

Our interest in mononuclear osmium complexes stems from the ability of some 18-electron pentacoordinate complexes of osmium to act as two electron donor ligands to coordinatively unsaturated metal centers such as \( \text{W(CO)}_5 \) in \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) (see Figure 1.1, page 3, and Chapter 3). The initial objective was to prepare a series of \( \text{Os(CO)}_3(L)(L') \) complexes (\( L = \text{CO}, \text{PMe}_3, \text{P(OMe)}_3; L' = \text{PMe}_3, \text{P(OMe)}_3, \text{P(OCH}_2\text{)}_3\text{CMe}, \text{P(o-Otol)}_3, \text{etc...} \) in which the electron density at the Os center would range from a relatively low amount as in \( \text{Os(CO)}_4(\text{Pc}) \) (\( \text{Pc} = \text{P(OCH}_2\text{)}_3\text{CMe} \)) to a high amount as in \( \text{Os(CO)}_3(\text{PMe}_3)_2 \). It was thought that an increase in the electron density on Os would make the resulting complex a stronger donor ligand. In the course of these studies we found that the \( \text{Os(CO)}_3(\text{PMe}_3)_2 \) complex (along with other bis-substituted Os complexes) has a potentially rich chemistry on its own. The presence of two strong \( \sigma \)-donor \( \text{PMe}_3 \) ligands in \( \text{Os(CO)}_3(\text{PMe}_3)_2 \) makes the metal center electron rich. As a consequence, \( \text{Os(CO)}_3(\text{PMe}_3)_2 \) readily undergoes oxidative addition reactions under mild conditions.

The synthesis of the mono- and and bis-substituted Os complexes, and some reactions of the bis-substituted complexes

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are described in this chapter.

2.2 Experimental.

Unless otherwise specified, manipulations of starting materials and products were carried out under an inert atmosphere with the use of standard Schlenk techniques and a Vacuum Atmospheres dry box (Model HE-63-P). Hexane and dichloromethane were distilled under nitrogen from potassium and calcium hydride, respectively. Dodecacarbonyltrirosium (Os$_3$(CO)$_2$) was prepared from OsO$_4$ by the literature method.$^{34}$ Osmium pentacarbonyl (Os(CO)$_5$) was prepared from Os$_3$(CO)$_2$ at $-270$ °C (external temperature) under CO (operating pressure $-510$ atm) according to the literature.$^{35}$ The phosphorus ligands were obtained commercially (Strem) with the exception of P(OCH$_2$)$_3$CMe which was prepared by the literature method.$^{36}$

A Parr 500 mL autoclave (with a rocking heater) was used for large scale reactions that required pressures that exceeded $\sim 1500$ psi. An Aminco Nitrogen-Operated Diaphram-Type compressor (model J46-14025) was employed to achieve pressures up to 3000 psi at room temperature. For reactions that required pressures not exceeding 1500 psi, a Parr 200 mL autoclave was used. Infrared spectra were obtained on a Perkin Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. Electron impact (70 eV) mass spectra were obtained with a Hewlett Packard 5985 GC-MS instrument. NMR spectra were
recorded on a Bruker WM400 spectrometer (operating frequencies were 100.6 MHz, 162 MHz and 400 MHz for $^{13}$C, $^{31}$P, and $^1$H NMR spectra, respectively) or on a Bruker WH100 spectrometer (operating frequency 100 MHz for $^1$H spectra). The microanalyses were obtained by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Synthesis of Monomeric Osmium Complexes. The descriptions given below are representative of the general reaction conditions and purification procedures used to prepare the monomeric osmium complexes. Analytical, yield, and mass and infrared spectral data for the compounds are given in Table 2.1, $^1$H and $^{31}$P NMR data in Table 2.2, and $^{13}$C (natural abundance) NMR data in Table 2.3.

Preparation of Os(CO)$_4$(PMe$_3$). The preparation of Os(CO)$_4$(PMe$_3$) followed the literature procedure and is included here for the sake of completeness. A weighed flask (equipped with a Teflon valve) that contained hexane (~50 mL) was transferred into the dry box. To this, PMe$_3$ (267 mg, 3.5 mmol) was added. The PMe$_3$ solution was then added into a 500 mL autoclave (outside the dry box) that contained Os$_3$(CO)$_{12}$ (1.006 g, 1.1 mmol) and hexane (80 mL). The flask was rinsed with hexane (~10 mL) and the rinse was added to the autoclave. The autoclave was sealed and flushed twice with CO (1000 psi) after which CO (3000 psi) was added. The vessel was heated to 270 °C (external temperature) for 20 h. After the vessel had returned to room temperature, the contents were transferred to a large sublimer.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass Spec</th>
<th>Spectra</th>
<th>Infrared</th>
<th>IR Stretches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(CO)(PMe₃)₂</td>
<td>66%</td>
<td>(hexane)</td>
<td>2062(m)</td>
<td>181(m)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>58%</td>
<td>(hexane)</td>
<td>2072(m)</td>
<td>1961(m)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>79%</td>
<td>(hexane)</td>
<td>2076(m)</td>
<td>2001(m)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>94%</td>
<td>(hexane)</td>
<td>1886(s)</td>
<td>(CH₂Cl₂)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>45%</td>
<td>(hexane)</td>
<td>2002(m)</td>
<td>1926(m)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>b</td>
<td>(CH₂Cl₂)</td>
<td>1913</td>
<td>(CH₂Cl₂)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>b</td>
<td>(CH₂Cl₂)</td>
<td>2032(s)</td>
<td>1661(s)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>b</td>
<td>(CH₂Cl₂)</td>
<td>2030(s)</td>
<td>159(s)</td>
</tr>
<tr>
<td>Os(CO)(PMe₃)₂[P(OMe)₃]</td>
<td>b</td>
<td>(CH₂Cl₂)</td>
<td>2043(s)</td>
<td>1968(s)</td>
</tr>
<tr>
<td>Os(CO)(O)(C≡CPh)</td>
<td>47.85</td>
<td>3.95</td>
<td>47.99</td>
<td>4.00</td>
</tr>
<tr>
<td>Os(CO)(O)(C≡CPh)</td>
<td>47.16</td>
<td>4.27</td>
<td>47.39</td>
<td>4.46</td>
</tr>
<tr>
<td>Os(CO)(O)(C≡CPh)</td>
<td>46.16</td>
<td>3.85</td>
<td>47.20</td>
<td>3.69</td>
</tr>
<tr>
<td>Os(CO)(O)(C≡CPh)</td>
<td>46.16</td>
<td>3.85</td>
<td>23.50</td>
<td>3.98</td>
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<tr>
<td>Os(CO)(O)(C≡CPh)</td>
<td>23.59</td>
<td>3.93</td>
<td>26.37</td>
<td>5.53</td>
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<td>Os(CO)(O)(C≡CPh)</td>
<td>26.1</td>
<td>5.33</td>
<td>18.25</td>
<td>3.42</td>
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<td>Os(CO)(O)(C≡CPh)</td>
<td>18.25</td>
<td>3.42</td>
<td>18.35</td>
<td>3.23</td>
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<td>Os(CO)(O)(C≡CPh)</td>
<td>18.25</td>
<td>3.42</td>
<td>19.35</td>
<td>3.23</td>
</tr>
</tbody>
</table>

(aPC = Ph₂CH₂Cl₂; Os; b) small scale reaction; wavenumbers in brackets for compounds 11 and 12 are assigned to stretching vibrations and deformation modes of the carbonate group.
Table 2.2. $^1$H and $^{31}$P NMR Data for the Mononuclear Osmium Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H$^a$</th>
<th>$^{31}$P{ $^1$H}$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-37.79(238.2), -4.60(237.8)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7.10 - 7.46 (ArH), 2.12, -144.7(275.4), 9.31(275.4) 1.77(10.3, 2.8)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.76(t, 4.12)</td>
<td>-33.4</td>
</tr>
<tr>
<td>11</td>
<td>1.68(t, 3.88)</td>
<td>-21.09</td>
</tr>
<tr>
<td>12</td>
<td>1.65(9.80), 1.52(t, 3.72)</td>
<td>-117.22(13.0), -129.41(t, 13.0)</td>
</tr>
</tbody>
</table>

Numbering scheme corresponds to that given in Table 2.1. Unless otherwise specified, spectra were recorded at 298 K in CD$_2$Cl$_2$. (a) Figures in parentheses are $J_{p-H}$; (b) Figures in parentheses are $J_{p-p}$; (c) CDCl$_3$.

Table 2.3. $^{13}$C NMR Shifts for the Carbonyl Ligands of the Osmium Carbonato Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ Carbonyl C</th>
<th>$\delta$ Carbonate C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(CO)$_2$(O(CO)O)(PMe$_3$)$_2$</td>
<td>179.5(t, 6.94)</td>
<td>167.3(br)</td>
</tr>
<tr>
<td>Os(CO)(O(CO)O)(PMe$_3$)$_3$</td>
<td>183.65(d, 10)</td>
<td>168.4</td>
</tr>
</tbody>
</table>

Spectra were obtained in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/4, v/v) solutions at ambient temperature; figures in parentheses are $J_{p-C}$.

The hexane was removed under vacuum and the Os(CO)$_4$(PMe$_3$) was purified by sublimation at $\sim$40 °C on to a coldfinger at $-78$ °C. In this way, Os(CO)$_4$(PMe$_3$) (830 mg, 66%) was obtained as a colorless powder. A small amount of Os(CO)$_3$(PMe$_3$)$_2$ (identified by IR spectroscopy) was also produced as a sublimable product. In addition, the tris-substituted Os(CO)$_2$(PMe$_3$)$_3$ complex was probably also a minor product of this reaction (see discussion below).
Preparation of Os(CO)$_4$(P(OMe)$_3$). A weighed flask equipped with a Teflon valve was taken into the dry box, and P(OMe)$_3$ (614 mg, 5.0 mmol) was added. The P(OMe)$_3$ was added to a solution of Os(CO)$_5$ (~1.2 mmol) in hexane (80 mL) (via several rinses of the flask with the Os(CO)$_5$ solution) contained in a 200 mL autoclave. A Teflon coated magnetic stir bar was added to the vessel. The vessel was sealed and CO (1000 psi) was added, after which the pressure was reduced to 400 psi. The solution was heated to 110 °C for 69 h. The solution components were separated by column chromatography on alumina (4 x 1 cm). The initial fraction eluted with hexane was believed to contain excess P(OMe)$_3$, since the fraction gave no IR bands in the carbonyl stretching region. The desired product was also eluted from the column as a colorless fraction with hexane as eluant. This fraction was transferred to a sublimer and the solvent was removed at 0 °C under vacuum. The desired product was purified by sublimation at ambient temperature on to a coldfinger at -78 °C. In this way, Os(CO)$_4$(P(OMe)$_3$) (288 mg, 58%) was obtained as a colorless powder.

Preparation of Os(CO)$_3$(PMe$_3$)$_2$. A solution of Os(CO)$_4$(PMe$_3$) (800 mg, 2.1 mmol) in hexane (35 mL) was placed in a Carius tube (~80 mL) fitted with a Teflon valve and equipped with a Teflon coated magnetic stir bar. The vessel and its contents were weighed and taken into the dry box, after which PMe$_3$ (226 mg, 3 mmol) was added. The tube was evacuated at -196 °C and thoroughly degassed via three freeze-pump-thaw cycles. The
solution was then heated to 170 °C for 22 h, degassed and heated for a further 16 h. An infrared spectrum of the solution after this time showed that no Os(CO)₄(PMe₃) remained. Components that were volatile at room temperature were removed under vacuum, and Os(CO)₃(PMe₃)₂ was purified by sublimation at 90 °C on to a coldfinger at -78 °C. In this way, Os(CO)₃(PMe₃)₂ (703 mg, 79%) was obtained as a colorless solid. A white powder that did not sublime under these conditions was dissolved in boiling C₆H₆, filtered through Celite, and allowed to crystallize from C₆H₆. In this way, Os(CO)₂[O(CO)O](PMe₃)₂ (102 mg, 11%) was obtained as a colorless solid.

Preparation of Os(CO)₃(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane). A Carius tube fitted with a Teflon valve and equipped with a magnetic stir bar was weighed, taken into the dry box, and dmpe (111 mg, 0.74 mmol) added. A solution of Os(CO)₅ (~175 mg, 0.53 mmol) in hexane (30 mL) was transferred (via syringe) into the Carius tube. The tube was evacuated at -196 °C and thoroughly degassed by three freeze-pump-thaw cycles. The vessel was then heated at 90 °C for 13.5 h. A cream colored solid formed during this time. The solution was degassed, heated for a further 8 h at 90 °C, degassed again, and heated at 100 °C for 12 h. The solution was degassed once more, and heated for a further 42.5 h at 90 °C: an IR spectrum of the solution after this time indicated nearly complete conversion to Os(CO)₃(dmpe) with a small amount of a product thought to be Os(CO)₄(dmpe). (IR bands at 2062, 1981, and 1937 cm⁻¹ ascribed

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to Os(CO)$_4$(dmpe) are very similar to those of Os(CO)$_4$(PMe$_3$) at 2062, 1981, and 1939 cm$^{-1}$.) Volatile materials were removed under vacuum, and fresh hexane (35 mL) was added. The solution was degassed as previously, and heated to 140 °C for 11.5 h after which an IR spectrum of the solution indicated complete conversion to Os(CO)$_3$(dmpe). An orange solid likely to be a triosmium cluster was also formed. The Os(CO)$_3$(dmpe) (in solution) was used directly without isolation for a reaction with W(CO)$_5$(THF) (see Chapter 3).

Reaction of Os(CO)$_3$(PMe$_3$)$_2$ with CH$_2$Cl$_2$ (small scale). A solution of Os(CO)$_3$(PMe$_3$)$_2$ (~5 mg) in CH$_2$Cl$_2$ was prepared in a Carius tube fitted with a Teflon valve and equipped with a Teflon coated magnetic stir bar. The tube was evacuated at -196 °C and thoroughly degassed with three freeze-pump-thaw cycles. The solution was stirred for 48 h at room temperature. No reaction was apparent (by IR spectroscopy) after this time. The solution was then stirred for a further 36 h under an atmosphere of nonpurified (i.e., commercial grade) nitrogen, after which an IR spectrum showed complete conversion to Os(CO)$_2$(Cl)$_2$(PMe$_3$)$_2$.$^\dagger$

Reaction of Os(CO)$_3$(PMe$_3$)$_2$ with O$_2$ (small scale). A solution of Os(CO)$_3$(PMe$_3$)$_2$ (~5 mg) in C$_6$H$_6$ (3 mL) was prepared in a 100 mL flask fitted with a Teflon valve and equipped with a

$^\dagger$The original sample of Os(CO)$_2$(Cl)$_2$(PMe$_3$)$_2$ which was fully characterized was obtained as a by-product from a large scale preparation of Os(CO)$_4$(PMe$_3$); the source of the chlorine was presumed to be from an impurity (such as CH$_2$Cl$_2$) in the solvent. It is unclear how the impurity became incorporated in the solvent.
Teflon coated magnetic stir bar. The vessel was evacuated at \(-196\) °C and degassed via two freeze-pump-thaw cycles, after which \(O_2\) (1 atm) was introduced into the vessel. No reaction was evident (by IR spectroscopy) after 25 h at ambient temperature. The solution was heated to 80 °C under \(O_2\) (2 atm) for 14 h during which complete conversion to \(\text{Os(CO)}_2[\text{O(CO)O}](\text{PMe}_3)_2\) was evident (by IR spectroscopy).†

**Raction of Os(CO)\(_3\)(PMe\(_3\))\(_2\) with \(S_8\).** A mixture of \(\text{Os(CO)}_3\)\(-(PMe\(_3\))_2\) (100 mg, 0.23 mmol) and \(S_8\) (15 mg, 0.046 mmol) in \(C_6H_6\) (11 mL) was prepared in a flask fitted with a Teflon valve and equipped with a Teflon coated magnetic stir bar. The vessel was evacuated at \(-196\) °C and thoroughly degassed by three freeze-pump-thaw cycles. The solution was then stirred at ambient temperature for 10 d. After removal of the solvent, an IR spectrum of the solid indicated incomplete reaction of \(\text{Os(CO)}_3(\text{PMe}_3)_2\). Benzene (≈5 mL) and additional \(S_8\) (10 mg, 0.039 mmol) were added, and the mixture was degassed as previously described. The mixture was stirred for a further 6 d at ambient temperature, after which additional \(S_8\) (10 mg, 0.039 mmol) was added. The mixture was again degassed as above and stirred at ambient temperature for a further 7 d. After this time, an IR spectrum of the solution showed CO stretching vibrations due only to the product. The mixture was dried under vacuum and the product was purified by chromatography on Florisil (10 x 1 cm) with

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†The original sample of \(\text{Os(CO)}_2[\text{O(CO)O}](\text{PMe}_3)_2\) that was fully characterized was produced as a by-product during the preparation of \(\text{Os(CO)}_3(\text{PMe}_3)_2\).
CH₂Cl₂/hexane (1/1, v/v) as eluant. The product, eluted as a yellow band, was further purified by recrystallization from hot hexane. In this way, bright yellow crystals of Os(CO)₂(PMe₃)₂⁻(S₄) (25 mg, 22%) were obtained.

2.3 Discussion

The experimental conditions for the preparation of the Os(CO)₄(L) complexes have either been briefly described previously⁷ or were similar to those conditions. The monosubstituted complexes Os(CO)₄(L) were readily prepared from the reaction of either Os₃(CO)₁₂ with the ligand (eq 2.1) or from Os(CO)₅ with the ligand (eq 2.2). The presence of CO in these reactions (~3000 psi and ~400 psi at ambient temperature for the reactions described in equations 2.1 and 2.2, respectively) is necessary in order to inhibit the formation of cluster products from the starting materials or from the monomeric products (eqs 2.3 and 2.4). Even with the large excess of CO, some cluster products

\[ \text{Os}_3(\text{CO})_{12} + 3L \xrightarrow{\Delta} 3\text{Os}(\text{CO})_4(L) \]  
\[ \text{Os}(\text{CO})_5 + L \xrightarrow{\Delta} \text{Os}(\text{CO})_4(L) \]

were formed. New clusters, which ranged from Os₃(CO)₉(L)₃ to
Os₃(CO)₄(L) were isolated and characterized (by IR and mass spectroscopy, and elemental analysis). It is apparent that some Os(CO)₃(PMe₃)₂ and Os(CO)₂(PMe₃)₃ also formed during the preparation of Os(CO)₄(PMe₃) since Os(Cl)₂(CO)₂(PMe₃)₂ and Os(CO)[O(CO)O](PMe₃)₃ derivatives were isolated (in separate instances) from the reaction (see below).

With the exception of Os(CO)₄(P(OCH₂)₃CMe) (which had to be purified by recrystallization), all of the monosubstituted complexes were purified by sublimation. The Os(CO)₄(Pc) complex (Pc = P(OCH₂)₃CMe) is also unlike most of the other monosubstituted complexes in that it is much less soluble in hexane. For example, Os(CO)₄(Pc) is only slightly to moderately soluble in hexane whereas the Os(CO)₄(L) (L = PMe₃, P(OMe)₃) complexes are very soluble in hexane. Other monosubstituted analogues (e.g., Os(CO)₄(PPh₃)₈) are, however, also only slightly soluble in hexane.

The bis-substituted complexes were prepared in a similarly straightforward way by the reaction of monosubstituted complexes with excess ligand at elevated temperatures (eq 2.5). With the exception of the preparation of Os(CO)₄(PMe₃) in which Os(CO)₂ was used as the starting material, the conditions used to prepare the bis-substituted complexes were much more forcing than those used to prepare the monosubstituted complexes. Thus, higher temperatures (170 °C for the preparation of Os(CO)₃-
(PMe₃)₂) or longer reaction times (~90 h for the preparation of Os(CO)₄(Pc)) were needed to effect the substitution of a CO in the Os(CO)₄(L) complexes (used as precursors for the preparation of Os(CO)₃(L)₂ complexes) than in Os(CO)₅ (used as a precursor for the preparation of most of the Os(CO)₄(L) complexes). This is consistent with increased backbonding of osmium to the carbonyl ligands in the Os(CO)₄(L) complexes compared to that in Os(CO)₅. It was necessary to add excess ligand to these reactions in order to inhibit the formation of triosmium clusters.

Whereas Os(CO)₃(PMe₃)₂ can be purified by sublimation at 80 to 90 °C (c.f., Os(CO)₄(PMe₃) sublimes readily at 30 to 40 °C), the other bis-substituted complexes are sufficiently nonvolatile that they cannot be conveniently sublimed, and require recrystallization for purification. The bis-substituted complexes, with the exception of Os(CO)₃(PMe₃)₂ which is moderately soluble in hexane, are only slightly soluble in hexane.

The Os(II) species Os(Cl)₂(CO)₂(PMe₃)₂, Os(CO)₂[O(CO)O]- (PMe₃)₂, and Os(CO)[O(CO)O](PMe₃)₃ were initially isolated as by-products during the preparations of Os(CO)₄(PMe₃) and Os(CO)₃(PMe₃)₂. Each of these by-products was purified by column chromatography and recrystallization; each compound has been fully characterized by elemental analysis and spectroscopic techniques (see discussion below).

The preparation of Os(CO)₄(PMe₃) from Os₃(CO)₁₂ and excess PMe₃ always results in the formation of some nonvolatile resi-
The carbonato derivative Os(CO)[O(CO)O](PMe$_3$)$_3$ was isolated by column chromatography from these residues. Given that Os(CO)$_3$(PMe$_3$)$_2$ reacts with O$_2$ to form Os(CO)$_2$[O(CO)O]-(PMe$_3$)$_2$ (see discussion below), it is probable that the Os(CO)-[O(CO)O](PMe$_3$)$_3$ is formed by the reaction of Os(CO)$_2$(PMe$_3$)$_3$ with O$_2$. (No attempt was made to isolate Os(CO)$_2$(PMe$_3$)$_3$ from the reaction.) In another instance, it is believed that CH$_2$Cl$_2$ was inadvertently added to the reaction solution, and Os(Cl)$_2$(CO)$_2$-(PMe$_3$)$_2$ was isolated as a nonvolatile by-product. It is probable that the Os(Cl)$_2$(CO)$_2$(PMe$_3$)$_2$ results from the reaction of Os(CO)$_3$(PMe$_3$)$_2$ with CH$_2$Cl$_2$ (see below).

All of the Os(CO)$_4$(L) and Os(CO)$_3$(L)$_2$ complexes gave a parent ion peak in the mass spectrum. The dichloride compound Os(Cl)$_2$(CO)$_2$(PMe$_3$)$_2$ gave a parent ion peak with a pattern as expected for the isotopic abundance of $^{35}$Cl and $^{37}$Cl. The carbonato complexes each gave a peak that corresponded to M$^+$-CO$_2$ for the highest molecular weight ion.

**Spectroscopic Properties of Mono- and Bis-Substituted Pentacoordinate Osmium Complexes.** The infrared spectra in the carbonyl stretching region of the Os(CO)$_4$(L) derivatives all exhibit a three band pattern; this is consistent with a trigonal bipyramidal geometry of C$_3$v symmetry with the noncarbonyl ligand in an axial position$^{38}$ as shown in Figure 2.1. (Four CO stretching vibrations would be expected for C$_2$v symmetry with the phosphorus ligand in an equatorial position.) As in the ruthenium analogue, the lowest energy CO band in Os(CO)$_4$[P(OMe)$_3$] is
Figure 2.1. Structures of Os(CO),_4(L) (left) and Os(CO),_3(L),_2 (right) in Solution.

split; this is believed to be caused by the one up, two down arrangement of the OMe groups (as was found in the crystal structure of the Ru(CO),_4[P(OMe),] molecule) which lowers the symmetry of the molecule from C,3v to C,5. The axial site preference of the phosphorus substituent is contrary to Bent's rule but in accord with theoretical and experimental studies which suggest that the better σ-donor ligand, or weaker π-acceptor ligand, will prefer the axial site.

The bis-substituted complexes Os(CO),_3(L),_2 each exhibit one strong IR band in the CO stretching region. This is consistent with trigonal bipyramidal geometry of D,3h symmetry (or pseudo D,3h symmetry for the complexes with mixed phosphorus ligands) with the phosphorus ligands in the axial positions as shown in Figure 2.1. (The X-ray crystal structure of Os(CO),_3(PPh),_2 showed that the PPh, ligands occupy the axial positions in this molecule.) The 31P NMR spectra of these complexes also
indicate $D_{3h}$ symmetry. For example, the $^{31}$P NMR spectrum of Os(CO)$_3$(PMe$_3$)(PPh$_3$) shows two sets of doublets with a large $^{31}$P-$^{31}$P coupling constant ($\sim$238 Hz). The large coupling can be attributed to a trans arrangement of the phosphorus ligands. (The cis $^{31}$P-$^{31}$P coupling in Os(CO)[O(CO)O](PMe$_3$)$_3$ is only 13 Hz and that in the cis isomer of (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$ is only 17 Hz (see Chapter 3).) That the Os(CO)$_3$(L)$_2$ complexes adopt $D_{3h}$ symmetry rather than $C_{2v}$ or $C_5$ symmetry is as expected based on steric and electronic (see above) effects.

**Spectroscopic Properties of Hexacoordinate Complexes of Osmium.** The IR spectra of the dichloride and carbonato species Os(Cl)$_2$(CO)$_2$(PMe$_3$)$_2$ (8) and Os(CO)$_2$[O(CO)O](PMe$_3$)$_2$ (11) in CH$_2$Cl$_2$ solution exhibit two strong bands in the CO stretching region at approximately 1956 cm$^{-1}$ and 2030 cm$^{-1}$. (A single band due to the osmium carbonyl ligand in Os(CO)[O(CO)O](PMe$_3$)$_3$ occurs at 1917 cm$^{-1}$.) Due to the increased oxidation state of the Os in these complexes, these bands occur at higher energy than the single band in Os(CO)$_3$(PMe$_3$)$_2$ (1875 cm$^{-1}$ in CH$_2$Cl$_2$ solution). The $^1$H and $^{31}$P NMR data indicate that the phosphorus ligands are trans in the axial positions in the dichloride and carbonato complexes (see discussion below). Therefore, Os(CO)$_2$-[O(CO)O](PMe$_3$)$_2$ must have $C_{2v}$ symmetry since two cis equatorial sites are occupied by the chelate CO$_3^{2-}$ ligand (see Figure 2.2). The two strong bands observed in the IR spectrum of the dichloride compound indicate that it also has $C_{2v}$ symmetry as shown in Figure 2.2 since a trans arrangement of the carbonyl
Figure 2.2. Proposed Structures of $\text{Os(CO)}_2[\text{O(CO)O}](\text{PMe}_3)_2$ (11) (left) and $\text{Os(CO)}_2(\text{Cl})_2(\text{PMe}_3)_2$ (8) (right).

ligands ($D_{2h}$ symmetry) would have only one band in the CO stretching region.

The osmium carbonato complexes exhibit additional IR bands near 1600 cm$^{-1}$ which can be attributed to the stretching vibration of the carbonate C=O. Carbon-oxygen stretching vibrations in organic carbonic acid derivatives occur in the region 1820-1630 cm$^{-1}$.

Bands at 1700 cm$^{-1}$ and 1675 cm$^{-1}$ have been observed for the analogous CO stretching vibrations in $\text{Os}[\text{O(CO)O}](\text{Cl})(\text{NO})(\text{PPh}_3)_2$ and $(\text{CH}_3)\text{Ir}[\text{P}(p\text{-tolyl})_3]_2(\text{CO})-\text{(O(CO)O)}$. Bands at 1700 cm$^{-1}$ and 1675 cm$^{-1}$ have been observed for the analogous CO stretching vibrations in $\text{Os}[\text{O(CO)O}](\text{Cl})(\text{NO})(\text{PPh}_3)_2$ and $(\text{CH}_3)\text{Ir}[\text{P}(p\text{-tolyl})_3]_2(\text{CO})-\text{(O(CO)O)}$. The presence of two CO stretching vibrations for $\text{Os(CO)}[\text{O(CO)O}](\text{PMe}_3)_3$ (1665 cm$^{-1}$ and 1641 cm$^{-1}$) may indicate a mixture of isomers in which the $\text{CO}_2^2$ is either monodentate or bidentate: both coordination modes are known.

Two bands were also observed for the carbonate C=O in $\text{Ir(CO)}(\text{O(CO)O})(\text{TDPME})$ (TDPME = 1,1,1-tris(diphenylphosphinomethyl)ethane). A solid state effect which may cause a single CO band to be split in the
KBr medium can be ruled out since the spectrum in CH₂Cl₂ also exhibits two bands in the same region; unlike the broad bands observed in the KBr medium, in CH₂Cl₂ the bands are sharp.

Infrared bands between 1265 cm⁻¹ and 1200 cm⁻¹ in the spectra of the carbonato species can be attributed to C-O stretching vibrations; this can be compared to a band at 1267 cm⁻¹ in (CH₃)Ir[P(p-tolyl)$_3$]$_2$(CO)(CO₃)$_2$. An infrared band at 1165 cm⁻¹ in Os[O(CO)O](Cl)(NO)(PPh₃)$_2$ was not assigned, but is presumably due to a similar C-O stretching vibration.

Finally, infrared bands in Os(CO)[O(CO)O](PMe₃)$_3$ (1022 and 829 cm⁻¹) and Os(CO)$_2$[O(CO)O](PMe₃)$_2$ (1000 and 823 cm⁻¹) can probably be attributed to a C=O symmetric stretching mode and a CO₃ deformation mode, respectively.

The 'H and ³¹P NMR spectra of Os(Cl)$_2$(CO)$_2$(PMe₃)$_2$ (8) and Os(CO)$_2$[O(CO)O](PMe₃)$_2$ (11) indicate a trans axial arrangement of the phosphine ligands. Complexes 8 and 11 each exhibit one triplet in the 'H NMR spectra for the methyl protons that arises from virtual coupling to two "equivalent" phosphorus nuclei. This is consistent with the C$_{2v}$ symmetry assumed for these complexes based on the infrared results (see above). The observation of only one resonance in the ³¹P NMR spectra of these complexes requires that the phosphorus ligands be in magnetically equivalent environments; again this is consistent with a trans axial arrangement of the phosphine ligands as indicated by the 'H NMR spectra.
The $^1$H NMR spectrum of Os(CO)[O(CO)O](PM$_3$)$_3$, (12) exhibits a doublet for one set of methyl protons that can be attributed to the methyl protons on a phosphine ligand that lies in the equatorial plane. The spectrum also exhibits a triplet that can be assigned to the methyl protons of two trans phosphine ligands. A structure that is consistent with these results is shown in Figure 2.3. The $^{31}$P NMR spectrum of 12 exhibits one doublet and one triplet (in a 2:1 ratio) with identical coupling constants. The triplet can be assigned to the phosphorus ligand in the equatorial plane, and the doublet can be assigned to the phosphorus ligands in the axial positions. Thus, the $^{31}$P NMR results also support the proposed structure of 12 shown in Figure 2.3.

The only complexes characterized by $^{13}$C NMR spectroscopy were the carbonato complexes 11 and 12; each complex exhibits resonances in the carbonyl region that can be assigned to metal carbonyl and carbonate carbonyl ligands. The metal carbonyl resonances for both complexes occur in the region that is typical for equatorial carbonyls on Os.

![Figure 2.3. Proposed Structure of Os(CO)[O(CO)O](PM$_3$)$_3$, (12).](image-url)
two equivalent carbonyl ligands in 11 appears as a triplet at \( \delta 179.5 \) due to coupling to two equivalent phosphorus nuclei. In \( \text{Os(CO)}[\text{O(CO)}\text{O}](\text{PMe}_3)_3 \), the metal carbonyl resonance appears as a doublet of broad peaks at \( \delta 183.7 \) due to primary coupling to the cis phosphorus nucleus in the equatorial plane. The peaks in the doublet are broad, presumably due to poorly resolved coupling to the two axial phosphorus nuclei.

The \(^{13}\text{C}\) resonances for the carbonate carbonyls of 11 and 12 occur as singlets at \( \delta 167.3 \) and \( \delta 168.4 \), respectively. The \(^{13}\text{C}\) resonance for the carbonyl carbon in the organic five membered ring carbonic acid \( \text{C}_2\text{H}_4\text{O}_2\text{CO} \) occurs at \( \delta 156.7 \).\(^\text{a,3}\)

**Oxidative Addition Reactions of \( \text{Os(CO)}_3(\text{PMe}_3)_2 \).** The isolation of \( \text{Os(CO)}_2(\text{Cl})_2(\text{PMe}_3)_2 \) and \( \text{Os(CO)}_2[\text{O(CO)}\text{O}](\text{PMe}_3)_2 \), which presumably formed by reactions of \( \text{Os(CO)}_3(\text{PMe}_3)_2 \) with \( \text{CH}_2\text{Cl}_2 \) and \( \text{O}_2 \), respectively, led us to investigate some oxidative addition reactions of \( \text{Os(CO)}_3(\text{PMe}_3)_2 \).

In a \( \text{CH}_2\text{Cl}_2 \) solution under a nonpurified nitrogen atmosphere, \( \text{Os(CO)}_3(\text{PMe}_3)_2 \) undergoes an oxidative addition reaction with \( \text{CH}_2\text{Cl}_2 \) to form the dichloride species \( \text{Os(CO)}_2(\text{Cl})_2(\text{PMe}_3)_2 \) (eq 2.6). Whereas the reaction was complete after a maximum of 36 h, no reaction was evident after 48 h in a \( \text{CH}_2\text{Cl}_2 \) solution that was thoroughly degassed. This probably indicates that the reaction occurs via a radical pathway that is catalyzed by trace
amounts of O₂ in the nitrogen. It is well known that small amounts of O₂ can promote a radical chain process.⁴⁹ For example, detailed studies on the oxidative addition reactions of alkyl halides to trans-Ir(Cl)(CO)(PMe₃)₂ showed that reaction rates were (in most cases) greatly accelerated by the presence of small amounts of O₂.⁵⁰ Interestingly, although no reaction occurred under thermal conditions, CH₂Cl₂ reacted with the Ir complex under photochemical conditions to give Ir(Cl)₂(CH₂Cl)⁻(CO)(PMe₃)₂. Homolytic cleavage of a C-Cl bond followed by oxidative addition of the radical fragments to the Ir center can account for the formation of the product. On the other hand, the formation of Os(CO)₂(Cl)₂(PMe₃)₂ under the reaction conditions employed appears to be somewhat unusual. A mechanism for its formation does not, on the surface, seem to be as straightforward. No attempt was made to isolate the organic products formed during the reaction, so it is not possible to propose a mechanism for this reaction. However, it is clear that there are two immediate sources of the two chlorine atoms in the product: both could have come from the same CH₂Cl₂ molecule, or one each could have come from separate CH₂Cl₂ molecules. In addition, the mechanism of formation may not involve simple oxidative addition to Os(CO)₃(PMe₃)₂. Since the presence of O₂ appears to be mandatory, it is possible that formation of an osmium oxo or dioxo species precedes the reaction with CH₂Cl₂. (For example, it has been suggested that an Ir(I)O₂ complex is formed followed by decomposition to Ir(II) and O₂⁻ prior to oxidative addition to Ir(Cl)(CO)(PMe₃)₂.⁵⁰) Oxidative addition to Os(CO)₃(PMe₃)₂
probably does not occur via the carbonato complex since this complex appears to be stable in CH₂Cl₂ (see below). More work on the reaction of Os(CO)₃(PMe₃)₂ with CH₂Cl₂ is needed, especially with respect to identification of the organic products.

Reaction of Os(CO)₃(PMe₃)₂ with O₂ (2 atm) in C₆H₆ at 80 °C yielded the carbonato complex Os(CO)₂[O(CO)O](PMe₃)₂ (eq 2.7).

\[ \text{Os(CO)₃(PMe₃)₂ + O₂} \rightarrow \text{Os(CO)₂[O(CO)O](PMe₃)₂} \] (2.7)

This reactivity mirrors that of Os(Cl)(CO)(NO)(PPh₃)₂ which reacts with O₂ to form Os(Cl)(O(CO)O)(PPh₃)₂.⁴⁴ The Os(CO)₃(PMe₃)₂ complex is sufficiently nucleophilic that it also reacts in the solid state with O₂ at -20 °C. Thus, a poorly sealed sample of Os(CO)₃(PMe₃)₂ stored at -15 to -20 °C for several months was found to have reacted with O₂ to form the carbonato complex.

Similar reactivity of Ir(Cl)(CO)(TDMPE) in solution and in the solid state has been observed.⁴⁶ Carbonato complexes have also been formed by reaction of dioxo complexes of Pd and Pt with free CO₂ and CO.⁵¹ In addition, (CH₃)Ir(CO)(O₂)[P(p-tolyl)₃]₂ reacts with CO to form (CH₃)Ir[P(p-tolyl)₃]₂(CO)(O(CO)O).³¹c

Other than these examples, carbonato derivatives of organometallic complexes seem to be relatively rare. Numerous carbonato coordination compounds, especially of Co, are, however, known.⁴⁵

The osmium carbonato product is probably formed by an initial dioxo complex which then rearranges to the carbonato compound. The mechanism shown in Scheme I was originally proposed for the formation of Os(Cl)(NO)[O(CO)O](PPh₃)₂ from O₂ and
Scheme I.

\[
\text{Scheme I.}
\]

\[
\begin{align*}
\text{L} & = \text{Cl}, \text{L}' = \text{NO}; \text{R} = \text{Ph} \text{ (work done by Roper)}^4^4 \\
\text{L} & = \text{CO}, \text{L}' = \text{CO}; \text{R} = \text{Me} \text{ (this work)} \\
\text{Os(Cl)(CO)(NO)(PPh}_3\text{)}_2. \text{ The mechanism that would convert 1A (in Scheme I) to the final product is uncertain. Both intermediates 2A and 2B (Scheme II) would seem to be possible precursors to Scheme II.}
\end{align*}
\]
the final product. An intermediate like 2B is more probable than an intermediate like 2A. This follows from experiments on $^{18}$O labeled $(\text{CH}_3)\text{Ir(CO)}(^{18}\text{O}_2)[\text{P}(\rho\text{-tolyl})_3]_2$ that, when reacted with unlabeled CO, gave a complex in which the $^{18}$O label was incorporated into the carbonate C=O. Similar studies on the sulfate complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(O)(O}_2\text{SO}_2)$ also showed that the $^{18}$O label was distributed statistically over all five positions. An intermediate such as 2B would allow the $^{18}$O label to be incorporated into the carbonate carbonyl, consistent with the results obtained for $(\text{CH}_3)\text{Ir(CO)}(^{18}\text{O}_2)[\text{P}(\rho\text{-tolyl})_3]_2$.

The reaction of Os(CO)$_3$(PM$_3$)$_2$ with elemental sulfur gives a product which is believed to be Os(CO)$_2$(PM$_3$)$_2$(S$_n$) (13) based on elemental analysis, mass and infrared spectral data (eq 2.8).

$$\text{Os(CO)}_3(\text{PM}_3)_2 + \text{S}_8 \rightarrow \text{Os(CO)}_2(\text{PM}_3)_2(\text{S}_n) \quad (2.8)$$

The IR spectrum of 13 contains two strong CO stretches at 2020 cm$^{-1}$ and 1959 cm$^{-1}$, similar to the spectra of the Os(II) complexes 8-11. By analogy to these Os(II) complexes (see above), a cis arrangement of the carbonyl ligands is assumed. This leaves the $\text{S}_n^{2-}$ moiety bonded to Os as a bidentate ligand that forms a five membered OsS$_n$ ring. A structure that is consistent with these observations is shown in Figure 2.4.

An infrared spectrum in the CO stretching region of Os(CO)$_2$(PM$_3$)$_2$(S$_n$) in hexane is shown in Figure 2.5. Each of the two strong bands has associated with it a weak band that may be due to a second conformer. A five membered MS$_n$ ring can adopt
Figure 2.4. Proposed Structure of $\text{Os(CO)}_2(\text{PMe}_3)_2(S_4)$ (13).

Figure 2.5. Carbonyl Stretching Region of the Infrared Spectrum of $\text{Os(CO)}_2(\text{PMe}_3)_2(S_4)$ in Hexane.
either an envelope or a half-chair conformation, analogous to cyclopentane. Both conformations have been observed in MS₄ complexes. For example, the five membered rings in [(η⁵-C₅H₅)Mo(S₄)₂]⁻ adopt an envelope conformation in the solid state whereas a half-chair conformation is formed by the MoS₄ and WS₄ rings in (η⁵-C₅H₅)₂Mo(S₄) (M = Mo, W) and in (η⁵-C₅Me₅)Re(O)-(S₄). The preference for one conformation versus the other is believed to be governed by interactions of the lone pair electrons on sulfur with the adjacent ligands. The proposed equilibrium between two conformers of Os(CO)₂(PMe₃)₂(S₄) is consistent with these results. The energy of activation for ring inversion in MS₄ complexes has been determined to be on the order of 50-70 kJ mol⁻¹ but barriers for the ring inversion or interconversion processes in MS₄ complexes have not been reported. The energy of activation might, however, be expected to be low given that the activation energy for the interconversion of the two conformational isomers in cyclopentane is very low.

The reaction of electron rich transition metal complexes with elemental sulfur is not unusual. These ring opening reactions mirror the sulfur scavenging ability of cyanide, sulfide, and phosphines. Complexes that contain two to nine sulfur atoms in an MSₓ ring are known, although rings that contain three or fewer sulfur atoms are generally formed by reactions of sulfide transfer reagents (e.g., Na₂S₂, SOCl₂, Li₂S₃, etc...) with metal halides or metallate ions. An excep-
tion is \((\eta^5-C_5Me_5)Rh_2(CO)_2(\mu-S)\) which is formed by the reaction of \((\eta^5-C_5Me_5)_2Rh_2(CO)_2\) with sulfur in a 1:1 stoichiometric ratio. Typically, reactions of metal complexes with elemental sulfur yield complexes that have MS₄ and MS₅ rings; those that have MS₅ rings are more prevalent. Rauchfuss states that steric factors and not electronic factors dictate the size of the rings in Ti complexes. Thus, a small MSₓ ring is formed when other sterically demanding ligands (e.g., C₅Me₅) are attached to the metal whereas larger MSₓ rings are formed when, for example, C₅H₅ is the adjacent ligand. On the other hand, Shaver has presented evidence which indicates that there may be an electronic component that governs the ring size in metallathiophane complexes. This evidence indicates that the ring size decreases with an increase in the electron density at the metal center, and vice versa.

The reaction of elemental sulfur with Os(CO)₃(PMe₃)₂ (4) is interesting in that there is apparently exclusive formation of OsS₄ rings. For example, 4 reacts with S₈ at ambient temperature to give Os(CO)₂(PMe₃)₂(S₄) as the only isolatable product; any excess 4 remains unreacted (by IR spectroscopy). Thus, no smaller or larger OsSₓ rings appear to be formed, and consumption of 4 remains incomplete until the molar ratio of S:Os-complex is at least 4:1.

Preference for the formation of a five membered ring in Os(CO)₂(PMe₃)₂(S₄) may be controlled by both steric and electronic factors. Based on the foregoing discussion, both of
these factors would seem to favor a small ring size. Thus, the steric requirements of the PMe₃ ligands as well as the high electron density at the Os center may combine to restrict the formation of a larger OsSₓ ring. It is interesting that Os(H)-[η²-P(Me)₂(CH₂)](PMe₃)₃, which is probably both more electron rich and more sterically crowded than 4, reacts with S₈ to give Os(PMe₃)₃(S₇). This latter result would seem to contradict both the electronic and steric influences on the MSₓ ring size. However, the S₇ system acts as a tridentate ligand in Os(PMe₃)₃(S₇) to form two fused five membered rings.

Very little mechanistic information on the reaction of S₈ with metal complexes has been published. The results of one study indicate that the complex Ti₂S₆ does not serve as a precursor to the Ti₂S₄ complex (i.e., ring contraction does not occur by successive loss of sulfur atoms). In another example, however, evidence suggests that the five membered rings in (η⁵-C₅Me₅)₂Rh₂(S₈) are formed by successive additions of S atoms to (η⁵-C₅Me₅)₂Rh₂(CO)₂. In the absence of kinetic studies, and given that the isolated yield of Os(CO)₂(PMe₃)₂(S₈) is only 22%, little can be said concerning the mechanism by which Os(CO)₃(PMe₃)₂ reacts with S₈ to yield the final product.

2.4 Conclusion

Monosubstituted complexes of the type Os(CO)₄(L) can be conveniently and routinely synthesized either from Os₃(CO)₁₂ with excess ligand (L = PMe₃) at high temperature and CO pres-
sure, or by reaction of Os(CO)$_5$ with the ligand (L = P(OMe)$_3$, P(OCH$_2$)$_3$CMe, etc...) under substantially milder conditions. Bis-substituted complexes of the type Os(CO)$_3$(L)$_2$ can be prepared in a straightforward way by reaction of Os(CO)$_4$(L) complexes with excess ligand in solution.

An unexpected result of these studies has been the discovery of the potentially rich oxidative addition chemistry of Os(CO)$_3$-(PMe$_3$)$_2$ (4). The susceptibility of 4 towards oxidative addition is indicated by reactions of 4 with O$_2$, CH$_2$Cl$_2$, and elemental sulfur under mild conditions to give clean conversion to Os(CO)$_2$-[O(CO)O](PMe$_3$)$_2$, Os(CO)$_2$(Cl)$_2$(PMe$_3$)$_2$, and Os(CO)$_2$(PMe$_3$)$_2$(S$_4$), respectively. The carbonato species joins a small but growing list of organometallic carbonato complexes. Carbonato complexes, and the synthesis of these compounds by direct reaction of O$_2$, are of significant interest with respect to the possible role of these species in oxidations of organic substrates, and as mimics of biological oxygen carriers.$^{63}$ The facile cleavage of two carbon chlorine bonds in CH$_2$Cl$_2$ to generate Os(CO)$_2$(Cl)$_2$(PMe$_3$)$_2$ represents an unusual reaction of CH$_2$Cl$_2$ with a metal complex. This reaction most likely proceeds via a radical pathway since it is catalyzed by trace amounts of O$_2$. Finally, Os(CO)$_2$(PMe$_3$)$_2$-(S$_4$) joins an important class of polysulfide organometallic complexes which may serve as models for catalytic processes.$^{64}$
3.1 Introduction

The concept of a dative bond has long been known in main group chemistry. Dative bonds result from the interaction of a Lewis acid with a Lewis base; in molecular orbital terms, it is the result of a HOMO LUMO interaction. Prototypical examples of compounds with dative bonds are ones in which BR₃ or AlR₃ (R = H, alkyl, halogen) acts as the Lewis acid and NR₃ or PR₃ (R = H, alkyl) functions as the Lewis base. An example of this type of complex is H₃NBH₃. Combination of BH₃ with CO also yields a dative bonded complex, H₃BCO. It has been observed that the strength of dative bonds between main group elements may be up to half the strength of a corresponding covalent bond, but usually are much weaker.⁶⁵

Equally well known are the many examples of dative bonds between main group and transition metal atoms. Examples abound of two-electron donor ligands containing P, N, O, etc... centers which act as Lewis bases towards unsaturated transition metal complexes.

Metal-metal bonds of orders one to four which result from the equal contribution of electrons from each of the metal fragments are well known and have been characterized fully.⁶⁶
Dative metal-metal bonds between a Lewis base transition metal fragment and a Lewis acid non-transition metal fragment are also known. For example, in $\text{Fe(CO)}_2(\text{PMe}_2\text{Ph})_2[\text{CS}_2\text{C}_2(\text{CO}_2\text{Me})_2]-(\text{HgCl}_2)$ the 18-electron Fe complex acts as a Lewis base to the Lewis acid HgCl$_2$, and in $(\eta^5\text{-C}_5\text{H}_5)\text{Rh(PMe}_3)_2(\text{Al}_2\text{Me}_2\text{Cl}_2)$ the 18-electron Rh complex is the Lewis acid towards the Al$_2$ Lewis base. Dative bonds between two transition metal species are, however, quite rare, and have been formulated primarily in order to achieve an 18-electron count at each metal center. Until recently, in those cases where a dative bond has been proposed, the metal-metal bond is invariably bridged by other ligands. The first example of a complex in which a dative metal-metal bond was proposed was in complex I. ($R = \text{OH}, R' = \text{Me}$). An alternate electron counting scheme which would result in a normal covalent single Fe-Fe bond can be proposed as in II. Similarly, Vahrenkamp, Geoffroy, and others have proposed dative metal-metal bonds in several phosphido- and carbonyl-bridged species in order to achieve an 18-electron count at each metal center. Again, an alternate electron counting scheme yields covalent metal-metal bonds as in III and IV. Numerous other
bridged bimetallic\textsuperscript{73} and cluster\textsuperscript{74} complexes have been described in which a dative metal-metal bond is postulated.

Since two bonding schemes can be constructed for these bridged species, this may indicate that there is delocalized metal-metal bonding. Therefore, it is not possible to describe the metal-metal bond unequivocally as either covalent or dative. Summerville and Hoffmann have noted that for triply-bridged species such as Fe\textsubscript{2}(CO)\textsubscript{9}, a delocalized bonding picture is the appropriate description of the Fe\textsubscript{2}(\mu-CO)\textsubscript{3} bonding interaction, and that in bridged complexes, electron counting conventions are not a good guide to the presence or absence of metal-metal bonding.\textsuperscript{75} In agreement with these conclusions, MO calculations on complexes thought to contain metal-metal dative bonds bridged by carbonyls indicate that there is little direct metal-metal interaction.\textsuperscript{76}

A dative metal-metal bond has been proposed in several bimetallic hydride species. In (H)\textsubscript{2}(\eta^5-C\textsubscript{5}H\textsubscript{5})\textsubscript{2}MM'(CO)\textsubscript{5} (M = Mo, W; M' = Cr, Mo, W) a dative metal-metal bond was formulated on the basis of the chemical shift and \textsuperscript{183}W-\textsuperscript{1}H couplings to the metal hydrides.\textsuperscript{77} The structure of the complex was believed to
be as in V. A semibridged structure (VI) with a single covalent bond would also be consistent with the NMR results. A metal-metal dative bond has also been postulated in the ionic binary complexes [(OC)$_5$M'M(CO)$_5$]$^-$ (M' = Mn, Re; M = Cr, Mo, W), as well as in the hydride complexes [(H)(OC)$_5$FeM(CO)$_5$]$^-$ (M = Cr, W). In these complexes it has been assumed that the negative charge is localized on the group 7 or group 8 metal atom; this yields an anionic 18-electron fragment and a neutral 16-electron group 6 metal fragment. While this would seem to violate Pauling's electroneutrality principle, this formulation is supported by ab initio calculations.

The first example of a neutral transition metal complex in which a dative metal-metal bond could be unambiguously assigned was (OC)$_5$OsOs(CO)$_3$(Cl)(GeCl)$_3$. The crystal structure shown in Figure 3.1 clearly indicates that there are no bridging ligands. Thus, the neutral 18-electron Os(CO)$_5$ complex acts as a two electron donor to the 16-electron Os(CO)$_3$(Cl)(GeCl)$_3$ fragment. In this way, the Os(CO)$_5$ can be described as a two electron donor ligand in much the same way as more classical ligands like PMe$_3$, NH$_3$, or CO. Since the original discovery, several other
bimetallic complexes containing dative metal-metal bonds have been reported from this laboratory and others but such complexes remain rare.

It has been found (by $^{13}$C and $^{31}$P NMR spectroscopy) that complexes of the type $(\text{Me}_3\text{P})(\text{OC})_5\text{OsM(CO)}_5$ ($\text{M} = \text{Cr, Mo, W}$) exist as two isomers in solution. An extension of this work has involved the synthesis of analogues of these complexes in which the cone angle and the electronic properties of the phosphorus ligand have been changed. The isomer ratios were found to vary substantially. In all of these complexes, CO migration between the two metal centers is facile. The details of this work have
been published.8

Another extension of this work has involved an investigation of the degree to which the dative metal-metal bond strengths are affected by the nucleophilic properties of the 18-electron Os donor species. The approach employed has involved the synthesis of bis-substituted Os(CO)₃(L)₂ complexes which are more electron rich at the Os center than the monosubstituted species; these were then used as donors towards group 6 M(CO)₅ species. An X-ray crystal structure of one of these derivatives, (Me₃P)₂(OC)₂OsW(CO)₅, has been obtained.83 Contrary to our expectations, the Os(CO)₃(L)₂ species seem to form less stable metal-metal bonded compounds with M(CO)₅. The UV/VIS spectra of a number of the mono- and bis-substituted bimetallic complexes also indicate that a weaker metal-metal bond is associated with an increase in the electron density on the Os donor atom.

An unexpected result of these investigations was the discovery of a linear trimetallic complex which was formulated as VII (see illustration below) based on ¹³C NMR evidence (Pc = P(OCH₂)₃CMe). An X-ray crystal structure of an isomer of VII confirmed the linear metal framework and the presence of metal-metal dative bonds in tandem. This bonding mode was heretofore unprecedented in the chemical literature.
3.2 Experimental

Unless otherwise stated, manipulations of starting materials and products were carried out under an inert atmosphere with the use of standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and dichloromethane were distilled under nitrogen from potassium, potassium benzophenone, and calcium hydride, respectively. The osmium compounds \( \text{Os(CO)}_3(L)(L') \) (\( L = \text{CO}, \text{PMe}_3, \text{P(OMe)}_3; \) \( L' = \text{CO}, \text{PMe}_3, \text{P(OMe)}_3, \text{PPh}_3, \text{P[O(O-tol)]}_3, \) \( \text{P(OCH}_2)_3 \text{CM} \)) were prepared as described in Chapter 2. The metal carbonyls \( \text{M(CO)}_6 \) (\( \text{M} = \text{Cr, Mo, W} \)) were obtained commercially.

An external medium-pressure mercury discharge lamp (200-W, Hanovia Model 654 A36) surrounded by a water-cooled quartz jacket was employed for the UV irradiations. The distance between the sample and the lamp was approximately 5 cm. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. UV/VIS
spectra were recorded on either a Cary 210 or a Phillips PU 8720 spectrometer. Electron impact (70 eV) mass spectra were obtained with a Hewlett-Packard 5985 GC-MS instrument. NMR spectra were recorded on a Bruker WM400 spectrometer (operating frequencies were 100.6 MHz, 162 MHz, and 400 MHz for $^{13}$C, $^{31}$P and $^1$H spectra, respectively). All samples used for $^{13}$C NMR were enriched with $^{13}$CO; these were prepared from $^{13}$CO enriched M(CO)$_6$ (see below). The microanalyses were obtained by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of M(CO)$_5$(THF) (M = Cr, Mo, W). In general, a quartz Carius tube that contained a Teflon coated magnetic stir bar was charged with M(CO)$_6$ (typically 0.1 to 0.2 mmol) and ~40 mL of THF. The tube was pneumatically sealed with a Teflon valve. Prior to irradiation, the solution was degassed either with two freeze-pump-thaw cycles or by slow evacuation of the vessel at room temperature. The solution was irradiated until an infrared spectrum of the reaction mixture showed no further conversion to the product. The Mo and W carbonyls reacted much quicker than the Cr carbonyl; the Cr and W carbonyls could be entirely converted to the M(CO)$_5$(THF) product, while the Mo species began to decompose long before the Mo(CO)$_6$ had completely reacted. After photolysis, the solution was concentrated under vacuum to approximately 1 to 2 mL in a Schlenk tube.

Preparation of $^{13}$CO-Labeled M(CO)$_6$ (M = Cr, Mo, W). Labeled M(CO)$_6$ was prepared by the treatment of preformed M(CO)$_5$(THF) with $^{13}$CO (1 atm). The reaction was stirred until the solution
became colorless. The reaction was subjected to further photolysis in the presence of the $^{13}$CO, after which it was stirred until it again became colorless. After removal of the solvent under vacuum, the labeled M(CO)$_6$ was purified via sublimation.

Preparation of (L)(OC)$_n$OsM(CO)$_5$ (L = P(OMe)$_3$, P(OCH$_2$)$_3$CMe; M = Cr, Mo, W) Derivatives. All of the complexes were prepared by the reaction of Os(CO)$_n$(L) with M(CO)$_5$(THF) in hexane. Details of three of the preparations are given below. The bimetallic products were all formed as insoluble precipitates in hexane. The desired products were purified by column chromatography followed by recrystallization from CH$_2$Cl$_2$/hexane. The complexes formed in yields of 70-80%, 20-30%, and 50-60%, for the Cr, Mo, and W species, respectively. They are bright yellow, light yellow, and pale yellow solids for the Cr, Mo, and W derivatives, respectively. The solids are all stable in air, though they are slightly light sensitive. The Mo and W complexes are slightly unstable in CH$_2$Cl$_2$ while the Cr analogues are very unstable in solutions of CH$_2$Cl$_2$ that are exposed to air. Yield, analytical, mass and infrared spectral data are given in Table 3.1, $^1$H and $^3$P{$^1$H} NMR data in Table 3.2, and $^{13}$C MMR data in Table 3.3. (The $^{13}$CO labeled samples were prepared by starting with $^{13}$CO labeled M(CO)$_5$(THF) starting material.)

Preparation of [(MeO)$_2$P](OC)$_n$OsMo(CO)$_5$. A solution of Mo(CO)$_6$ (300 mg, 1.14 mmol) in THF (~50 mL) was irradiated for 2.5 h to yield Mo(CO)$_5$(THF). After irradiation, the solution was evaporated to near dryness under vacuum and cooled to -196 °C. A
Table 3.1. Microanalysis, Mass Spectral, Yield, and Infrared Spectral Data for New Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Calcd. C</th>
<th>% Found C</th>
<th>Mass Spectrum&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield</th>
<th>Infrared Stretches νCO&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="OC">(MeO)₃P</a>₂OsCr(CO)₅ (7)</td>
<td>23.27 1.45</td>
<td>23.33 1.33</td>
<td>--</td>
<td>63%</td>
<td>2063(w) 2021(s) 1915(s) 1895(m,sh)</td>
</tr>
<tr>
<td><a href="OC">MeC(CH₃O)₃P</a>₂OsCr(CO)₅ (8)</td>
<td>26.18 1.41</td>
<td>26.32 1.48</td>
<td>M⁺</td>
<td>91%</td>
<td>2107(vw) 2029(s) 1915(s) 1887(m,sh)</td>
</tr>
<tr>
<td><a href="OC">(MeO)₃P</a>₂OsMo(CO)₅ (9)</td>
<td>21.76 1.36</td>
<td>21.96 1.32</td>
<td>--</td>
<td>28%</td>
<td>2097(vw) 2048(m) 2013(s) 1927(s) 1886(m)</td>
</tr>
<tr>
<td><a href="OC">(MeO)₃P</a>₂OsW(CO)₅ (10)</td>
<td>19.26 1.20</td>
<td>19.33 1.13</td>
<td>--</td>
<td>51%</td>
<td>2102(w) 2048(m) 2015(s) 1925(s) 1886(m)</td>
</tr>
<tr>
<td><a href="OC">MeC(CH₃O)₃P</a>₂OsW(CO)₅ (5)</td>
<td>21.72 1.17</td>
<td>21.74 1.20</td>
<td>M⁺</td>
<td>29%</td>
<td>2108(w) 2044(m) 2030(s) 1915(s) 1881(m)</td>
</tr>
<tr>
<td>(Me₃P):(OC)₂OsW(CO)₅ (1)</td>
<td>22.41 2.42</td>
<td>22.58 2.44</td>
<td>--</td>
<td>40%</td>
<td>2060(m) 2053(m) 2012(m) 2002(ms) 1957(s) 1906(s) 1875(m)</td>
</tr>
<tr>
<td><a href="OC">(MeO)₃P</a>₂OsW(CO)₅ (11)</td>
<td>----</td>
<td>----</td>
<td>--</td>
<td>--</td>
<td>2072(mw) 2030(m) 1975(s) 1912(s) 1863(m)</td>
</tr>
<tr>
<td>[(o-to10)₃P(Me₃P)(OC)₂OsW(CO)₅ (6)</td>
<td>37.44 2.92</td>
<td>37.40 2.86</td>
<td>c</td>
<td>32%</td>
<td>2060(m) 2026(m) 1997(m) 1976(s) 1901(s) 1874(m)</td>
</tr>
<tr>
<td>(dmpe)(OC)₂OsW(CO)₅ (12)</td>
<td>22.24 2.12</td>
<td>22.46 1.99</td>
<td>--</td>
<td>--</td>
<td>2059(m) 2014(m) 1980(m) 1958(s) 1904(s) 1862(m)</td>
</tr>
<tr>
<td>(PC)(OC)₂OsOs(CO)₅(PC)W(CO)₅ (4)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>22.08 1.52</td>
<td>21.86 1.53</td>
<td>--</td>
<td>13%</td>
<td>2126(w) 2114(w) 2051(s) 2041(s) 2008(m,sh) 1973(m,sh) 1957(s) 1904(s) 1844(m)</td>
</tr>
<tr>
<td>(PC)(OC)₂OsOs(CO)₅W(CO)₅ (3)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>22.08 1.52</td>
<td>22.33 1.54</td>
<td>--</td>
<td>22%</td>
<td>2101(m) 2059(s) 2022(vs) 1977(vs) 1902(s) 1856(m)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Unless otherwise specified, the complexes did not give satisfactory EI mass spectra; <sup>b</sup> Solution IR spectra were recorded in CH₂Cl₂; <sup>c</sup> M⁺ = W(CO)₅; <sup>d</sup> Pc = P(OCH₃)₃CMe.
Table 3.2. $^1$H and $^{31}$P NMR Data for New Bimetallic and Trimetallic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H$\delta$</th>
<th>$^{31}$P($^1$H)$\delta$</th>
<th>Isomer Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 A</td>
<td>3.68(13.2)</td>
<td>100.6</td>
<td>~50</td>
</tr>
<tr>
<td></td>
<td>3.74(12.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 A</td>
<td>4.37(5.0), 0.85</td>
<td>84.2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>4.33(5.0), 0.80</td>
<td>81.5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 A</td>
<td>3.71(13.1)</td>
<td>102.9</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>3.77(12.0)</td>
<td>87.1</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 A</td>
<td>3.73(13.0)</td>
<td>99.6</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>3.78(11.8)</td>
<td>83.4</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 A</td>
<td>4.37(5.0), 0.85</td>
<td>82.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>4.33(5.0), 0.81</td>
<td>80.4</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 A</td>
<td>1.88(9.36), 1.79(9.26), -59.4(17.2), -64.5(17.1)</td>
<td>~1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.86(4.2)</td>
<td>-65.7</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>7.33-7.10 (ArH)</td>
<td>2.35, 86.3(25.8), -62.8(26.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.81(10.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.78(9.85), 1.97(10.05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 A</td>
<td>4.44(5.1), 4.21(4.9)</td>
<td>91.9(3.6), 73.5(3.6)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4.35(5.1), 4.20(4.9)</td>
<td>92.0(3.5), 76.3(b)</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td></td>
<td>78.1</td>
<td></td>
</tr>
</tbody>
</table>

Numbering scheme corresponds to that given in Table 3.1. Unless otherwise specified, all spectra were obtained at -20 or -30 °C in CH$_2$Cl$_2$. Numbers in parentheses for the $^1$H NMR data correspond to J$_{p-H}$. Numbers in parentheses for the $^{31}$P NMR spectra correspond to J$_{p-p}$. a, ambient temperature; b, coupling not resolved;
Table 3.3. $^{13}$C NMR Shifts for the Carbonyl Ligands of New Bimetallic and Trimetallic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M(CO)$_5$</th>
<th>Os(CO)$<em>{4-n}$(L)$</em>{1+n}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ ax-CO</td>
<td>$\delta$ rad-CO</td>
<td>$\delta$ axial/equatorial CO</td>
</tr>
<tr>
<td>7$^a$</td>
<td>227.7</td>
<td>222.8</td>
<td>186.8(5.2)</td>
</tr>
<tr>
<td>8 A$^a$</td>
<td>230.1</td>
<td>222.6</td>
<td>184.6</td>
</tr>
<tr>
<td>B</td>
<td>229.3</td>
<td>221.0</td>
<td>187.0(19.0), 179.9(120.9), 167.0(10.5)</td>
</tr>
<tr>
<td>9 A$^a$</td>
<td>216.7</td>
<td>210.3</td>
<td>186.4</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>209.3</td>
<td></td>
</tr>
<tr>
<td>10 A$^a$</td>
<td>204.4</td>
<td>202.3(124.6)$^c$</td>
<td>184.1(5.0)</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>201.8</td>
<td></td>
</tr>
<tr>
<td>5 A$^a$</td>
<td>204.1$^g$</td>
<td>202.2(124.5)$^c$</td>
<td>182.3(5.2, 91.5$^d$)</td>
</tr>
<tr>
<td>B</td>
<td>203.3</td>
<td>201.7(125)$^c$</td>
<td>183.7(19.0), 177.6(122.0), 167.2(11.3)</td>
</tr>
<tr>
<td>1 A$^a$</td>
<td>205.9</td>
<td>205.1(125.3)$^c$</td>
<td>195.3(14.6), 185.3(74.6)</td>
</tr>
<tr>
<td>B</td>
<td>203.8</td>
<td>204.8(125.2)$^c$</td>
<td>197.2(10.1), 177.6(10.2)</td>
</tr>
<tr>
<td>6</td>
<td>204.9$^h$</td>
<td>203.7(126.8)$^c$</td>
<td>191.8(14.1), 181.6(dd; 67.4, 6.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>* * trimetallic complexes * *</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 A</td>
<td>206.4</td>
<td>203.8(123.9)$^c$</td>
<td>195.8(19.2)$^e$ 192.4(121.4)$^e$, 179.9(6.7)$^f$</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>203.9</td>
<td>195.4(20.2)$^e$, 180.2(18.4)$^f$</td>
</tr>
<tr>
<td>3</td>
<td>206.4$^l$</td>
<td>204.1(125.1)$^c$</td>
<td>193.3$^e$, 183.2(16.1)$^f$, 165.6(11.1)$^f$</td>
</tr>
</tbody>
</table>

Numbering scheme corresponds to that given in Table 3.1. All spectra were obtained in either CD$_2$Cl$_2$ or CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/4, v/v) solutions; figures in parentheses are $J_{p-C}$ unless stated otherwise; $a$, spectrum at -20 or -30 °C; $b$, not observed; $c$, $J_{W-C}$; $d$, $J_{OS-C}$; $e$, CO ligands on the central Os; $f$, CO ligands on the terminal Os; $g$, $J_{p-C}$ 4.7 Hz, $J_{W-C}$ 178 Hz; $h$, $J_{p-C}$ 4.0 Hz; $j$, $J_{W-C}$ 177 Hz.
solution of Os(CO)₄[P(OMe)₃] (185 mg, 0.43 mmol) in hexane (20 mL) was added. The mixture was allowed to warm slowly to -78 °C, and stirred for 30 min with the exclusion of light, whereupon a yellow solid formed. The mixture was stirred for a further 20 min at room temperature. After removal of the solvent, the remaining solid was chromatographed on a Florisil column (11 x 1 cm) with CH₂Cl₂/hexane (1/5, v/v followed by 1/1, v/v) as eluant. The desired product, eluted from the column as a yellow band, was contaminated with traces of a deep red compound identified as (OC)₅Mo{Os(CO)₃[P(OMe)₃]}₂.⁸⁻ The impure product was purified by two recrystallizations from CH₂Cl₂/hexane, followed by chromatography on a silica gel column (5 x 1 cm), and finally by a third recrystallization from CH₂Cl₂/hexane. In this way, [(MeO)₃P](OC)₄OsMo(CO)₅ (79 mg, 28%) was obtained as pale yellow air-stable crystals. An X-ray crystal structure of the deep red contaminant showed that it contained [(MeO)₃P]-(OC)₄OsMo(CO)₅ and (OC)₅Mo{Os(CO)₃[P(OMe)₃]}₂ co-crystallized in a 1:1 ratio. The molecular structure of [(MeO)₃P](OC)₄OsMo(CO)₅ is shown in the Appendix.⁸⁵

Preparation of [(MeO)₃P](OC)₄OsW(CO)₅. A solution of W(CO)₅(THF) was prepared from W(CO)₆ (300 mg, 0.85 mmol) as described previously. The solution was reduced in volume under vacuum to ca 5 mL, and then added dropwise to a vigorously stirred solution of Os(CO)₄[P(OMe)₃] (200 mg, 0.46 mmol) in hexane (40 mL). The W(CO)₅(THF) was added until the infrared spectrum showed no bands due to the starting Os compound. The
reaction was dried under vacuum and the crude solid was purified by column chromatography on Florisil (17 x 1 cm) with CH$_2$Cl$_2$/hexane (2/5, v/v) as the eluant. A deep red band that contained (OC)$_5$W[Os(CO)$_3$[P(OMe)$_3$]]$_2$ (identified by IR spectroscopy) was eluted from the column ahead of the yellow band that contained the desired product. Recrystallization of the product from CH$_2$Cl$_2$/hexane removed trace amounts of the cluster to give [(MeO)$_3$P](OC)$_4$OsW(CO)$_5$ (192 mg, 51%) as pale yellow air-stable crystals.

Preparation of [MeC(CH$_2$O)$_3$P](OC)$_4$OsW(CO)$_5$. A solution of W(CO)$_5$(THF) was prepared from W(CO)$_6$ (200 mg, 0.57 mmol) as described previously, and reduced to ca 2 mL under vacuum. The W(CO)$_5$(THF) was added dropwise to a vigorously stirred solution of Os(CO)$_4$(Pc) (Pc = P(OCH$_2$)$_3$CMe) in 10 mL of hexane/CH$_2$Cl$_2$ (~50/1, v/v) until all of the starting osmium complex was consumed (as indicated by IR spectroscopy). A dull yellow solid precipitated from the reaction. The solvent was removed under vacuum, and the crude product was purified by chromatography on alumina (11 x 1 cm). The desired product, [MeC(CH$_2$O)$_3$P](OC)$_4$OsW(CO)$_5$, was eluted with CH$_2$Cl$_2$/hexane (1/1). A small amount of the cluster (OC)$_5$W[Os(CO)$_3$[P(OCH$_2$)$_3$CMe]]$_2$ was eluted as a faint red band with the same solvent mixture. A second yellow compound eluted with CH$_2$Cl$_2$/hexane (2/1, v/v) was not identified, but the IR spectrum (in the $\nu$CO region) resembled the spectra of 3 and 4 (see below). A third yellow compound was eluted with CH$_2$Cl$_2$; this was subsequently identified as (Pc)(OC)$_4$OsOs(CO)$_3$(Pc)W(CO)$_5$. 

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The desired product was recrystallized from CH$_2$Cl$_2$/hexane to give [MeC(CH$_2$O)$_3$P](OC)$_4$OsW(CO)$_5$ (45 mg, 29%) as yellow air-stable crystals.

Preparation of (L)(L')(OC)$_3$OsW(CO)$_5$ (L = PMe$_3$, P(OMe)$_3$; L' = PMe$_3$, P(OMe)$_3$, P[O(o-tol)]$_3$) Derivatives. These compounds were all prepared in an analogous manner to the Os(CO)$_n$(L) derivatives. The yields, elemental analyses, mass and infrared spectral data are given in Table 3.1, $^1$H and $^{31}$P{$^1$H} NMR data in Table 3.2, and $^{13}$C NMR data in Table 3.3. The complexes are all reasonably air-stable yellow solids, but much less stable in CH$_2$Cl$_2$ than the monosubstituted derivatives. The details of one preparation are given below.

Preparation of (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$. A solution of W(CO)$_5$(THF) was prepared from W(CO)$_6$ (158 mg, 0.5 mmol) as previously described, dried, and cooled immediately to -196 °C. A solution containing Os(CO)$_3$(PMe$_3$)$_2$ (192 mg, 0.5 mmol) in 15 mL hexane/2 mL CH$_2$Cl$_2$ was added dropwise from a dropping funnel. Upon warming the mixture to room temperature in the dark, a dull yellow solid formed. The reaction was stirred for a further 2 hr at room temperature. After solvent removal, the crude product was chromatographed on silica gel (11 x 1 cm) with CH$_2$Cl$_2$ as the eluant. The product was further purified by recrystallization from CH$_2$Cl$_2$/hexane. In this way, (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$ (120 mg, 40%) was obtained as yellow, air-stable crystals. One of these crystals was used for the X-ray diffraction study.
Preparation of \((\text{Pc})_2(\text{OC})_3\text{OsOs(CO)}_4\text{W(CO)}_5\) (\text{Pc} = \text{P(OCH}_2)_3\text{CMe})

A solution of \([\text{MeC(CH}_2\text{O})_3\text{P}](\text{OC})_4\text{OsW(CO)}_5\) (56 mg, 0.072 mmol) and \(\text{Os(CO)}_4(\text{Pc})\) (42 mg, 0.09 mmol) in 4 mL of hexane/THF (3/1) was pneumatically sealed in a Carius tube equipped with a Kontes Teflon valve and a Teflon coated magnetic stir bar. The vessel was evacuated at -196 °C and degassed via two freeze-pump-thaw cycles and heated to 90 °C for 6.4 d. A yellow solid began precipitating after several days. The crude product was purified by chromatography on alumina (12 x 1 cm) with CH$_2$Cl$_2$/hexane (1/2 v/v) as the eluant. The desired product was further purified by recrystallization from C$_6$H$_5$Cl/CH$_2$Cl$_2$ with a top layer of hexane. In this way, \((\text{Pc})_2(\text{OC})_3\text{OsOs(CO)}_4\text{W(CO)}_5\) (3) (23 mg, 22%) was recovered as bright yellow crystals. One of these crystals was used for an X-ray diffraction study.

Reaction of Complexes Containing Dative Metal-Metal Bonds with Two Electron Donor Ligands (CO, PPh$_3$). These reactions were typically carried out on very small scales and monitored by infrared spectroscopy. The bimetallic species (ca 5 mg) were dissolved in CH$_2$Cl$_2$. The vessels were evacuated at -196 °C and the solutions degassed either after the addition of PPh$_3$ or prior to the addition of CO (1 to 2 atm). Both light and dark reaction conditions were employed. Products of these reactions were identified by their characteristic $\nu$CO infrared bands.
3.3 Results and Discussion

Syntheses of Complexes with Dative Metal-Metal Bonds.

Complexes \((L)_{n}(OC)_{5-n}OsM(CO)_{5}\) (\(L = PMe_3, P(OMe)_3, Pc, \text{etc...; } \)) \(M = \text{Cr, Mo, W}; n = 1, 2\) were readily prepared by reaction of 18-electron Os compounds with freshly prepared \(M(CO)_{5}(THF)\) as in equation 3.1. The bimetallic products were all readily purified by column chromatography followed by recrystallization to give yellow solids. The solids are stable in air, slightly photosensitive, and insoluble in nonpolar organic solvents. It has been suggested that the low solubility in nonpolar solvents may be due to the polar nature of the dative metal-metal bond (viz \((\delta^+M---M(\delta^-))\)).

\[
\text{Os(CO)}_{5-n}(L)_n + \text{M(CO)}_{5}(\text{THF}) \rightarrow (L)_n(OC)_{5-n}\text{OsM(CO)}_{5} \tag{3.1}
\]

(Complexes with covalent metal-metal bonds tend to be much more soluble.)

The \((L)(OC)_{4}OsM(CO)_{5}\) complexes were all produced along with a small, although varying, amount of the trimetallic cluster species \((OC)_{5}M[Os(CO)_{3}(PR_{3})]_{2}\) (see Chapter 4). The yields of the \((L)(OC)_{4}OsM(CO)_{5}\) complexes differed substantially; they were typically 70-80\%, 20-30\%, and 50-60\%, for the Cr, Mo, and W derivatives, respectively. The greater yields of the Cr complexes compared to the W analogues are likely the result of more favorable kinetic conditions for the Cr species since the W derivatives are chemically more stable (see below). The substantially lower yields observed for the Mo derivatives are likely attributable to the much lower stability of \(Mo(CO)_{5}(THF)\). When the phosphorus ligand was Pc
(Pc = P(OCH₂)₃CMe), only a trace amount of the triangular cluster species formed; a possible explanation is given below.

During the preparation of [MeC(CH₂O)₃P](OC)₄OsW(CO)₅, an unexpected compound was also produced; the bright yellow compound was identified as (Pc)(OC)₄OsOs(CO)₃(Pc)W(CO)₅ (4) (shown above as VII) based on the ¹³C NMR spectrum (see below) and elemental analysis. It was thought that the reaction of WOs(CO)₅(Pc) with excess Os(CO)₄(Pc) would yield the linear trimetallic compound. These reagents, heated at 90 °C in hexane/THF for 6 d, gave (Pc)₂(OC)₃OsOs(CO)₄W(CO)₅ (3) (an isomer of VII) in 22% yield. (No reaction occurred under mild conditions in the presence of Me₃NO.) It was purified by chromatography and recrystallization. Its structure was determined by X-ray crystallography. A view of the structure is shown in Figure 3.4. In the absence of labeling experiments, there is no experimental evidence to suggest a mechanism for the formation of 3. It is certain, however, that 3 does not result from 4 via thermal isomerization (see below). This suggests that loss of Pc from WOs(CO)₅(Pc) is involved. The mechanism for the formation of 4 during the preparation of WOs(CO)₅(Pc) is equally uncertain. It could be that a CO is lost from WOs(CO)₅(Pc) due to decreased π-backbonding, or that a CO is abstracted from WOs(CO)₅(Pc) by excess W(CO)₅(THF). The linear trimetallic complexes are even less soluble than the bimetallic species; they are, for example, only slightly to moderately soluble in CH₂Cl₂. Some possible reasons for the decreased solubility are
Only two complexes of the type \((L)_2(OC)_3OsM(CO)_5\) were isolated in quantities suitable for complete characterization; these were \((Me_3P)_2(OC)_3OsW(CO)_5\) (60% yield) and \([(o-tolO)_3P]-\(Me_3P\))(OC)_3OsW(CO)_5\) (34% yield). There is compelling infrared evidence for the formation of two others, \([(MeO)_3P]_2(OC)_3Os-W(CO)_5\) and \((dmpe)(OC)_3OsW(CO)_5\) (dmpe = 1,2-bis(dimethylphosphino)ethane). No evidence was obtained for the formation of the corresponding Cr derivatives. Given the shorter metal-metal bond lengths in the latter derivatives, it is likely that steric factors prevented the formation of the Cr complexes. Similarly, no cluster species were observed for the Os(CO)_3(L)_2 derivatives, presumably due to excessive steric strain in the equatorial plane of the incipient cluster. (We have found that these complexes, unlike the monosubstituted derivatives, cannot be converted into clusters (see below).) Syntheses of the Mo derivatives were not attempted.

**Structure of \((Me_3P)_2(OC)_3OsW(CO)_5\) (1).** The crystal structure of 1 is shown in Figure 3.2; selected bond lengths and angles are given in Table 3.4. The molecule contains a crystallographically imposed \(C_2\) axis that lies along the \(C(7)-Os-W-C(4)\) axis. The coordination about each metal center is is octahedral, though that about Os is quite distorted in the equatorial plane. While the equatorial carbonyls on Os lean inward towards the \(W(CO)_5\) fragment \((C(8)-Os-C(8) = 155.4 (3)°)\), the shortest contact distance between W and one of the carbonyl ligands on Os
Figure 3.2. Molecular Structure of (Me₃P)₂(OC)₃OsW(CO)₅ (1).

is 3.328 (6) Å. Thus, the Os-W bond cannot be considered semibridged; it can, therefore, be unambiguously described as a dative bond between an 18-electron Os(CO)₃(PMe₃)₂ group and a 16-electron W(CO)₅ fragment.

A view of 1 along the P-Os-P bond is shown in Figure 3.3. The inward leaning of the equatorial carbonyls on Os is significantly greater than in the monophosphine analogue (Me₃P)(OC)₄Os-W(CO)₅ (2) (168.5 (4)°). It has been suggested that the inward leaning of carbonyls in [Mn₃(CO)₁₄]⁻ is due to an Mdπ-COπ*
Table 3.4. Selected Bond Lengths (Å) and Angles (deg) for (Me₃P)₂(OC)₃OsW(CO)₅ (1) and (Pc)₂(OC)₃OsOs(CO)₄W(CO)₅ (3).

<table>
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<th>Bond/Angle</th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>Os-W</td>
<td>3.1417(6)</td>
<td>Os(1)-Os(2)</td>
</tr>
<tr>
<td>Os-P</td>
<td>2.391(2)</td>
<td>Os(2)-W(1)</td>
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<tr>
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<td>Os(1)-P(1)</td>
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<td>Os(1)-P(2)</td>
</tr>
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<td>W-C(6)</td>
<td>2.034(7)</td>
<td>W-C(11)</td>
</tr>
<tr>
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<td>W-C(12)</td>
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<td>W-C(14)</td>
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<td>C(7)-O(7)</td>
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<td>Os(1)-C(20)</td>
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<td>C(8)-O(8)</td>
<td>1.120(7)</td>
<td>Os(1)-C(30)</td>
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<td>Os(2)-C(21)</td>
<td>Os(2)-C(22)</td>
</tr>
<tr>
<td>P-Os-P</td>
<td>173.83(5)</td>
<td>Os(2)-C(23)</td>
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<tr>
<td>C(7)-Os-C(8)</td>
<td>155.4(3)</td>
<td>Os(2)-C(24)</td>
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<td>C(15)-O(15)</td>
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</tr>
<tr>
<td></td>
<td>C(14)-W(1)-C(12)</td>
<td>W(1)-C(14)</td>
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</table>

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Figure 3.3. View of \((\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5\) Along the P-Os-P Bond.

backbonding interaction\(^8\) (see illustration above). Similar inward leaning of the equatorial groups has been observed in \([\text{RFeM(CO)}_5^-\) (\(R = \text{H}, \text{Ph}_3\text{PAu}; M = \text{Cr}, \text{W}\)) complexes in which
dative metal-metal bonds are formulated,\textsuperscript{79} and in the complexes Mn\textsubscript{2}(CO)\textsubscript{10},\textsuperscript{88} Mn\textsubscript{2}Fe(CO)\textsubscript{14},\textsuperscript{89} HRe\textsubscript{2}Mn(CO)\textsubscript{14},\textsuperscript{90} [Mo\textsubscript{2}(CO)\textsubscript{10}]\textsuperscript{2-},\textsuperscript{91} and \{Zn(Fe(CO)\textsubscript{4})\textsubscript{2}\}\textsuperscript{2-}\textsuperscript{92} that contain covalent metal-metal bonds. The greater inward leaning of the equatorial carbonyls in 1 compared to its monosubstituted analogue is consistent with this model. Greater electron density on the Os center in 1 compared to 2 would be expected to lower the energy of the $\pi^*$ orbitals on the carbonyls by virtue of increased $\pi$-backbonding. In turn, the $\pi^*$ orbitals would become more favorable for bonding with the d$\pi$ orbitals of the adjacent W atom, thus increasing the inward leaning of these carbonyls. However, it is interesting that the CO bond lengths of the carbonyls bonded to Os in (Me\textsubscript{3}P)\textsubscript{2}(OC)\textsubscript{5}Os-W(CO)\textsubscript{5} (1.120 (7) Å) are identical within the experimental error to the similar CO bond lengths in (Me\textsubscript{3}P)(OC)\textsubscript{4}OsW(CO)\textsubscript{5} (1.13 (1) Å). This may be due to a simultaneous decrease in the Os-CO backbonding with an increase in the CO backbonding of those carbonyls to W.

The view in Figure 3.3 suggests that the coordination about Os can be equally well described as either a distorted octahedron, or as a distorted edge-bridged trigonal bipyramid. With a C(8)-Os-C(8) bond angle of 155.4 (3)°, the geometry is approximately half-way between the two. The phosphine ligands are mutually trans to each other and cis to the Os-W bond in the solid state, and are slightly bent away from the W(CO)\textsubscript{5} fragment (P-Os-P = 175.83 (5)°); presumably this decreases steric interactions with the radial carbonyls on W. A trans arrangement
of the phosphines also minimizes the steric interactions between the PMe₃ groups. However, the concentration of this isomer in solution is approximately equal to that of an isomer in which the PMe₃ ligands are cis to each other with one trans and one cis to the metal-metal bond (see below). More favorable polar interactions in the solid state may cause preferential crystallization of the trans isomer. Interestingly, in 2, it is the isomer in which the PMe₃ is trans to the metal-metal bond that is found in the solid state, and is the more highly populated in solution as well.⁸

The Os-W bond length in 1 is 3.1417 (6) Å. This can be compared to the Os-W bond length of 3.0756 (5) Å in (Me₃P)(OC)₄Os-W(CO)₅ (2).⁸ It is uncertain whether the increased bond length is caused by steric or electronic effects. Based on a steric argument, two PMe₃ ligands cis to the Os-W bond would be expected to result in significant steric strain between the Os and W fragments. This is consistent with our inability to prepare the Cr derivatives since the Os-Cr dative bond would be expected to be ca 0.1 Å shorter than an Os-W dative bond (e.g., the Os-M bond length in (Me₃P)(OC)₄OsCr(CO)₅ is 2.9787 (14) Å⁸ compared to 3.0756 (5) Å in 2). On the other hand, there are several electronic arguments which may be used to account for the longer Os-W bond in 2. The increased electron density on Os(CO)₃(PMe₃)₂ compared to Os(CO)₄(PMe₃) may cause an increase in electron-electron repulsion between the Os and W fragments. The filled t₂g set of orbitals on the Os fragment are of the
correct symmetry and energy to interact with the filled $t_{2g}$ set of orbitals on the W fragment. This would result in a destabilizing two-orbital four-electron interaction; this would cause the metal-metal bond to be weakened and, hence, lengthened. Evidence suggests that poorer $\sigma$-donor and better $\pi$-acceptor phosphorus ligands on Os do indeed result in a stronger metal-metal bond (see below). Similar observations have been made in $(L)(OC)_4$Os[Os$_2$(CO)$_{11}$] complexes. However, there may be an optimal limit. For example, in $\{(H)[(MeO)_3P](OC)_3FeW(CO)_5\}^-$, the dative Fe-W bond is 0.023 Å shorter than in the the carbonyl derivative $\{(H)(OC)_4FeW(CO)_5\}^-$. In a different way, it may be argued that in 2 (with the PMe$_3$, trans to the $\sigma$-donor orbital on Os) the PMe$_3$, ligand donates two electrons directly into the orbital on Os which interacts with the empty $a_1$ orbital on W(CO)$_5$. Calculations have shown that PMe$_3$, versus CO in a position trans to the metal-metal bond raises the energy of the donor orbital above that of a pure "d" orbital by mixing in of "p" character. Thus, the directional characteristics and energy of the donor orbital in Os(CO)$_4$(PMe$_3$) (in a square pyramidal geometry with PMe$_3$, at the apex) should be better suited for bonding to W(CO)$_5$, than in Os(CO)$_3$(PMe$_3$)$_2$ (in a square pyramidal geometry with the two PMe$_3$, ligands trans in the basal
plane). Given that basicity increases from first row to third row transition metals, it might also be argued that the W(CO), group cannot easily accommodate the more nucleophilic Os(CO), PM,e, species. This argument, however, would suggest that the Cr derivatives should be more stable; this is not consistent with the experimental results. It is likely that both steric and electronic factors combine to cause the metal-metal bond to be longer in 1 than in 2. Evidence will be presented below which suggests that the two-orbital four-electron destabilizing interaction is of greater significance.

The W-Cax bond length (1.95 (1) Å) in 1 is significantly shorter than the W-Ceq bond lengths (2.032 (7) to 2.034 (7) Å). This can be attributed to increased π-backbonding to the axial carbonyl. Although the difference is barely significant, a lengthened axial C-O bond (1.17 (1) Å) compared to the equatorial C-O bond lengths (1.139 (8) to 1.12 (1 Å) is consistent with this interpretation. Similarly lengthened M-Cax bond lengths were found in (Me3P)(OC),OsM(CO), (M = Cr, W)8 and (η5-C5Me5)(OC),IrW(CO), complexes,95 and in [(R)FeM(CO)],- (R = H, Ph3Au; M = Cr, W).79 Interestingly, the W-Cax bond length in 2 (1.965 (8) Å) is not significantly different from that in 1.

Structure of (Pc),OsOs(CO),W(CO), (Pc = P(OCH2),3CMe) (3). A view of the molecular structure of 3 is shown in Figure 3.4. Selected bond lengths and angles are given in Table 3.4. The lack of any bridging groups is evident from the figure. An electron count at each metal center indicates that the two
metal-metal bonds can be described as dative bonds. In this way, the Os(CO)$_4$ moiety acts as both a two electron acceptor and a two electron donor. This is the first example of a complex with dative bonds in tandem. The coordination geometry around each metal center is approximately octahedral. The terminal Os and W fragments are rotated with respect to the central Os(CO)$_4$ group such that the radial carbonyls and Pc ligands are staggered with respect to the radial ligands on the adjacent metal centers. The Os-Os-W angle is 172.07 (4)$^\circ$, virtually identical to the P-Os-W
angle in 2 (171.31 (4)°). The bent M-M-M backbone in 3 is unusual for trimetallic chain-like complexes. The equatorial carbonyls on Os(1) lean inward towards Os(2), though the angle, 162.5 (9)°, is less than that in (Me₃P)₂(OC)₃OsW(CO)₅ (1). Since the Os(CO)₃(PC)₂ group is expected to be a poorer electron donor than Os(CO)₃(PMe₃)₂, the decreased inward leaning in 3 may be attributable to decreased dπ-π* interaction between the carbonyls on Os(1) and the Os(2) metal center (see above). Given the respective cone angles of PMe₃ and PC (118° and 101°) the difference may also be attributed to greater steric interactions in 1 versus 3. The radial carbonyls of Os(CO)₄ also lean inward towards the W(CO)₅ fragment; the C(24)-Os(2)-C(22) and C(23)-Os(2)-C(21) angles are 168.8 (9)° and 165.0 (9)°, respectively. Since there are no apparent steric interactions that cause CO(24) and CO(22) to lean inward, this provides some support for the dπ-π* bonding argument (see above). The greater inward leaning of CO(23) and CO(21) may, however, be at least partially attributable to steric interactions with the phosphite ligands. The trans C-W-C angles are very nearly linear (177 (1)° to 178 (1)°).

The Os-Os bond length (2.940 (1) Å) is similar to the Os-Os dative bond lengths found in the three independent molecules in the unit cell of (OC)₅OsOs(CO)₃(Cl)(GeCl₃) (2.916 (2), 2.927 (2), 2.931 (2) Å), and the covalent Os-Os bond lengths in the linear molecules Os₃(CO)₁₂(SiCl₃)₂ (2.9120 (9) Å) and Os₃(CO)₁₂(I)₂ (2.935 (2) Å). The Os-W distance is 3.039 (1) Å;
this is shorter than the dative Os-W bonds in either 2 or 1. A reason for the shorter bond in 3 is not apparent. For example, the relative donor ability of Os(CO)$_4$(L) ($L = Os(CO)$_4$(Pc)) compared to Os(CO)$_4$(PMe$_3$) or Os(CO)$_3$(PMe$_3$)$_2$ is unknown. The steric interaction between the Os(2) and W fragments in 3 is expected to be very similar to that in (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (2). The shorter Os-W bond in 3 may possibly account for the increased stability of 3 compared to other bimetallic complexes with dative bonds between osmium and tungsten (see below).

Spectroscopic Properties of (L)(L')(OC)$_3$OsM(CO)$_5$ Complexes, and WOs$_2$(CO)$_2$(Pc)$_2$ Complexes; Carbonyl Site Exchange and Isomerization of (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$ (1). An Infrared spectrum of 1 (in CH$_2$Cl$_2$) is shown in Figure 3.5. The IR spectra of all the complexes with dative metal-metal bonds exhibit CO stretching bands attributable to terminal carbonyls only. This indicates that the unbridged metal-metal bonds observed in the solid state structures are maintained in solution. There are three more $\nu$CO bands in the spectrum of 1 than in its monosubstituted analogue (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (2); the greater number of bands can be attributed to the nearly equal population of two isomers (see below). If coupling of CO stretching vibrations between those on the donor half and those on the acceptor half of the molecule is neglected, six bands would be expected for each of the isomers (three bands for the mer-Os(CO)$_3$(L)$_2$ fragment in each isomer, and three for a $C_{4v}$ W(CO)$_5$ fragment). It is likely that some of these bands are not resolved in
Figure 3.5. Carbonyl Stretching Region of the Infrared Spectrum of (Me₃P)₂(OC)₃OsW(CO)₅ (1) in CH₂Cl₂.
CH$_2$Cl$_2$, but the observation of eight bands in the CO stretching region may be taken to indicate the presence of isomers. The spectra of the bis-substituted (dmpe)(OC)$_3$OsW(CO)$_5$ and [(o-tolO)$_3$P](Me$_3$P)(OC)$_3$OsW(CO)$_5$ complexes which exist as only one isomer in solution (see below) with one phosphorus bonded cis the Os-W bond and one trans to the Os-W bond, exhibit a six band pattern; the two additional bands in 1 must therefore be derived from a second isomer. The intense low energy band at 1906 cm$^{-1}$ is assigned to an e mode of the W(CO)$_5$ group based on a comparison to spectra of W(CO)$_5$(L) complexes. A similar assignment has been made in [HFeW(CO)$_9$]$^-$ complexes.$^{79}$ The energy of this band can thus be taken as a measure of the electron donating ability of a ligand attached to an M(CO)$_5$ group. Accordingly, this band is shifted from 1913 cm$^{-1}$ in 2 to 1906 cm$^{-1}$ in 1. A similar shift to low energy was observed for other bis-substituted derivatives (see Table 3.1). In the monosubstituted derivatives (L)(OC)$_4$OsM(CO)$_5$, the same band is shifted to the highest energy when L is P(OCH$_2$)$_3$CMe. This indicates that amongst the phosphorus ligands, P(OCH$_2$)$_3$CMe is the weakest $\sigma$-donor or the strongest $\pi$-acceptor.

The infrared spectrum in the $\nu$CO region of (Pc)$_2$(OC)$_3$Os-Os(CO)$_4$W(CO)$_5$ (3) in CH$_2$Cl$_2$ (Figure 3.6) shows seven clearly distinguishable bands and one shoulder band. Since there appears to be only one isomer of 3 in solution (see below), and again if it is assumed that no vibrational coupling of the carbonyls of one metal fragment with those of the adjacent metal fragment

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Figure 3.6. Carbonyl Stretching Region of the Infrared Spectra of $(\text{Pc})_2(\text{OC})_3\text{OsOs(OC)}_3\text{W(CO)}_5$ (3) (left) and $(\text{Pc})(\text{OC})_4\text{OsOs(OC)}_3(\text{Pc})\text{W(CO)}_5$ (4) (right) in $\text{CH}_2\text{Cl}_2$. 
occurs, seven IR bands are predicted in the CO stretching region. Broadening of some of the bands and the presence of a shoulder on one band may be attributable to vibrational coupling. (The bands are also expected to be broadened in CH2Cl2.) The two lowest energy bands can be assigned to the carbonyls on W by analogy to the bimetallic complexes. They can also be assigned with reasonable certainty by comparison to the spectrum of \((\text{Pc})(\text{OC})_4\text{OsOs(CO)}_3(\text{Pc})\text{W(CO)}_5(4)\), an isomer of 3, shown in Figure 3.6. Interestingly, the intense bands at 1902 cm⁻¹ and 1904 cm⁻¹ in 3 and 4, respectively, occur at slightly lower energy than that in \((\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5(1)\). This is surprising since it is likely that more electron density is being donated to \(\text{W(CO)}_5\) in 1 than in either 3 or 4. Comparison of the spectra of 3 and 4 reveals that the most intense of the low energy bands (e \(\text{W(CO)}_5\)) is shifted to slightly higher energy in 4 than in 3; this result is again surprising since the central Os moiety in 4 would be expected to be more electron rich than that in 3, and hence be a better electron donor. Delocalized bonding along the trimetallic chain may account for the difference in \(\nu\text{CO}\) bands in 3 and 4 as well. It is possible that the Os-W bond in 4 is slightly longer than that in 3 due to the cis Pc ligand: this would result in less electron density being donated to W, and thus result in the higher \(\nu\text{CO}\) stretching frequency in 4. Unfortunately, attempts to grow a suitable quality crystal of 4 for X-ray diffraction studies were unsuccessful.
The UV/VIS spectra of some of the complexes with metal-metal dative bonds were recorded. Values of $\lambda_{\text{max}}$ are given in Table 3.5 (page 95). A typical spectrum is shown in Figure 3.7. The spectra of the complexes all exhibit a near-UV absorption between 360 nm and 380 nm that can likely be attributed to a $\sigma \rightarrow \sigma^*$ transition associated with the metal-metal bond. In this respect these complexes are similar to bimetallic complexes that contain covalent metal-metal bonds such as $\text{Mn}_2(\text{CO})_6$. Further discussion of the UV/VIS data is given in the discussion on bonding and stability (see below).

**Figure 3.7.** UV/VIS Spectrum of $[(\text{MeO})_3\text{P})(\text{OC})_4\text{OsW(CO)}_5]$. 

$\lambda_{\text{max}} = 366.4$ nm

$\varepsilon = 3266$ L\(\cdot\)mol\(^{-1}\)\(\cdot\)cm\(^{-1}\)
With the exception of \([(o-tolO)P(Me_3P)(OC)_3OsW(CO)_5\), (6), the $^{13}$C NMR spectra of the bimetallic complexes ($^{13}$CO enriched) indicated the presence of two isomers in solution. The $^{13}$C NMR spectra of \([MeC(CH_2O)_2P](OC)_3OsCr(CO)_5\), (8) and 1 are shown in Figures 3.8 and 3.9, respectively, as representative examples. Spectra of other \((L)(OC)_3OsM(CO)_5\), and \(LL'(OC)_3OsM(CO)_5\), \((L = P(OMe)_3, P(OCH_2)_3CMe; M = Cr, W)\) complexes are given in the Appendix.) The spectral assignment of 8A is straightforward based on the signal intensities, the characteristic region of the carbonyls, and on $^{31}$P coupling. In this way, the signal at $\delta$ 230.1 of relative intensity one can be assigned to the axial carbonyl on Cr in isomer 8A. We have found that, for these complexes, the resonance for the CO trans to the metal-metal bond on the acceptor fragment always occurs at the lowest field; the only exception is in isomer 1B of \((Me_3P)_2(OC)_3OsW(CO)_5\). The resonance at $\delta$ 222.6 of relative intensity four can be unambiguously assigned to the four equivalent radial carbonyls b on Cr. Finally, the signal at $\delta$ 184.6 of relative intensity four can be unequivocally assigned to the four
Figure 3.8. $^{13}$C NMR Spectrum of $[\text{MeC(CH}_2\text{O})_3\text{P}]_2\text{P(OC)}_4\text{OsCr(CO)}_5$ (8). The remaining signals in the spectrum can be assigned to isomer 8B in a similarly straightforward way. That the four radial carbonyls on Cr in 8B
Figure 3.9. $^{13}$C NMR Spectrum of (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$ (1); Asterisk: W(CO)$_6$.

are equivalent indicates that there is unrestricted rotation about the metal-metal bond. This is consistent with the MO bonding description (see below). The assignment of the resonance at $\delta$ 179.9 to carbonyl f of 8B is unambiguous due to the large trans $^{31}$P coupling. The resonance at $\delta$ 187.0 of relative
intensity two can then be assigned to carbonyls g; this leaves the $\delta$ 167.0 signal as due to carbonyl h that is trans to the metal-metal bond. In general, $^{13}$C resonances for carbonyls on the donor Os fragment that are trans to the metal-metal bond have been found to occur at unusually high fields. This can possibly be attributed to a deshielding effect brought about as a result of electron donation from the Os center to the group 6 metal center. Deshielding would ordinarily be expected to cause a downfield shift. However, changes in the $^{13}$C chemical shifts opposite to that expected from simple theory is a common problem in the study of metal-carbonyl derivatives. These anomalous changes have usually been rationalized in terms of changes in the $\Delta \varepsilon$ parameter in the paramagnetic contribution to the chemical shift.

The $^{13}$C NMR spectrum of $(\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5$ (1) can be assigned in a similar way. The spectrum is consistent with the presence of nearly equal concentrations of two isomers, 1A and 1B; i.e., the signals due to the radial carbonyls on W are of approximately the same area for both isomers (see Figure 3.9).
The chemical shift of the resonance assigned to carbonyl \( e \) (\( \delta 203.8 \)) (see illustration above) is unusual; this represents the only example among these complexes in which the \( ^{13}C \) resonance of the CO on the \( W(CO)_5 \) fragment that is trans to the dative metal-metal bond occurs at a higher field than the radial carbonyls on \( W \). The assignment of this resonance to the axial CO on \( W \) in \( 1B \) is based on the observation that the analogous CO in the monosubstituted complexes occurs at higher field in the isomer where the phosphorus ligand is cis to the metal-metal bond, \( i.e. \), isomer \( B \). The resonance at \( \delta 195.3 \) assigned to carbonyl \( c \) of \( 1A \) shows coupling to only one cis phosphorus ligand. It is likely that it is the coupling to the axial phosphorus ligand which is not observed; coupling between phosphorus and the radial carbonyls of \( 8A \) was also not observed. Isomers \( 1A \) and \( 1B \) are in equilibrium (see below). No evidence was detected for the presence of the third possible isomer in which the phosphine ligands would be mutually cis to each other and cis to the Os-W bond. Substitution of one \( PMe_3 \) with \( P[O(o-tol)]_3 \) yielded a complex (6) which exists in only one isomer form in solution: the \( ^{13}C \) NMR spectrum of 6 is shown in Figure 3.10.

The \( ^{13}C \) NMR spectra of \( (Pc)_2(OC)_3OsOs(CO)_4W(CO)_5 \) (3) and \( (Pc)(OC)_4OsOs(CO)_3(Pc)W(CO)_5 \) (4) are given in Figure 3.11, and the spectral assignments are as indicated on page 82. Assignment of the \( ^{13}C \) resonances for carbonyls on the Os centers is facilitated by \( ^{31}P \) coupling, and by the chemical shifts and intensities of the signals. For example, in 3 the resonance at
Figure 3.10. $^{13}$C NMR Spectrum of $\left[(o\text{-}t\text{o}1O)_3P\right]\left(\text{Me}_3P\right)\left(\text{OC}\right)_3\text{OsW(CO)}_5$ (6) in the Carbonyl Region.
Figure 3.11. $^{13}$C NMR Spectra of $(\text{Pc})_2(\text{OC})_3\text{OsOs(CO)}_3\text{W(CO)}_5$ (3) (top) and $(\text{Pc})(\text{OC})_4\text{OsOs(CO)}_3(\text{Pc})\text{W(CO)}_5$ (4) (bottom).
δ 193.3 of intensity four shows no 31P coupling and is in the region of the spectrum associated with carbonyls attached to osmium;48 it can, therefore, be assigned to the four equivalent carbonyls on the central Os. The 13C signals of the carbonyls on the terminal Os center can be likewise assigned based on chemical shifts, 31P coupling, and intensities. The resonance for the axial CO of the terminal Os occurs as a triplet at δ 165.6, consistent with previous observations (see above). The 13C resonances of the axial and radial carbonyls on W can be unambiguously assigned based on chemical shifts, 183W coupling, and intensities; these occur at δ 206.4 and δ 204.1, respectively. Thus, the solution 13C NMR spectrum of 3 is consistent with the solid state structure. It is interesting that 3 exists as only one isomer in solution. Since two isomers of (Me3P)2(OC)3OsW(CO)5 were observed in solution (see above), the lack of a second isomer of 3 cannot be the result of steric repulsion since the cone angle of PMe3 is 118° while that of P(OCH2)3CMe is only 101°.96 The necessarily electronic reasons for the absence of a cis-axial,equatorial isomer are not apparent. The 13C NMR spectrum of 4 is consistent with the presence of two isomers, 4A and 4B; 4A is the dominant form in solution. (The concentration of 4B was not sufficient to detect resonances for single nonequivalent carbonyls.) It is noteworthy that the equivalence of the radial carbonyls on W in 4A and 4B indicates free rotation about the Os-W bond, while the equivalence of the four radial carbonyls on the terminal Os in 4A indicates that there is also free rotation about the Os-Os bond.
Carbonyl Site Exchange and Isomerization in Complexes with Dative Metal-Metal Bonds. The $^{13}$CO label was introduced into all the complexes discussed in the previous section via labeled M(CO)$_6$ starting material for the bimetallic complexes, and by $^{13}$CO labeled [MeC(CH$_2$O)$_3$P](OC)$_4$OsW(CO)$_5$ for 3. Migration of the $^{13}$CO from the W center to the Os center is thought to occur via the well known bridge-terminal exchange process (Scheme I).

**Scheme I.**

![Chemical structure](image)

Previous studies have shown that the exchange does not involve an intermolecular process. Thus, introduction of free $^{13}$CO to a sample that contained unlabeled (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (2) in solution showed no evidence (by $^{13}$C NMR) for incorporation of $^{13}$CO into the complex. In 1, this process may only be accessible for isomer 1B. In 1A the all cis isomer, (1C) (see below), would have to be an intermediate. No evidence for the existence of 1C has been observed, although this does not rule out the possibility that it may be present at a concentration that is too low to detect by NMR spectroscopy. However, if the assumption is made that 1c is an energetically unfavorable isomer, then bridge-terminal exchange should not be possible.
from 1A. Therefore, it was thought that the use of a phosphorus ligand with a large cone angle in place of one of the PMe3 groups might force the bimetallic complex to exist in only the isomer form of 1A, and this would not allow CO migration via the bridge-terminal exchange process. Substitution of one PMe3 in 1 with P[O(o-tol)]3 (cone angle = 141°) does indeed yield a complex (6) that, by 13C NMR, exists only in the form of isomer 1A in solution. However, as indicated by the fact that a good 13C NMR spectrum could be obtained for 6 (see Figure 3.10), the 13CO was clearly able to migrate from the labeled W(CO)5 group to Os. Unfortunately, these results do not preclude the possibility that 6 may exist in the same form as 1B at very low concentration (i.e., the concentration of the isomer may be too low for detection by NMR methods), and that during that time the carbonyls can migrate freely in the horizontal plane. It was thought that a chelating phosphine ligand on Os might sort this problem out since a trans phosphine isomer (i.e., like 1B) would not be possible (see below). If it is again assumed that an isomer like 1c is not accessible, then CO migration should not
be possible via the proposed bridge-terminal exchange process. The lack of CO migration would suggest that the exchange mechanism and the isomerization process (see below) are perhaps interrelated. While the dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) derivative has been isolated (see Table 3.1), attempts to prepare sufficient quantities of Os(CO)$_3$(dmpe) to make this study possible were unsuccessful. In addition to the use of chelating ligands, other phosphine/phosphite substituted Os donor complexes (e.g., Os(CO)$_3$(PMe$_3$)(Pc), Os(CO)$_3$(Pc)$_2$, etc...) may yield valuable information about the exchange and isomerization processes; i.e., phosphorus ligands of different sizes and with different electronic properties may preferentially adopt one isomer form over another, and this may have an effect on the ligand exchange and isomerization processes. Work is in progress in this area.

Given that very low energy barriers for carbonyl exchange in the equatorial planes of (OC)$_5$M[Os(CO)$_3$(PR$_3$)]$_2$ (M = Cr, W) clusters have been observed (see Chapter 5), it is noteworthy that CO exchange in the unobstructed equatorial plane of (Pc)$_2$(OC)$_3$OsOs(CO)$_4$W(CO)$_5$ (3) is not rapid on the NMR time scale.
at room temperature. The activation energy for the exchange process in clusters as well as in bimetallic complexes seems to be related to the electron density on the metal centers. For example, CO exchange is rapid on the NMR time scale at ambient temperature in \((\eta^5-C_5Me_5)(OC)_{2}IrW(CO)_5\)\(^9\) and \([FeCr(CO)_5]^{2-}\).\(^7\)

It has been shown previously that the two isomers of \((Me_3P)(OC)_4OsW(CO)_5\)\(^2\) (2) are in rapid equilibrium, and that the equilibrium occurs via an intramolecular process.\(^8\) Similarly, a \(^1\)H spin saturation transfer experiment on \((Me_3P)_2(OC)_3OsW(CO)_5\) (1) (Figure 3.12) showed that 1A and 1B are in rapid equilibrium on the NMR time scale. Saturation of the signal at \(\delta 1.78\) corresponding to 1A caused transfer to the "triplet" signal at \(\delta 1.86\) assigned to 1B. By analogy to 2, it is assumed that the isomerization takes place intramolecularly, presumably via a trigonal-twist process at the Os center (Scheme II).

It has been found that in the monosubstituted complexes \((L)(OC)_4OsM(CO)_5\), the isomer ratio is intimately related to the steric bulk of the phosphorus ligand and the length of the metal-metal bond.\(^8\) Those complexes substituted with bulky ligands (e.g., \(PPh_3\), \(PMe_2Ph\)) exist almost entirely in the form in which the bulky ligand is trans to the metal-metal bond (i.e., like that in isomer 8A (see page 75)). In contrast, when \(L\) is \(P(OCH_2)_3CMe\) the A:B isomer ratio in \([MeC(CH_2O)_3P](OC)_4Os-W(CO)_5\) (5) is only 1.5:1. In addition, while the isomer ratios of the Mo and W derivatives are very similar (probably due to the nearly equal covalent radii of Mo and W), the trans form is
Figure 3.12. $^1$H Spin Saturation Transfer Spectrum of (Me$_3$P)$_2$(OC)$_3$OsW(CO)$_5$. Spectrum A is the $^1$H NMR spectrum of 1 in the phosphorus methyl region. The arrow indicates the signal saturated. B is the difference spectrum after irradiation that shows saturation transfer to the other signals.

Scheme II.
significantly more favored for the Cr derivatives. Since the substituents on phosphorus are splayed out towards the adjacent radial carbonyls on W in the cis form but are directed back from the radial carbonyls on Os in the trans form, the isomer ratio dependence upon the cone angle of the phosphorus ligand and the Os-M bond length is as anticipated. Similar conclusions can be made for 4 in which the dominant isomer has the Pc ligand on the terminal Os trans to the Os-Os bond. The results for the P(OMe), complexes may seem anomalous since this ligand has a smaller cone angle than PMe,\(^3\). For example, the A:B isomer ratio is 13.5:1 when L is P(OMe), but only 3.3:1 for PMe,\(_3\). These observations can, however, be readily rationalized if the protrusion of the methyl groups beyond the O-P-M-P-O angle (i.e., the angle used to determine the cone angle) is taken into account.\(^3\) Thus, the P(OMe), ligand is expected to have a greater preference for the least sterically crowded position. Theoretical calculations suggest that the position trans to the metal-metal bond will be the electronically preferred position for an electron donor ligand as well.\(^9\)

Similar conclusions concerning ligand site preference can be made for the bis-substituted bimetallic complexes. In 1, the steric interactions of PMe, with the four radial carbonyls on W in 1A must be approximately equal to those between two cis PMe, ligands in 1B; i.e., the A:B isomer ratio is ca 1:1. The nearly equal A:B isomer ratio in 1 may also be the result of electronic factors. For example, isomer A with one phosphorus ligand trans
to the metal-metal bond may be the preferred geometry for electronic reasons (see above), but the electronic factors may be nearly equal to the unfavorable steric interactions between the two cis phosphine ligands. Thus, the electronic factors which favor isomer A may be equally balanced by unfavorable steric factors which tend to favor isomer B.

Substitution of one of the PMe₃ ligands with P[O(O-tol)], yielded a complex which, by ¹³C NMR spectroscopy (see Figure 3.10 above), existed as only one isomer in solution with the phosphite trans to the metal-metal bond. (The magnitude of the ³¹P-¹³C coupling of a phosphine to a trans CO is usually substantially less than 100 Hz, while the coupling of a phosphite to a trans CO is usually substantially greater than 100 Hz in these complexes.) The trans ³¹P-¹³C coupling in 6 (67.4 Hz) indicates that the PMe₃ is trans to a CO, and that the P[O(O-tol)], must, therefore, be trans to the metal-metal bond. As was found in the monosubstituted complexes, these results indicate that a radial position on Os that is cis to the metal-metal bond is sterically more crowded than the position trans to the metal-metal bond.

Since one phosphorus ligand must necessarily be cis to the metal-metal bond in the bis-substituted complexes, this conclusion is also consistent with our inability to prepare the Cr analogues. However, there may be an as yet unrecognized electronic preference for one site versus another. For example, the BuNC ligands in the thermodynamically preferred isomer of
(Bu<sup>1</sup>NC)<sub>2</sub>(OC)<sub>3</sub>OsCr(CO)<sub>5</sub> are both mutually cis to each other and cis to the metal-metal bond. In addition, it was noted above that the phosphorus ligand with the smallest cone-angle (P(OCH<sub>2</sub>)<sub>3</sub>CMe) occupied only radial sites on the terminal Os in ((Pc)<sub>2</sub>(OC)<sub>3</sub>OsOs(CO)<sub>4</sub>W(CO)<sub>5</sub>) (3). However, the electronic preference in 3 may be intrinsically associated with the linear trimetallic structure (see above). We have observed what appears to be an electronic preference for various isomers in clusters (see Chapter 4). A study of bis-substituted complexes such as (Me<sub>3</sub>P)(Pc)(OC)<sub>3</sub>OsW(CO)<sub>5</sub> may reveal some information concerning electronic versus steric effects on the isomer ratios in these complexes. Work is in progress in this area.

Bonding in Complexes with Dative Metal-Metal Bonds. A covalent metal-metal bond with a bond order of one is formed by the combination of two radical fragments, each of which donates one electron to the bonding molecular orbital. A typical example is Mn<sub>2</sub>(CO)<sub>10</sub>: the bonding has been described by an orbital interaction diagram as shown in Figure 3.13. Typically, complexes with metal-metal bonds are colored due to absorption of visible light. The frequency of the absorbed radiation corresponds to the energy required to effect the transition of a σ-bonding electron to the σ-antibonding level. The photochemistry of complexes with covalent metal-metal bonds can be almost entirely explained in terms of these σ→σ* transitions. The dative metal-metal bond description is similar except that both bonding electrons come from only one metal center: an orbital interac-
tion diagram clearly distinguishes the dative bond as resulting from the overlap of frontier orbitals of \( \sigma \)-symmetry between the donor HOMO and the acceptor LUMO (see Figure 3.13b).\(^9\) This bonding description readily accounts for the insolubility and color of complexes with dative metal-metal bonds. Since the \( \sigma \)-acceptor and \( \sigma \)-donor orbitals are not at the same energy, the bonding electrons will be localized more on the donor than on the acceptor. Williams and Marder have carried out calculations on these complexes; they concluded that in \((OC)_{5}OsOs(CO)_{3}(Cl)-(GeCl_{3})\) the electron density is largely localized on the Os(CO)$_{5}$ fragment (see Figure 3.14).\(^9\) Halpin and Hall reached the same conclusions for \([HFe(CO)_{4}Mo(CO)_{5}]^{-}\).\(^{80}\) The unequal distribution of electron density between the metal atoms causes the

\[\text{Figure 3.13. Orbital Interaction Diagrams for Covalent (a) and Dative (b) bonds.}\]
Figure 3.14. Electron Density Map for the Dative Metal-Metal Bond in (OC)₅OsOs(CO)₃(Cl)(GeCl₃).

metal-metal bond to be polar, this accounts for the low solubility in nonpolar solvents. The similarity in the bonding descriptions for complexes with covalent and dative metal-metal bonds suggests that $\sigma \rightarrow \sigma^*$ electron transitions should also be observed for the latter complexes. Indeed, a near-UV absorption was observed for each of the complexes studied. This is consistent with the yellow color observed for all of the complexes prepared to date. A typical UV/VIS spectrum is shown in Figure 3.7 (p 74). The energy of the $\sigma \rightarrow \sigma^*$ transitions can be correlated with the strength of the metal-metal bond (see below).
Stability of Bimetallic Complexes with Dative Metal-Metal Bonds. The initial reason for the study of complexes with dative metal-metal bonds beyond those already known was to determine the effect on the strength of the metal-metal bond caused by a change in electron density at the Os donor center. It was expected that increasing the electron density at the Os center would result in a stronger metal-metal bond. Theoretical arguments also suggest that substitution of the CO trans to the metal-metal bond on the donor species with a good electron donor should increase the stability of the metal-metal bond. However, contrary to expectations, it has been found that an increase in the electron density on the donor Os can in some cases actually destabilize the metal-metal bond.

Studies have indicated that the energy of the $\sigma \rightarrow \sigma^*$ transition can be related to the strength of a metal-metal bond. This relationship results because a strong sigma bond yields a $\sigma$-bonding orbital of low energy, and a $\sigma$-antibonding orbital of correspondingly high energy. Thus, $\Delta E(\sigma \rightarrow \sigma^*)$ will be large. By the same argument, $\Delta E(\sigma \rightarrow \sigma^*)$ will be small for a weak bond. Accordingly, we have found that the energy of the $\sigma \rightarrow \sigma^*$ transition in the bimetallic complexes with dative metal-metal bonds roughly parallels the chemical stability of the complexes. A list of several closely related bimetallic complexes arranged in order of increasing $\lambda_{max}$ (i.e., decreasing $\Delta E(\sigma \rightarrow \sigma^*)$) is given in Table 3.5. Among the monosubstituted P(OMe), complexes of Cr, Mo, and W, the chromium derivative is expected to have
Table 3.5. Electronic Absorption Maxima ($\lambda_{\text{max}}$) of Selected Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$<a href="%5Ctext%7BOC%7D">(\text{MeO})_3\text{P}</a>_4\text{OsMo(CO)}_5$</td>
<td>360.0</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BOC%7D">\text{MeC(CH}_2\text{O})_3\text{P}</a>_4\text{OsW(CO)}_5$</td>
<td>362.5</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BOC%7D">(\text{MeO})_3\text{P}</a>_4\text{OsW(CO)}_5$</td>
<td>364.0</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5$</td>
<td>365.5</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BMe%7D_3%5Ctext%7BP%7D">(\text{o-tolO})_3\text{P}</a>(\text{OC})_3\text{OsW(CO)}_5$</td>
<td>369.0</td>
</tr>
<tr>
<td>$(\text{dmpe})(\text{OC})_3\text{OsW(CO)}_5$</td>
<td>369.5</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5$</td>
<td>370.3</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BOC%7D">(\text{MeO})_3\text{P}</a>_4\text{OsCr(CO)}_5$</td>
<td>402.0</td>
</tr>
</tbody>
</table>

the weakest metal-metal bond based on the trends in metal-metal bonding. In agreement with this prediction, the near-UV absorption for the Cr complex (402 nm) is indeed at lower energy than those for the Mo and W derivatives. The Cr complex is correspondingly bright yellow, the W complex is light yellow, and the Mo complex is pale yellow.

Experimental observations also support the conclusion that the metal-metal bond is weakest in the Cr derivatives. A series of infrared spectra of $[(\text{MeO})_3\text{P}](\text{OC})_4\text{OsCr(CO)}_5$ (in CH$_2$Cl$_2$) recorded over ca 45 min is shown in Figure 3.15. The spectra indicate that after only 5 min there is considerable decomposition resulting in the formation of Cr(CO)$_6$. After 45 min, the bimetallic complex is essentially decomposed. (The decomposition is likely catalyzed by O$_2$ since a degassed solution
Figure 3.15. Changes in the Infrared Spectrum of $(\text{MeO})_3P(\text{OC})_4\text{OsCr(CO)}_5$ in $\text{CH}_2\text{Cl}_2$ as a Function of Time.
showed little decomposition after several days.) In contrast, after 30 min the decomposition of the Mo derivative is approximately equal to that of the Cr derivative after only 10 min under the same conditions. Furthermore, \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\), which is expected to have a weaker metal-metal bond than the \(\text{P(OMe)}_3\) derivative (see above), is only slightly decomposed after 85 min, and remains largely intact after 3 h under these conditions. In addition to the difference in decomposition between the Cr and W analogues, it was found that the Os-Cr bond in \([(\text{MeO})_3\text{P})(\text{OC})_4\text{OsCr(CO)}_5\] was displaced by \(\text{PPh}_3\) after only 1 h whereas displacement of the Os-W bond in \([(\text{MeO})_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\] required more than 29 h. It is noteworthy that the displacement reactions were carried out under ambient light: no reaction was observed under the same conditions in the absence of light. The observed stability of the complexes, therefore, parallels the general trends in covalent metal-metal bonding between first row and third row transition metals.\(^{10a}\) A possible decomposition pathway is given in Scheme III.\(^8\) Although the \(\lambda_{\text{max}}\) values lead to the conclusion that \([(\text{MeO})_3\text{P})(\text{OC})_4\text{OsMo(CO)}_5\] should be more stable than \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\), the lower chemical stability of the Mo complex may be the result of either a different decomposition pathway \((i.e.,\ loss\ of\ a\ ligand)\) or the result of kinetic rather than thermodynamic instability.

A comparison of the series of monosubsstituted W derivatives \((\text{L})(\text{OC})_4\text{OsW(CO)}_5\) shows that the highest energy \(\sigma \rightarrow \sigma^*\) transition is observed when \(\text{L}\) is \(\text{P(OCH}_2)_3\text{CMe}\), and the lowest when \(\text{L}\) is
PMe₃, with that for the P(OMe)₃ complex half-way between. Thus, [MeC(CH₂O)₃P](OC)₄OsW(CO)₅ (5) would be expected to have the strongest metal-metal bond, and (Me₃P)(OC)₄OsW(CO)₅ the weakest in this series. There is experimental evidence to support this conclusion. For example, the decomposition of 5 is at most only very slow at 90 °C since 3 is prepared from 5 at this temperature over a 6 d period. On the other hand, the P(OMe)₃ and PMe₃ derivatives either decompose or form heterotrimetallic clusters under much milder conditions (see Chapter 4). Since the cis to trans isomer ratio for [MeC(CH₂O)₃P](OC)₄OsW(CO)₅ (5) is much greater than that for (Me₃P)(OC)₄OsW(CO)₅ (2) (see NMR discussion above), it might be assumed that steric interactions do not cause weakening of the metal-metal bond. However, it is possible that decomposition only occurs from the cis isomer of (Me₃P)(OC)₄OsW(CO)₅, in which unfavorable steric interactions are maximized. Electronic factors may also be responsible for the observed trend: this would be consistent with the foregoing discussion concerning two-orbital four-electron interactions.
between the two metal centers (see Molecular Structure section). That is, P(OCH₃)₃CMe would be expected to cause the least destabilization and PMe₃ the most; P(OMe)₃ would be intermediate between these two. Weakening of the metal-metal bonds in clusters⁴⁸a and bimetallic complexes¹⁰³c has been observed upon substitution of CO (a relatively poor electron donor) with better electron donor PR₃ groups. Again, steric and electronic effects cannot be separated based on the limited data.

A final comparison between the UV/VIS data for monosubstituted and bis-substituted complexes of osmium and tungsten leads to the prediction that the Os-W bonds in the latter complexes are weaker than in the former compounds given that the \( \sigma \rightarrow \sigma^* \) transitions are lower in energy for the bis-substituted derivatives. Again, experimental evidence supports this interpretation. In CH₂Cl₂, \((\text{Me}_3\text{P})_2(\text{OC})_3\text{OsW(CO)}_5\) (1) was found to be substantially less stable than \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) (2). In this case, and that of the other bis-substituted complexes, it is uncertain whether the Os-W bond is weakened due to increased steric interactions or electronic factors. In the bis-substituted complexes, one of the phosphorus ligands is forced into a position cis to the metal-metal bond; this undoubtedly results in unfavorable steric interactions which could weaken the metal-metal bond. On the other hand, the metal-metal bond may be weakened as a result of a more pronounced two-orbital four-electron interaction as discussed above. As was discussed previously in the description of the molecular structure of 1,
it is not possible to separate the two effects based on the limited experimental data. It is interesting to note that among the bis-substituted derivatives, the lowest energy $\sigma \rightarrow \sigma^*$ transition is associated with 1. This may be because the Os-W bond is weakened by the presence of two cis phosphines in isomer 1B (see page 88) while only one phosphine is cis to the Os-W bond in the two other bis-substituted complexes, or because of the increased electron density on the Os in 1.

Like the monosubstituted complexes, the dative metal-metal bond in 1 is displaced by the two electron donor PPh$_3$ in a degassed CH$_2$Cl$_2$ solution over ca 21 h (equation 3.2). The products were identified by their characteristic carbonyl stretches in the IR spectrum.\textsuperscript{105} Reaction of 1 with CO (2 atm) in CH$_2$Cl$_2$ also resulted in displacement of the Os-W bond; the products, identified by infrared spectroscopy, were mainly W(CO)$_6$ and Os(CO)$_3$(PMe$_3$)$_2$. Unlike the monosubstituted derivatives, 1 decomposes in CH$_2$Cl$_2$ to give either Os(CO)$_2$(PMe$_3$)$_2$(Cl)$_2$ or Os(CO)$_2$(PMe$_3$)$_2$(CO$_3$) (see Chapter 2). In addition, Os(CO)$_3$(PMe$_3$)$_2$ was not displaced from 1 by Os(CO)$_4$(PMe$_3$) in CH$_2$Cl$_2$ solution before decomposition occurred.

\textbf{Stability of Trimetallic Complexes with Dative Metal-Metal Bonds.} The formation of linear trinuclear complexes

\begin{equation}
\text{Me}_3\text{P}_2(\text{OC})_3\text{OsW(CO)}_5 + \text{PPh}_3 \rightarrow \text{Os(CO)}_3(\text{PMe}_3)_2 \quad (3.2)
+ \text{W(CO)}_5(\text{PPh}_3)
\end{equation}
(Pc)(OC)₄OsOs(CO)₃(Pc)W(CO)₅ (3) and (Pc)₂(OC)₃OsOs(CO)₄W(CO)₅ (4) appears to be unique for the phosphorus ligand P(OCH₂)₃CMe. (An analogue of these complexes has recently been prepared where the substituted ligand is BuNC; an X-ray crystal structure of this complex has confirmed the presence of dative metal-metal bonds in tandem.¹⁰⁶) Both 3 and 4 are stable at 90 °C with respect to interconversion between these two isomers. Thus, prolonged heating of a solution of 3 did not result in the formation of detectable amounts of 4, and vice versa. This was surprising since the reaction of Os(CO)₄(Pc) with WOS(CO)₉(Pc) would reasonably have been expected to yield 4 as the primary product. In addition, both 3 and 4 show little evidence for any decomposition at 90 °C. Prolonged heating of 4 does result in its conversion to the cluster (OC)₅W{Os(CO)₃[P(OCH₂)₃CMe]}₂, though some 3 remained even after 3 d. Therefore, the linear trimetallic species are much more robust than all of the bimetallic species that contain dative metal-metal bonds.

A reason for the increased stability of the linear trimetallic complexes is not apparent. It was noted that the Os-W bond distance in (Pc)₂(OC)₃OsOs(CO)₄W(CO)₅ (3) is shorter than that of the dative bond in (Me₃P)(OC)₄OsW(CO)₅ (see Molecular Structure section above). However, while the difference in the Os-W bond lengths is crystallographically significant, any chemical significance is probably negligible given that the force constants for metal-metal bonds are relatively small: thus, the metal-metal bonds can be easily deformed."
It is noteworthy that during the preparation of [MeC(CH₂O)₃P](OC)₄OsW(CO)₅, (Pc)(OC)₄OsOs(CO)₃(Pc)W(CO)₅ (4) is formed as a by-product but very little triangular cluster (see Chapter 4) is formed. On the other hand, the triangular cluster is the only heterometallic by-product isolated from the preparation of all the other monosubstituted bimetallic complexes. It was found that 4 could be cleanly converted to the triangular cluster by photolysis in C₆F₆, or thermally as described above. This suggests that 4 may be an intermediate in the cluster formation. It may be that linear trimetallic complexes like 4 are formed during the preparation of the other bimetallic species, but that once formed they rapidly decompose to form the triangular clusters. The thermal stability of the linear complexes may be related to the electron donating ability of the phosphorus ligand. For example, the bent OsOsW backbone (172°) in 3, and presumably in 4 as well, is unusual amongst M₃ chain-like complexes. It has been suggested that some bending of an M-M bond may occur in order to facilitate a stabilizing Mₙπ-COπ* interaction between a metal center and a CO on an adjacent metal center (see illustration below). Since there is more electron density on the terminal Os in 4 than on a terminal metal in a binary carbonyl complex, bending in 4 (like that observed in 3) may occur as a result of this interaction. Substitution of Pc with a much better electron donor such as PMe₃ may result in increased bending due to an increased d-π* interaction. The bending may approach the transition state needed to form the cluster. Hence, a low energy pathway to
triangular cluster formation is achieved for all those cases where the phosphorus ligand is a better donor than Pc. This may account for the formation of the triangular clusters to the exclusion of trimetallic chain complexes and vice versa.

**Photochemistry of Complexes with Dative Metal-Metal Bonds.**

As described above, bimetallic complexes with dative metal-metal bonds resemble complexes with covalent metal-metal bonds such as Mn$_2$(CO)$_{10}$ in that they all absorb light in the near-UV region; this can be attributed to $\sigma \rightarrow \sigma^*$ transitions associated with the metal-metal bond. The origin of these $\sigma \rightarrow \sigma^*$ transitions in terms of a molecular orbital description of the metal-metal bonding is also similar for covalent and dative metal-metal bonds. However, the similarity seems to end there. For example, at ambient temperature, the photochemical reactivity of complexes with covalent metal-metal bonds is dominated by homolytic cleavage of the metal-metal bond into radical fragments.$^{10}$ Typically these radical fragments recombine to form homobimetallic or heterobimetallic (when M$_2$(CO)$_{10}$ and M'$_2$(CO)$_{10}$ are used as reactants) complexes. The photochemical reactivity of complexes with dative metal-metal bonds appears to
be different. When photolyzed in the inert solvent C₆F₆, hetero-
trimetallic clusters are formed (see Chapter 4). The formation
of clusters by this route is unprecedented in organometallic
photochemistry.

In an attempt to determine whether the primary photoprocess
involves homolytic or heterolytic cleavage of the metal-metal
bond, or ligand loss from the intact bimetallic species, several
reactions that employed (Me₃P)(OC)₄OsW(CO)₅ as the bimetallic
species were carried out. In one, AIBN (NCMe₂CN₂CMe₂CN, a radi-
cal initiator) was added to both a thermal and a photochemical
reaction mixture. Formation of the heterotrimetallic cluster
would have indicated a radical pathway, and hence homolytic
metal-metal bond fission, as a possible primary photoprocess.
However, no cluster was formed in either reaction. In another
photochemical reaction, CCl₄ (a radical trap) was added.
Formation of the cluster in this reaction would have suggested a
primary photoprocess other than homolytic metal-metal bond
fission, while the absence of cluster formation would have
provided evidence of a radical pathway. No cluster was formed in
this reaction, but the result is in conflict with that of the
reaction with AIBN. A final photochemical reaction was carried
out with added PPh₃. The lack of formation of cluster complex
would have indicated heterolytic metal-metal bond fission or
ligand loss as possible primary photoprocesses, while cluster
formation would have suggested a radical pathway. Again, no
cluster was formed. (The products of this reaction were
Os(CO)$_3$(PMe$_3$)(PPh$_3$), Os(CO)$_4$(PMe$_3$), and W(CO)$_5$(PPh$_3$), as identified by infrared spectroscopy.)

The results of these experiments are, unfortunately, completely inconclusive since two experiments suggested a possible radical pathway while one suggested a nonradical pathway. These results are, however, highly preliminary. As noted in Chapter 4, another interesting aspect of at least one of the bimetallic complexes, (Me$_3$P)(OC)$_4$OsW(CO)$_5$, is that the photochemical and thermal reactivity appears to be the same since the cluster is formed by either route. This represents a rare example of such behavior. A detailed research proposal to study the photochemistry of complexes with dative metal-metal bonds has been proposed.$^{109}$

3.4 Conclusion

Two major features about transition metal complexes with dative metal-metal bonds have been established. First, it is apparent from chemical stability and spectroscopic studies that the stability of complexes with dative metal-metal bonds between Os and a group 6 metal M(CO)$_5$ fragment is often decreased as the electron density on the donor metal center is increased; this is contrary to what was anticipated. It was also found that the stability of complexes with W(CO)$_5$ as the acceptor species were more stable than those with Cr(CO)$_5$ as the acceptor fragment. This is the expected result based on general periodic trends in metal-metal bonding. Like complexes with covalent metal-metal
bonds, the energy of the near-UV ($\sigma \rightarrow \sigma^*$ transition) absorption appears to parallel the chemical stability of complexes with a dative metal-metal bond. However, a description of the bonding clearly distinguishes one from the other.

Second, the photochemistry of complexes with dative metal-metal bonds is distinctly different from that of complexes with covalent metal-metal bonds. Photolysis of monosubstituted $(L)(OC)_4OsM(CO)_5$ complexes in C$_6$F$_6$ yields heterotrimetallic cluster compounds: the formation of metal clusters from metal-metal bonded species by photolysis is unprecedented in organometallic photochemistry. The primary photoprocess in these reactions has not been established as yet.

Two linear trimetallic complexes were isolated and characterized: these are believed to contain two dative metal-metal bonds in tandem. As far as we are aware, this type of bonding mode is unprecedented in either main group or transition metal chemistry. The trimetallic complexes are thermally much more robust than the bimetallic compounds. This may be due to unusual bonding along the metal chain. One of these complexes was readily converted to a triangular cluster by photolysis. Thus, the linear trimetallic complexes may be intermediates formed during the photolysis of bimetallic complexes on the route to the triangular clusters. A method to remove a ligand (e.g., CO) from one of the intact trimetallic molecules and replace it with an 18-electron donor complex to extend the chain length has not yet been attempted. Future work in this area must include such
studies.
CHAPTER 4
SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF HETEROTRIMETALLIC CLUSTERS CONTAINING OSMIUM AND A GROUP 6 METAL

4.1 Introduction

It is well known that heterogeneous catalysts with two or more metal centers are often more active than the individual metal atoms.\(^{110}\) There are several well-established synthetic strategies for the preparation of heterometallic cluster complexes.\(^{112a}\) The elegant use of the isolobal analogy for organometallic complexes employed by Stone\(^{113}\) has, in particular, yielded many examples of heterotrimetallic clusters. A significant usefulness for these species as catalysts or as synthetic reagents has not yet been demonstrated, but the potential value of combining early and late transition metals in one cluster molecule has long been recognized. Therefore, strategies for the synthesis of heterometallic cluster species are of paramount importance in enabling the chemist to design target cluster molecules.

In the studies on heterobimetallic complexes with dative metal-metal bonds\(^{8}\) it was noted that deep red compounds were produced as minor by-products during the preparation of the bimetallic species (see Chapter 3). One of these products was determined to be \((\text{OC})_3\text{Mo}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2\), a heterotrimetallic cluster complex, by X-ray crystallography.\(^{8a}\) Methods to synthesize these novel clusters were, therefore, investigated. Here we
report that these clusters can be prepared in moderate yields at room temperature in C\textsubscript{6}F\textsubscript{6} by the photolysis of complexes that contain dative metal-metal bonds (equation 4.1). This synthetic strategy allows the synthesis of diosmium-group 6 metal clusters that cannot be obtained by other existing routes. The chromium derivatives represent the first chromium-osmium clusters to be reported, and the molybdenum analogues are rare examples of clusters that contain this metal and osmium. Only three other clusters that contain molybdenum and osmium have been reported.\textsuperscript{111} Preliminary evidence shows that these clusters react with H\textsubscript{2} under mild conditions, and that one CO ligand, presumably the axial carbonyl on the group 6 metal, is labile towards substitution by a two electron donor ligand. The details of these studies along with the X-ray crystal structures of (OC)\textsubscript{5}M[Os(CO)\textsubscript{3}(PMe\textsubscript{3})]\textsubscript{2} (M = Cr, W), (OC)\textsubscript{5}Mo[Os(CO)\textsubscript{3}[P(OMe)\textsubscript{3}]]\textsubscript{2}, and (μ-H)\textsubscript{2}(OC)\textsubscript{6}W[Os(CO)\textsubscript{3}(PMe\textsubscript{3})]\textsubscript{2} are described below. Some of these results have been reported in preliminary form.\textsuperscript{112}

4.2 Experimental

All of the dative metal-metal bonded bimetallic starting materials (L)(OC)\textsubscript{4}OsM(CO)\textsubscript{5} (M = Cr, Mo, W; L = PMe\textsubscript{3}, P(OMe)\textsubscript{3}, P(OCH\textsubscript{2})\textsubscript{3}CMe), were synthesized according to literature methods,\textsuperscript{8} and were handled under inert atmosphere conditions with the use
of standard Schlenk techniques. Hexane and CH$_2$Cl$_2$ were distilled under nitrogen from K and CaH$_2$, respectively, prior to use. Benzene and C$_6$F$_6$ were distilled under nitrogen from K and P$_2$O$_5$, respectively, prior to use. An external, medium-pressure mercury discharge lamp (200-W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the irradiations; there were ~5 cm between the source and the edge of the reaction vessel.

Infrared spectra were obtained on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. Electron-impact (70 eV) mass spectra were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility); the pattern of the envelope of ions for the parent ion or the species of highest mass matched the computer simulated pattern for most of the species involved. NMR spectra were recorded on a Bruker WM400 spectrometer (operating frequencies; 400 MHz for $^1$H, 100.6 MHz for $^{13}$C, and 162 MHz for $^{31}$P). The $^{13}$C NMR spectra were obtained on samples that were enriched with $^{13}$CO. These were prepared either by using labeled starting materials or by stirring the cluster products under 1 atm of $^{13}$CO (99% $^{13}$C) at 50-80 °C for 21 to 22 hours. The labeled compounds were purified by column chromatography and recrystallization. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory at Simon Fraser University.
Preparation of \((\text{OC})_5M[\text{Os(CO)}_3(L)]_2\) \((M = \text{Cr}, \text{Mo}, \text{W}; L = \text{P(OMe)}_3, \text{P(OCH}_2)_3\text{CMe}, \text{PMe}_3)\) Derivatives. The cluster complexes were all prepared by the photolysis of a supersaturated solution of the appropriate bimetallic complex in \(\text{C}_6\text{F}_6\) (or \(\text{C}_6\text{H}_6\) for \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\)) in Pyrex Carius tubes. The solutions were thoroughly degassed by several freeze-pump-thaw cycles prior to photolysis. Typical irradiation times ranged from \(-2\) hr \((M = \text{W}; R = \text{Me})\) to \(17\) hr \((M = \text{Mo}; R = \text{Me})\); the times varied depending on the amounts of starting materials used. The initially pale yellow solutions turned deep red with small amounts of solid decomposition products. (Prolonged irradiation of the clusters did not result in any detectable decomposition.) After photolysis, the \(\text{C}_6\text{F}_6\) was removed under vacuum. (Impure \(\text{C}_6\text{F}_6\) was redistilled from \(\text{P}_2\text{O}_5\) prior to further use.) The crude solid was dissolved in a minimum amount of \(\text{CH}_2\text{Cl}_2\) and chromatographed on an alumina (neutral) column with \(\text{CH}_2\text{Cl}_2/\text{hexane} (1/1\) to \(1/3, \text{v/v})\) as the eluant. The purified products were recrystallized from either \(\text{CH}_2\text{Cl}_2\) and hexane, or from a mixture of \(\text{C}_6\text{H}_5\text{Cl}, \text{CH}_2\text{Cl}_2,\) and hexane prior to spectroscopic and elemental analysis. Yields were typically \(30\%\) to \(40\%\). Yield, analytical, mass and infrared spectral data are given in Table 4.1; \(^{31}\text{P}\{^1\text{H}\}\) and \(^1\text{H}\) NMR data (where recorded) are given in Table 4.2; \(^{13}\text{C}\) NMR data for various complexes are given in Table 4.3. All of the complexes except \((\text{OC})_5\text{W[Os(CO)}_3[\text{P(OCH}_2)_3\text{CMe}])_2\) are reasonably soluble in nonpolar organic solvents. Two variations of the preparation of the clusters are given below.
<table>
<thead>
<tr>
<th>Compound</th>
<th>% Calcd. C</th>
<th>% Found C</th>
<th>Mass Spectrum</th>
<th>Yield</th>
<th>Infrared Stretches (\nu)CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>((OC)_2Cr[Os(CO)]_2(PMe)_3); (1)</td>
<td>22.87 2.03</td>
<td>23.09 2.04</td>
<td>M+</td>
<td>32%</td>
<td>(hexane) 2073(w) 2003(s) 1991(s) 1980(w,sh) 1973(w,sh) 1956(w) 1940(m) 1920(w) 1886(w,br)</td>
</tr>
<tr>
<td>((OC)_2Cr[Os(CO)]_2(POMe)_3); (7)</td>
<td>20.65 1.84</td>
<td>20.78 1.89</td>
<td>M+</td>
<td>22%</td>
<td>(hexane) 2084(w) 2026(m) 2005(vs) 1983(m,sh) 1942(m) 1921(m)</td>
</tr>
<tr>
<td>(OC)_2Mo[Os(CO)]_2(PMe)_3); (14)</td>
<td>21.80 1.94</td>
<td>22.03 1.90</td>
<td>M+</td>
<td>32%</td>
<td>(hexane) 2074(w) 2018(s) 2004(m) 1988(vs) 1951(m) 1947(m) 1941(w,sh) 1937(w) 1908(w)</td>
</tr>
<tr>
<td>(OC)_2Mo[Os(CO)]_2(POMe)_3); (2)</td>
<td>19.77 1.76</td>
<td>19.86 1.89</td>
<td>M+</td>
<td>22.3%</td>
<td>(hexane) 2084(w) 2027(s) 2015(m) 2000(s) 1982(w) 1974(w) 1968(w) 1951(m) 1936(w)</td>
</tr>
<tr>
<td>((OC)_2W[Os(CO)]_2(PMe)_3); (3)</td>
<td>19.93 1.77</td>
<td>20.27 1.71</td>
<td>M+</td>
<td>39%</td>
<td>(hexane) 2075(w) 2014(s) 2007(m) 1989(vs) 1944(m) 1925(w) 1904(w)</td>
</tr>
<tr>
<td>((OC)_2W[Os(CO)]_2(POMe)_3); (8)</td>
<td>18.22 1.62</td>
<td>18.25 1.62</td>
<td>M+</td>
<td>30%</td>
<td>(hexane) 2085(w) 2027(s) 2018(m,sh) 2002(vs) 1982(w) 1947(m) 1929(m)</td>
</tr>
<tr>
<td>((OC)_2W[Os(CO)]_2(POMe)_3); (9)</td>
<td>21.58 1.55</td>
<td>21.54 1.59</td>
<td>--</td>
<td>53%</td>
<td>(CHCl_3); 2090(w) 2027(s) 2008(s) 1918(m,br)</td>
</tr>
<tr>
<td>([\text{MeO}]_2P)(OC)_2W[Os(CO)]_2(PMe)_3); (6)</td>
<td>20.36 2.40</td>
<td>20.40 2.44</td>
<td>b</td>
<td>60%</td>
<td>(hexane) 2050(w) 1999(m) 1980(s) 1961(w) 1944(w) 1930(w) 1916(w,sh) 1887(m) 1866(w)</td>
</tr>
<tr>
<td>((\mu-H)_2(OC)_2Cr[Os(CO)]_2(PMe)_3); (10)</td>
<td>--</td>
<td>--</td>
<td>c</td>
<td>(CHCl_3); 2089(w) 2036(w) 2005(vs) 1886(m) 1839(m)</td>
<td></td>
</tr>
<tr>
<td>((\mu-H)_2(OC)_2Mo[Os(CO)]_2(PMe)_3); (11)</td>
<td>a</td>
<td>d</td>
<td>(CHCl_3); 2089(w) 2037(w) 2005(vs) 1895(m,br) 1841(m,br)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\mu-H)_2(OC)_2Mo[Os(CO)]_2(POMe)_3); (12)</td>
<td>19.09 2.00</td>
<td>19.26 2.16</td>
<td>--</td>
<td>d</td>
<td>(CHCl_3); 2103(w) 2051(w,sh) 2022(vs) 1986(m,sh) 1971(m,sh) 1956(w,sh) 1902(m,br) 1849(m,br)</td>
</tr>
<tr>
<td>((\mu-H)_2(OC)_2W[Os(CO)]_2(PMe)_3); (4)</td>
<td>19.24 2.00</td>
<td>19.45 1.82</td>
<td>a</td>
<td>63%</td>
<td>(CHCl_3); 2092(m) 2040(m) 2004(vs) 1950(m) 1880(m) 1839(m)</td>
</tr>
<tr>
<td>((\mu-H)_2(OC)_2W[Os(CO)]_2(POMe)_3); (13)</td>
<td>--</td>
<td>--</td>
<td>c</td>
<td>(CHCl_3); 2107(wn) 2056(w) 2924(vs) 1985(w) 1886(m) 1841(m)</td>
<td></td>
</tr>
</tbody>
</table>

a. decomposed; b. M+ - CO; c. small scale reaction; d. produced as by-product.
Table 4.2. $^1$H and $^3$P NMR Data for New Trimetallic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H$_\delta$</th>
<th>$^3$P{$^1$H}$\delta$</th>
<th>Isomer Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A</td>
<td>--</td>
<td>-40.4$^d$</td>
<td>~1.4</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-37.9</td>
<td></td>
</tr>
<tr>
<td>7 A</td>
<td>--</td>
<td>100.6</td>
<td>~6</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>104.5</td>
<td></td>
</tr>
<tr>
<td>14 A</td>
<td>--</td>
<td>-41.0</td>
<td>~3</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-38.2</td>
<td></td>
</tr>
<tr>
<td>2 A</td>
<td>--</td>
<td>103.5$^{a,d}$</td>
<td>~5.5</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>107.5</td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td>1.9(12)$^f$</td>
<td>-42.3$^d$</td>
<td>~2.6</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-37.9</td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td></td>
<td>-41.0 -44.0$^{c,e}$</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-37.9</td>
<td></td>
</tr>
<tr>
<td>8 A</td>
<td>--</td>
<td>100.6</td>
<td>~5.3</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>105.0</td>
<td></td>
</tr>
<tr>
<td>9 A</td>
<td>--</td>
<td>95.1 92.8$^d$</td>
<td>~9</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>96.8</td>
<td></td>
</tr>
<tr>
<td>6 A</td>
<td>3.59(11.9) 1.82(9.9)$^{d,f}$</td>
<td>143.5 -45.0 -49.0$^d$</td>
<td>~1</td>
</tr>
<tr>
<td>B</td>
<td>3.59(11.9) 1.82(9.9)$^f$</td>
<td>142.1 -42.1</td>
<td></td>
</tr>
<tr>
<td>10 A</td>
<td>1.87(10.0) 1.54</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.06(10.0) -19.86(16)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2.06(10.4) -16.91(19.2)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3.81(12.3) -16.27(17.9)</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.12(16) -16.25(16.8)</td>
<td>-45.8</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>3.83(20) -16.03(16)</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Numbering scheme corresponds to that given in Table 4.1 Unless otherwise specified, all spectra were run at 298 K in CDCl$_3$. Figures in parentheses are $^3$PJ-$^1$H. $^a$, 251 K; $^b$, 236 K; $^c$, 152 K; $^d$, CD$_2$Cl$_2$; $^e$, CH$_2$Cl$_2$/CHCl$_2$F ~1:3 v/v; $^f$, signals due to different isomers were not resolved.
### Table 4.3. $^{13}$C NMR Shifts for the Carbonyl Ligands of New Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{M(CO)}_5$</th>
<th>$\text{Os}_2(\text{CO})_6(\text{L})_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ ax-CO</td>
<td>$\delta$ rad-CO</td>
</tr>
<tr>
<td>1 A (151)</td>
<td>232.0</td>
<td>221.2</td>
</tr>
<tr>
<td>B</td>
<td>232.0</td>
<td>223.3</td>
</tr>
<tr>
<td>7 A (205)</td>
<td>231.1</td>
<td>219.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 A (151)</td>
<td>205.9</td>
<td>200.9(117.6)$^a$</td>
</tr>
<tr>
<td>B</td>
<td>206.3</td>
<td>203.5(119.1)$^a$</td>
</tr>
<tr>
<td>4 (298)</td>
<td>204.7$^d$</td>
<td>202.2(127)$^a$</td>
</tr>
<tr>
<td>6 A (298)</td>
<td>210.3(12.6)</td>
<td>108.0</td>
</tr>
<tr>
<td>B</td>
<td>210.2(12.2)</td>
<td>107.8</td>
</tr>
<tr>
<td>8 A (213)</td>
<td>205.3</td>
<td>199.5(117.0)$^a$</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>194.9</td>
</tr>
<tr>
<td>9 A (243)</td>
<td>205.1</td>
<td>199.1(119)$^a$</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>192.2(10)</td>
</tr>
</tbody>
</table>

Numbering scheme corresponds to that in Table 4.1; numbers in parentheses associated with the compound numbers correspond to the temperature (in Kelvin) at which the spectrum was recorded unless stated otherwise, other numbers in parentheses are $J_{p-C}$; a. $J_{w-C}$; b. intensity too low to detect; c. appears as a shoulder on the $\delta$ 194.9 resonance; d. $J_{w-C}$ 164 Hz.
Preparation of \((\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\) in \(\text{C}_6\text{H}_6\). A supersaturated solution that contained \((\text{Me}_3\text{P})(\text{OC})_6\text{OsW(CO)}_5\ (5)\ (100 \text{ mg}, 0.14 \text{ mmol})\) in \(\text{C}_6\text{H}_6\) (20 mL) was pneumatically sealed in a Pyrex Carius tube fitted with a Teflon valve. The solution, evacuated at \(-196^\circ\text{C}\) and degassed by three freeze-pump-thaw cycles, was irradiated for 37 min, degassed with two freeze-pump-thaw cycles, and irradiated for a further 90 min. During the irradiation the initially pale yellow solution turned red, and some solid decomposition product formed. An IR spectrum of the solution after 127 min of irradiation showed no bands attributable to the starting material. The \(\text{C}_6\text{H}_6\) was removed under vacuum and the crude reaction mixture dissolved in \(\text{CH}_2\text{Cl}_2\) and chromatographed on an alumina (neutral) column (11 x 1 cm). A deep red band that contained \((\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\ (3)\) was eluted from the column with \(\text{CH}_2\text{Cl}_2/\text{hexane (1/2, v/v)}\). A bright yellow band that contained \((\mu-\text{H})_2(\text{OC})_4\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\ (4)\) (see below) was eluted with \(\text{CH}_2\text{Cl}_2/\text{hexane (3/1, v/v)}\). In this way, 3 (28 mg, 39%) and 4 (16 mg 23%) were obtained as deep red, and yellow solids, respectively. Deep red crystals of 3 suitable for an X-ray crystal structure determination were grown from a mixture of \(\text{C}_6\text{H}_5\text{Cl}\) and \(\text{CH}_2\text{Cl}_2\) with hexane layered on top. Bright yellow crystals (of similar quality) of 4 were grown from \(\text{C}_6\text{H}_6\) with hexane layered on top.

The \((\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe}_3)]_2\ (3)\) cluster was also prepared via a thermal route. A solution of 5 (30 mg, 0.03 mmol) in \(\text{C}_6\text{H}_6\) (20 mL) was pneumatically sealed in a Carius tube fitted with a
Teflon valve, evacuated at -196 °C and degassed by two freeze-pump-thaw cycles. The stirred reaction was heated at 70 to 80 °C for 42.2 h during which the initially pale yellow solution turned red. The product was purified as above to yield 3 (5 mg, 33%).

Preparation of \((\text{OC})_5\text{Cr}[\text{Os(CO)}_3(\text{PMe})_3]\)_2 (1). A solution of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsCr(CO)}_5\) (6) (100 mg, 0.18 mmol) in \text{C}_6\text{F}_6 (10 mL) was sealed in a Pyrex Carius tube equipped with a Kontes Teflon valve, evacuated at -196 °C and degassed by two freeze-pump-thaw cycles. The solution, which was irradiated for a total of 11 h, was degassed after 5 hr and 9.5 hr; the reaction mixture turned from pale yellow to deep red during this time. The \text{C}_6\text{F}_6 was recovered via vacuum distillation for further use. The crude solid was dissolved in \text{CH}_2\text{Cl}_2 and placed on an alumina (neutral) column (12.5 x 1 cm). A deep red band that contained 1 was eluted with \text{CH}_2\text{Cl}_2/hexane (1/3, v/v). A pale amber band that contained \((\mu-\text{H})_2(\text{OC})_4\text{Cr}[\text{Os(CO)}_3(\text{PMe})_3]\)_2 (IR spectral identification) was eluted with \text{CH}_2\text{Cl}_2/hexane (1/1, v/v). After recrystallization from \text{C}_6\text{H}_5\text{Cl}/\text{CH}_2\text{Cl}_2 with pentane layered on top (-20 °C), 1 (33 mg, 37%) was obtained as deep red crystals: one of these crystals was used for an X-ray crystal structure determination.

Reaction of \((\text{OC})_5\text{W}[\text{Os(CO)}_3(\text{PMe})_3]\)_2 (3) with CO. A mixture of 3 (~5 mg) in hexane (3 mL) was placed in a round-bottom flask fitted with a Kontes Teflon valve. The solution was thoroughly degassed by repeated freeze-pump-thaw cycles, after which 1 atm
of CO was added above the frozen solution. The solution was stirred for 4 d at 80 °C. An IR spectrum at the end of this time showed that most of the starting material remained intact, and that very little decomposition to Os(CO)$_4$(PMe$_3$) and W(CO)$_6$ occurred. This same procedure, with the use of $^{13}$CO (99% $^{13}$C) was employed to make $^{13}$CO-enriched 3.

**Reaction of (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) with P(OMe)$_3$.** A solution of 3 (47 mg, 0.05 mmol) in hexane (20 mL) was prepared in a 100 mL round-bottom flask equipped with a Kontes Teflon valve. To this, P(OMe)$_3$ (64 mg, 0.5 mmol) was added. The solution was degassed by one freeze-pump-thaw cycle. The reaction, which was heated to 50 °C for a total of 31 h, was degassed after 12 h and 22 h. Volatile materials were removed under vacuum, and the crude solid dissolved in CH$_2$Cl$_2$ and placed on an alumina (neutral) column (12 x 1 cm). Unreacted 3 was eluted from the column with CH$_2$Cl$_2$/hexane (1/3, v/v) as the eluant, followed by a purple band which contained an unidentified compound. Elution with CH$_2$Cl$_2$/hexane (1/2, v/v) removed a deep orange band that contained the major product, and a final red band of unknown identity. The major product was recrystallized from CH$_2$Cl$_2$/hexane at -20 °C to afford [(MeO)$_3$P](OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (28 mg, 60%) as dark-red crystals.

**Reaction of (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) with H$_2$.** A solution that contained 3 (47 mg, 0.021 mmol) in C$_6$H$_6$ (15 mL) was placed in a Carius tube fitted with a Kontes Teflon valve. The solution was evacuated at -196 °C and degassed by three freeze-pump-thaw
cycles, after which H₂ (1 atm) was added. The reaction was stirred at 50 °C for 21.25 h during which the initially deep red solution turned bright yellow and a small amount of dark solid formed. Volatile materials were removed under vacuum, and the crude product dissolved in CH₂Cl₂ and placed on an alumina (neutral) column. The yellow band that contained the desired product was eluted with CH₂Cl₂/hexane (2/1, v/v). In this way, (μ-H)₂(OC)₄W[Os(CO)₃(PMe₃)]₂ (4) (13 mg, 63%) was obtained as a bright yellow solid. The ¹³CO-labeled 3 was obtained from labeled starting materials (see above).

4.3 Results

Molecular Structures of (OC)₅M[Os(CO)₃(PR₃)]₂ (M = Cr, W; R = Me; M = Mo; R = OMe) and (μ-H)₂(OC)₄W[Os(CO)₃(PMe₃)]₂. The Cr, Mo, and W clusters of (OC)₅M[Os(CO)₃(PR₃)]₂ all adopt similar structures in the solid state. The structures of the Cr (1) and Mo (2) derivatives have been published in preliminary communications;¹¹² views of these molecules are shown in the Appendix. The structure of the W cluster 3 shown in Figure 4.1 is exemplary of the isomer found for all three species. For the purpose of the discussion of the structures of these clusters, the numbering of the phosphorus and osmium atoms, and the carbonyls, conforms to that given for 3 in Figure 4.1.

Structure of (OC)₅W[Os(CO)₃(PMe₃)]₂ (3). A view of the molecular structure of of 3 is shown in Figure 4.1, and selected bond lengths and angles are given in Table 4.4. The metal atoms
are in a triangular arrangement, and there are no bridging ligands. The phosphines occupy equatorial sites on separate Os centers, one trans and one cis to an Os-W bond. The Os-W bond lengths are 3.0427 (8) Å and 3.0646 (8) Å; the longer bond is cis to PMe₃. These lengths are shorter than the unbridged dative bond in (Me₃P)(OC)_5OsW(CO)_5 (3.0756 (5) Å)⁸ and in (η⁵-C₅H₅)W-Os₃(CO)₁₂(μ₃-CC₆H₄CH₃)(μ-H)₂ (3.097 (1) Å),¹¹³ but significantly longer than the unbridged Os-W bonds in the nearly planar (η⁵-C₅H₅)WO₃(CO)₁₁[μ₃-η²-OCCH₂Tol] (2.914 (1) Å)¹¹⁴ cluster.

Figure 4.1. Molecular Structure of (OC)₅W[Os(CO)₃(PMe₃)]₂ (3).
Table 4.4. Selected Bond Lengths (Å) and Angles (deg) for (OC)₅Cr[Os(CO)₃(PMe₃)]₂ (1), (OC)₅Mo[Os(CO)₃(PMe₃)]₂ (2), (OC)₅W[Os(CO)₃(PMe₃)]₂ (3), and (μ-H)₂(OC)₄W[Os(CO)₃(PMe₃)]₂ (4).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1)-Os(2)</td>
<td>2.8384(8)</td>
<td>2.854(2)</td>
<td>2.8545(7)</td>
<td>2.964(3)</td>
</tr>
<tr>
<td>Os(1)-M</td>
<td>3.024(2)</td>
<td>3.079(3)</td>
<td>3.0642(7)</td>
<td>3.154(2)</td>
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<tr>
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<td>3.041(3)</td>
<td>3.0423(8)</td>
<td>3.156(3)</td>
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<tr>
<td>Os(1)-P(1)</td>
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<td>2.299</td>
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<td>2.32(1)</td>
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<td>Os(2)-P(2)</td>
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<td>1.83(6)</td>
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<td>1.82(1)</td>
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</tr>
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<td>1.90(3)</td>
<td>1.94(1)</td>
<td>1.94(5)</td>
</tr>
<tr>
<td>M-C(31)</td>
<td>1.84(2)</td>
<td>2.06(3)</td>
<td>2.04(1)</td>
<td>1.95(5)</td>
</tr>
<tr>
<td>M-C(32)</td>
<td>1.90(2)</td>
<td>2.02(3)</td>
<td>2.02(1)</td>
<td>1.90(5)</td>
</tr>
<tr>
<td>M-C(33)</td>
<td>1.88(2)</td>
<td>2.05(3)</td>
<td>2.01(1)</td>
<td>2.04(5)</td>
</tr>
<tr>
<td>M-C(34)</td>
<td>1.90(2)</td>
<td>2.03(3)</td>
<td>2.02(1)</td>
<td>1.82(5)</td>
</tr>
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<td>M-C(35)</td>
<td>1.82(2)</td>
<td>1.93(3)</td>
<td>1.97(1)</td>
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</table>

and in the closo clusters (η⁵-C₅H₅)WO₃(CO)₅(C₂To₁₂)H (2.831 (1), 2.910 (1), and 2.891 (1) Å),¹¹⁵ (μ-H)₃W(η⁵-C₅H₅)Os₃(CO)₁₁ (2.890 (3) Å),¹¹⁶ and (μ-H)Os₃W(CO)₁₂(η⁵-C₅H₅) (2.909 (2) to 2.934 (2) Å).¹¹⁷ The Os-Os bond length of 2.8548 (7) Å is comparable to those in the Cr and Mo analogues, and slightly shorter than that in Os₃(CO)₁₂ (2.877 Å).¹¹⁸ A view from the middle of the Os-Os vector to the W atom indicates that the four radial carbonyls on the W are staggered, though not perfectly;
the dihedral angle \( \tau \) is 23° (see Figure 4.2). While the W-C bond lengths to the radial carbonyls (average: 2.028 Å) are not significantly different, the W-C bond length of 1.968 (6) Å to the unique axial CO is 0.06 Å shorter. The bond angle C(32)-W-C(34) which corresponds to the carbonyls that most closely eclipse the plane of the metals is substantially distorted from linearity (161.3 (5)°). The C(31)-W-C(33) bond angle of the carbonyls that are closer to being perpendicular to the metal plane is approximately linear (177.6 (5)°).

X-ray crystal structure of \((OC)_5Cr[Os(CO)_3(PMe_3)]_2\) (1). A list of selected bond lengths and angles is given in Table 4.4. The major features of 1 are identical to those of 3. The metal atoms are in a triangular arrangement with no bridging carbonyl ligands. The phosphine ligands occupy equatorial positions on separate Os centers with one trans and the other cis to Os-Cr.

Figure 4.2. View of 3 From the Middle of the Os-Os Vector to the W Atom.
metal-metal bonds. The Os-Cr bond vectors are 2.996 (2) Å and 3.023 (2) Å. These bond lengths are slightly longer than the dative metal-metal bond length of 2.9787 (14) Å found in \((\text{Me}_3\text{P})(\text{OC})_4\text{OsCr(CO)}_5\), and also longer than those found in \((\text{Bu}^\text{t}\text{NC})(\text{OC})_4\text{OsCr(CO)}_5\) (2.966 (2) Å) and \((\text{Bu}^\text{t}\text{NC})_2(\text{OC})_3\text{OsCr(CO)}_5\) (2.9693 (12) Å). The longer of the two Os-Cr bonds in 1 is cis to a phosphine ligand. It has been observed that the metal-metal bond that is cis to a phosphine ligand in Os\(_3\)(CO)\(_{11}\)(L) complexes is generally longer than the other Os-Os bonds in the cluster. It has been previously noted that the dative metal-metal bond is slightly longer than a single covalent metal-metal bond, so the Os-Cr bond in 1 represents a "long" single bond. (The bonding in these clusters is discussed in Chapter 5.) The Os-Os bond length (2.838 (1) Å) is somewhat shorter than that found in Os\(_3\)(CO)\(_{12}\) (2.877 Å), and in the Mo and W analogues. The Cr-C bond length of 1.84 (2) Å to the carbonyl trans to the Os\(_2\) fragment is shorter than the Cr-C bond lengths to three of the radial carbonyls (average 1.895 Å); the Cr-C bond length to C(32) is shortened to 1.82 (2) Å. The dihedral angle \(\tau\) (see Figure 4.2) between the plane that contains the two Os atoms and the plane of C(34)-Cr-C(35) is 26°; this indicates that the four radial carbonyls on Cr are clearly not perfectly staggered. The bond angle C(34)-Cr-C(35) is significantly nonlinear (164.3 (8)°) while that of C(31)-Cr-C(33) is approximately linear (177.7 (7)°). Thus, the carbonyls which are most closely coplanar with the CrOs\(_2\) plane are bent away from the nearest equatorial ligands on the Os centers. This bending can likely be
attributed to steric effects.

**Structure of (OC)₅Mo{Os(CO)₃[P(OMe)₃]}₂ (2).** This compound was originally formed as a by-product in the preparation of [(MeO)₃P](OC)₄OsMo(CO)₅. The cluster molecule was co-crystallized with the bimetallic molecule in a 1:1 ratio. A list of selected bond lengths and angles for 2 is given in Table 4.4. Like 1 and 3 the metals form a triangle that contains only terminally bonded carbonyl ligands; the phosphite ligands occupy equatorial sites on separate osmium centers, one trans and one cis to a Mo-Os bond. The Os-Os bond length (2.8537 (13) Å) is similar to those in 1 and 3. The Os-Mo bond lengths are 3.041 (2) Å and 3.079 (2) Å. These bond lengths are significantly longer than the unbridged osmium-molybdenum bond lengths in (μ-H)₂(η⁵-C₅H₅)₂Mo₂Os₃(CO)₁₂·C₆H₆ (2.830 (1) Å to 2.908 (1) Å) and (μ-H)₃(η⁵-C₅H₅)MoOs₃(CO)₁₁ (2.919 (1) Å to 2.950 (1) Å), but similar to the osmium-molybdenum dative bond length in [(MeO)₃P](OC)₄OsMo(CO)₅ (3.075 (2) Å). The Os-Mo bond lengths in 2 are actually much closer to those found for H-bridged Os-Mo bonds (2.999 (1) Å to 3.092 (1) Å). Like the corresponding bonds in 1 and 3, the longer Os-Mo bond in 2 is cis to a phosphorus ligand which is bent back towards the molybdenum atom (Os(2)-Os(1)-P(1) = 167.0 (2)°). The radial carbonyls on Mo are slightly staggered with respect to the MoOs₂ plane; the dihedral angle τ is 26° (see Figure 4.2). The radial carbonyls that lie close to the plane of the metal triangle are bent back from the osmium centers (C(32)-Mo-C(34) = 162 (1)°) while those which are
more perpendicular to the plane are approximately linear
(C(31)-Mo-C(33) = 179 (1°)). The Mo-C_{radial} bond lengths are
equal within experimental error; the Mo-C_{axial} length is
slightly shorter. The equatorial CO on Os(2) which is cis to the
Os-Mo bond is inclined toward the Mo; the Os(1)-Os(2)-C(22)
angle is 164.7 (7)°. The cis ligand-osmium-ligand angles range
from 89° to 95°. Exceptions are for the equatorial carbylns
C(22) and C(12) that are cis to the P(1) phosphite ligand and
are bent further away; these have angles of approximately 98°.

Structure of (μ-H)_{2}(OC),W[Os(CO)_{3}(PMe_{3})]_{2} (4). A view of the
molecular structure of 4 is shown in Figure 4.3, and selected
bond lengths and angles are given in Table 4.4. The metals are
in a triangular arrangement with all the carbylns in terminal
positions. The two phosphine ligands occupy equatorial positions
on separate Os centers, each is cis to an Os-W bond; this
arrangement of the phosphorus ligands is different from that of
custers 1, 2, and 3 (see above). The two bridging hydrogen
ligands were not located in the X-ray structure, but the
positions were unambiguously established by NMR spectroscopy
(see below). Each hydrogen atom bridges a separate Os-W bond,
consistent with the observation that the Os-W distances, 3.154 (2)
Å and 3.156 (3) Å, are identical. These bonds are
significantly longer than those in (μ-H)_{3}Os_{3}W(CO)_{11}(η^{5}-C_{5}H_{5})
(3.073 (2) Å and 3.082 (3) Å). The Os-Os bond length in 4
(2.964 (3) Å) is approximately 0.1 Å longer than the Os-Os bond
length in 3 and in Os_{3}(CO)_{12}, and also longer than Os-Os bonds
Figure 4.3. Molecular Structure of $(\mu-H)_2(OC)_4W[Os(CO)_3(PMe_3)]_2 (4)$.

in mutually trans-substituted $\text{Os}_3(\text{CO})_{10}(\text{L})_2$ complexes. The bond length in 4 is closer in length to the "long" Os-Os bond lengths found in $\text{Os}_4(\text{CO})_6(\text{PMe}_3)_8^{1 c}$ and in $\text{Os}_4(\text{CO})_{15}$. The bond angles $\text{P}(1)-\text{Os}(1)-\text{C}(12)$, $\text{C}(12)-\text{Os}(1)-\text{Os}(2)$, and $\text{Os}(1)-\text{Os}(2)-\text{C}(22)$ range from 90° to 94° as expected for octahedral coordination. The $\text{C}(22)-\text{Os}(2)-\text{P}(2)$ angle (98°) is slightly larger. The carboxyls on W that are cis to the phosphines are pushed together, making the $\text{C}(32)-\text{W}(1)-\text{C}(34)$ angle 86 (2)°. The axial carboxyls on all the metal centers are
slightly rotated with respect to each other; the torsion angles are $C(13)-Os(1)-Os(2)-C(23) \ (4.7^\circ)$, $C(23)-Os(2)-W(1)-C(33) \ (4.7^\circ)$, and $C(33)-W(1)-Os(1)-C(13) \ (7.5^\circ)$. The $C_{ax}-M-C_{ax}$ angles are all approximately $173^\circ$.

**Spectroscopic Properties of $(OC)_{5}M[Os(CO)_3(PR_3)]_2$ and $(\mu-H)_{2}(OC)_4W[Os(CO)_3(PMe_3)]_2$ Clusters.** An infrared spectrum of $(OC)_{5}W[Os(CO)_3(PMe_3)]_2 \ (3)$ in hexane is shown in Figure 4.4; similar spectra were obtained for all $(OC)_{5}M[Os(CO)_3(PR_3)]_2$ analogues of 3. There was no evidence for bridging carbonyls in the IR spectra of these clusters in solution. This agrees with the X-ray results which showed that all the CO ligands are terminal.

The $^{31}P$, $^{13}C$, and $^1H$ NMR spectra are all similar for clusters 1, 2, and 3; the data are given in Tables 4.2 and 4.3. These clusters all exhibit fluxional behavior at room temperature; three of the exchange processes become static at very low temperatures. (A detailed discussion of these fluxional processes is presented in Chapter 5.) The $^{13}C$ NMR spectra of $(OC)_{5}W[Os(CO)_3(PMe_3)]_2 \ (3)$ and $(OC)_{5}Cr[Os(CO)_3(PMe_3)]_2 \ (1)$ recorded at 151 K are shown in Figures 4.5 and 4.6, respectively. Both spectra are consistent with the presence of two isomers, A and B, as shown for the W analogue (Me and axial CO groups have been omitted for clarity). These two isomers have been shown to be in equilibrium (see Chapter 5). Based on the characteristic region of the resonances of the carbonyls, the presence of $^{183}$W satellites, the intensities, and the mode of
Figure 4.4. Carbonyl Stretching Region of the Infrared Spectrum of $(\text{OC})_5\text{W}[(\text{OsCO})_3(\text{PMe}_3)]_2$ (3) in Hexane Solution.
Figure 4.5. $^{13}$C NMR Spectrum of (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) at 151 K in CD$_2$Cl$_2$/CHFCl$_2$ (1/3, v/v).
Figure 4.6. $^{13}$C NMR Spectrum of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1) at 151 K in CD$_2$Cl$_2$/CHFCl$_2$ (1/3, v/v).
collapse of the signals at higher temperatures, the spectrum of 3 can be assigned as indicated by the letters a through j. The spectrum of 1 can be assigned similarly, and is consistent with the presence of two isomers, 1A and 1B. It is apparent that even at 151 K, all of the resonances attributed to isomer 3A, with the exception of the signal assigned to carbonyl e, remain slightly broadened; this indicates that the exchange process that involves the other carbonyls is not static on the NMR time scale at 151 K. Warming the sample of 3 to 157 K causes nearly complete collapse of all signals due to isomer A except that of carbonyl e. It is also apparent that the four radial carbonyls on W are equivalent in each particular isomer. We have interpreted this as due to unrestricted rotation of the M(CO)$_5$ group relative to the Os$_2$ fragment since no static conformation of the M(CO)$_5$ group would render all four radial carbonyls equivalent.$^{112}$ No $^{31}$P-$^{13}$C coupling was observed; this is not unusual for carbonyl carbons that are cis to phosphorus in osmium clusters, though this is more generally the case for
equatorial rather than axial carbonyls.

The $^{31}$P NMR spectra of 3 recorded at 151 K and 240 K are shown in Figure 4.7. These spectra are also representative of the $^{31}$P spectra for the Cr and Mo analogues. The interpretation of the spectrum obtained at 151 K is consistent with the presence of two isomers, A and B (see above). Upon warming, the high field signals at $\delta$ -41.0 and $\delta$ -44.0 coalesce to a singlet at $\delta$ -42.2; these signals can, therefore, be assigned to isomer 3A. (A fluxional process that accounts for this behavior is presented in Chapter 5.)

The $^1$H NMR of 3 at room temperature shows only one doublet at $\delta$ 1.90 ($J_\text{P-C} = 12$ Hz) for the methyl groups on the two inequivalent PMe$_3$ ligands; apparently the protons are unaffected by the slight change in environment between isomers A and B.

An infrared spectrum of ($\mu$-H)$_2$(OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (4) in CH$_2$Cl$_2$ is shown in Figure 4.8; similar spectra were obtained for all analogues of 4. The IR band pattern is much simpler than that of 3 probably due to the greater symmetry in 4 and because there is only one isomer of 4 in solution (see below).

The $^1$H NMR of 4 in the high field region consists of a doublet centered at $\delta$ -16.25 ($J_\text{P-H} = 16.7$ Hz) with $^{183}$W satellites ($J_{W-H} \approx 36$ Hz). The position of the hydride signal is in the region expected for bridging hydrides of Os and W. That the signal shows $^1$H-$^{183}$W coupling, and it is not a triplet due to coupling to two equivalent phosphorus atoms, unambiguously
establishes the location of the bridging hydrides on Os-W bonds rather than on the Os-Os bond. The $^{31}$P{'H} NMR spectrum shows only one singlet at $\delta$ -45.8; this indicates chemically equivalent environments for each of the phosphines, and, therefore, precludes the possibility that both hydrogen atoms bridge the...
Figure 4.8. Carbonyl Stretching Region of the Infrared Spectrum of $(\mu-H)_{2}(OC)_{4}W[Os(CO)_{3}(PMc_{3})]_{2}$ (4) in CH$_2$Cl$_2$ Solution.
same Os-W bond.

The $^{13}$C NMR spectrum of 4 recorded at room temperature is shown in Figure 4.9. The spectrum is consistent with the solid-state structure which, therefore, indicates that there is only one isomer present in solution. The spectrum also shows that unlike the (OC)$_5$M[Os(CO)$_3$(PR$_3$)]$_2$ clusters, 4 is completely static at room temperature. The resonances to low field of 200 ppm can be unequivocally assigned to the carbonyls on W. The resonance due to the axial carbonyls on W cannot, however, be unambiguously distinguished from that due to the equatorial

![Figure 4.9. $^{13}$C NMR Spectrum of $(\mu-\text{H})_2$(OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (4) in CDCl$_3$.](image-url)
carbonyls on W. The signal at $\delta$ 202.2 is slightly broadened, possibly due to $^1H-^{13}C$ coupling, which suggests that this signal is due to the equatorial carbonyls. Only two resonances were observed for the axial and equatorial carbonyls on W; this implies the presence of a $C_2$ axis that passes through the center of the Os-Os bond vector to the W atom. This two-fold axis, together with the $^1H-^{183}W$ coupling (see above), requires the two bridging hydrogen atoms to lie along separate Os-W bonds, in agreement with the X-ray results (see above). The resonance of intensity four at $\delta$ 183.8 is attributable to the four equivalent axial carbonyls on the Os centers; the resonances for axial carbonyls on Os have previously been observed to occur downfield from those for equatorial carbonyls on Os.$^{122,48}$ The signal due to the axial carbonyls on Os shows some degree of coupling to the phosphorus, but the coupling is not resolved. Not surprisingly, the sharp resonance at $\delta$ 174.7 attributable to the two equatorial carbonyls on the Os atoms shows no evidence for any coupling to phosphorus.

4.4 Discussion

The $(OC)_5M[Os(CO)_3(PR_3)]_2$ clusters are all formed in very low yields as by-products during the preparation of $(L)(OC)_6Os-M(CO)_5$ complexes, and heretofore a higher yield route to their formation was unknown. The use of the isolobal analogy to generate heterotrimetallic clusters by the addition of an
ethylene-like bimetallic species to an \( \text{M(CO)}_5 \) (\( \text{M} = \text{Cr, Mo, W} \)) fragment\(^{123} \) is precluded as a synthetic strategy to prepare the \( \text{(OC)}_5\text{M[Os(CO)}_3(\text{PR}_3)]_2 \) clusters since stable species with Os=Os double-bonds are exceedingly rare and unstable.\(^{124} \)

Heterotrimetallic complexes \( \text{(OC)}_5\text{Cr[Os(CO)}_3(\text{PMe}_3)]_2 \) (1), \( \text{(OC)}_5\text{Mo[Os(CO)}_3(\text{PMe}_3)]_2 \) (2), and \( \text{(OC)}_5\text{W[Os(CO)}_3(\text{PMe}_3)]_2 \) (3) are readily prepared by photolysis of the appropriate \( \text{(L)(OC)}_4\text{Os-M(CO)}_5 \) complexes in the inert solvent \( \text{C}_6\text{F}_6 \) at room temperature. Attempts to prepare the W and Mo clusters by either the thermal or photochemical reaction of \( \text{W(CO)}_4(\text{NCMe})_2 \) or \( \text{(C}_7\text{H}_8)\text{Mo(CO)}_4 \) with \( \text{Os(CO)}_4(\text{L}) \) complexes gave the desired products in yields of 5% or less. All of the complexes are deep red, air-stable solids which were readily isolated in pure form following column chromatography and recrystallization. Each has been fully characterized by elemental analysis, infrared and mass spectroscopy, and by either \(^{13}\text{C} \) and/or \(^{31}\text{P} \) NMR spectroscopy. The \( \text{(OC)}_5\text{Cr[Os(CO)}_3(\text{PMe}_3)]_2 \) complex represents the first example of a cluster which contains both osmium and chromium, and the Mo derivative represents a rare example of a cluster that contains molybdenum and osmium.\(^{111} \)

Based on spectroscopic evidence, all three clusters adopt the same two isomer forms A and B (see page 130) in solution, though the isomer ratios vary significantly from one complex to the next. It is apparent from the isomer ratios given in Table 4.2 that isomer A is the preferred geometry for the \( \text{(OC)}_5\text{M-[Os(CO)}_3(\text{PR}_3)]_2 \) complexes. This geometry corresponds to the
major isomer found in solution for $\text{Os}_3(\text{CO})_9(\text{PR}_3)_2$ complexes as well.\textsuperscript{125} There is likely to be a greater repulsive interaction between the methyl groups on a syn phosphorus ligand and the four carboxyls on the square pyramid-like $\text{M(\text{CO})}_5$ fragment (when the phosphorus ligand is cis to an Os-W bond) than between it and only one equatorial carboxyl on an adjacent Os center (when the phosphorus ligand is trans to an Os-W bond). Therefore, for steric reasons, isomer $B$ is expected to be less favorable for the $(\text{OC})_5\text{M}[\text{Os(\text{CO})}_3(\text{PR}_3)]_2$ complexes. A problem arises, however, in attempts to rationalize the isomer ratios based purely on steric interactions. For example, in 3 which has an $A:B$ isomer ratio of $2.6:1$, substitution of $\text{PMe}_3$ by a ligand with a smaller cone angle would be expected to increase the relative population of isomer $B$. However, in $(\text{OC})_5\text{W}[\text{Os(\text{CO})}_3(\text{P(OMe)}_3)]_2$ the $A:B$ ratio is approximately $5.3:1$. A similar increase in the $A:B$ ratio is also observed for the $\text{P(OMe)}_3$ versus the $\text{PMe}_3$ derivatives of the Cr and Mo analogues. Based on a steric argument, this observation is not especially surprising since the well known protrusion of the methyl groups outside the cone angle of $\text{P(OMe)}_3$, may cause an increased steric interaction beyond that expected based purely on a cone angle comparison. But a problem again arises with this simple steric argument since substitution of $\text{P(OMe)}_3$ with $\text{P(OC(\text{CH}_2)}_3\text{CMe}$ (which has a cone angle of $101^\circ$\textsuperscript{9,6}) results in an $A:B$ isomer ratio of approximately $9:1$ in $(\text{OC})_5\text{W}[\text{Os(\text{CO})}_3(\text{P(OC(\text{CH}_2)}_3\text{CMe})]_2$. Thus, it is apparent that as the phosphorus ligand becomes a poorer $\sigma$-donor and a better $\pi$-acceptor, the relative population of isomer $A$ increases. In
addition, a comparison of the isomer ratios for 3 and

\[ ((\text{MeO})_3\text{P})(\text{OC})_4\text{W(Os(CO))}_3(\text{PMe}_3)]_2 \] (6) shows that substitution of

the axial CO on the W(CO)_5 fragment by the better σ-donor, but

poorer π-acceptor, P(OMe)_3 group leads to an A:B isomer

distribution in which the relative population of isomer B is

slightly greater than that of A. Taken together, these

observations lead to the conclusion that isomer A will become

increasingly favored as electron density is removed from the

Os_2(CO)_6(PR)_3)_2 fragment. The difference in isomer ratios between

1 and 3 may be the result of poorer overlap between the LUMO on

the Cr(CO)_5 group with the HOMO on the Os_2 fragment which would

result in less electron removal by Cr(CO)_5 than by W(CO)_5.

With the exception of the preparation of (OC)_4W(Os(CO))_3-

(PMe)_3)]_2, when C_6H_6 was used as the solvent for photolysis, all

the dative bonded species yielded products that appeared to

result from oxidative-addition to Os(CO)_4(PR)_3).† (Infrared

spectra of the reaction products indicated the presence of

fac-Os(CO)_3(PR)_3(X)_2 species.) It is probable that C-H activa-
tion of C_6H_6 occurs in these reactions given that this is a well

known result of the photolysis of Ir(η^5-C_5Me_5)(H)_2(PR)_3)_2^1a and

Ir(η^5-C_5Me_5)(CO)_2^1b in C_6H_6. In addition, Os complexes that

contain phosphine ligands are known to activate C-H bonds under

mild thermal conditions. 126 For the case of (Me_3P)(OC)_4OsW(CO)_5

(5) which produced 3 in good yield upon photolysis in C_6H_6, it

was found that heating 5 in C_6H_6 also produced 3 in good yield.

†We have recently found that the use of a GWV light filter
(300 nm cutoff) does allow the use of C_6H_6 as solvent.
This represents a rare example where the photochemical and thermal reactivity of a compound with a metal-metal bond appears to be the same.

The reactivity of complexes with dative metal-metal bonds appears, on the surface at least, to be different from that of complexes with covalent metal-metal bonds. The primary photo-process at room temperature in species such as $M_2(CO)_{10}$ ($M = \text{Mn, Re}$), $\text{MnRe(CO)}_{10}$, $\text{Cp(O)}_2\text{ReMn(CO)}_5$, and other metal-metal single bonded species has been found to involve homolytic cleavage of the metal-metal bond to generate radical fragments. To our knowledge, metal clusters have never been observed upon the photolysis of complexes with covalent metal-metal bonds. There are several reasons why the mechanism of formation of the cluster species may not involve homolytic cleavage of the dative metal-metal bond. First, homolytic fission of the metal-metal bond would yield ionic radical species. In a nonpolar solvent

$$M' \rightarrow M' \xrightarrow{h\nu} [M^+] + [M^-]$$

such as $C_6F_6$ it may be unlikely that the two oppositely charged radical species would be able to diffuse far enough away from each other to undergo chemical reactions. While homolytic cleavage cannot be ruled out, it is likely that it would be rapidly followed by combination of the radical ions to regenerate the starting material. There is precedent for the formation of radical ions following photolysis but these result from a thermal electron transfer process, and not from
the initial photolysis. Secondly, we have recently identified a nearly linear trimetallic complex, which may be a precursor to the cluster species. This complex, produced as a minor product during the preparation of \([\text{MeC(CH}_2\text{O)}_3\text{P}](\text{OC})_4\text{OsW(CO)}_5\)\(^{128}\) readily forms the heterotrimetallic cluster upon photolysis in \(\text{C}_6\text{F}_6\).

Like the cluster species, there is no precedent for the formation of a linear trimetallic product from the photolysis of complexes with metal-metal bonds. At this point, however, a mechanism for the formation of the clusters or the linear trimetallic species is not obvious, and neither homolytic nor heterolytic metal-metal bond cleavage processes can be ruled out (see p 104). Preliminary results suggest that the mechanism may involve only the bimetallic complex. For example, photolysis of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) in the presence of added \(\text{Os(CO)}_4(\text{PMe}_3)\) did not increase the yield of 3; \(\text{Os(CO)}_4(\text{PMe}_3)\) was mostly converted to \(\text{Os}_3(\text{CO})_{10}(\text{PMe}_3)_2\) and \(\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3\) (identified by elemental analysis, and by IR and mass spectroscopy).

The solid-state structures of the \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PR}_3)]_2\)
\((\text{M} = \text{Cr} \ (1), \ \text{Mo} \ (2), \ \text{W} \ (3))\) clusters are similar. Each is
composed of a triangular arrangement of metal atoms with only terminal carbonyl ligands, and each molecule has a phosphorus ligand trans to an Os-W bond on one of the Os atoms while the phosphorus ligand on the other Os atom is cis to an Os-W bond.

The Os-Os bond lengths are all in the range of 2.84 Å to 2.85 Å, a length similar to the single bond length of 2.877 Å in Os₃(CO)₁₂. The average Os-Mo and Os-W bond lengths in 2 and 3 are 3.06 Å and 3.05 Å, respectively. These bond lengths are more like those found for hydrogen-bridged Os-Mo and Os-W bonds. The lengthened bonds may be a reflection of the bonding mode in these clusters (see Chapter 5). The lengthened bonds may also be due to some inherent difference in bond lengths in trinuclear clusters versus the higher nuclearity clusters that are the only species known to which comparisons can be made. It has been found that the metal-metal bond distances in tetranuclear clusters are generally 0.05 Å to 0.10 Å shorter than in trinuclear clusters. Since 1 represents the only cluster that contains osmium and chromium, the average Os-Cr bond length of 3.01 Å cannot be judged to be either long or short. Compared to the dative metal-metal bond in bimetallic Os-Cr complexes (see above), the Os-Cr bond in 1 would seem to represent a "long" Os-Cr bond. It should be pointed out, however, that a general comparison between the lengths of metal-metal bonds in clusters versus those in complexes with dative metal-metal bonds cannot be made since, unlike 1, the Os-W bond in 3 is shorter than that in the corresponding bimetallic complex. In all cases, the
longer Os-M bond in the \((\text{OC})_2M[\text{Os(CO)}_3(PR_3)]_2\) complexes is the one that is cis to the phosphorus ligand; this has been observed to be a general trend in bis-substituted \(\text{Os}_3(\text{CO})_2(L)_2\) complexes.\(^{120}\)

The arrangement of the phosphorus ligands in the solid state is unlike that found in disubstituted triosmium clusters. For example, the solid-state structures of \(\text{Os}_3(\text{CO})_{10}(L)_2\) \((L = \text{PPh}_3, \text{PPh(OMe)}_2, \text{P(OMe)}_3)\) complexes show that the two phosphorus ligands occupy equatorial positons on adjacent Os centers, each trans to the same metal-metal bond.\(^{120}\) It has been argued that the mutually trans disposition of the phosphorus ligands results in the least amount of steric crowding. This argument does not, however, hold for complexes 1 to 3. In each of these cases there is no preference in the solid state for a mutually trans arrangement of the phosphorus ligands even with increasing cone angle: \(i.e.,\) the cone angles of \(\text{P(OMe)}_3\) and \(\text{PMe}_3\) are \(107^\circ\) and \(118^\circ\) respectively.\(^{130}\) The structural difference between the triosmium species and that of 1 to 3 may simply be due to increased steric strain imposed by a square-pyramid shaped \(\text{M(CO)}_5\) group versus a sawhorse-shaped \(\text{Os(CO)}_4\) group.

Like the \(\text{Os}_3(\text{CO})_{10}(L)_2\) complexes, there is some twisting at each of the metal centers in the \((\text{OC})_5M[\text{Os(CO)}_3(PR_3)]_2\) \((M = \text{Cr (1), Mo (2), W (3)})\) clusters to relieve steric strain. The torsional angles between the two osmium centers is on the order of \(5^\circ\). The degree of rotation of the \(\text{M(CO)}_5\) fragment with respect to the plane formed by the metal atoms is approximately the same.
in complexes 1, 2, and 3 ($\tau = 23^\circ$ to $26^\circ$). In contrast, the Mo(CO)$_5$ moiety is essentially perfectly staggered in MoRh$_2$(μ-CO)$_2$(CO)$_5$(η$^5$-C$_5$Me$_5$)$_2$ in the solid state, and is averaged to a perfectly staggered arrangement in CoMoRh(μ-CO)$_2$(CO)$_5$(η$^5$-C$_5$Me$_5$)$_2$ in solution at -60 °C.$^{123}$ Clearly, a perfectly staggered conformation would minimize repulsive steric interactions in 1, 2, and 3, and this suggests that there may be an electronic preference for the eclipsed form. Extended Hückel molecular orbital calculations on M(CO)$_5$(C$_2$H$_4$) complexes (Os$_2$(CO)$_6$(PR$_3$)$_2$ is isolobal with C$_2$H$_4$) have shown that there is an electronic preference for an eclipsed conformation of the C$_2$H$_4$ with respect to the metal carbonyl ligands,$^{131}$ though similar calculations on the "inorganic alkene" MoRh$_2$ complex above indicated a slight preference for the staggered form.$^{123a}$ It is stressed, however, that the energy difference between any conformation of the M(CO)$_5$ moiety in 1, 2, and 3 must be very small since the M(CO)$_5$ unit is observed to be freely rotating in solution at 151 K.

The trans OC-M-CO angles about the M(CO)$_5$ moiety in 1, 2, and 3 are all approximately $178^\circ$ between the carbonyls that are nearly perpendicular to the plane of the metal atoms, and approximately $162^\circ$ for those nearly in the plane. Two views of 3 which illustrate these angles are shown in Figure 4.10. It is again stressed that in solution all the carbonyl ligands become equilibrated in 1, 2, and 3. Thus, the time-averaged OC-Mo-CO angles must be equal, and whether in the solid state or in
Figure 4.10. Top View (A) and Side (B) View of (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3).
solution, the coordination about the M(CO)_5 is best described as octahedral with the Os_2(CO)_6(PR_3)_2 group occupying one coordinate position. View A in Figure 4.10 also indicates the octahedral coordination about the osmium centers.

The dihydride clusters (μ-H)_2(OC)_4W[Os(CO)_3(PMe_3)]_2 (4) and the Cr and Mo analogues of 4, represent a departure from the (OC)_5M[Os(CO)_3(PR_3)]_2 clusters in that they are bright yellow, and exist as one isomer which is static in solution at room temperature with respect to carbonyl migration between the metal centers. (The ^1H NMR of (μ-H)_2(OC)_4Cr[Os(CO)_3(PMe_3)]_2 indicates that there are two isomers of this cluster in solution, and that these may be in rapid equilibrium via a trigonal twist process at the Os centers.) The solid-state structure of 4 is also quite different from those of 1, 2, and 3. The location of the phosphorus ligands mutually trans to the same metal-metal bond, the slight twisting of the ML_4 units, and the geometry about each Os center is reminiscent of the structural features of Os_3(CO)_10(L)_2 complexes. The geometry about the W is clearly octahedral except that, unlike (OC)_5W[Os(CO)_3(PMe_3)]_2, two coordination sites are used in bonding to the Os_2 fragment and to the hydrogen atoms. The positions of the bridging hydrogen atoms on separate Os-W bonds were unambiguously established by NMR spectroscopy (see above). In addition, the metal-hydride ligands were placed with the HYDEX program of Orpen: the calculations revealed that the minimum energy positions for the hydrogen atoms occur when each hydrogen bridges a separate Os-W
bond, and with the bridging hydrogen atoms in the plane formed by the three metal atoms.$^{107a}$

The metal-metal contact distances are of particular interest in this molecule. The Os-Os bond length is 2.964 (3) Å, a length that is closer to that of the long Os-Os bonds in Os$_4$(CO)$_5$ (2.99 Å) which have been assigned a bond order of less than one,$^{121}$ than those in Os$_3$(CO)$_2$ (2.877 Å).$^{118}$ Applying Pauling's equation for the calculation of bond order$^{134}$ and using 2.877 Å

$$d(n) = d(1) - 0.6\log(n)$$

for the length of an Os-Os single bond, yields a bond order of 0.7 for the Os-Os bond in 4. The donation of electron density to the electron deficient W(CO)$_5$ fragment from the Os$_2$ HOFO (highest occupied fragment orbital) would be expected to lead to a weakening of the Os-Os bond if the HOFO has substantial metal-metal bonding character. But since a similar lengthening of the Os-Os bond was not observed in 1, 2, and 3, this suggests the possibility that it is an Os$_2$(CO)$_6$(PR$_3$)$_2$(H)$_2$ unit bonded to W(CO)$_5$ in 4: i.e., the Os-Os bond in an isolated Os$_2$(CO)$_6$(PR$_3$)$_2$ fragment would best be described as a double bond, while that in an Os$_2$(CO)$_6$(PR$_3$)$_2$(H)$_2$ fragment would be a single bond in order that each osmium center achieves an 18-electron count, and as such, the HOFO for Os$_2$(CO)$_6$(PR$_3$)$_2$ would be expected to be different from that of Os$_2$(CO)$_6$(PR$_3$)$_2$(H)$_2$. This interpretation would also be consistent with the observed W-H coupling (ca 36 Hz) which is approximately half that found for a hydrogen
atom bonded directly to W (ca 62 Hz);\textsuperscript{77} this may indicate that the hydrogen atoms are closer to the osmium centers than to the tungsten atom. It should be pointed out, however, that the metal-metal bond length may not be an accurate measure of the bond order. This reason for this is that the force constant for a metal-metal bond is small (compared, for example, to that of a carbon-carbon bond for which bond lengths and bond orders are much more closely related), and therefore, easily distorted by steric interactions.\textsuperscript{135}

To our knowledge, the hydrogen-bridged metal-metal bonds in $(\mu^{-}H)_{2}(OC)_{4}W[Os(CO)_{3}(PMe_{3})]_{2}$ (4) represent the longest Os-W bonds known (average 3.15 Å). The bonds are on the order of 0.1 Å longer than the unbridged osmium-tungsten bonds in $(OC)_{5}W[Os(CO)_{3}(PMe_{3})]_{2}$; this is consistent with studies by Churchill in which H-bridged Os-W bonds in clusters were found to be approximately 0.13 Å longer than unbridged Os-W bonds,\textsuperscript{136} and with studies which have shown that H-bridged metal-metal bonds are generally lengthened by 0.1 Å or more compared to the analogous unbridged bonds.\textsuperscript{137} The unusually long H-bridged Os-W bonds in 4 may be attributable to the structural differences between the open Os$_{2}$W triangular core of 4 and that of the closo tetrahedral core clusters to which the bond length comparisons must be made (see above). The possibility that the Os-H-W bonds are unsupported is disregarded here since such bond lengths tend to be on the order of 3.3 Å to 3.4 Å in complexes that contain metals with smaller covalent radii than W.\textsuperscript{138} Furthermore, the
sum of the M-H and M'-H bond lengths is generally very close to the observed M-M' separation in complexes that have unsupported M-H-M bonds. In 4 the sum of the W-H length (~1.685 (3) Å)‡ and the Os-H length (1.637 (4) to 1.668 (4) Å) is much longer than the observed Os-W bond length of 3.16 Å.

The chemical reactivity of clusters 1, 2, and 3 has only been briefly explored. We were prompted to investigate the substitution of one of the CO ligands by two electron donors since we were able to introduce $^{13}$CO into the clusters simply by stirring hexane solutions of the clusters at 50° to 80 °C under 1 atm of $^{13}$CO. Thus, it appeared that loss of CO was facile in these complexes. As noted above, (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) reacted under mild conditions with H$_2$ to yield (μ-H)$_2$(OC)$_4$W-[Os(CO)$_3$(PMe$_3$)]$_2$. Similarly, the Cr and Mo analogues of 3 reacted with H$_2$ to give the corresponding dihydride clusters; these products were identified by IR and $^1$H NMR spectroscopy. In addition, 3 reacted with P(OMe)$_3$ in solution at 50 °C to yield [(MeO)$_3$P](OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (6). By comparison, substitution of a CO in Os$_3$(CO)$_{12-χ}$(L)$_χ$ requires much more forcing conditions, or the use of a decarbonylation reagent such as Me$_3$NO. The $^{13}$C NMR spectrum of 6 indicated that the P(OMe)$_3$ ligand occupies the axial position on W (as shown below), and that there are two isomers in solution that correspond to those of 3A

and 3B. The $^{13}$C NMR spectrum also showed that rotation of the W(CO)$_4$(L) group remains unrestricted at room temperature, but that all other CO-exchange processes observed in 3 are static on the NMR time scale at ambient temperature in 6. Like the parent complex, 6 is deep red; this can be taken to indicate that the metal-metal bonding in 6 is relatively unchanged upon substitution of a CO for P(OMe)$_3$. (i.e., The energy of the $\sigma \rightarrow \sigma^*$ transition would be expected to change if the metal-metal bonding had been altered, and this would result in a color change in the complex.) Preliminary studies on 3 have also shown that it reacts under similar conditions with C$_2$Ph$_2$ to form an as yet unidentified bright yellow complex. Research has been proposed to study reactions of the trinuclear cluster complexes with two-electron donor ligands such as olefins, acetylenes, RS$^-$, and Os(CO)$_4$(L) complexes.

4.5 Conclusion

A convenient method has been developed for preparation of the heterotrimetallic clusters (OC)$_3$M[Os(CO)$_3$(PR$_3$)]$_2$ (M = Cr, Mo, W) by photolysis in C$_6$F$_6$ of bimetallic complexes with dative
metal-metal bonds. The clusters with osmium and chromium are the first examples of clusters that contain these two metals. The number and composition of the heterotrimetallic clusters appears to be limited only by the number of bimetallic starting materials that are available, and the stability of the resultant metal cluster complexes. Therefore, this synthetic approach represents a versatile method for the preparation of heterotrimetallic clusters of a desired composition. The mechanism of formation of these clusters remains uncertain, though preliminary evidence suggests that they may be formed through a linear trimetallic intermediate.

The \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PR}_3)]_2\) clusters that have been structurally characterized all adopt the same geometric features in the solid state. The phosphorus ligands are bound to separate osmium centers in the equatorial plane. The arrangement of the phosphorus ligands, one cis and one trans to the Os-Os bond, is unlike that found in \(\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_2\) complexes; the difference is attributed to steric interactions between a cis phosphorus ligand and the square pyramid-like \(\text{M(CO)}_5\) fragment. The \(^{31}\text{P}[^1\text{H}]\) and \(^{13}\text{C}\) NMR spectra showed that each complex exists as two isomers in solution, one which corresponds to that found in the solid state, and one in which the phosphorus ligands are both trans to the Os-Os bond. There is a significant variation in the isomer ratios in solution at room temperature. The available data indicates that poorer \(\sigma\)-donor (or better \(\pi\)-acceptor) phosphorus ligands stabilize the trans-trans isomer whereas
better $\sigma$-donor (or poorer $\pi$-acceptor) phosphorus ligands stabilize the cis-trans isomer. With the exception of (OC)$_5$W[Os(CO)$_3$[P(OCH$_2$)$_3$CMe]$_2$, all of the (OC)$_5$M[Os(CO)$_3$(PR$_3$)]$_2$ clusters showed evidence ($^3$P or $^{13}$C NMR) for rapid CO site exchange at room temperature. Two of the complexes, 1 and 3, showed $^{13}$C NMR spectra consistent with static structures of the two isomers only at 151 K.

Substitution of one CO on the M(CO)$_5$ fragment is facile in the (OC)$_5$M[Os(CO)$_3$(PR$_3$)]$_2$ complexes. Under mild conditions (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) reacted with H$_2$ to form ($\mu$-H)$_2$(OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (4), and with P(OMe)$_3$ to form [(MeO)$_3$P](OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (6). At 3.154 (2) Å and 3.156 (3) Å, the H-bridged Os-W bonds in 4 represent the longest Os-W bonds known. The bright yellow color of 4 indicates that the bonding in the metal framework has been altered from that of the deep red starting material (3). On the other hand, the deep red color of 6 indicates that substitution of an axial CO on W with P(OMe)$_3$ does not significantly alter the metal-metal bonding; this is consistent with the NMR results. Reactions of (OC)$_5$M[Os(CO)$_3$(PR$_3$)]$_2$ complexes with other two electron donor ligands, including 18-electron organometallic complexes, will form the basis for future research in this area.
CHAPTER 5

FLUXIONAL BEHAVIOR AND BONDING IN \((\text{OC})_5\text{M}[\text{Os(CO)}_3(\text{PR}_3)]_2\) CLUSTERS

5.1 Introduction

The field of organometallic cluster chemistry has expanded tremendously since Muetterties first proposed that metal clusters may serve as models for the study of metal surface chemistry.\(^{140}\) In particular, it was suggested that migration of small molecules on a molecular cluster surface, which could be studied by conventional spectroscopic techniques (e.g., NMR spectroscopy), may reveal valuable information with respect to migration of molecules on the surface of a bulk metal catalyst. Ligand exchange processes in clusters are common.\(^{141}\) Carbonyl site exchange in \(\text{Fe}_3(\text{CO})_{12}\), for example, remains fast on the NMR time scale even at \(-150\) °C. The \(^{13}\text{C}\) NMR spectrum of \(\text{Ru}_3(\text{CO})_{12}\) also exhibits only one singlet at temperatures down to \(-100\) °C.\(^{142}\) On the other hand, the \(^{13}\text{C}\) NMR spectrum of \(\text{Os}_3(\text{CO})_{12}\) at room temperature exhibits two singlets attributable to the axial and equatorial carbynols; these singlets do broaden and coalesce in the base line at \(90\) °C,\(^{143}\) indicative of axial/equatorial exchange. There are a number of other metal clusters in which carbonyl and hydride site exchange processes have been observed. There do not appear to be any well defined rules for fluxional behavior in clusters that can be used to predict whether or not ligand exchange will be facile. Therefore, the study of ligand exchange processes in organometallic clusters remains of
A brief description of the CO site exchange processes in the heterometallic cluster (OC)₅Cr[Os(CO)₃(PMe₃)]₂ has been recently published in communication form.¹² A discussion of the fluxional processes exhibited by the (OC)₅M[Os(CO)₃(PR₃)]₂ (M = Cr, W; R = Me, OMe; PR₃ = P(OCH₂)₃CMe) complexes as indicated by variable temperature¹³C and³¹P NMR spectroscopic studies is presented in this chapter.

5.2 Experimental

The (OC)₅M[Os(CO)₃(PR₃)]₂, [(MeO)₃P](OC)₄W[Os(CO)₃(PMe₃)]₂, and (μ-H)₂(OC)₄W[Os(CO)₃(PMe₃)]₂ complexes were prepared as described in Chapter 4. All variable temperature¹³C and³¹P NMR spectra were obtained on a Bruker WM400 spectrometer at operating frequencies of 100.6 MHz and 162 MHz, respectively. The¹³C NMR spectra were obtained on¹³CO enriched samples in a CD₂Cl₂/CH₂Cl₂ solvent mixture for the temperature range of 180 K to 300 K, a 1/3 (v/v) CD₂Cl₂/CHFCl₂ solvent mixture for temperatures lower than 180 K, and C₆D₅CD₃ for temperatures greater than 300 K.
5.3 Results and Discussion

The $^{13}$C and $^{31}$P NMR data for the relevant complexes are listed in Tables 4.2 and 4.3. Variable temperature $^{13}$C NMR spectra for (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) are shown in Figure 5.1. At 151 K the spectrum indicates that there are two isomers of 3; these correspond to isomers 3A and 3B. A discussion of the spectral assignments is given in Chapter 4; the $^{13}$C resonances for the carbonyls are indicated by the letters a through j on the 151 K spectrum. The $^{31}$P NMR spectrum of 3 at 151 K is also consistent with the presence of 3A and 3B. The major isomer is 3A.

![Diagram](image_url)

The $^{13}$C NMR spectrum at 151 K shows that even at this low temperature, the four radial carbonyls on the W(CO)$_5$ fragment are equivalent in both isomers. The equivalence in 3B could be explained simply by assuming perfect staggering of the four carbonyls with respect to the Os-Os bond vector. However, a perfectly staggered arrangement would not render all the radial carbonyls in 3A equivalent since the magnetic environment at
Figure 5.1. Variable Temperature $^{13}$C NMR Spectra of (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) from 151 K to 323 K.
each osmium center is different. For 3A these carbonyls will only become equivalent if there is rapid rotation of the W(CO)$_5$ group with respect to the Os$_2$ fragment (see Scheme I). Since

Scheme I.

there is no detectable broadening due to exchange of the NMR signal at 151 K, this implies that the rate of exchange is in the fast exchange region, i.e., $k > 2.22\Delta\nu$. A chemical shift difference of 2.47 ppm for the two inequivalent sets of carbonyls of the W(CO)$_5$ unit in the dihydride derivative of 3 (see Chapter 4) can be used to approximate the chemical shift difference of the radial carbonyls for a static W(CO)$_5$ fragment in 3. If it is assumed that 151 K corresponds to the coalescence temperature for the resonances of the axial carbonyls, this results in an exchange rate of $5.5 \times 10^2$ s$^{-1}$ and a $\Delta G^\dagger$ of $28$ kJ mol$^{-1}$ for the rotation process.† The calculated value of $\Delta G^\dagger$ is, however, clearly an upper limit to the rotational barrier since the NMR signal shows no broadening. For example, for two sites that undergo fast exchange, the rate constant required to observe detectable broadening (of 0.5 Hz) due to

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† The chemical shift difference may be unrealistic since there are obvious chemical differences between a W(CO)$_5$ group and a $(\mu-\text{H})_2\text{W(CO)}_4$ group, but chemical shift differences of $>10$ ppm for axial and equatorial carbonyls in Os clusters are common.
exchange is given by $\pi(\Delta \nu)^2$ where $\Delta \nu$ is the chemical shift difference between the two signals when the molecule is rigid.\textsuperscript{145} This gives a rate of at least $\sim 1.9 \times 10^5$ s\textsuperscript{-1} for the rotation. The calculated $\Delta G^\ddagger$ from this rate is $\sim 20$ kJ mol\textsuperscript{-1}. The difference between these two $\Delta G^\ddagger$ values suggests that the true coalescence temperature must be well below 151 K. Therefore, this indicates that there is essentially unrestricted rotation of the W(CO)$_5$ fragment at this temperature. (Compare, for example, the energy barriers of 54.4 \pm 2.1, and 67.8 \pm 2.1 kJ mol\textsuperscript{-1} calculated for the rotation about the metal-metal single bonds in Mo$_2$(η\textsuperscript{5}-C$_5$H$_5$)$_2$(CO)$_5$CNMe\textsuperscript{146} and [W(η\textsuperscript{5}-C$_5$H$_5$)(CO)$_3$],\textsuperscript{147} respectively.) It has been proposed that this indicates a strong centrally-directed three-center, two-electron bond in the Cr analogue of 3.\textsuperscript{112a} Stone has observed similar rotation in MoCoRh(μ-CO)$_2$(CO)$_5$(η\textsuperscript{5}-C$_5$Me$_5$)$_2$ (15)\textsuperscript{123a} and [PtRh$_2$(μ-H)(μ-CO)$_2$(L)(L')(η\textsuperscript{5}-C$_5$Me$_5$)$_2$]{BF$_4$} (16).\textsuperscript{148} The barrier to rotation in 15 was calculated to be 52.3 ± 1.3 kJ mol\textsuperscript{-1} at the coalescence temperature ($\sim -16$ °C), while those for three PtRh$_2$ derivatives of 16 were 49.3, 56.0, and 58.1 kJ mol\textsuperscript{-1}, respectively. These barriers to rotation are significantly higher than in 3. Furthermore, whereas spectra consistent with the solid state structures were obtained at 213 K and 223 K for 15 and 16, respectively, the rotation of the W(CO)$_5$ fragment was still fast on the NMR time scale for 3 even at 151 K. In contrast to (OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ and (μ-H)$_2$(OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$, it is only the hydrogen bridged [PtRh$_2$(μ-H)]$^+$ species that exhibit this type of rotation while
the neutral PtRh$_2$ clusters do not undergo this rotation.

Substitution of the axial CO on the W(CO)$_5$ fragment of 3 with P(OMe)$_3$ (see Chapter 4) has no effect on the rotational process. The $^{13}$C NMR spectrum of [(MeO)$_3$P](OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (6) at 253 K is shown in Figure 5.2; it is consistent with the presence of two isomers, 6A and 6B. Further evidence for unrestricted rotation of the M(CO)$_5$ group is presented below. This rotation appears to be independent of other fluxional processes in 3 and its analogues. For example, in (OC)$_5$W-[Os(CO)$_3$(P(OCH$_2$)$_3$CMe)]$_2$ which is rigid with respect to inter-metal carbonyl exchange at 261 K (see below), no broadening of the radial W(CO)$_5$ resonances was observed upon cooling to 183 K.

At 151 K the resonances assigned to carbonyls a, b, c, d, and f, of isomer 3A are all broadened (see Figure 5.1); this indicates that a fluxional process involving these carbonyls is not quite static even at this temperature. As the temperature is increased to 157 K the resonances of these carbonyls broaden simultaneously. The resonances due to carbonyls d and f (the axial carbonyls on the Os centers) coalesce separately from the other signals and sharpen to a singlet in the 278 K spectrum. Therefore, carbonyls d and f do not participate in the fluxional process of carbonyls a, b, and c, but are instead rendered e-equivalent by that exchange process. The signals due to carbonyls a, b, and c, emerge as a single resonance in the 249 K spectrum. Note that the resonance attributed to carbonyl e of 3A remains sharp over the complete temperature range.
A site exchange mechanism consistent with these observations is shown in Scheme II (carbonyls above and below the WOs$_2$ plane have been omitted for clarity). The mechanism involves a partial

Figure 5.2. $^{13}$C NMR Spectrum of [(MeO)$_3$P](OC)$_4$W[Os(CO)$_3$(PMe$_3$)]$_2$ (6) at 253 K.
equatorial merry-go-round process. In order to preserve an 18-electron configuration at each metal center, synchronous movement of carbonyls to generate the intermediate 3i with three bridging carbonyls is proposed; the intermediate must have a low concentration since there is no evidence for any bridging-carbonyl species in the $^{13}\text{C}$ NMR at 151 K. This type of intermediate has been proposed for several bimetallic$^{149}$ and cluster$^{150}$ species. However, merry-go-round carbonyl exchange processes that take place in the equatorial plane are rare, especially for triosmium clusters. The "clicking" motion of the phosphorus ligands renders these ligands equivalent with the same rate as the merry-go-round process. This accounts for the concomitant broadening of the carbonyl resonances of d and f with those of carbonyls a, b, and c. This mechanism is also consistent with
the observation of a sharp singlet for carbonyl e over the experimental temperature range since the magnetic environment of e is unchanged throughout this process. In addition, although this mechanism requires the signal due to carbonyl a to collapse at a rate twice that of carbonyl b, all the carbonyls on W are ultimately brought into the equatorial exchange process. This strongly supports the above description of a freely rotating W(CO)$_5$ group.

Further support for a merry-go-round mechanism in the equatorial plane is obtained from the room temperature $^{13}$C NMR spectrum of 6 (see Figure 5.2 above). With the P(OMe)$_3$ ligand on W in the equatorial plane of the three metal atoms, the merry-go-round process is inactivated up to 253 K; this provides strong evidence that the exchange process must occur in the equatorial plane.

Isomer 3B remains static over the entire temperature range since the merry-go-round process is blocked at all times by the two phosphorus ligands, one of which would have to migrate from Os to W to enable this process. (Except in rare cases,$^{151}$ phosphine and phosphite ligands do not form intermediates in which these ligands bridge a metal-metal bond, and so do not migrate from one metal center to another via an intramolecular process.) The static nature of 3B is, therefore, also consistent with the proposed mechanism shown above in Scheme II.
As the sample is warmed to 323 K the resonance attributed to carbonyl e of 3A collapses to the baseline. This may result from a trigonal-twist process at the Os centers (see below) such that carbonyl e becomes equivalent to carbonyls d and f.

The variable temperature $^3\text{P}$ NMR spectra of 3, shown in Figure 5.3, are equally consistent with the equatorial exchange mechanism. From the chemical shift separation of the phosphorus resonances of 3A at 151 K, $\Delta G^\dagger$ for the two site exchange process is calculated to be $\sim 31 \text{ kJ mol}^{-1}$ at the coalescence temperature (175 K). The low energy exchange barrier in 3A for the in-plane merry-go-round process is unprecedented for equatorially substituted trinuclear clusters. Energy barriers for merry-go-round exchange processes in the equatorial plane are typically much greater for trinuclear carbonyl clusters that contain neutral ligands in the exchange plane. A low activation energy for an all equatorial merry-go-round process has been determined for the bis-axially substituted species $(\text{C}_8\text{H}_8\text{N}_2)\text{Ru}_3(\text{CO})_{10}$ ($\sim 26.4 \text{ kJ mol}^{-1}$). A similar mechanism has been proposed for Os$_3$(CO)$_{10}$(C$_7$H$_8$), with an activation energy of $\sim 42.8 \text{ kJ mol}^{-1}$ calculated for this process.

Substitution of the phosphorus ligand on the Os center has a large effect on the barrier to the merry-go-round exchange process. In $(\text{OC})_5\text{W}[\text{Os(OC)}_3[\text{P(OMe)}_3]]_2$ (8) this process becomes static at 207 K; an energy barrier of $\sim 50 \text{ kJ mol}^{-1}$ is calculated at the coalescence temperature of 250 K. As in 3, there is no evidence for equatorial exchange in isomer B of 8. The variable
temperature $^{13}$C NMR spectra of 8 are shown in Figure 5.4. In
(OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ (3) the $^{31}$P NMR resonances for
isomer A are sharp at 261 K, and are only slightly broadened at
291 K; they finally coalesce between 333 K and 354 K. An
exchange barrier of $\sim$67 kJ mol$^{-1}$ at the coalescence temperature
is calculated for 9. Again, isomer B of 9 remains rigid. The
variable temperature $^3$P NMR spectra of $(OC)_5W\{Os(CO)_3[P(OCH_2)_2-CMe]\}_2$ are shown in Figure 5.5.

These results suggest that the energy barrier for the equatorial exchange process increases as the phosphorus ligand becomes a poorer $\sigma$ donor and a better $\pi$ acceptor. There is some precedent for the dependence of the energy barrier for CO site exchange on the electronic properties of the ligand. For example, it has been observed that the activation energy for the bridge-terminal exchange process in $\text{Os}_3(CO)_{11}(L)$ complexes is
Figure 5.5. Variable Temperature $^{31}\text{P}$ NMR Spectra of $(\text{OC})_5\text{W}[\text{Os(CO)}_3[\text{P(OCH}_2)_3\text{CMe}]]_2$ (9).
lowered as the $\sigma$ donor ability of the ligand increases.\textsuperscript{152} This is thought to be due to an expansion of the filled $d$ orbitals which could in turn result in better overlap of the carbonyl $\pi^*$ orbital with the 5$d$ orbital of an adjacent Os center; this would facilitate the formation of the intermediate bridged structure.\textsuperscript{4,6a} It has also been observed that the barrier to axial-equatorial exchange is decreased as the ligand becomes a better donor in $\text{HM}_3(\text{CO})_9[C_2\text{C(CH}_3)_3]\ (M = \text{Ru, Os})$ complexes\textsuperscript{153} as well as in mononuclear Fe complexes.\textsuperscript{154} Alternatively, it may be argued that the same exchange barrier decreases as the steric requirements of the phosphorus ligand increase; the relative cone angles of the three phosphorus ligands are $\text{PMe}_3 > \text{P(OCH}_3)_3 > \text{P(OCH}_2)_3\text{CMe}$. The larger cone-angle ligands may force the carbonyls into positions that approach the transition state for site exchange; this would facilitate the exchange process. A decrease in the activation energy of a trigonal-twist process with a corresponding increase in the size of the ligand has been observed in $[\text{PPN}]\text{Os}_X(\text{CO})_1\) (X = Cl, Br, I, NCO) complexes.\textsuperscript{150d} Given that the merry-go-round and trigonal-twist processes are different, and that there is only a limited amount of data available, it is not possible to separate whether electronic or steric effects have the dominant influence on the energy barriers.

The Cr analogue of 3, (OC)$_5\text{Cr}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$ (1), undergoes the same two low energy CO site exchange processes as 3. The variable temperature $^{13}\text{C}$ NMR spectra of 1 are shown in Figures
The resonances in the spectrum at 151 K have been assigned in Chapter 4. The labels a through j for the carbonyls on 1 follow that illustrated above for 3, consistent with the presence of two isomers, 1A and 1B. There is no evidence for any broadening of the resonances due to the radial carbonyls of the Cr(CO)₅ group of either isomer in the 151 K spectrum. This indicates that the Cr(CO)₅ group is freely rotating at this temperature. As in 3, the signals due to carbonyls a, b, c, d, and f, all broaden simultaneously as the temperature of the sample is increased above 151 K; this is consistent with the partial merry-go-round process described in Scheme II above. At the assumed coalescence temperature of ~167 K, an activation barrier of ~33 kJ mol⁻¹ is calculated for the "exchange" of the axial carbonyls on the Os centers. The energy barrier for the partial merry-go-round process in 1 is, therefore, slightly greater than that in 3. A comparison of the spectra recorded at 151 K for 1 and 3 shows that the signal attributed to carbonyl c is slightly broadened in 3, but sharp in 1; this is consistent with the slightly higher energy barrier calculated for 1. As observed in the W analogue, a change in the phosphorus ligand to P(OMe)₃ raises the energy barrier for the equatorial exchange process. In (OC)₅Cr{Os(CO)₃[P(OMe)₃]}₂ (7) the low temperature limiting spectrum is reached at 199 K; the activation barrier is ~46 kJ mol⁻¹ at the coalescence temperature of 239 K. The variable temperature ¹³C NMR spectrum of 7 is shown in Figure 5.8.
Figure 5.6. Variable Temperature $^{13}$C NMR Spectra of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1) from 151 K to 246 K.
Figure 5.7. Variable Temperature $^{13}$C NMR Spectra of $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$ (1) from 225 K to 299 K.
Figure 5.8. Variable Temperature $^{13}$C NMR Spectra of (OC)$_5$Cr{Os(CO)$_3$[P(OMe)$_3$]}$_2$ (7).
Slightly below 225 K a separate exchange process begins to occur in 1B. Inspection of the $^{13}$C NMR spectra (see Figure 5.7 above) shows that the resonances assigned to carbonyls g, h, i, and j, of 1B broaden and diminish simultaneously, and finally collapse to the baseline as the temperature is raised to 298 K. These results are consistent with a merry-go-round exchange of carbonyls between Os and Cr in the axial planes as shown below in Scheme III. This type of process is blocked in 1A by the phosphorus ligands which spend a finite period of time in the planes in which exchange occurs. Given that the partial merry-go-round process in the equatorial plane occurs much more rapidly in 1A than the axial-plane exchange process in 1B, it is not surprising that no evidence is seen for the axial exchange process in 1A even at 298 K. This type of exchange was not detected in the W complexes. This may be a consequence of the longer Os-W bonds which leads to a higher activation energy to form the bridged intermediate, although this seems unlikely.

Scheme III.
given the similar ease of exchange of carbonyls in the equator-
ial planes of 1 and 3.

A fourth fluxional process in 1 can be inferred from the series of $^{31}P\{^1H\}$ NMR spectra shown in Figure 5.9. When the same sample of 1 was dissolved in solvents of different polarity, a change in the relative proportion of isomers 1A and 1B was observed. While 1A was the dominant form in acetone, the relative population of 1B increased as the solvent polarity was lowered ($CD_2Cl_2$), became approximately equal to 1A in $CDCl_3$, and finally became the dominant form in toluene. A final spectrum of the same sample in acetone-$d_6$ restored the isomer ratio to that observed originally. Thus, drying the sample (by a stream of $N_2$) between spectral observations did not cause a change in the isomer ratio as a result of preferential crystallization of one isomer form. These results indicate that isomers 1A and 1B can interconvert, presumably via a trigonal-twist mechanism at the Os centers (Scheme IV). (Trigonal-twist processes have been proposed to account for the exchange of axial and equatorial

![Scheme IV](image_url)
Figure 5.9. $^{31}$P NMR Spectra of $(OC)_5Cr[OS(CO)_3(PMe_3)]_2$ (1) in Solvents of Different Polarity.

carbonyls in substituted triosmium clusters.$^{48a,150b}$ We have observed similar behavior in 3. It is apparent that the process which interconverts 1A and 1B has a much higher activation energy than the merry-go-round processes in the equatorial and
axial planes. This is in accord with earlier studies which showed that the trigonal-twist mechanism in Os₃(CO)₁₀[P(OMe)₃]₂ occurred at substantially higher temperatures than axial in-plane carbonyl exchange.

**Bonding in (OC)₅M[Os(CO)₃(PR₃)]₂ Metal Clusters.** A covalent single bond results from the sigma overlap of two half-occupied orbitals to give one bonding and one antibonding molecular orbital (MO). Metal-metal bonds are not an exception. For example, the Mn-Mn bond in Mn₂(CO)₁₀ has been fully characterized in terms of the diagram below. The metal-metal bond results from

![Diagram of Mn-Mn bond in (OC)₅Mn(Mn(CO)₅)]

the sigma overlap of a half-occupied a₁ orbital on Mn(CO)₅ with an identical orbital of a second Mn(CO)₅ group. A description of the metal-metal bonding in polyhedral clusters is not as simple. In clusters there are many orbital overlap interactions which contribute to the total metal-metal bonding. The polyhedral skeletal electron pair theory (PSEPT) first advanced by Wade and quantified by Mingos has been used extensively to count cluster bonding electrons and predict geometries. In a slightly different way, Lauher describes the bonding in terms of
edge-bridging and centrally directed orbitals, but the electron count concerns only the metal atoms and the energies of metal centered orbitals. This model has been derived from detailed MO calculations but is conceptually easily understood. Finally, using the frontier orbital and isolobal analogy approach, Hoffmann has reduced the metal-metal bonding description in clusters to one that is both relatively simple and elegant at the same time. These various models yield the same conclusions in a quantitative MO sense, but differ slightly in how they are presented. All these models conclude that there is bonding around the periphery of the cluster as well as bonding directed towards the center of the metal framework. For the purposes of the cluster species discussed above, Hoffmann's frontier orbital description will be used to describe the bonding.

It was noted previously that the upper limit of the barrier to rotation of the W(CO)$_5$ unit was estimated to be ~28 kJ mol$^{-1}$ in (OC)$_6$W[Os(CO)$_3$(PMe$_3$)]$_2$. The actual barrier is, however, certain to be lower than that estimated since the $^{13}$C resonance for the four radial carbonyls on W shows no broadening even at 151 K (see above). The equivalence of the radial carbonyls in [(MeO)$_3$P](OC)$_5$W[Os(CO)$_3$(PMe$_3$)]$_2$ and (OC)$_5$W[Os(CO)$_3$[P(OCH$_2$)$_3$-CMe]]$_2$ persists at 151 K and 183 K, respectively, even though all other CO site-exchange processes are static up to ~260 K. This suggests that rotation of the M(CO)$_5$ group must occur independently of other CO site exchange processes. This in turn implies that the M(CO)$_5$ group can be viewed as a separate frag-
ment in the metal cluster. The isolobal concept and its basis in frontier molecular orbitals can be used to describe, in a qualitative way, the bonding between the two separate fragments $\text{M(CO)}_5$ and $\text{Os}_2(\text{CO})_6(\text{PR}_3)_2 \ (\text{Os}_2(\text{L})_8)$.

The $d^8 \text{ML}_4$ fragments of $\text{Os}_2(\text{L})_8$ are isolobal with $\text{CH}_2$. Therefore, $\text{Os}_2(\text{L})_8$ can be viewed as an ethylene-like molecule.

$$\text{(R}_3\text{P})(\text{OC})_3\text{Os}=\text{Os(OC)}_3(\text{PR}_3) \underset{\sigma}{\longrightarrow} \text{H}_2\text{C}=\text{CH}_2$$

Although $\text{Os}_2(\text{CO})_6(\text{PR}_3)_2$ is unknown as an isolated stable complex, this formulation is appealing since it results in an 18-electron count at each Os center. The frontier orbitals of the $\text{M(CO)}_5$ fragment can then be overlapped with those of the $\text{Os}_2(\text{L})_8$ fragment to construct the cluster. This approach is analogous to that employed by Stone et al., for the isolobally equivalent complex $[\text{MoRh}_2(\mu-\text{CO})_2(\text{CO})_5(\pi^5-\text{C}_5\text{H}_5)]$ (17). The frontier orbitals of $\text{M(CO)}_5$ fragments have been described. The four orbitals shown on the left side of Figure 5.10 are those that are important for bonding of the $\text{M(CO)}_5$ fragment to the $\text{Os}_2$ fragment. The orbitals that are of particular importance are the $2a_1$ orbital and the degenerate e set composed of the $b_1$ and $b_2$ orbitals. The $2a_1$ LUMO is a hybrid of $z^2$, $z$, and $s$ orbitals and is strongly directed away from the basal plane of the flat square pyramidal $\text{M(CO)}_5$. The filled e set is composed of $dxz$ and $dyz$ orbitals. The frontier fragment orbitals of an $\text{Os}_2(\text{L})_8$ species are depicted on the right of Figure 5.10. The representation of the orbitals of $\text{Os}_2(\text{CO})_6(\text{L})_2$ were adapted from
those of Os$_2$(CO)$_8$, a molecule that has been recently isolated in an argon matrix at 10-12 K. (Although the orbital energies of the $M_2$ fragments may be different, the bonding arguments are qualitatively the same since these two species are isoelectronically and isolobally equivalent.) The two most significant bonding interactions are between the $2a_1$ acceptor orbital (LUMO) and...
of M(CO)$_5$ and the 16a$_1$ donor orbital (HOMO) of Os$_2$(L)$_8$, and between the b$_2$ and b$_1$ donor orbitals (HOMO) of M(CO)$_5$ and the 15b$_1$ acceptor orbital (LUMO) of Os$_2$(L)$_8$. These are the only stabilizing metal-metal interactions which will have significant overlap, are energetically favorable, and are symmetry allowed. The bonding is distinctly similar to that of an olefin bonded to a d$^6$ ML$_5$ group.$^{131}$

By analogy to [MoRh$_2$(μ-CO)$_2$(CO)$_5$(η$^5$-C$_5$H$_5$)$_2$],$^{123d}$ the energy separation between the 16a$_1$ HOMO and the 2a$_1$ LUMO interaction is expected to be smaller than that of the e HOMO and 15b$_1$ LUMO interaction. Therefore, the strongest metal-metal bonding is achieved through the former combination. (The 16a$_1$-2a$_1$ bonding MO is, however, destabilized by the a$_1$-16a$_1$ interaction.) The 16a$_1$-2a$_1$ combination yields a bonding MO that is localized largely at the center of the metal triangle, i.e., a three-center, two-electron bond. Similar bonding models have been proposed for M$_3$(CO)$_{12}$ (M = Fe, Ru, Os) clusters in which a centrally localized MO provides for strong metal-metal bonding.$^{160}$ A similar description of the bonding of an M(CO)$_5$ (M = Cr, Mo, W) group to the triangular face of Ni$_3$(CO)$_6$ in the clusters [Ni$_3$M$_2$(CO)$_{16}$]$_2^-$ has also been proposed.$^{161}$ The 15b$_1$-b$_1$ interaction results in edge-bridged metal-metal bonds. By a valence bond approach, the two M-Os bonds will have a bond order
of one-half since the Os-M-Os bonding arrangement is a three-center, two-electron interaction. Alternatively, edge-bridging metal-metal bonds can also be constructed by simple d-orbital overlap around the deltahedral MOs2 perimeter, again like that proposed for M3(CO)12 clusters. The combination of the edge-bridging orbitals cannot, however, result in three metal-metal bonds of bond order one since there is always a node associated with the overlap. Since both the centrally-directed bond and edge-bridging bonds have a bond order of less than one, it may be inferred that the combination of the edge-bridging bonds plus the centrally-directed metal-metal bond is required for strong metal-metal bonding. Therefore, the ability to form a strong centrally-directed bond may account for the robustness of clusters built up of deltahedra such as Os3(CO)12 and the (OC)3M[Os(CO)3(PR3)]2 complexes. It has been proposed that the inability of Os4(CO)16 to form a centrally-localized bonding MO may account for its chemical instability.12
Relevance of Metal-Metal Bonding to the Unrestricted Rotation of the \( \text{M(CO)}_5 \) Group. It is clear from the bonding description that the \( a_1 \) overlap will not result in any barrier to rotation of the \( \text{M(CO)}_5 \) group. Since the \( \text{M(CO)}_5 \) \( b_1 \) and \( b_2 \) orbitals are degenerate, any linear combination of the two yields an equivalent result. Therefore, there will be no angular rotational requirement for the formation of two metal-metal bonds.\(^{162} \) In this way, the \( \text{M-Os}_2 \pi^* \) bonding interaction has cylindrical symmetry, and no barrier to rotation is to be expected. The only other interaction of significance is a weak two-orbital, four-electron destabilizing interaction between the \( \text{M(CO)}_5 \) \( a_1 \) orbital and the \( 16a_1 \) orbital on the \( \text{Os}_2 \) fragment, and it also has no rotational preference. Due to the lack of \( d \) orbitals on an olefin, a similar interaction in \( \text{M(CO)}_5(\text{olefin}) \) complexes does have an orientational preference; this makes the barrier to rotation of an organic alkene greater than that of an "inorganic" alkene.\(^{163} \) It can be concluded that there will be little, if any, electronic barrier to rotation of the \( \text{M(CO)}_5 \) groups, and that any such barrier must arise primarily from steric interactions. An energy barrier of \(~23 \text{ kJ mol}^{-1} \) was calculated by the EHMO method for the rotation of \( \text{Mo(CO)}_5 \) in \([\text{MoRh}_2(\mu-\text{CO})_2(\text{CO})_9(\eta^5-\text{C}_5\text{H}_5)_2]^{123a} \) The calculated barrier is only approximately half the experimentally determined value for the \( \text{CoRh} \) analogue \((\text{OC})_5\text{MoCoRh(\mu-CO)}_2(\eta^5-\text{C}_5\text{Me}_5)_2 \) (15). The discrepancy has been attributed to interactions which were not included in the model. As previously mentioned, the extreme upper limit for the barrier to rotation in the complexes described
above is estimated to be less than 28 kJ mol⁻¹, or roughly half the actual limit found in 15. Therefore, the steric requirements of the \( \text{Os}_2(\text{CO})_6(\text{PR}_3)_2 \) group must be less than those of \( \text{CoRh}(\mu-\text{CO})_2(\eta^5-\text{C}_5\text{Me}_5)_2 \).

5.4 Conclusion

The present work has shown that CO site exchange is facile in \( (\text{OC})_5\text{M[Os(CO)_(3)(PR_3)]_2} \) clusters. In at least one of these \( (\text{M} = \text{Cr}) \), the exchange can occur via four different mechanisms, each of which has a different activation energy. Furthermore, this work represents the first observation of a very low energy barrier for an equatorial merry-go-round exchange process in a trinuclear cluster containing two equatorial ligands other than CO. While we are not much further ahead in terms of predicting in which clusters CO exchange will occur, we have observed an ancillary ligand effect on the rate of CO exchange, and we can at least predict the most likely mechanisms for exchange. This may have some potential value with respect to the use of metal clusters as catalysts in view of the fact that two reagents on different metal centers must be brought together before reaction can occur. Finally, the stability of the \( (\text{OC})_5\text{M[Os(CO)_(3)(PR_3)]_2} \) complexes along with the unrestricted rotation of the \( \text{M(CO)}_5 \) fragment provides evidence for a centrally-directed bonding interaction since the edge-bridging combination of orbitals alone would not be expected to result in strong metal-metal bonding. This leads to the general conclusion that both bonding modes
contribute to the stability of the deltahedral arrangement of metal atoms in polyhedral cluster molecules. It also indicates that the metal-metal bonding in trinuclear metal carbonyl clusters should not be described in terms of two center, two electron bonds as has often been done in the past.\textsuperscript{112a}
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APPENDIX

The (Me₃P)(OC)₅OsMo(CO)₅, (OC)₅Cr[Os(CO)₃(PMe₃)]₂, and (OC)₅Mo[Os(CO)₃(PMe₃)]₂ complexes were discussed in Chapters 2 and 3, respectively. The molecular structures of (Me₃P)(OC)₅OsMo(CO)₅, (OC)₅Cr[Os(CO)₃(PMe₃)]₂, and (OC)₅Mo[Os(CO)₃(PMe₃)]₂ are shown in Figures A-1, A-2, and A-3, respectively.

The ¹³C NMR spectra of [(MeO)₃P](OC)₄OsCr(CO)₅, [MeC(CH₂O)₃P](OC)₄OsCr(CO)₅, [(MeO)₃P](OC)₄OsW(CO)₅, and [MeC(CH₂O)₃P](OC)₄OsW(CO)₅ were discussed in Chapter 3. These spectra are shown in Figures A-4, and A-5, respectively.
Figure A-1. Molecular Structure of \([(\text{MeO})_3\text{P})(\text{OC})_4\text{OsMo(CO)}_5\].
Figure A-2. Molecular Structure of \((\text{OC})_5\text{Cr}[\text{Os(CO)}_3(\text{PMe}_3)]_2\).
Figure A-3. Molecular Structure of (OC)$_3$Mo[Os(CO)$_3$P(OME)$_3$]$_2$. 
Figure A-4. $^{13}$C NMR Spectra of [(MeO)$_3$P](OC)$_4$OsCr(CO)$_5$ (top) and [MeC(CH$_2$O)$_3$P](OC)$_4$OsCr(CO)$_5$ (bottom) in the Carbonyl Region.
Figure A-5. $^{13}$C NMR Spectra of [(MeO)$_3$P](OC)$_4$OsW(CO)$_5$ (top) and [MeC(CH$_2$O)$_3$P](OC)$_4$OsW(CO)$_5$ (bottom) in the Carbonyl Region.