SYSTEMATIC SYNTHESIS OF TETRA AND PENTANUCLEAR CLUSTERS OF OSMIUM

by

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SYSTEMATIC SYNTHESIS OF TETRA AND

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Abstract

Routes for the systematic synthesis of tetra and pentanuclear clusters containing osmium have been established:

The clusters $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**) and $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (**3**) ($Cp^* = C_5Me_5$) were prepared by addition of $Re(CO)_4(PPh_3)(H)$ and $Cp^*Os(CO)_2(H)$, respectively, to $Os_3(CO)_{10}(COE)_2$ (COE = cyclooctene). Although both **2** and **3** are 62-electron clusters, the former cluster has a planar whereas the latter cluster has a nonplanar (butterfly) arrangement of metal atoms. The difference in the structures has been rationalized in terms of stabilization of the dative Os-Os bond in **3** by the electron-donating $Cp^*Os(CO)_2$ fragment.

Addition of two moles of $Re(CO)_3(PMe_3)_2(H)$ to $Os_3(CO)_{10}(COE)_2$ gave $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (**5**) in which the hydride ligands bridge the Re-Os bonds. This is unlike $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$ where the hydride ligands bridge Os-Os bonds. These results are consistent with the view that where a choice exists a hydride ligand will bridge the more electron-rich metal-metal bond. This observation may be of general applicability to hydrido-metal cluster compounds.

Carefully controlled pyrolysis of **3** gave $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**11**), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4(CH_2)]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**12**), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4(CH_2)]Os_4(CO)_{11}$ (**13**), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**). This series provides an interesting example of sequential C-H activation of the C_5Me_5 ligand on a cluster. It is also a unique example of a closely related series of clusters containing Os_4, Os_4H, Os_4H_2, and Os_4H_3 units.

The reaction of $Os(CO)_5$ with $Os_4(CO)_{14}$ afforded the known $Os_5(CO)_{19}$ (**15**) which on careful heating gave the hitherto unknown $Os_5(CO)_{18}$ (**16**). The latter cluster was shown to have a planar, "raft-like" skeleton rather than the bent structure that had been assumed. The clusters $Os_5(CO)_{18}(L)$ (L = PMe_3, **18**; $CNBu^t$, **23**) were synthesized in a similar manner to **15**, and like **15** shown to have a "bow-tie" configuration of metal atoms. Subsequent pyrolysis of **18** and **23** gave $Os_5(CO)_{17}(L)$ (L = PMe_3, **19**; $CNBu^t$, **24**) and $Os_5(CO)_{15}(L)$ (L = *ax*-PMe_3, **20**; *eq*-PMe_3, **21**; $CNBu^t$, **25**). Structural studies on clusters **18**$\cdot CH_2Cl_2$, **19-21**, **23** and **25** show that the PMe_3 and $CNBu^t$ ligands have different site preferences, as has been found in $Os_3(CO)_{11}(L)$ compounds. A remarkable aspect of this part of the study was the isolation and characterization of the two isomers **20** and **21** and the finding that the sterically more hindered isomer **21** was the thermodynamically more stable form.

The HYDEX program of Orpen (*J. Chem. Soc., Dalton Trans.* **1980**, 2509) has been used to give "*I numbers*" for coordination sites in mononuclear and polynuclear carbonyl compounds. The I numbers reflect the steric interactions at coordination sites and are in agreement with the general views of these interactions in simple metal carbonyl compounds. The method, however, provides a crude measure of the magnitude of steric interactions at sites in more complex molecules such as $Os_5(CO)_{16}$. It is believed the technique will be of general use in the study of metal carbonyl compounds.

Dedication

To my wife, Meihua Gao

and son, Ray Wang

Acknowledgement

My sincere gratitude to my senior supervisor, Dr. R. K. Pomeroy, for his continual encouragement and guidance (and the beers on Fridays!) during the course of this project.

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My thanks to Mr. M. Yang for microanalyses.

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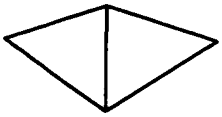
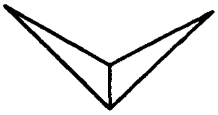
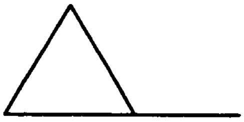
I. Descriptors for cluster shapes used in this thesis:



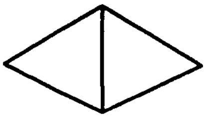
kite



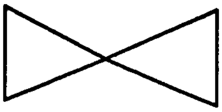
butterfly



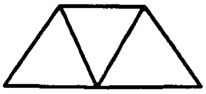
spiked triangle



rhomboidal



bow-tie



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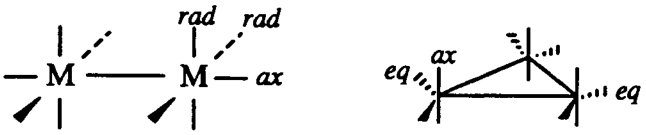
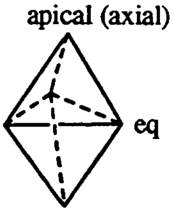
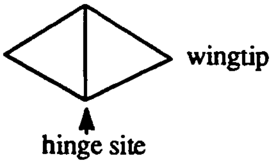


radial, equatorial and axial sites





II. Definitions and explanations of terms used in this thesis:

a. **Site energy**: Relative potential energy of a coordination site to the other sites in the same molecule.

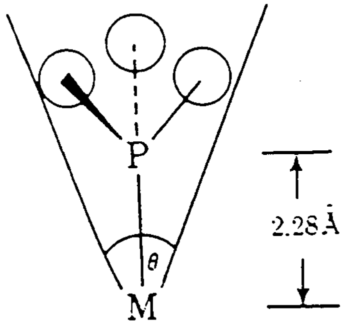
b. **HYDEX program:** The program of Orpen's that is used to calculate the positions of minimum energies for a hydride ligand (see ref. 37).

c. **Dative bond:** A formal description of a metal-metal bond in which both of the pair of electrons of the bond are thought to come from the same fragment of the two fragments bonded. (cf. H_3NBH_3 and $(OC)_5OsCr(CO)_5$)

d. **Isolobal analogy:** A concept popularized by R. Hoffmann. Two fragments are isolobal if the number, symmetry properties, approximate energies, and the shapes of their frontier orbitals are similar, and the number of electrons in them are same. Isolobal fragments may be organic, main group or transition metal fragments (e. g., CH_2, $SnMe_2$, $Os(CO)_4$ are isolobal). Such fragments are expected to have similar bonding properties.

e. **σ-donor, π-acceptor:** A σ-donor is a unit which donates electron density to another unit through a filled σ-orbital. A π-acceptor is a unit which accepts electron density from another unit through its empty π-orbitals.

f. **Cone angle:** A concept proposed by C. A. Tolman to indicate the steric effect of a ligand (see references 76b-c). The cone in question is one that can just enclose the van der Waals surface of all ligand atoms over all rotational orientations about the M-P bond as shown below.



g. **Polyhedral skeletal electron pair theory (PSEPT):** A set of rules (sometimes known as Wade's rules) used to predict the shape of cluster compounds based on the number of skeletal electron pairs. (see references 3 (page 72) and 4 (page 81); also see W. W. Porterfield *Inorganic Chemistry*, Addison-Wesley Publishing Company, 1983, P. 546).

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Chapter 1. Introduction

A metal cluster compound is usually considered as a compound containing three or more metal atoms in a closed array and in which metal-metal bonding is significant. The first organometallic cluster (i.e., a cluster complex with metal-carbon bonds) reported is apparently $Fe_3(CO)_{12}$ described by Dewar and Jones in 1907.[1] It was, however, not until the late 1960's with the improvements to structure determination by X-ray crystallography that the study of organometallic compounds began in earnest. Aspects of metal cluster chemistry such as their synthesis, structure, reactivity, relation to interactions on a metallic surface, and potential application in both homogeneous and heterogeneous catalysis have been widely studied such that it is now an important area of inorganic chemistry. Several textbooks on the subject have appeared.[2-6]

Metal carbonyl clusters are the largest group of cluster compounds and new carbonyl cluster compounds of higher nuclearity are reported virtually every day. The systematic preparation of metal cluster compounds has been a major challenge to synthetic organometallic chemists for the past thirty years. In the book *Transition Metal Clusters* (published in 1980) it is stated, "the preparation of clusters remains almost entirely an accidental affair and few systematic routes have been devised." [2] Recently, however, a few systematic routes have been described for the synthesis of metal carbonyl cluster compounds.[3,4,7-9]

A brief outline of the important methods for building up cluster compounds from precursors of lower nuclearities is now presented.

Pyrolysis of a metal carbonyl cluster compound of lower nuclearity is the most common way to synthesize compounds of higher nuclearities. One of the best know examples is the pyrolysis of $Os_3(CO)_{12}$, reported by Eady, Johnson and Lewis in 1975 (eq 1.1).[10] The primary product is $Os_6(CO)_{18}$ although other clusters with five to eight Os atoms are also produced.

$$Os_3(CO)_{12} \xrightarrow{210\ ^\circ C} Os_5(CO)_{16} + Os_6(CO)_{18} + Os_7(CO)_{21} + Os_8(CO)_{23} \qquad (1.1)$$

Photolysis of organometallic compounds is another way frequently used to generate cluster compounds. For instance, photolysis of $CpRh(CO)_2$ with ultraviolet light at room temperature yielded $Cp_3Rh_3(CO)_3$ as one product (eq 1.2).[11]

$$CpRh(CO)_2 \xrightarrow{h\nu} Cp_2Rh_2(CO)_3 + Cp_3Rh_3(CO)_3 \qquad (1.2)$$

Both pyrolysis and photolysis often result in a variety of cluster compounds in low yields.

Redox condensation, first reported by Hieber and Schubert is another route for building cluster compounds. Their first example of a redox condensation reaction was the reaction of $[Fe_3(CO)_{11}]^{2-}$ with $Fe(CO)_5$ to form $[Fe_4(CO)_{13}]^{2-}$ (eq 1.3).[12]

$$[Fe_3(CO)_{11}]^{2-} + Fe(CO)_5 \longrightarrow [Fe_4(CO)_{13}]^{2-} \qquad (1.3)$$

A further example is the reaction of $[Rh_6(CO)_{15}]^{2-}$ with $Rh(CO)_4^-$ to give $[Rh_7(CO)_{16}]^{3-}$ reported by Martinengo and Chini (eq 1.14).[13]

$$[Rh_6(CO)_{15}]^{2-} + [Rh(CO)_4]^- \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} [Rh_7(CO)_{16}]^{3-} \tag{1.4}$$

Another approach is the base-promoted condensation reaction. The reaction of a metal carbonyl compound with hydroxide ion can cause the loss of a CO ligand and consequent formation of a higher nuclearity cluster, as shown in eq 1.5.[14]

$$Rh_4(CO)_{12} \xrightarrow[\text{Pr}^i\text{OH, N}_2]{80^\circ\ \text{OH}^-} [Rh_{15}(CO)_{27}]^{3-} \tag{1.5}$$

Yet another approach is the condensation of low nuclearity clusters that contain labile ligands such as acetonitrile. For example, $Os_3(CO)_{10}(MeCN)_2$ is stable in solutions of dry solvents without added acetonitrile.[15,16] It does, however, undergo condensation in the presence of a $PdCl_2$ catalyst (eq 1.6).[17]

$$\begin{aligned} Os_3(CO)_{10}(MeCN)_2 \xrightarrow{PdCl_2} \ & Os_6(CO)_{20}(MeCN) + Os_6(CO)_{19}(MeCN)_2 \\ & + Os_6(CO)_{21} + Os_6(CO)_{18} + \text{others} \end{aligned} \tag{1.6}$$

Some compounds undergo chemically induced condensation reactions under very mild conditions. An example is the reaction of $RhFe(CO)_5\{\mu\text{-}Ph_2P\text{-}C(CH_2)PPh_2\}$ with $Me_3NO{\cdot}2H_2O$ at room temperature to give $Rh_2Fe_2(CO)_8\text{-}\{\mu\text{-}Ph_2PC(CH_2)PPh_2\}_2$ (eq 1.7).[18]

$$RhFe(CO)_5(\eta^2,\mu\text{-L}) + 2\ (Me_3NO{\cdot}2H_2O) \longrightarrow Rh_2Fe_2(CO)_8(\eta^2,\mu\text{-L})_2 \tag{1.7}$$

Addition of a coordinatively unsaturated mononuclear complex fragment to a cluster compound is another method to generate a cluster compound of higher nuclearity.[7] This mononuclear fragment may arise from a polynuclear species in the reaction. For example, $Fe_3(CO)_9(PR)_2$ can coordinate with "$Fe(CO)_4$" arising from $Fe_3(CO)_{12}$ to form $Fe_4(CO)_{13}(PR)_2$; this cluster can then rapidly lose CO to give the observed product $Fe_4(CO)_{11}(PR)_2$ (eq 1.8).[19]

$$Fe_3(CO)_9(PR)_2 \xrightleftharpoons[\text{-"}Fe(CO)_2\text{"}]{Fe_3(CO)_{12}} Fe_4(CO)_{11}(PR)_2 \qquad (1.8)$$

Compounds that are formally unsaturated or have metal-metal multiple bonds readily react with mononuclear species to form clusters of higher nuclearities. An example is the reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$[20] with mononuclear species (eq 1.9).[21]

$$Os_3(\mu\text{-}H)_2(CO)_{10} + CpCo(CO)_2 \xrightarrow{90\ ^\circ C} Os_3Co(\mu\text{-}H)_2(Cp)(CO)_{10} \qquad (1.9)$$

Metal-carbene and metal-carbyne complexes also undergo addition with organometallic compounds. Studies by Stone and co-workers using the analogy between metal-carbene complexes and olefins, and between metal-carbyne complexes and alkynes have led to the successful synthesis of many novel cluster compounds.[22]

Weakly coordinated ligands such as cyclooctene, acetonitrile, tetrahydrofuran, etc. can be easily replaced with organometallic species. The compounds $Os_3(CO)_{10}(COE)_2$[15] (COE = cyclooctene; prepared by Shapley and co-workers) and $Os_3(CO)_{12\text{-}n}(MeCN)_n$ (n = 1,[16] 2[15,16]; prepared by Johnson, Lewis and co-workers) are probably the most widely used precursors for the generation of cluster compounds of osmium.[23-26]

The application of the last method to the systematic synthesis of cluster compounds has resulted in some significant results from this laboratory. One of these is the formation of $(Me_3P)(OC)_4OsW(CO)_5$ by the reaction of $Os(CO)_4(PMe_3)$ with $W(CO)_5(THF)$ (eq 1.10).[27]

$$Os(CO)_4(PMe_3) + W(CO)_5(THF) \longrightarrow (Me_3P)(OC)_4OsW(CO)_5 \qquad (1.10)$$

Although not strictly a cluster compound it is believed to be the first example of a compound containing an unbridged donor-acceptor bond between different transition-metal atoms. Compounds of this type are precursors to novel trinuclear clusters containing osmium and a group 6 metal.[28]

Another significant result was the synthesis of $Os_4(CO)_{15}$ by the reaction of $Os_3(CO)_{10}(COE)_2$ with $Os(CO)_5$ (eq 1.11).[29]

$$Os_3(CO)_{10}(COE)_2 + Os(CO)_5 \longrightarrow Os_4(CO)_{15} \qquad (1.11)$$

This was the first tetranuclear binary carbonyl of osmium. Subsequently, $Os_4(CO)_{16}$[30] and $Os_4(CO)_{14}$[31] were prepared from the carbonylation and decarbonylation of $Os_4(CO)_{15}$, respectively. These binary carbonyls of osmium have filled the gap between $Os_3(CO)_{12}$ and the higher nuclearity carbonyls of osmium.[32]

The structure determinations of the 62-electron compounds $Os_4(CO)_{15}$ and related clusters such as $Cp^*IrOs_3(CO)_{12}$[29] and $Os_4(CO)_{14}(PMe_3)$[33] reveal they have unusual planar, "kite-like" metal skeletons with adjacent short (~2.8 Å) and long (~3.0 Å) peripheral metal-metal bonds. Previously, Churchill and Hollander[34] had described the structure of $Os_3Re(H)(CO)_{15}$. It was also found to possess a planar rhomboidal arrangement of metal atoms but with equal peripheral metal-metal bonds.

Another 62-electron tetranuclear cluster compound, $Os_4(\mu\text{-}H)(CO)_{14}$-

$(SnMe_3)$,[35] prepared by Pomeroy and co-workers, also has a planar Os_4 arrangement but with only one long Os-Os bond; the other Os-Os lengths were within the range expected for Os-Os single bonds (the average value is 2.88 Å in $Os_3(CO)_{12}$[36]). Bond angle data, calculations with the HYDEX program,[37] and NMR spectroscopic evidence were all consistent with the view that the long Os-Os bond was not bridged by the hydride ligand.[35] This is contrary to what would be expected from the behavior of trinuclear metal carbonyl clusters where a bridging hydride ligand usually causes a lengthening of the metal-metal bond with which it is associated.[38,39]

These differences stimulated us into attempting to gain a better understanding of the bonding in these tetranuclear clusters and the location of hydride ligands within them. Part of this thesis describes the synthesis of some related 62-electron tetranuclear cluster compounds and their characterization, especially by X-ray diffraction.

The synthesis and structure[40] of $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ are reported in Part I of Chapter 2. The molecular structures reveal that these two 62-electron clusters have different metal skeletons. A structural comparison between $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ and $HReOs_3(\mu\text{-}H)(CO)_{15}$ is presented and a rationale for the different metal skeletons in $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ is discussed.

The synthesis and structure of $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_nOs_3(CO)_{12\text{-}n}$ (n = 1, 2[41]) are reported in Part II of Chapter 2. There is a change of the coordination sites of the hydride ligands in $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_nOs_3(CO)_{12\text{-}n}$ (n = 1, 2) compared to those in the corresponding carbonyl compounds $(OC)_5ReOs_3(\mu\text{-}H)\text{-}(CO)_{10}(NCMe)$[42] and $[(OC)_5Re(\mu\text{-}H)]_2Os_3(CO)_{10}$.[43]

From the careful pyrolysis of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ at different temperatures the four compounds, $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$, $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$, $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$, and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ were prepared. The synthesis and structure of these compounds are reported in Chapter 3. This work demonstrated a stepwise C-H cleavage of two methyl groups of the Cp* ligand on a metal cluster. The study also allowed a crystallographic comparison of Os_4, $Os_4(\mu\text{-}H)$, $Os_4(\mu\text{-}H)_2$ and $Os_4(\mu\text{-}H)_3$ in a closely related series of clusters.

Systematic synthesis of cluster compounds of higher nuclearities from precursors of lower nuclearities has been a goal of research in this laboratory for some time.[32] Of the transition metals osmium forms the most binary carbonyls. Before 1987, there were nine binary carbonyls of osmium known:[32] $Os(CO)_5$,[44] $Os_2(CO)_9$,[45] $Os_3(CO)_{12}$,[36] $Os_5(CO)_{16}$,[10,46] $Os_5(CO)_{19}$,[47] $Os_6(CO)_{18}$,[10,48] $Os_6(CO)_{21}$,[17] $Os_7(CO)_{21}$,[10,49] and $Os_8(CO)_{23}$.[10,32] The gap between $Os_3(CO)_{12}$ and the higher nuclearity carbonyls of osmium was filled with the synthesis of $Os_4(CO)_n$ (n = 14, 15, 16)[29-31] in this laboratory in 1987-88 (see page 5).

The rich structural diversity exhibited by the tetranuclear clusters of osmium previously prepared in this laboratory as well as those described in Chapters 2 and 3 of this thesis, prompted the obvious extension to the systematic synthesis of pentanuclear clusters of osmium. This is the subject of the second half of this thesis.

Pentaosmium binary carbonyls, $Os_5(CO)_{16}$[10,46] and $Os_5(CO)_{19}$[47], were first reported by Johnson, Lewis and co-workers in 1976 and 1981, respectively. The former was a minor product from the pyrolysis[10] of $Os_3(CO)_{12}$ (mentioned above) while the latter was obtained from the reaction of $Os_6(CO)_{18}$ with CO at

160 °C and 90 atm.[47] A trigonal bipyramidal arrangement of metal atoms is present in $Os_5(CO)_{16}$ whereas $Os_5(CO)_{19}$ has the so-called bow-tie metal skeleton. Their derivatives such as $Os_5(CO)_{15}\{P(OMe)_3\}$[50] and $Os_5(CO)_{16}\{P(OMe)_3\}_3$[47b] also have similar metal skeletons to their parent carbonyls. In order to probe other possible structures and synthetic routes for pentaosmium clusters, studies were carried out on the synthesis of pentaosmium clusters under less forcing conditions. In Chapter 4 the systematic synthesis of $Os_5(CO)_n$ (n = 19, 18, 16)[51] from species of lower nuclearity is reported. The crystal structure of $Os_5(CO)_{18}$ reveals a new arrangement of metal atoms in the series of pentaosmium clusters..

Binary carbonyls of osmium are, in general, relatively more difficult to make than their derivatives. The derivatives, however, can sometimes provide more information about the compounds such as their bonding and skeletal formation. Studying the site preference of different ligands in clusters can also provide insight into the coordination environment in clusters. These factors prompted our research on the derivatives of $Os_5(CO)_{19-n}$ (n = 0, 1, 3). In Chapter 5 the syntheses of $Os_5(CO)_{19-n}(L)$ (L = PMe_3,[52] $CNBu^t$;[53] n = 1, 2, 4) and their structures (except $Os_5(CO)_{17}(CNBu^t)$) are reported. The $Os_5(CO)_{15}(PMe_3)$ clusters were found to exhibit an unexpected form of isomerism (both isomers were structurally characterized).

Some preliminary attempts at the systematic synthesis of hexanuclear clusters of osmium resulted in the preparation of $Os_6(CO)_{20}(L)$ clusters, albeit in low yields.

The HYDEX program of Orpen[37] has been used to calculate the hydride positions in several clusters described in Chapters 2 and 3 of this thesis. A set of parameters of the program have been changed to calculate relative potential energies (denoted as "*I numbers*") that give an indication of the relative magnitude of steric interactions at different coordination sites in mono- and polynuclear carbonyl compounds. The *I number* magnitudes agree with the expected views of steric interactions at sites in simple metal carbonyl compounds and give an insight into the steric interactions in more complicated compounds where it is less obvious which the most sterically crowded site is in the molecule.

Chapter 2. 62-Electron Tetranuclear Clusters Containing Osmium and Site Preference of Bridging Hydride Ligands in Metal Clusters

2.1 Introduction

Tetranuclear metal-carbonyl clusters usually adopt a tetrahedral or butterfly arrangement of metal atoms.[3,54,55] In some cases they adopt a planar arrangement of metal atoms.[56] In the absence of bridging ligands other than bridging hydride ligands, however, a planar configuration of metal atoms is rarely found. Previous co-workers from this laboratory have reported the preparation and structure of $Os_4(CO)_{14}(L)$ (L = CO,[29] PMe_3[33]) and $(\eta^5\text{-}C_5Me_5)Ir\text{-}Os_3(CO)_{12}$[29] which have a planar metal skeleton with adjacent short (~2.8 Å) and long (~3.0 Å) peripheral metal-metal bonds. In unpublished work, $Os_4(CO)_{14}(CNBu^t)$ and $Os_4(CO)_{13}(PMe_3)[P(OMe)_3]$ have been found to have similar "kite-like" skeletons. As mentioned in Chapter 1 (page 6), the bond lengths and location of the hydride ligand in $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ are contrary to what would be expected from the behavior of trinuclear metal carbonyl clusters where a bridging hydride ligand usually causes a lengthening of the metal-metal bond with which it is associated.[38,39]

The structure of $Os_3Re(H)(CO)_{15}$ (**1**) has been described by Churchill and Hollander.[34] It was found to possess a planar rhomboidal arrangement of metal atoms with all equal peripheral metal-metal bonds. In a cluster containing both osmium and rhenium atoms, it is difficult to distinguish the two by X-ray crystallography.

Studies were undertaken in order to further probe the metal geometries, unusual bonding and location of hydride ligands in this family of clusters. In this chapter the synthesis and structure of $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**) and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (**3**) are reported.[40] One of the precursor compounds used in the synthesis of **2** was $Re(OC)_4(PPh_3)(H)$.[57] Given the mild conditions involved in the synthesis of **2** (see the next page), the reasonable assumption was made that the PPh_3 ligand would remain attached to the Re atom in the product and hence would make the Re atom readily identifiable by X-ray crystallography. The structure of **2**, which unlike **1** was not disordered, reveals a planar configuration of metal atoms with a long Re-Os bond that is believed to be unbridged. However, the structure of **3** has a nonplanar butterfly arrangement of the Os_4 atoms. The bonding in **2** and **3** is discussed and a reason offered for the difference in the structures (Part I).

In this chapter the synthesis and structure of $(OC)_3(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (**4**) and $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (**5**) are also reported. The location of the hydride ligands in these clusters was unexpected; this result has provided a deeper understanding of the site preference of bridging hydride ligands in cluster compounds (Part II).

2.2 Results and Discussion

2.2.1 Part I. 62-Electron Tetranuclear Clusters Containing Osmium

The clusters $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**) and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (**3**) were prepared by the addition of $Re(CO)_4(PPh_3)(H)$[57] (for **2**) and $(Cp^*)Os(CO)_2(H)$[58] (for **3**; $Cp^* = \eta^5\text{-}C_5Me_5$), respectively, to $Os_3(CO)_{10}(COE)_2$ (COE = cyclooctene)[15] in CH_2Cl_2/hexane at 0 °C (e.g., eq 2.1). Clusters **2** and **3** are air stable, red crystalline solids.

$$Os_3(CO)_{10}(COE)_2 + Re(CO)_4(PPh_3)(H) \xrightarrow{0\ ^\circ C} \underset{\mathbf{2}}{(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}} \qquad (2.1)$$

2.2.1.1 Structure Assignment

$(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (2). The structure of **2** as determined by X-ray crystallography (Figure 2.1) shows an almost planar arrangement of metal atoms; the dihedral angle between the Re-Os(1)-Os(2) and Os(1)-Os(2)-Os(3) planes is 175.2°. A carbonyl ligand moved from the Re atom to an Os atom. There are three carbonyl ligands attached to one of the hinge osmium atoms (Os(1)), but four to the other hinge metal atom (Os(2)). The bulky PPh_3 ligand occupies one of the least hindered sites in the molecule, namely, the equatorial site at the rhenium atom that is also cis to the lone equatorial carbonyl ligand on Os(1).

Although the Os-Os lengths in the Os_3 triangle of **2** (Table 2.1) vary significantly (Os(1)-Os(2) = 2.927 (1) Å, Os(1)-Os(3) = 2.825 (1) Å, Os(2) - Os(3) = 2.953 (1) Å) they are, nevertheless, in the range expected for unbridged Os-Os

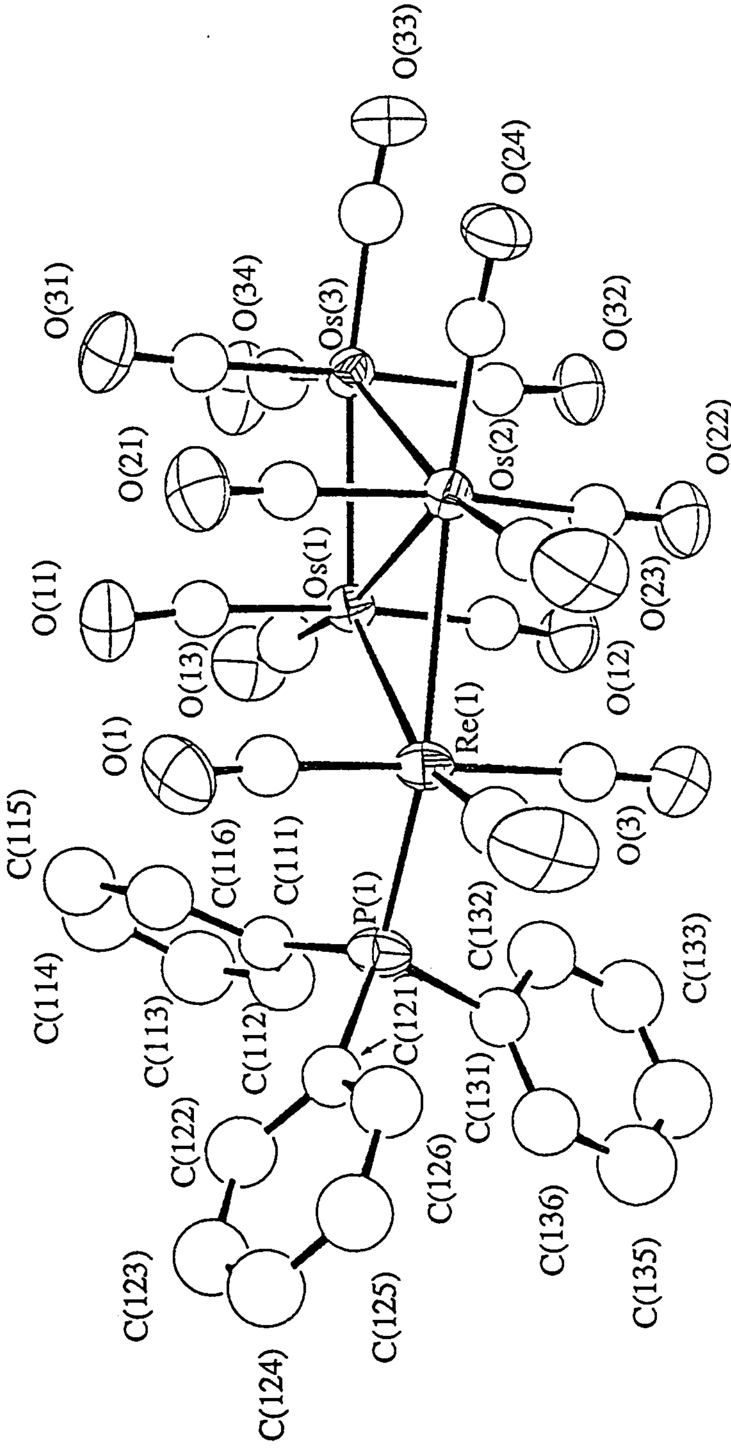

Figure 2.1. The molecular structure of $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ **(2)**

Table 2.1. Selected Bond Lengths (Å) and Angles (°) for $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**)

Bond Lengths

Os(1) - Os(2)	2.927 (1)	Re - P(1)	2.386 (3)
Os(1) - Os(3)	2.825 (1)		
Os(1) - Re	2.962 (1)	(Os-C)	1.86 (2) - 1.98 (2)
Os(2) - Os(3)	2.953 (1)	(Re-C)	1.91 (2) - 1.98 (2)
Os(2) - Re	3.108 (1)	(C-O)	1.11 (3) - 1.18 (3)

Bond Angles

Os(3) - Os(1) - Os(2)	61.75 (2)	C(13) - Os(1) - Os(3)	105.5 (4)
Re - Os(1) - Os(2)	63.70 (2)	C(13) - Os(1) - Re	128.9 (4)
Os(3) - Os(2) - Os(1)	57.42 (2)	C(23) - Os(2) - Re	75.1 (4)
Re - Os(2) - Os(1)	58.71 (2)	C(24) - Os(2) - Os(3)	74.8 (3)
Os(2) - Re - Os(1)	57.59 (2)	C(33) - Os(3) - Os(2)	110.3 (4)
Os(2) - Os(3) - Os(1)	60.82 (2)	C(34) - Os(3) - Os(1)	89.3 (4)
P(1) - Re - Os(1)	105.27 (8)	C(3) - Re - Os(2)	101.3 (4)
P(1) - Re - Os(2)	162.84 (8)	C(3) - Re - P(1)	95.9 (4)

single bonds. The lengths may be compared with the average Os-Os distance of 2.88 Å in $Os_3(CO)_{12}$.[36]

The Re-Os bonds are also of markedly different lengths: Re-Os(1) = 2.962 (1) Å, Re-Os(2) = 3.108 (1) Å. It is usually found in trinuclear metal carbonyl clusters that a singly bridging hydride ligand causes a lengthening of the metal-metal vector with which it is associated.[38] For example, the Os-Os lengths of Os(μ-H)Os linkages are usually around 3.0 Å.[36,38,39,59]

Unbridged Re-Os bonds would be expected to have a length close to 2.959 Å, the mean of the Re-Re bond length in $Re_2(CO)_{10}$ (3.041 (1) Å)[60] and the average Os-Os length in $Os_3(CO)_{12}$ (2.88 Å).[36] The Re-Os lengths in **2**, therefore, suggest that Re-Os(2) and not Re-Os(1) is bridged by the hydride ligand. But **2** is a member of the class of planar, 62-electron clusters that, as mentioned in the Introduction, has some metal-metal bonds that are exceptionally long and are also unbridged.[29,33,35] Indeed, other evidence strongly favors the location of the hydride ligand as bridging the shorter Re-Os bond. Calculations using the HYDEX program[37] yielded a site energy of 2.3 for the hydride ligand symmetrically bridging Re-Os(1) whereas all other positions investigated resulted in site energies of greater than 9 (Table 2.2). In his original study, Orpen estimated the site energies for 41 bridging hydrides with the HYDEX program and found them to occur in the range 0.2-10.6 with an average value of 2.8.[37] The site energy for the hydride bridging Re-Os(1) in **2** is almost identical to that found for $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$, a cluster also believed to have a long, unbridged metal-metal bond.[35]

In Figure 2.2 the ORTEP diagram of the molecular framework in the metal plane of **2** is superimposed on the corresponding framework of $Os_4(CO)_{14}(PMe_3)$. The latter cluster contains no hydride ligands and has adjacent short (2.779 (2), 2.784 (2) Å) and long (2.982 (2), 3.013 (2) Å) Os-Os bonds around the Os_4 periphery.[33] As can be seen from the figure, the displacement of the in-plane ligands of **2** relative to those in $Os_4(CO)_{14}(PMe_3)$ is entirely consistent with the hydride ligand bridging the short Re-Os(1) bond. Another point to note is that the Os-Os bond in $Os_4(CO)_{14}(PMe_3)$ that corresponds to the bridged Re-Os bond in **2** has an unusually short length of 2.799 (2) Å. The Re-Os distance of the $Re(\mu\text{-}H)Os$ in **2** of 2.962 (1) Å therefore represents a significant lengthening over this distance, even when the different covalent radii of rhenium and osmium are taken into account.

The P-H coupling constant of 13.0 Hz exhibited by the hydride resonance in the ^1H NMR spectrum of **2** is also consistent with the placement of the hydride

Table 2.2. Site Energies[a] for a Hydride Ligand in Various Positions in $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**) and $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (**3**)

Molecule **2**		Molecule **3**	
Position	Site Energy	Position	Site Energy
Os(1)(μ-H)Re	2.3	Os(1)(μ-H)Os(2)	1.68
Os(2)(μ-H)Re	10.9	Os(1)(μ-H)Os(3)	11.1
Os(1)(μ-H)Os(2)	9.4	Os(1)(μ-H)Os(4)	9.7
Os(1)(μ-H)Os(3)	24.3	Os(2)(μ-H)Os(3)	12.0
Os(2)(μ-H)Os(3)	13.7	Os(2)(μ-H)Os(4)	11.3
Os(1)-H	9.4	Os(1)-H[b]	7.2
Os(2)-H	19.3	Os(2)-H[c]	7.6
Os(3)-H	17.6	Os(3)-H	13.8
Re-H	19.3	Os(4)-H[d]	-0.7
		Os(1)Os(2)Os(3)(μ_3-H)	1.4
		Os(1)Os(2)Os(4)(μ_3-H)	0.6

[a] Calculated with the HYDEX program.[9] [b] H···Os(1) = 2.02 Å, H···Os(2) = 2.79 Å. [c] H···Os(2) = 2.03 Å, H···Os(1) = 2.54 Å. [d] H···C(3) = 0.84 Å.

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ligand proposed above;[61] that is, the triphenylphosphine and hydride groups have a cis arrangement in the cluster. It is usually found in metal carbonyl clusters that contain phosphorus-donor and hydride ligands that the hydride ligands will, as far as possible, bridge metal-metal bonds that are cis to the phosphorus ligand.[62] This observation will be of central importance in Part II of this chapter.

The $^{13}C/^{13}C\{^1H\}$ NMR spectra for **2** (discussed in page 19) is less definitive as to the location of the hydride ligand in the cluster. Although an

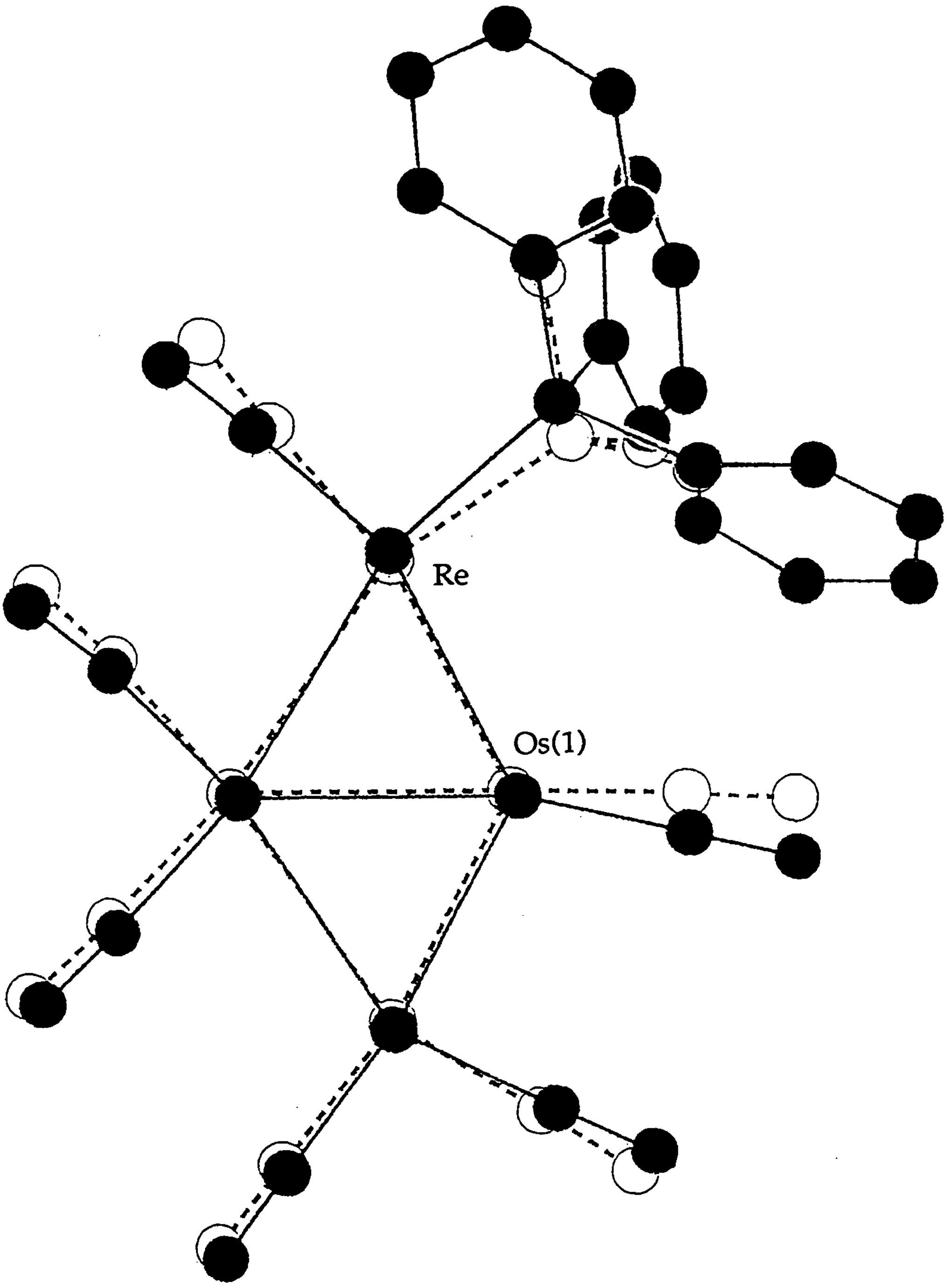

Figure 2.2. Superimposition of the structure of 2 (filled circles) on that of $Os_4(CO)_{14}(PMe_3)$ (open circles). Axial carbonyls have been omitted and Os(1) and Re atoms (shown above) of 2 superimposed with Os(1) and Os(2) atoms of $Os_4(CO)_{14}(PMe_3)$.

obvious increase of intensities for the resonances assigned (see page 19) to the three carbonyls on Os(1) was observed in the $^{13}C\{^{1}H\}$ NMR spectrum compared to that in the ^{13}C NMR spectrum, the intensities for the resonances assigned to the carbonyls on the Re atom remained approximately unchanged. We believe, however, that the available evidence more strongly supports the hydride ligand as located along the short Re-Os(1), rather than the long Re-Os(2), bond.

Churchill and Hollander[34] have reported the structure of $ReOs_3(H)(CO)_{15}$ (**1**) prepared by Knight and Mays by the acidification of an anion presumed to be $[ReOs_3(CO)_{15}]^-$ (i.e., a route different to that used to prepare **2**).[63] The structure of **1** was disordered. In that disordered model the wingtip positions were occupied by $Os(CO)_4$ groups and the hinge positions by $Re(CO)_4$ and $Os(H)(CO)_3$ (i.e., a terminal hydride ligand) groups statistically distributed over the two sites. The model was supported by the thermal motion parameters of the heavy atoms.

A model for the structure of **1** based on that of **2** in which the PPh_3 ligand has been replaced by a carbonyl group appears to also agree with the results of Churchill and Hollander. There are only two crystallographically distinct metal-metal distances for **1**, namely, the average peripheral metal-metal length and the hinge metal-metal length.[34] It is noteworthy that the former length (2.962 Å) is close to the average value for these lengths in **2** (2.957 Å). Furthermore, the hinge metal-metal length in **1** (2.944 (1) Å) is close to that in **2** (2.927 (1) Å). If one of the hinge positions in **1** were occupied by a Re atom, then by analogy to **2** it would be expected that this length would be somewhat longer than 2.959 Å which as discussed above, is the length expected for a Re-Os single bond. In $Re_2Os_3(\mu\text{-}H)_2(CO)_{20}$ (**7**) which has two unbridged Re-Os bonds, the average Re-Os distance was found to be 2.962 Å (there were two independent molecules in the unit cell).[43] For these reasons, it is possible that **1** has a structure similar to **2** with the Re atom in a wingtip position and the hydride ligand bridging one of the Re-Os bonds. However, the infrared spectra in the carbonyl stretching region of **1** and **2** are different, as are their solubilities.[43b,63]

The ^{1}H NMR spectrum of **2** in acetone-d_6 exhibits a doublet centered at δ -12.14. As mentioned previously, the P-H coupling constant (of 13.0 Hz) is consistent with a cis arrangement of the H and PPh_3 ligands.[61] The ^{1}H NMR resonances for bridging hydrogen ligands in Os(μ-H)Os linkages usually occur to high field (i.e., a more negative value) of -15 ppm whereas those of terminal Os-H linkages usually appear to low field of -15 ppm.[59] The hydride resonance for **2** therefore has a chemical shift in the region expected if the hydride ligand were in a terminal position on Os(1), a position analogous to that originally proposed for the hydride ligand in **1** (see page 18). If the hydride ligand did, however, occupy such a position the ^{1}H NMR resonance would not be expected to indicate any P-H coupling.

The $^{13}C\{^{1}H\}$ NMR spectrum of **2** (^{13}CO-enriched) in CD_2Cl_2 at room temperature (Figure 2.3) is consistent with a rigid structure in solution that is identical to that in the solid state. (It is assumed that one of the resonances due to one set of axial carbonyls on an Os atom is degenerate with the signal due to an equatorial CO on an Os atom; page 21.) A partial assignment of the resonances in the spectrum is possible. The two signals to lowest field at δ 202.3 and 195.3 are confidently assigned to the axial and equatorial carbonyl carbon atoms on the Re atom, respectively, on the basis of their chemical shift, their intensity, and because they exhibit P-C coupling. The resonance at δ 192.1 is attributed to the axial carbonyls on Os(1) since it is in the region associated with axial carbonyls of $Os(CO)_3(L)$ groupings,[64,65] has an intensity of 2, and because it

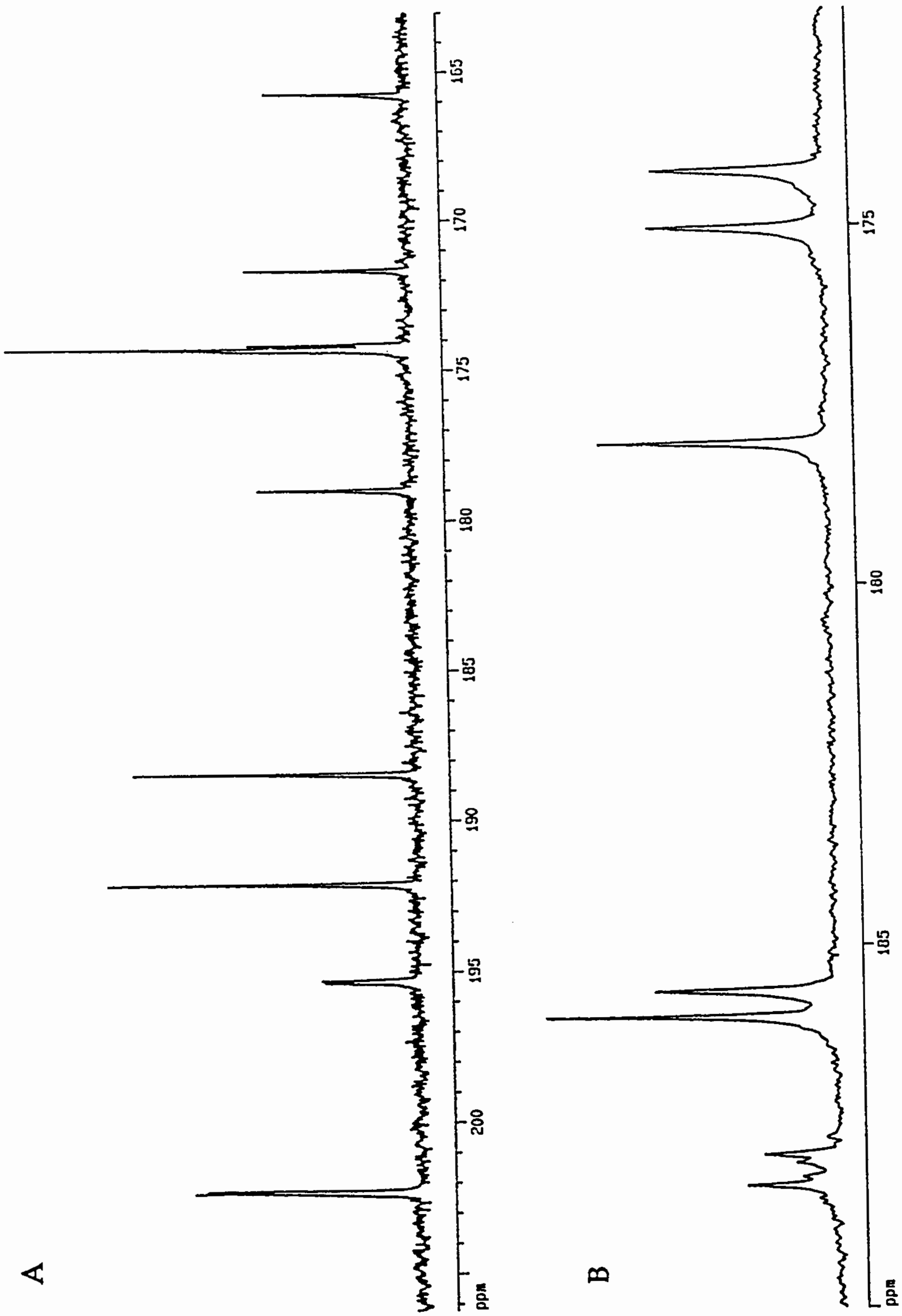

Figure 2.3. $^{13}C\{^1H\}$ NMR spectra of **2** (A) and **3** (B)

shows a small coupling constant in the ^{1}H-coupled ^{13}C NMR spectrum (Figure 2.4) and an increase of intensity in the ^{13}C{^{1}H} NMR spectrum. The peak at δ 188.4 is assigned to the axial carbonyls attached to Os(3) since the peak also appears in the chemical shift region for axial carbonyls of $Os(CO)_4$ units that are attached to the rest of the metal cluster via two metal-metal interactions. The remaining signal of intensity 2, believed isochronous with one of intensity 1, at δ 174.3 is, therefore, assigned to the axial carbonyls of Os(2). This is an unusual chemical shift for such resonances; as noted previously for related clusters,[33] this may be attributed to the unusual bonding in these tetranuclear clusters (this is discussed below).

The signal of intensity 1 at δ 179.0 is assigned to the equatorial carbonyl on Os(1) (i.e., C(13), Figure 2.1) on the basis that it shows a small coupling to hydrogen (broad peak, coupling unresolved) in the ^{1}H-coupled ^{13}C NMR spectrum (Figure 2.4) and an increase of intensity in the ^{13}C{^{1}H} NMR spectrum and because, in a similar manner to the resonance of the axial carbonyls on Os(1), the resonance is shifted downfield from the region normally associated with equatorial carbonyls in osmium carbonyl clusters.[64] The resonance at highest field (of intensity 1) is assigned to the carbon trans to the long Re-Os(2) bond (i.e., C(24), Figure 2.1). As discussed below, we believe this is a dative metal-metal bond and we have previously observed that resonances for carbonyl ligands trans to such bonds occur at particularly high fields.[65] The assignment of the remaining signals of intensity 1 to C(23), C(33), and C(34) is uncertain at present.

$(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3). Like **2**, **3** is a 62-electron cluster, but the X-ray structure determination reveals that it has a nonplanar butterfly rather

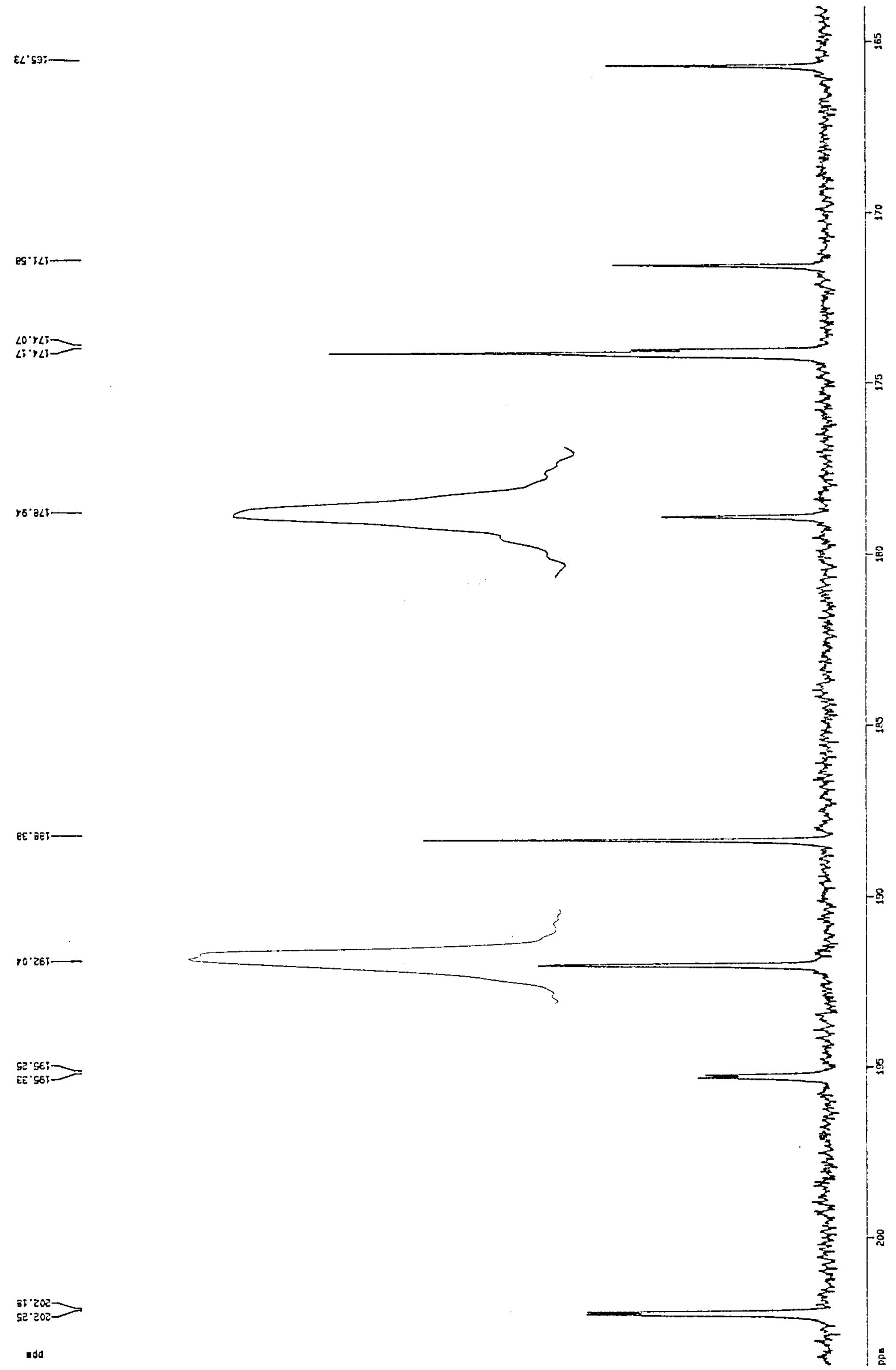

Figure 2.4. ^{13}C NMR spectrum of $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**)

than a planar skeleton of metal atoms (Figure 2.5). The dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(2)Os(4) planes in **3** is 115.4°. The Os-Os bond lengths are given in Table 2.3, along with other selected bond length and angle data. As in **2**, the location of the hydride ligand in **3** was studied in detail (Experimental Section). The final difference map based on low-angle reflections, results from the HYDEX program[37] (Table 2.2), and a comparison of bond angle data with related clusters, were consistent with the hydride ligand as located across the hinge Os(1)-Os(2) bond (although the HYDEX program also gave low values for the face-capping mode of the hydride). Remarkably, this bond at 2.793 (2) Å is the shortest Os-Os bond in **3**. Similar behavior was observed for the Os-Os bond lengths in $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$[62f] and $Os_4(CO)_{11}(\mu\text{-}H)_3$-(CHCHPh).[66] The differences in the Os-Os lengths in these clusters can, in part, be attributed to the different coordination numbers of the metal atoms in the clusters: the shorter Os-Os bond lengths involve osmium atoms with only three terminal ligands.

The $^{13}C\{^1H\}$ NMR spectrum (Figure 2.3) of **3** (^{13}CO-enriched) in toluene-d_8 at -30 °C exhibits seven signals in the carbonyl region in an approximate ratio of 1:1:2:2:2:2:2. This is consistent with the view that **3** has the same structure, (i.e., with a mirror plane) in solution as found in the solid state, with the hydride ligand either in the mirror plane or rapidly oscillating about the plane. In the ^1H-coupled ^{13}C NMR spectrum (Figure 2.6) only one of the signals that was a singlet in the $^{13}C\{^1H\}$ NMR spectrum is split into a doublet, indicative of coupling to hydrogen. Furthermore, this signal is to higher field compared to those of $Os(CO)_4$ units[67] where we have previously observed the resonances of the carbonyls of $Os(CO)_3$ groups to occur. We believe the only reasonable interpretation of these results is that the hydride ligand is stereochemically rigid

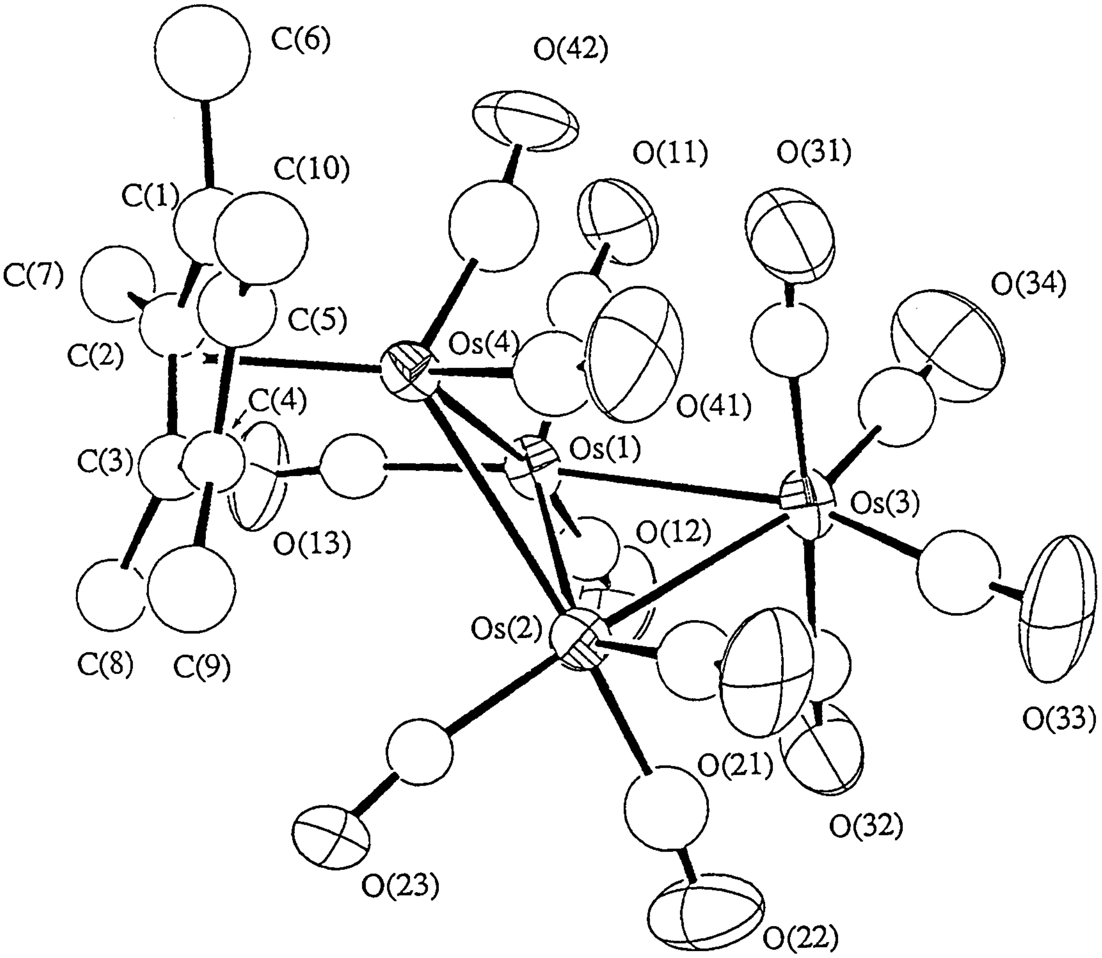

Figure 2.4. The molecular structure of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3)

Table 2.3. Selected Bond Lengths (Å) and Angles (°) for $(Cp^{*})(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (**3**)

Bond Lengths

Os(1) - Os(2)	2.793 (1)	(Os-C)	1.80 (3) - 1.99 (3)
Os(1) - Os(3)	2.875 (1)	(C-O)	1.09(3) - 1.19(3)
Os(1) - Os(4)	3.023 (1)	$(C\text{-}C)_{ring}$	1.41 (3) - 1.43 (3)
Os(2) - Os(3)	2.886 (1)	$(C\text{-}C_{Me})$	1.51 (3) - 1.57 (3)
Os(2) - Os(4)	3.004 (1)		

Bond Angles

Os(2) - Os(3) - Os(1)	58.01 (3)	C(11) - Os(1) - Os(2)	141.5 (7)
Os(2) - Os(4) - Os(1)	55.21 (3)	C(12) - Os(1) - Os(2)	110.7 (7)
Os(3) - Os(1) - Os(2)	61.19 (3)	C(13) - Os(1) - Os(2)	114.9 (7)
Os(3) - Os(2) - Os(1)	60.80 (3)	C(21) - Os(2) - Os(1)	142.7 (7)
Os(4) - Os(1) - Os(2)	62.05 (4)	C(22) - Os(2) - Os(1)	111.6 (8)
Os(4) - Os(2) - Os(1)	62.74 (4)	C(23) - Os(2) - Os(1)	116.2 (6)

on the NMR time scale at this temperature and bridges the hinge, Os(1)-Os(2), bond. The chemical shift of the hydride resonance (δ -15.67) in the ^1H NMR spectrum of **3** is consistent with a bridging, rather than terminal, hydride ligand.[59]

The ^{13}C NMR signal at δ 175.1 that exhibits the coupling to hydrogen (Figures 2.4 & 2.6) is assigned to the carbon atoms trans to the hydride ligand, namely, C(11) and C(21) (Figure 2.5). Assignment of the remaining resonances in the ^{13}C NMR spectrum is as follows. The peaks at δ 188.3 and 187.9 are assigned to the axial carbons on Os(3) (i.e., C(31), C(32)): they are the only peaks of intensity 1 and, furthermore, they exhibit $^{13}C\text{-}^{13}C$ coupling, as expected for

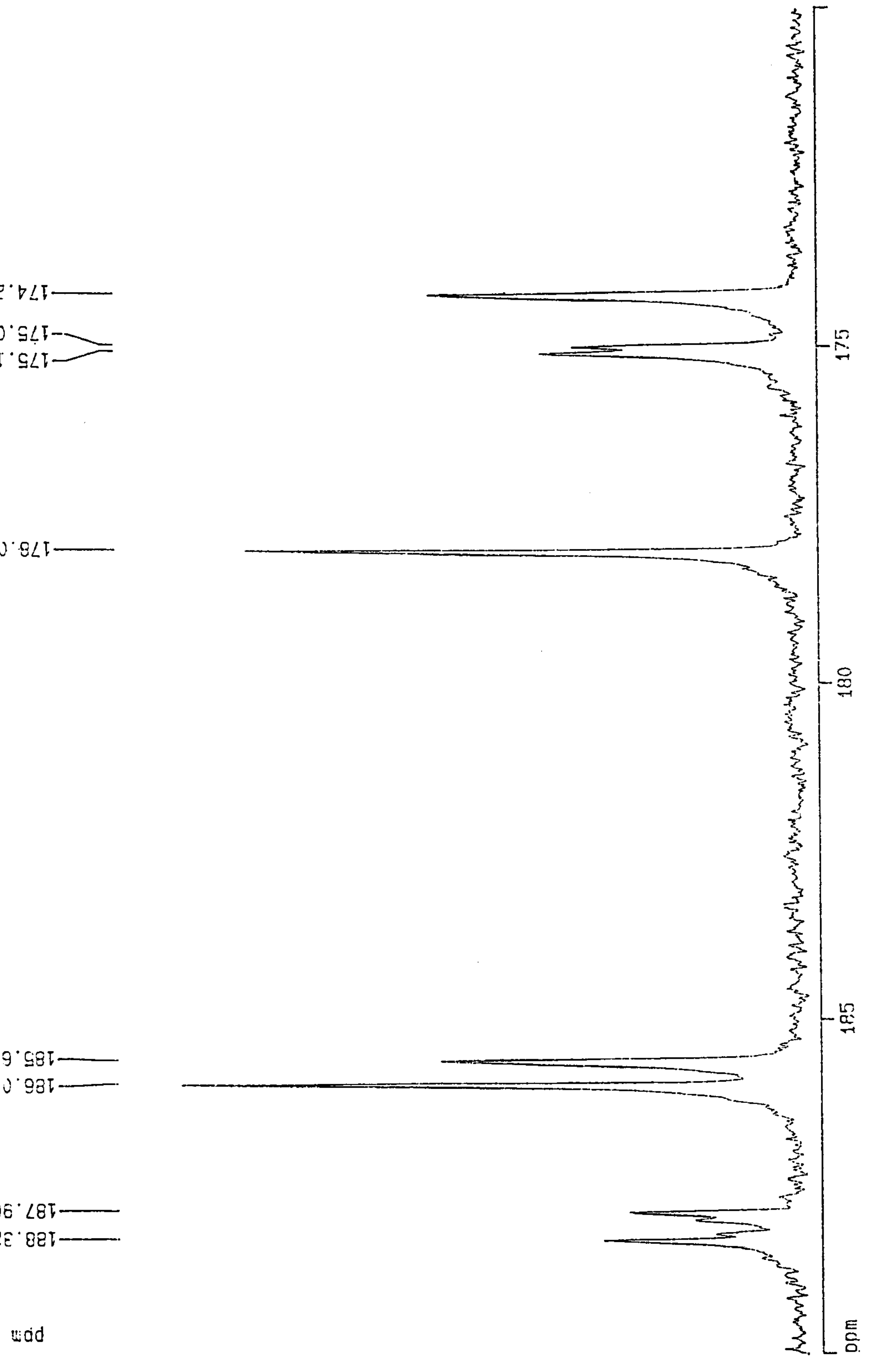

Figure 2.6. ^{13}C NMR spectrum of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3)

chemically different carbonyls in a trans arrangement (the precursor of **3** contained ~35% ^{13}CO).[68] The resonance at δ 186.0 is tentatively assigned to the carbonyl carbons on Os(4) (C(41), C(42)). This resonance is more intense than the other signals, nominally of intensity 2. Because of their close proximity to the methyl hydrogens these carbon atoms are expected to have a shorter T_1 which would lead to a somewhat more intense ^{13}C NMR signal. For the same reason, the signal for these carbonyls is expected to exhibit an NOE in the $^{13}C\{^1H\}$ NMR spectrum; this was indeed observed. It is also commonly observed that the resonances of carbonyls attached to a metal atom to which electron donating ligands are coordinated are shifted downfield, rather than upfield.[69] The peak at δ 185.7 is attributed to the equatorial carbonyls on Os(3) (i.e., C(33), C(34)): it is in the region expected for the signals of equatorial carbonyls of $Os(CO)_4$ groups, downfield from the region where the resonance of $Os(CO)_3$ groupings occur.[64,67] The signal at δ 178.1 is assigned to carbon atoms C(13) and C(23) since it is more intense than the other signals attributed to the $Os(CO)_3$ units; this would be expected for the carbons of these units that are closest to the methyl hydrogens, for reasons given above. It is also expected that the remaining carbons of the $Os(CO)_3$ units would have similar ^{13}C NMR chemical shifts since they are both directed away from the Cp* ligand and towards the $Os(CO)_4$ grouping. The remaining signal, at δ 174.3, is therefore assigned to C(12) and C(22).

2.2.1.2 Bonding in 2 and 3

A simple view of the bonding in **2** is depicted in Chart 2.1. In order for each metal atom to achieve an 18-electron configuration it is proposed that the

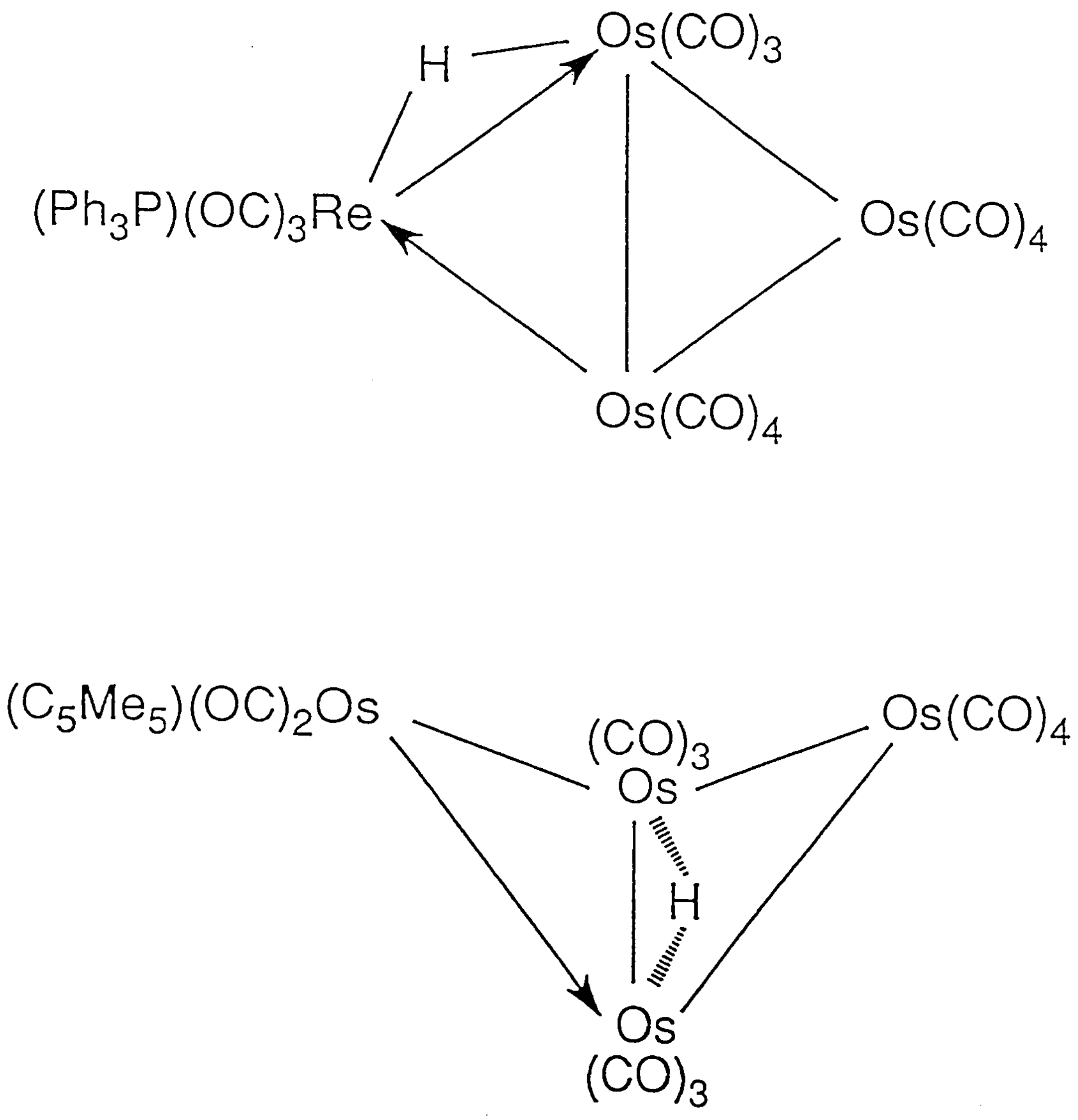
H
Os(CO)3
(Ph3P)(OC)3Re
Os(CO)4
Os(CO)4
(C5Me5)(OC)2Os
(CO)3
Os
Os(CO)4
H
Os
(CO)3

Chart 2.1

bond between the osmium atom of the hinge $Os(CO)_4$ unit to the rhenium atom is a dative bond and that the bond of the rhenium atom to the other hinge osmium atom is a three-center, two-electron Re(μ-H)Os linkage. That dative metal-metal bonds might be present in the metal framework of metal cluster compounds was first proposed in 1979.[70] Numerous complexes have also been described that have an unbridged, donor-acceptor dative bond between an osmium and a second transition metal atom.[65,71] The structures of two complexes that are believed to have two unbridged dative metal-metal bonds in tandem have been reported by Pomeroy and coworkers.[65a,72] Complexes in which three-center, two-electron Re(μ-H)M (M = transition metal) bonds are believed to be present have been well characterized.[73]

A proposal for the metal-metal bonding in 3 is also depicted in Chart 2.1. In the proposed view, the 17-electron $(Cp^*)Os(CO)_2$ fragment is bound to the rest of the cluster via one dative and one nondative Os-Os bond (these bonds may be transposed to the arrangement shown in Chart 2.1).

A comparison of the positions of the CO stretching frequencies of $(Cp^*)Os(CO)_2(H)$ (2001, 1941 cm^{-1})[58] to those of $Re(CO)_4(PPh_3)(H)$ (2082, 1991, 1977, 1964 cm^{-1})[57] indicates that there is more electron density on the osmium atom in $(Cp^*)Os(CO)_2$ than on the rhenium atom in $Re(CO)_4(PPh_3)$ (or $Re(CO)_3(PPh_3)$). This increased electron density would be expected to favor the structure found for 3 rather than one similar to that found for **2**. This is because the osmium atom to which the Cp* ligand is attached acts as the donor atom in the dative metal-metal bond in 3, whereas it would be the acceptor atom in a structure analogous to **2**. We and others have observed that, in general, apparently stronger dative metal-metal bonds are formed when stronger σ-donor ligands are attached to the donor metal atom.[65,72,74]

Relevant to this discussion is that a changeover has been observed in the structures of $Os_4(CO)_{15}(L)$ (L = CO, P-donor ligand, $CNBu^t$) clusters upon changing the ligand L. A changeover from a puckered-square arrangement of metal atoms with no dative metal-metal bonds to a spiked triangular geometry with one dative and three non-dative metal-metal bonds (i.e., $(L)(OC)_4Os\rightarrow Os_3(CO)_{11}$) has been observed upon an increase in the σ-donor properties of L.[71a]

An alternative view of the bonding in **3** is that it is a formally unsaturated cluster similar to $Os_3(\mu\text{-}H)_2(CO)_{10}$,[75] but with one of the bridging hydride ligands replaced by the isolobal $(Cp^*)Os(CO)_2$ unit. In other words, the $(Cp^*)Os(CO)_2$ fragment is bound to the rest of the cluster via a three-center, two-electron bond where each unit contributes one electron to the bond. Given the propensity of osmium to form dative metal-metal bonds in organometallic complexes, the former interpretation for the bonding in **3** is favored.

2.2.1.3 Structure and Stoichiometry of 2, 3 and 5

As has been previously pointed out, 62-electron clusters that contain osmium appear to adopt a planar metal arrangement when one of the hinge metal atoms has four terminal ligands. On the other hand, a butterfly (bent) configuration is found when both hinge atoms have only three terminal ligands.[62f] For example, $Os_4(CO)_{14}(PMe_3)$ has a planar Os_4 metal framework[33] whereas $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ has a butterfly Os_4 skeleton.[62f] In this way, the hinge metal atoms have approximately octahedral coordination if the hinge metal-metal bond is ignored. The structures of **2** and **3** are in agreement with this generalization: **2** has an $Os(CO)_4$ grouping in a hinge position and a planar arrangement of metal atoms; **3** has $Os(CO)_3$ groupings in both the hinge sites and possesses a butterfly configuration of metal atoms.

As also mentioned previously, the tetranuclear cluster $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**) was prepared by the addition of $Re(CO)_4(PPh_3)(H)$ to $Os_3(CO)_{10}(COE)_2$. The compound $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (**5**), a pentanuclear cluster, was similarly prepared by the addition of $Re(CO)_3(PMe_3)_2(H)$ to $Os_3(CO)_{10}(COE)_2$ (molar ratio 2:1). There was no evidence in the latter reaction for an intermediate analogous to **2**, i.e., $(OC)_2(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (**8**). When $Os_3(CO)_{10}(COE)_2$ and $Re(CO)_3(PMe_3)_2(H)$ in a 1:1 molar ratio were stirred together in solution, **5** resulted with no definitive spectroscopic evidence for **8**. Furthermore, $Re(CO)_5(H)$ has been reported to react with $Os_3(CO)_{10}(COE)_2$ to form $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$ (**7**),[43] a compound that has a similar metal skeleton to **5**.

It is interesting that **2**, **3** and **5** (and **7**) have these different skeletons of metal atoms, even though they are made from analogous reactions under similar reaction conditions. An argument based mainly on steric effects is given below.

It is known that the donor properties of CO, PPh_3 and PMe_3 follow the order CO < PPh_3 < PMe_3.[76a] That **2** is a tetranuclear cluster whereas both **5** and **7** have five metal atoms suggests that the change in the electronic character of the fragment $Re(CO)_{5-n}(L)_n$ ($n = 1$, L = CO, PPh_3; $n = 2$, L = PMe_3) does not have a large affect on the formation of the different arrangements of metal atoms.

It is also known that the ligands PMe_3 and PPh_3 in $Ni(CO)_3(L)$ (L = PMe_3, PPh_3) complexes have cone angles of 118° and 145°, respectively.[76b] Carbon monoxide has a cone angle of ~95°,[76b] i.e., in terms of size the ligands decrease in the order PPh_3 > PMe_3 > CO. Upon coordination of $Re(CO)_4(PPh_3)(H)$ to $Os_3(CO)_{10}(COE)_2$ (eq 2.1) to form $(OC)_3(Ph_3P)Re(\mu\text{-}H)Os_3(CO)_{11}$ (**2**), the migration of a CO ligand from the Re center to a hinge Os center is favored because of the larger cone angle of PPh_3 and steric interaction of the PPh_3 and the carbonyl ligands on the Re atom. This migration thus prevents formation of the pentanuclear cluster and forms a planar arrangement of metal atoms. Furthermore, the bulky PPh_3 ligand in both **2** and $Re(CO)_4(PPh_3)(H)$ might prevent attack of a second $Re(OC)_4(Ph_3P)(H)$ molecule at Os(1) (or Os(2)) in **2**.

In **3** there may be less steric interactions between the Cp* and the two carbonyl ligands in the $Cp^*Os(CO)_2$ fragment and therefore, one of these two carbonyls is not "forced" to migrate to another Os atom in the formation of **3**. Furthermore, the increased electron density of the osmium atom in $Cp^*Os(CO)_2$ favors the formation of a dative M-M bond, as mentioned previously (page 29), and as a result a butterfly arrangement of the metal atoms is adopted.

Curiously, addition of $Os(CO)_5$ or $Cp^*Ir(CO)_2$ to $Os_3(CO)_{10}(COE)_2$ produced compounds $Os_4(CO)_{15}$ and $Cp^*(CO)IrOs_3(CO)_{11}$ with tetranuclear arrangements of metal atoms.[29] Whereas the $Re(OC)_4(Ph_3P)$ and $Cp^*Os(CO)_2$ are 17-electron fragments, $Os(CO)_5$ and $Cp^*Ir(CO)_2$ are 18-electron units. The bonds needed for the latter two moieties to form spiked triangular clusters would be unbridged, dative metal-metal bonds. Dinuclear complexes in which the $Os(CO)_5$ or $Cp^*Ir(CO)_2$ forms the donor half of a dative metal-metal bond are known but, with the exception of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$,[77] are unstable.[78,65c] Therefore, compounds with nondative covalent bonds between the $Os(CO)_5$ (or $Cp^*Ir(CO)_2$) and $Os_3(CO)_{10}$ are, in general, favored whenever possible. In order for $Os(CO)_5$ (or $Cp^*Ir(CO)_2$) to form nondative covalent bonds with other species, a vacant site on $Os(CO)_5$ (or $Cp^*Ir(CO)_2$) needs to be generated in the reaction. This requirement of a vacant site leads to the movement of a carbonyl ligand from $Os(CO)_5$ (or $Cp^*Ir(CO)_2$) to an osmium atom of the $Os_3(CO)_{10}$ fragment. As a result, planar compounds form.

2.2.2 Part II. Site Preference of Bridging Hydride Ligands in Metal Clusters

As discussed above, $Os_3Re(H)(CO)_{15}$ (**1**) was thought to have a terminal hydride ligand on Os(1), while $[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ (**2**) is believed to have a hydride ligand bridging the Re-Os(1) bond cis to the phosphine ligand. In order to more fully understand the factors that influence the site preference of hydride ligands in clusters, further rhenium-osmium hydrido clusters have been synthesized and the site of hydride coordination investigated.

The clusters $(OC)_3(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (**4**) and $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2$-$Os_3(CO)_{10}$ (**5**) were prepared by the addition of $Re(CO)_3(PMe_3)_2(H)$[41] to $Os_3(CO)_{11}(NCMe)$[16] (eq 2.2) and to $Os_3(CO)_{10}(COE)_2$[15] (eq 2.1, page 12), respectively, at room temperature.

$$Os_3(CO)_{11}(NCMe) + Re(CO)_3(PMe_3)_2(H) \longrightarrow \underset{\mathbf{4}}{(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}} \qquad (2.2)$$

Clusters **4** and **5** are air stable, orange crystalline solids.

2.2.2.1 Structure Assignment

The molecular structures of **4** (Figure 2.7) and **5** (Figure 2.8) reveal that both **4** and **5** have a "spiked" triangular metal atom arrangement. The arrangements of non-hydrogen ligands in the two clusters are similar to that in $(OC)_5ReOs_3(\mu\text{-}H)(CO)_{10}(NCMe)$[42] (**6**) and $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$[43] (**7**), respectively. The metal-metal bond lengths (and angles) in **4** (Table 2.4) and **6**, and **5** (Table 2.5) and **7**, however, are very different as are shown in Figures 2.9 and 2.10.

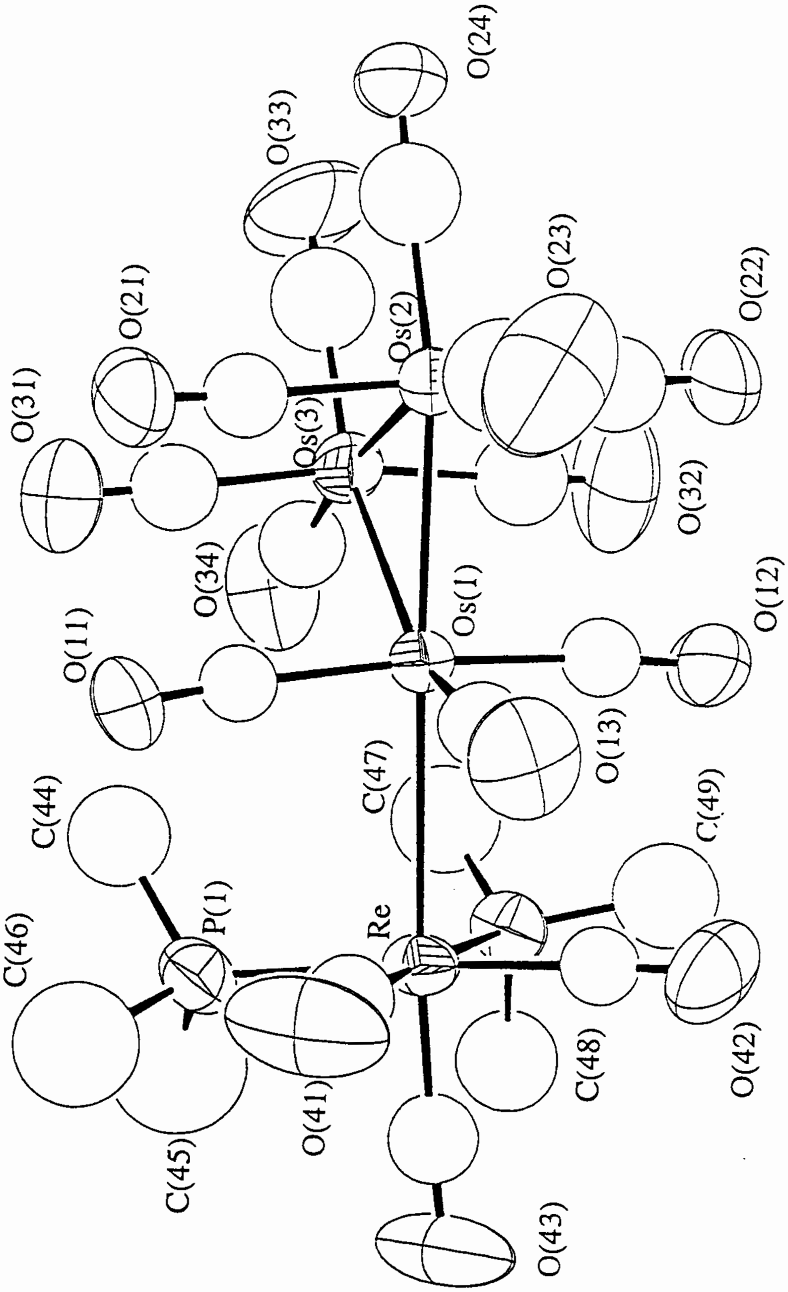

Figure 2.5. The molecular structure of $(OC)_3(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (4)

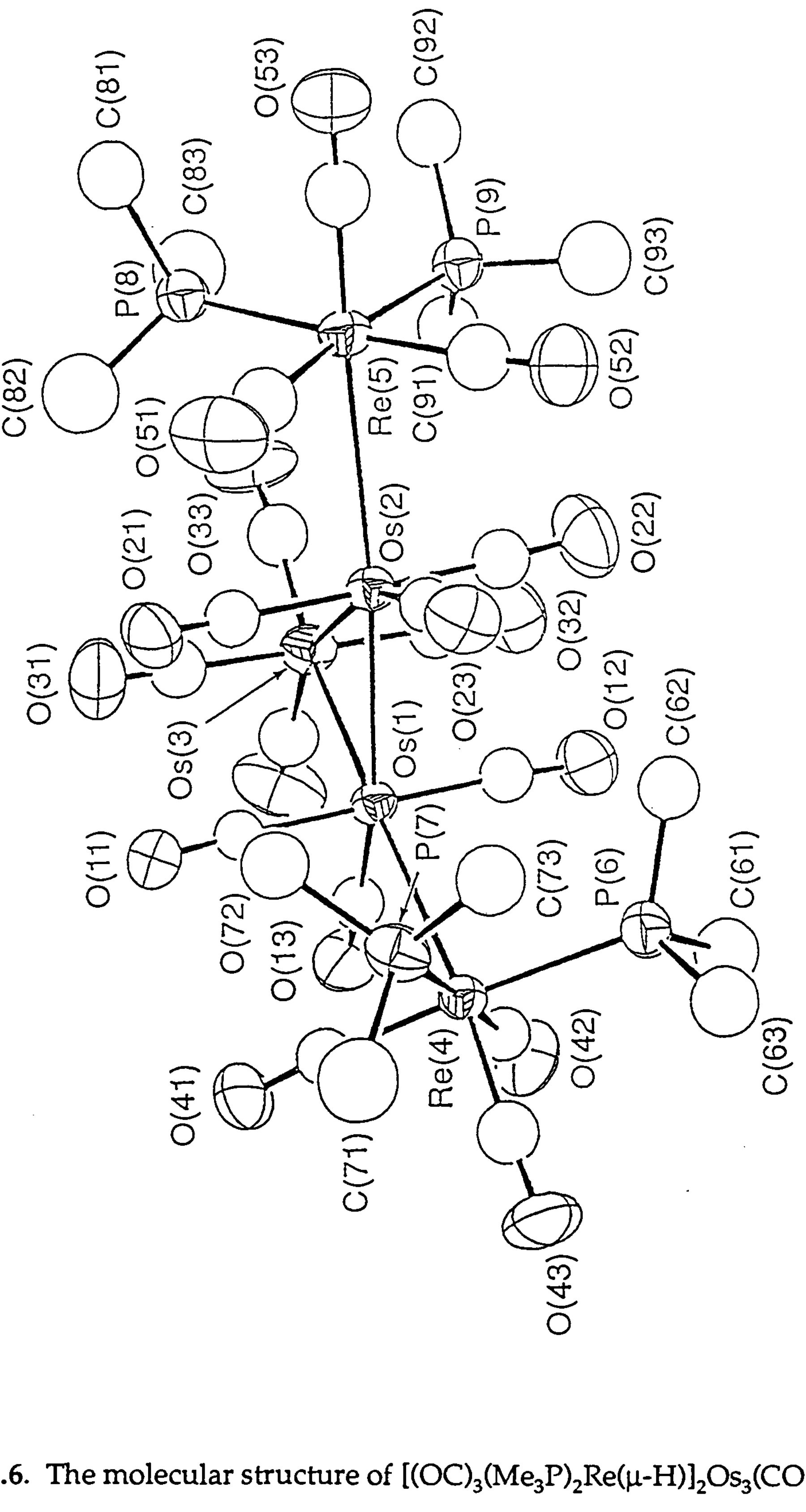

Figure 2.6. The molecular structure of $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5)

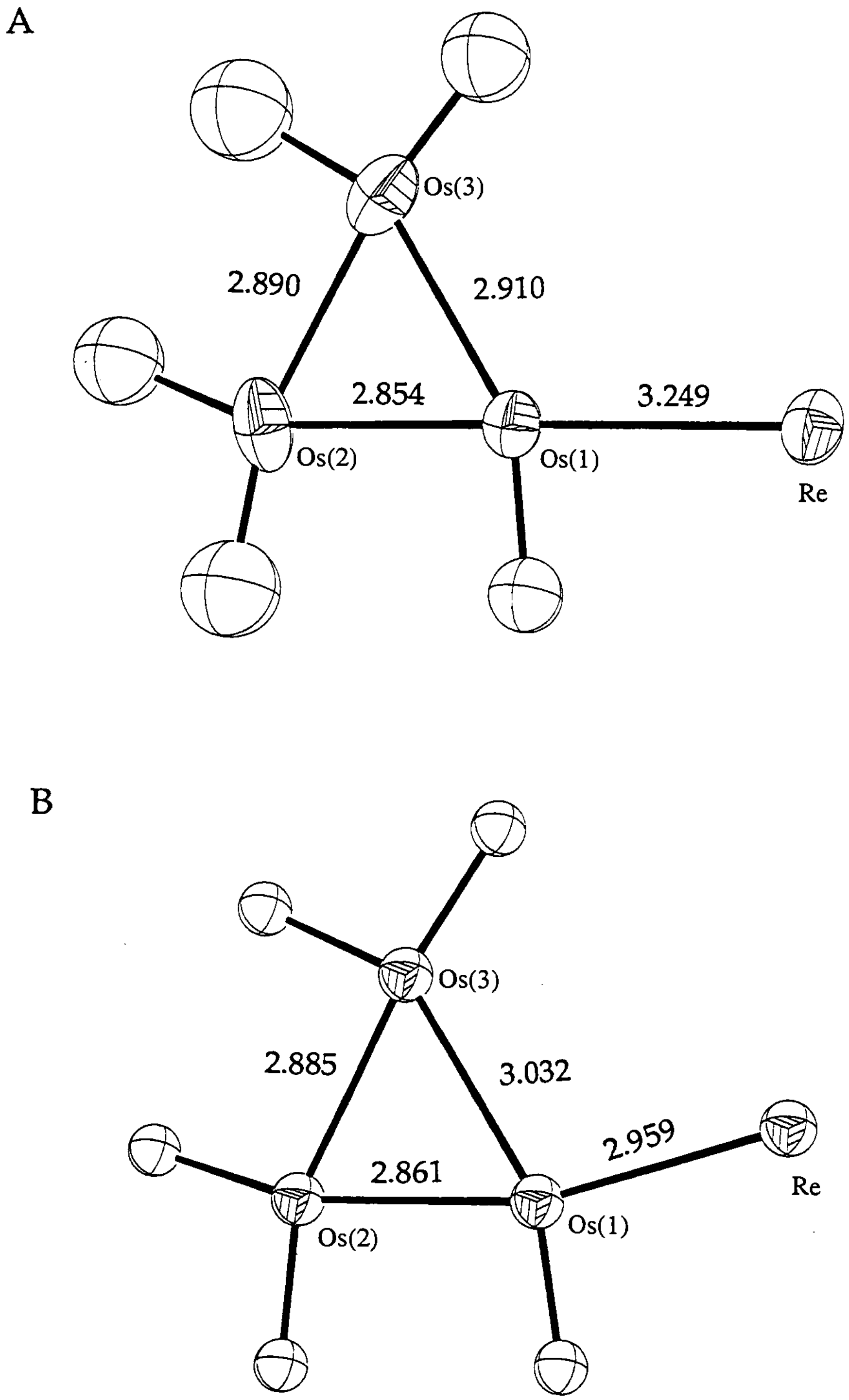

Figure 2.9. ORTEP drawings of the inner atoms of $(OC)_3(Me_3P)_2Re(\mu\text{-}H)\text{-}Os_3(CO)_{11}$ (4) (A) and $(OC)_5ReOs_3(\mu\text{-}H)(CO)_{10}(NCMe)$ 6 (B) with the M-M bond lengths (Å).

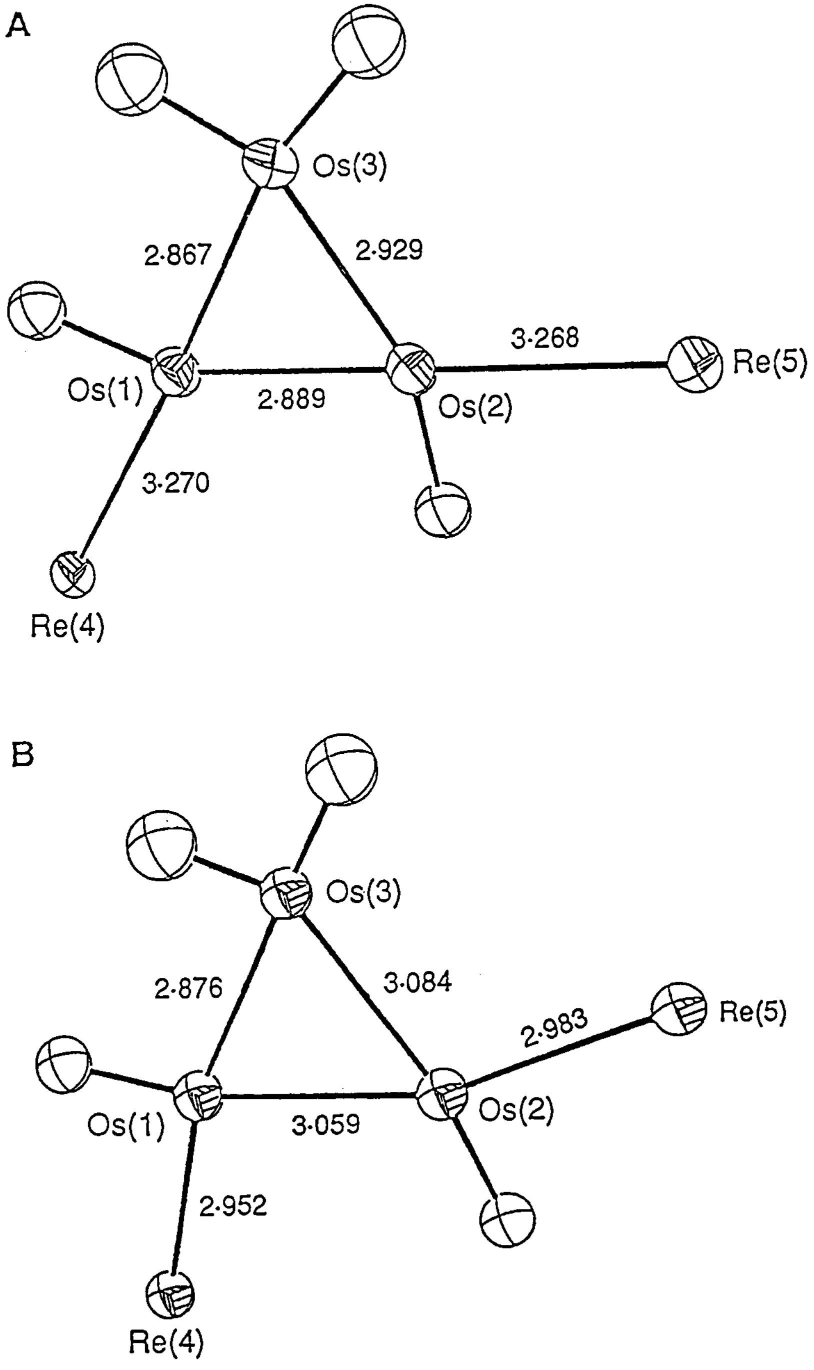

Figure 2.10. ORTEP drawings of the inner atoms of $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2\text{-}Os_3(CO)_{10}$ (5) (A) and molecule A of $[(OC)_5Re]_2Os_3(\mu\text{-}H)_2(CO)_{10}$ (7) (B) with the M-M bond lengths (Å).

Table 2.4. Selected Bond Lengths (Å) and Angles (°) for $(OC)_3(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (4)

Bond Lengths

Os(1) - Os(2)	2.854 (1)	Re - P(2)	2.469 (3)
Os(1) - Os(3)	2.910 (1)	(Os-C)	1.86 (3) - 1.96 (3)
Os(1) - Re	3.249 (1)	(Re-C)	1.84 (3) - 1.98 (3)
Os(2) - Os(3)	2.890 (1)	(P-C)	1.75 (3) - 1.85 (3)
Re - P(1)	2.474 (4)	(C-O)	1.10 (2) - 1.20 (2)

Bond Angles

Os(3) - Os(1) - Os(2)	60.18 (2)	P(2) - Re - Os(1)	99.26 (9)
Os(3) - Os(2) - Os(1)	60.88 (2)	P(2) - Re - P(1)	94.4 (1)
Re - Os(1) - Os(2)	178.15 (2)	C(33) - Os(3) - Os(2)	91.9 (6)
Re - Os(1) - Os(3)	120.18 (2)	C(34) - Os(3) - Os(1)	111.4 (6)
P(1) - Re - Os(1)	99.0 (1)		

It is well established that the presence of a single bridging hydride ligand is generally associated with a lengthening of the metal-metal bond as compared to that when it is unbridged.[38] In trinuclear osmium carbonyl clusters, the lengths of unbridged Os-Os bonds are usually around 2.88 Å, the average Os-Os length in $Os_3(CO)_{12}$,[36] whereas the Os-Os distances in Os(μ-H)Os linkages are normally around 3.0 Å.[36,39,59] As can be seen from Figure 2.9, the Os-Os bond lengths in **6** clearly indicate that the hydride ligand bridges Os(1)-Os(3).[42] Furthermore, the Re-Os distance in the molecule is as expected for an unbridged bond: 2.959 Å, exactly equal to the mean of the bond length in $Re_2(CO)_{10}$ (3.041 (1) Å)[60] and the average Os-Os length in $Os_3(CO)_{12}$ (2.88 Å).[36]

In contrast, the Os-Os lengths in **4** (Figure 2.9) indicate that none is bridged by a hydride ligand; the longest Os-Os distance is 2.910 (1) Å. On the

Table 2.5. Selected Bond Lengths (Å) and Angles (°) for $[(OC)_3(Me_3P)_2Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (**5**)

Bond Lengths

Os(1) - Os(2)	2.889 (1)	2.889[a]	Os(2) - Re(2)	3.268 (1)	3.269[a]
Os(1) - Os(3)	2.867 (1)	2.869[a]	(Os-CO)	1.84 (2) - 1.93 (2)	
Os(1) - Re(1)	3.270 (1)	3.272[a]	(Re-CO)	1.85 (2) - 1.94 (2)	
Os(2) - Os(3)	2.929 (1)	2.931[a]	(C-O)	1.13 (3) - 1.19 (3)	

Bond Angles

Os(3) - Os(1) - Os(2)	61.18 (2)	Re(2) - Os(2) - Os(1)	175.01 (2)
Os(3) - Os(2) - Os(1)	59.04 (2)	Re(2) - Os(2) - Os(3)	118.79 (2)
Os(2) - Os(3) - Os(1)	59.78 (2)	P(2) - Re(1) - P(1)	95.5 (1)[b]
Re(1) - Os(1) - Os(2)	120.96 (2)	P(4) - Re(2) - P(3)	94.7 (3)[b]
Re(1) - Os(1) - Os(3)	176.44 (2)		

[a] Corrected values based on rigid body motion of the metal atoms.
[b] Atoms were affected by restraints.

other hand, the Os-Re length in **4** (3.250 (1)Å) is some 0.3 Å longer than the corresponding length in **6**. The metal-metal bond lengths in **4** are, therefore, consistent with the view that the hydride ligand bridges the Re-Os rather than an Os-Os bond. The bond angles in **4** (Table 2.4) support this view. For example, the Os(3)-Os(1)-Re angle in **4** is 120.18 (3)°, whereas in **6** the corresponding angle is 104.84 (2)°. The ^1H NMR spectrum of **4** exhibits a triplet at δ -17.08 (J_{PH} = 13.9 Hz), consistent with the view that in solution **4** has the same structure as that found in the solid state. Furthermore, the size of the P-H coupling constant suggests that the hydride ligand is cis to the two PMe_3 groups.[61]

Analysis of the structures of 5 and 7 gives similar results. From Figure 2.10, the M-M bond lengths in 7 indicate that the hydride ligands bridge Os(1)-Os(2) and Os(2)-Os(3) rather than the Re-Os bonds. However, the M-M lengths in 5 (Figure 2.10) clearly indicate that the hydride ligands bridge the Re-Os bonds. The larger bond angles (Os(2)-Os(1)-Re(1) = 120.96 (2)° and Os(3)-Os(2)-Re(2) = 118.79 (2)°) in 5 compared to the corresponding angles (103.93 (10)° and 103.97 (9)°) in molecule A of 7 are also consistent with this location of the hydride ligands. (The molecular dimensions of the two independent molecules of 7 are not, in a chemical sense, significantly different.[43a])

The ^1H NMR spectrum of 5 in toluene-d_8 exhibits two strong triplets in a 1:1 ratio at δ -16.96 (J_{PH} = 13.8 Hz) and -17.30 (J_{PH} = 14.8 Hz). This indicates that the major form of 5 in solution has the same structure as that found in the solid state. The size of the P-H coupling constants also suggests that a given hydride ligand is cis to the two nearest PMe_3 groups.[61] It is impossible from the available evidence to determine if there is free rotation about the Re(μ-H)Os bonds of 5 in solution.

There is also a minor triplet in the spectrum at δ -17.17 (J_{PH} = 14.3 Hz). This signal increased in intensity relative to the other hydride signals when the spectrum was recorded in acetone-d_6. This behavior is interpreted in terms of a second isomer of 5 (with the $Re(CO)_3(PMe_3)_2(H)$ ligands trans to the same Os-Os bond) in equilibrium with the major isomer. Similar behavior has been observed in $Os_3(CO)_{10}(PR_3)_2$ and $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W) clusters.[64d,79,80]

The $Re(CO)_3(PMe_3)_2(H)$ ligands are assumed to be bound to their respective osmium atoms via three-center, two-electron bonds. This type of bonding was proposed many years ago by Kaesz and co-workers to be present in $(OC)_5Re(\mu\text{-}H)ReMn(CO)_9$[73] and is also believed to be present in **2** as mentioned above.

Changes in the site of coordination of a hydride ligand upon replacement of a carbonyl by a phosphine ligand have been observed previously. For example, in $Ru_4(\mu\text{-}H)_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ hydrogen atoms bridge all three edges of the tetrahedron that are connected to the Ru atom to which both phosphorus atoms are coordinated[81] (Chart 2.2). This leaves two adjacent tetrahedral edges free of hydrogen atoms. In the parent compound, $Ru_4(\mu\text{-}H)_4(CO)_{12}$, two opposite edges are left unbridged (D_{2d} structure)[82] (Chart 2.2). In $Os_3(\mu\text{-}H)(\mu\text{-}S_2CH)(CO)_{10}$ both bridging ligands span the same Os-Os bond, whereas in $Os_3(\mu\text{-}H)(\mu\text{-}S_2CH)(CO)_9(PMe_2Ph)$ the hydride bridges the Os-Os bond that is cis to the PMe_2Ph group and the sulfur ligand bridges a second Os-Os bond[83] (Chart 2.2).

As mentioned previously (page 16), it is usually found in carbonyl cluster compounds that contain both phosphine and bridging hydride ligands that, as far as possible, the hydride ligands bridge the metal-metal bonds that are cis to the phosphorus atoms,[59,62,81,83] even though these metal-metal bonds are invariably the more sterically hindered bonds. These bonds are, however, also expected to be more electron rich: because of the poorer π-acceptor properties of phosphine ligands compared to CO groups, there should be less delocalization of the electron density in the metal-metal bond onto the neighboring ligands as shown in Chart 2.3 ($L = PMe_3$). Molecular orbital calculations for $Ru_3(CO)_{12}$ have shown that this type of interaction (i.e., L = CO) is significant.[84]

Fehlner has discussed the energetics of E-H-M versus M-H-M formation (E = main group element, M = transition metal). He concluded that, for a fixed metal atom type, as the electronegativity of the main group increases, M-H-M is

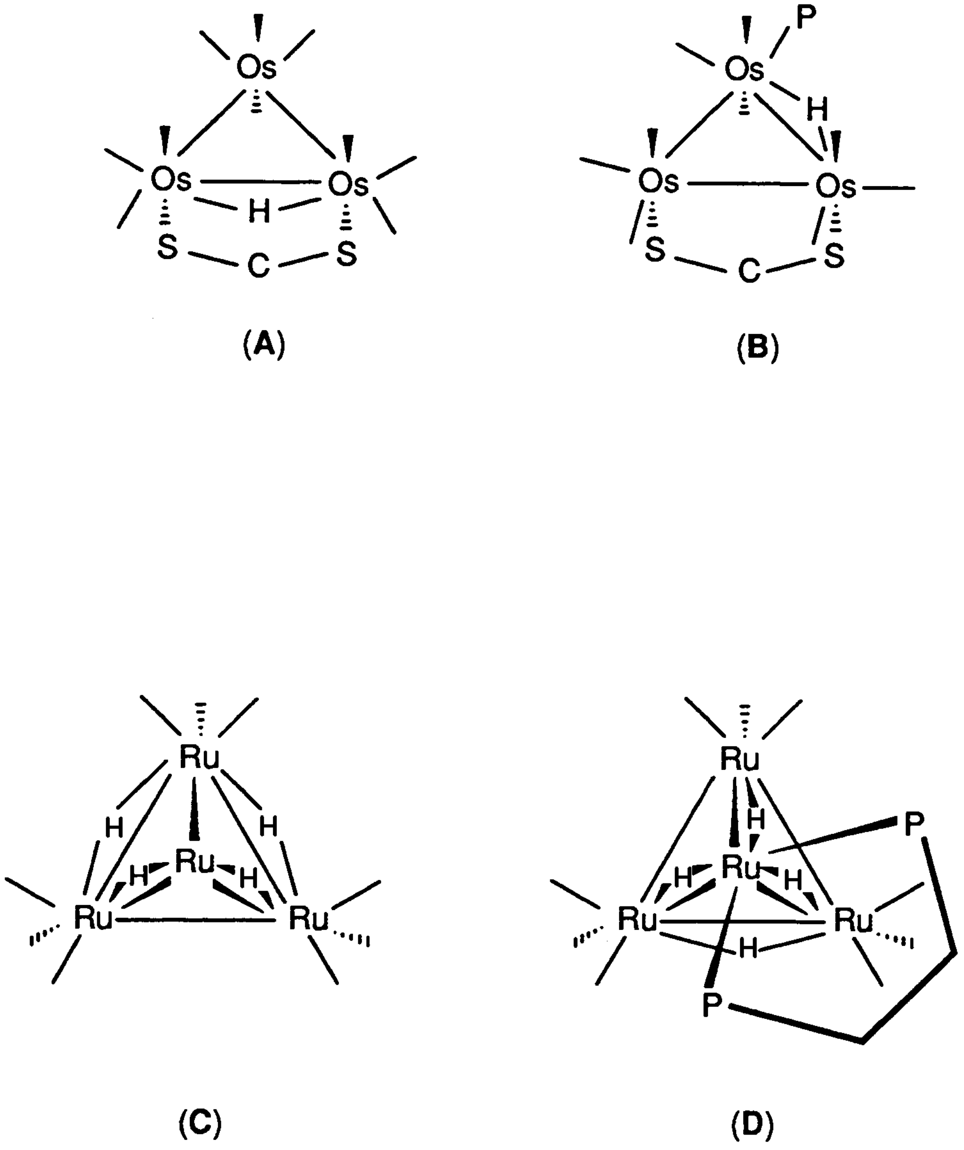

Chart 2.2. Sketches of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (**A**), $Ru_4(\mu\text{-}H)_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ (**B**), $Os_3(\mu\text{-}H)(\mu\text{-}S_2CH)(CO)_{10}$ (**C**) and $Os_3(\mu\text{-}H)(\mu\text{-}S_2CH)(CO)_9(PMe_2Ph)$ (**D**) (carbonyl ligands attached to the central Ru atom in **C** and **D** are omitted)

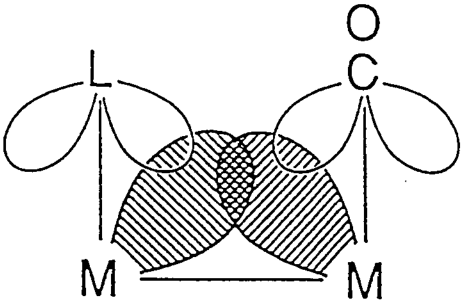

Chart 2.3.

favored over E-H-M; for a constant main group atom, as the electronegativity of the metal increases, E-H-M is favored over M-H-M.[85] Although a somewhat different approach, Fehlner's views are consistent with that presented above.

The view that a hydride ligand will bridge the most electron-rich metal-metal bond may be of general applicability. For example, a number of osmium carbonyl clusters with ER_3 (E = Si, Sn; R = organic group) and bridging hydride ligands have been reported by Pomeroy and co-workers.[35,86] In all cases there is a bridging hydride across the Os-Os bond that is also cis to the ER_3 ligand.

2.3 Experimental Section

2.3.1 Preparations

General Procedures. The following general procedures were applied to all the experimental work reported in this thesis unless otherwise stated. Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was treated similarly, except CaH_2 was used as the drying agent.

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 and found accurate to ± 1 cm^{-1}. NMR spectra were recorded on either a Bruker WM400 or Bruker SY-100 spectrometer; the $^{31}P\{^1H\}$ NMR spectra are referenced with respect to external 85% H_3PO_4. Fast-atom-bombardment mass spectra were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility). Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory at Simon Fraser University.

The preparations of $Re(CO)_5(H)$,[87] $Re(CO)_4(PPh_3)(H)$,[57] $(Cp^*)Os(CO)_2(H)$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[58] $Os_3(CO)_{10}(COE)_2$ (COE = cyclooctene)[15] and $Os_3(CO)_{11}$-(NCMe)[16] were carried out by literature procedures. The ^{13}CO-enriched compounds were synthesized from ^{13}CO-enriched $Os_3(CO)_{12}$ (~ 35 % ^{13}C).[88]

Preparation of $Re(CO)_3(PMe_3)_2(H)$. This compound was prepared in good yield from the reaction of excess PMe_3 with $Re(CO)_5(H)$ in benzene at room temperature.[57] The reaction was complete after 3.5 h. The residue after removal of the solvent and excess reagents on the vacuum line was recrystallized from toluene/hexane at -78 °C to yield the desired product as a white, air-stable solid. IR (hexane) ν(CO) 2010 (s), 1929 (s), 1914 (vs) cm^{-1}. ^1H NMR (C_6D_6) (δ): major isomer, 1.18, 1.17, 1.16 (intensity ratio 5.0:2.7:4.8), -4.74 (t, J_{PH} = 28.7 Hz); minor isomer, 1.41, 1.40, 1.39 (ratio 1.3:1.1:1.4), -5.80 (t, J_{PH} = 20.9 Hz). MS (EI): *m/z* 424

(M+). Anal. Calcd for $C_9H_{19}O_3P_2Re$: C, 25.53; H, 4.52. Found: C, 25.54; H, 4.48.

Preparation of $[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ (2). A solution of $Os_3(CO)_{10}(COE)_2$ was prepared from $Os_3(\mu\text{-}H)_2(CO)_{10}$ (34 mg, 0.040 mmol) and cyclooctene in the presence of ethylene.[15] The excess cyclooctene was removed under vacuum at *ca.* 40 °C. To the solid $Os_3(CO)_{10}(COE)_2$ was added CH_2Cl_2 (2 mL) and hexane (10 mL) and the resulting solution cooled to 0 °C. $Re(CO)_4(PPh_3)(H)$ (22 mg, 0.039 mmol) was then added to the solution and the solution was stirred at 0 °C for 0.5 h over which time the color changed from amber to red. The solution was evaporated to dryness on the vacuum line and the remaining solid chromatographed on a silica gel column (2.5 x 20 cm). Elution with CH_2Cl_2/hexane (1/4) gave the desired product, **2** (22 mg, 39%). The analytical sample was obtained as air-stable, red crystals by recrystallization from toluene/hexane: IR (CH_2Cl_2) ν(CO) 2118 (m), 2070 (s), 2050 (m), 2036 (vs), 2013 (w), 1969 (w), 1933 (w) cm^{-1}; ^1H NMR (acetone-d_6, room temperature) δ -12.14 (d, J_{PH} = 13.0 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, room temperature, 85% H_3PO_4 external reference) δ 22.89 (s); $^{13}C/^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temperature) δ 202.3 (2C, J_{PC} = 7 Hz), 195.3 (1C, J_{PC} = 8 Hz), 192.1 (2C, J_{HC} = 2 Hz), 188.4 (2C), 179.0 (1C), 174.3 (3C), 174.1 (1C), 171.7 (1C), 165.8 (1C). Anal. Calcd for $C_{32}H_{16}O_{14}ReOs_3$: C, 27.22%; H, 1.14%. Found: C, 27.39%; H, 1.21%.

Preparation of $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3). The procedure used to prepare **3** was similar to that used to make **2** except $(Cp^*)Os(CO)_2(H)$ replaced $Re(CO)_4(PPh_3)(H)$, and a reaction time of 2 h was employed; the yield was 66% after recrystallization. The analytical sample of **3** was obtained as air-stable, red crystals by recrystallization from CH_2Cl_2/hexane: IR (CH_2Cl_2) ν(CO) 2117 (w), 2095 (s), 2047 (vs), 2013 (vs), 1977 (m), 1959 (m), 1918 (w); ^1H NMR (toluene-d_8, room temperature) δ 1.60 (s), -15.67 (s); $^{13}C/^{13}C\{^1H\}$ NMR (toluene-d_8, -30 °C) δ 188.3 (1C), 187.9 (1C, the CC coupling was ambiguous), 186.0 (2C), 185.7 (2C), 178.1 (2C), 175.1 (2C, J_{CH} = 9.0 Hz), 174.3 (2C). Anal. Calcd for $C_{22}H_{16}O_{12}Os_4$: C, 21.43%; H, 1.31%. Found: C, 21.65%; H, 1.40%.

Preparation of $(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (4). To a solution of $Os_3(CO)_{11}(NCMe)$ (43 mg, 0.047 mmol) in CH_2Cl_2 (15 mL) was added $Re(CO)_3(PMe_3)_2(H)$ (20 mg, 0.047 mmol). The solution turned from yellow to amber soon after the addition; the solution was allowed to stir at room temperature for ~1.5 h. The solvent was removed on the vacuum line and the residue recrystallized from CH_2Cl_2/hexane to yield 4 (42 mg, 69%) as orange, air-stable crystals. IR ν(CO) (CH_2Cl_2) 2105 (m), 2049 (s), 2036 (s), 2014 (s, br), 1982 (w), 1962 (w), 1916 (m) cm^{-1}. ^1H NMR ($C_6D_5CD_3$) δ 1.08 - 1.06 (m), -17.08 (t, J_{PH} = 13.9 Hz). Anal. Calcd for $C_{20}H_{19}O_{14}Os_3P_2Re$: C, 18.45; H, 1.47; ($C_{20.5}H_{20}O_{14}ClOs_3P_2Re$: C, 18.31; H, 1.50). Found: C, 18.48; H, 1.44.

Preparation of $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5). A solution of $Os_3(CO)_{10}(COE)_2$ (0.035 mmol) in CH_2Cl_2 (1 mL) and hexane (12 mL) was prepared by a procedure similar to that used to make 2. The solution was cooled to 0 °C. To the solution was added $Re(CO)_3(PMe_3)_2(H)$ (31 mg, 0.073 mmol) and the mixture allowed to warm with stirring to room temperature; the stirring was continued for 1.5 h. The solvent was removed on the vacuum line and the residue washed with hexane to remove any remaining $Re(CO)_3(PMe_3)_2(H)$. The solid was recrystallized twice from CH_2Cl_2/hexane (~1:5) to yield 5 (52 mg, 88%) as bright orange, air-stable crystals. IR ν(CO) (CH_2Cl_2) 2079 (m), 2029 (vs), 1987 (s), 1953 (m), 1907 (m) cm^{-1}. ^1H NMR ($C_6D_5CD_3$) (δ): 1.23 - 1.16 (m); major isomer, -16.96 (t, J_{PH} = 13.8 Hz), -17.30 (t, J_{PH} = 14.8 Hz); minor isomer, -17.17 (t, J_{PH} = 14.3 Hz). Anal. Calcd for $C_{28}H_{38}O_{16}Os_3P_2Re_2$: C, 19.81; H, 2.26. Found: C, 19.97; H, 2.09.

2.3.2 X-ray Structure Determinations

General Procedure. The following procedure was employed for all the structure determinations discussed in this thesis unless otherwise stated. A crystal of suitable size was mounted on an Enraf Nonius diffractometer and intensity data collected with the use of graphite-monochromated Mo Kα radiation. Background measurements were made by extending the scan width by 25% on each side of the scan unless otherwise stated. The final unit cell was determined from 25 well-centered high-angle reflections (values given in Tables) that were widely scattered in reciprocal space. Two intensity standards were measured at fixed time intervals (stated in each case) during data collection. Absorption corrections by Gaussian integration (checked against Ψ-scan measurements) were applied to the measured intensity data. Data reduction included the small corrections for intensity scale variation, and Lorentz and polarization effects.

The positions of the Os (and Re) atoms were determined by direct methods unless otherwise stated. Subsequent electron density difference syntheses revealed the remaining non-hydrogen atoms. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and initially given isotropic thermal parameters 10% larger than the thermal parameter of the carbon to which they were attached. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme, based on counting statistics, was adopted for which $<w(|F_o|-|F_c|)^2>$ was near constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$. Complex scattering factors[89] for neutral atoms were used in the calculation of structure factors. The programs used for data reduction, structural solution and initial refinement were from the

NRCVAX Crystal Structure System;[90] the final refinement employed the program suite CRYSTALS.[91] All computations were carried out on a MicroVAX-II computer. All U(iso) values without errors in this thesis are equivalent isotropic temperature factors. Each of them is derived from the cube root of the product of the principal axes of the thermal ellipsoid.

X-ray Structure Determinations for 2-5. Two intensity standards, measured every 1 h during data collection, varied up to ±2% for **2** and ±3% for **5** and decreased 9% for **3** and 8% for **4**$\cdot$1/2(CH_2Cl_2). Crystallographic data are summarized in Table 2.6. The final fractional coordinates for the non-hydrogen atoms of **2**, **3**, **4**$\cdot$1/2(CH_2Cl_2) and **5** are given in Tables 2.7, 2.8, 2.9, and 2.10, respectively (pages 54-59). Other crystallographic data are included in the supplementary tables of this thesis.

[(Ph_3P)($OC)_3$Re](μ-H)$Os_3(CO)_{11}$ (2). The coordinates and thermal parameters of carbon atoms with attached hydrogen atoms were linked so that the derived shifts in coordinates and thermal parameters included contributions from appropriate derivatives from the atom sites. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Re, Os, P and O atoms, and isotropic thermal parameters for C atoms.

(Cp*)($OC)_2$OsOs_3(μ-H)$(CO)_{10}$ (3). Static background measurements were made at positions 0.025° beyond each edge of the scan width. The positions of the Os atoms were determined from the Patterson map. The coordinates and thermal parameters of carbon atoms with attached hydrogen atoms were dealt with similarly to their counterparts in **2**. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal

Table 2.6. Summary of Crystal Data and Details of Intensity Collection for **2**, **3**, **4**·1/2(CH_2Cl_2) and **5**.

compound	**2**	**3**
formula	$C_{32}H_{16}O_{14}ReOs_3$	$C_{22}H_{16}O_{12}Os_4$
fw	1412.2	1233.2
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	Pbca
a, Å	9.496(2)	11.802(2)
b, Å	9.751(2)	15.037(2)
c, Å	20.079(3)	31.061(4)
α, deg	77.83(2)	
β, deg	82.12(2)	
γ, deg	86.62(2)	
V, Å^3	1799	5513
2θ range of unit cell, deg	30-45	29-38
Z	2	8
D_{calc}, g cm^{-3}	2.61	2.97
μ(Mo, Kα), cm^{-1}	140.78	184.59
cryst size, mm	0.081x0.13x0.30	0.22x0.21x0.20
transmission coeff range[a]	0.31-0.46	0.050-0.089
scan method	ω-2θ	ω-2θ
scan range (2θ), deg	4-45	4-45
scan width (ω), deg	$0.9 + 0.35\tan\theta$	$0.9 + 0.35\tan\theta$
scan rate (ω), deg min^{-1}	0.82-5.5	0.69-5.5
No. of unique rflns	4677	3570
No. of obsd rflns[b]	3346	2129
No. of variables	301	234
R[c]	0.028	0.037
Rw[d]	0.035	0.042
k[d]	0.0005	0.00012
G.O.F.[e]	1.2	1.6
extinction (g)	0.23(2)	0.197(17)

Table 2.6 cont'd

compound	$4 \cdot 1/2(CH_2Cl_2)$	5
formula	$C_{20.5}H_{20}O_{14}ClOs_3P_2Re$	$C_{28}H_{38}O_{16}Os_3P_2Re_2$
fw	1344.6	1697.5
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	16.480(3)	9.421(3)
b, Å	8.764(1)	14.920(2)
c, Å	24.316(4)	17.214(2)
α, deg		71.19(1)
β, deg	108.45(1)	78.25(2)
γ, deg		79.22(2)
V, $Å^3$	3331.2	2223.1
2θ range of unit cell, deg	30-36	30-40
Z	4	2
D_{calc}, g cm^{-3}	3.051	2.536
μ(Mo, Kα), cm^{-1}	174.40	142.53
cryst size, mm	0.15x0.20x0.23	0.078x0.16x0.24
transmission coeff range[a]	0.043-0.22	0.12-0.39
scan method	ω-2θ	ω-2θ
scan range (2θ), deg	3-45	4-45
scan width (ω), deg	0.9 + 0.35tanθ	1.0 + 0.35tanθ
scan rate (ω), deg min^{-1}	0.82-5.5	0.86-3.3
No. of unique rflns	4353	5779
No. of obsd rflns[b]	3186	3983
No. of variables	275	347
R[c]	0.032	0.028
Rw[d]	0.039	0.034
k[d]	0.0001	0.0002
G.O.F.[e]	1.2	2.1
extinction (g)	0.24 (2)	0.27 (2)

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[a] Absorption corrections. [b] $Io > 2.5(Io)$. [c] $R = \sum||Fo| - |Fc||/\sum|Fo|$.
[d] $Rw = (\sum w(|Fo| - |Fc|)^2/\sum w|Fo|^2)^{1/2}$, $w = [\sigma^2(Fo) + k(Fo)^2]^{-1}$.
[e] $GOF = (\sum w(|Fo| - |Fc|)^2/(\text{degrees of freedom}))^{1/2}$.

parameters for the Os and O atoms, and isotropic thermal parameters for C atoms.

$(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}\cdot 1/2(CH_2Cl_2)$ (4-solvate). Only the coordinates of carbon atoms (except the solvent carbon atom) with attached hydrogen atoms were linked so that the derived shifts in coordinates included contributions from appropriate derivatives from the atom sites. The thermal parameters of these hydrogen atoms were allowed to have the same shifts. The final least-squares refinement included an extinction parameter, coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Os, Re, Cl (solvate), P, and O atoms, and isotropic thermal parameters for C atoms.

$[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5). The thermal parameters for P(3), P(4) and two each of the attached carbon atoms, were large; these six atoms were divided into two half-atom pairs and each pair given a single isotropic thermal parameter. The coordinates of carbon atoms with attached hydrogen atoms were linked, similar to the treatment used for $4\cdot 1/2(CH_2Cl_2)$. The final least-squares refinement (with 22 restraints for distances between Re(2) and the four half-occupancy phosphorus atom sites and for the lengths of all P-C bonds) included an extinction parameter, coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the Os, Re, P(1), P(2), and O atoms, and one isotropic thermal parameter for each full C atom.

2.3.3 Placement of the Hydrides Ligand in 2, 3, 4-solvate and 5.

$[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ (2) and $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3\text{-}(CO)_{10}$ (5). Although the ^1H NMR data suggested the hydride ligands bridged Os(1)-Re in 2 and both Os-Re bonds in 5, there was no conclusive evidence for the hydride ligands in the final difference maps. Results of calculations of the "site energy" of the hydride ligand in various positions in **2** with the HYDEX program[37] are shown in Table 2.2. As can be seen, these calculated results clearly favored the hydride ligand occupying a position bridging the Os(1)-Re bond. Similar calculations for **5** also showed that hydride ligands bridging Os-Re bonds had the minimum "site energies". The hydride ligands in **2** and **5** were therefore placed in the calculated positions and included as fixed contributions in the final refinement.

$(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3). Immediately before the final refinement of **3** a difference map based on low-angle reflections ($(\sin\theta)/\lambda <$ 0.35 $Å^{-1}$) revealed the largest peak (x = 0.605, y = 0.404, z = 0.131) with electron density 0.57 (13) $eÅ^{-3}$ was 1.6 Å from Os(1) and 1.7 Å from Os(2) and a second peak with electron density 0.52 (13) $eÅ^{-3}$ was 1.4 Å from Os(1) and 1.2 Å from C(11). The "site energy" of a hydride ligand in each of these two approximate positions was calculated with the HYDEX program[37] (Table 2.2). The calculations showed that a hydride ligand (x = 0.628, y = 0.411, z = 0.130) at 1.8 Å from both Os(1) and Os(2) had the minimum site energy in agreement with the largest peak in the difference map.

This conclusion was further supported by a comparison of the appropriate bond angles in the geometries of $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (**8**),[62f] $Os_3Pt(\mu\text{-}H)(CO)_{11}[P(c\text{-}C_6H_{11})_3]$ (**9**),[62d] and $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)$ (**10**)[92] as shown in Table 2.11. In both **8** and **9** a hydride ligand is believed to bridge the hinge metal atoms, whereas in **10** these atoms are thought to be unbridged. The bond angles about the hinge metal atoms clearly show the similarity between **3**, **8**, and **9**, and the difference between these clusters and **10**.

All the evidence was therefore consistent with the hydride ligand as

Table 2.11. Comparison of Selected Angles (°) for Compounds **3**, **8**, **9** and **10**.

	3	**8**	**9**	**10**
Os(2)-Os(1)-C(11)	141.5	142.1	142.0	167.9
Os(2)-Os(1)-C(12)	110.7	104.4	106.1	95.0
Os(2)-Os(1)-C(13)	114.9	119.2	115.0	85.5
Os(1)-Os(2)-C(21)	142.7	137.2	141.7	158.5
Os(1)-Os(2)-C(22)	111.6	111.7	103.1	91.2
Os(1)-Os(2)-C(23)	116.2	117.7	116.5	102.2

placed in the position derived from the difference map based on the low-angle reflections; it was included as a fixed contribution in the final refinement.

$(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (4). Similar to **3**, a difference map based on low-angle reflections ($(\sin\theta)/\lambda < 0.35$ Å^{-1}) revealed the largest peak with electron density 0.6 (1) eÅ^{-3} was 1.7 Å from Os(1) and 1.8 Å from Re. Therefore, the hydride ligand was placed in this position and its coordinates and thermal parameter were refined in the final refinement.

Table 2.7. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ (**2**)

Atom	x/a	y/b	z/c	U(iso)
Os(1)	2327.4 (4)	3228.3 (4)	1444.5 (2)	333
Os(2)	1526.6 (4)	411.9 (4)	1378.0 (2)	326
Os(3)	2490.8 (4)	2530.2 (5)	139.7 (2)	348
Re	1626.9 (5)	1263.3 (5)	2777.3 (2)	366
P(1)	1952 (3)	2550 (3)	3630 (2)	404
O(11)	5401 (9)	2211 (10)	1593 (5)	611
O(12)	-673 (9)	4585 (10)	1489 (5)	632
O(13)	3329 (11)	6225 (10)	1163 (5)	741
O(21)	4583 (9)	-801 (9)	1488 (5)	579
O(22)	-1567 (9)	1602 (10)	1404 (5)	615
O(23)	404 (12)	-2172 (11)	2397 (5)	752
O(24)	1238 (9)	-1033 (9)	210 (5)	551
O(31)	5575 (9)	1324 (10)	180 (5)	613
O(32)	-602 (8)	3639 (8)	107 (5)	519
O(33)	2209 (11)	1479 (12)	-1158 (5)	714
O(34)	3650 (10)	5426 (10)	-482 (6)	743
O(1)	4636 (10)	-98 (9)	2933 (5)	606
O(2)	-1621 (10)	2004 (11)	2882 (5)	710
O(3)	655 (14)	-1454 (11)	3753 (5)	759
C(11)	4265 (13)	2547 (12)	1504 (6)	453 (29)
C(12)	410 (13)	4044 (12)	1458 (6)	436 (29)
C(13)	2942 (13)	5062 (14)	1276 (7)	554 (33)
C(21)	3507 (13)	-302 (12)	1432 (6)	440 (29)
C(22)	-414 (13)	1240 (12)	1389 (6)	458 (29)
C(23)	824 (13)	-1175 (13)	2059 (7)	497 (31)
C(24)	1370 (12)	-458 (12)	616 (6)	429 (28)
C(31)	4445 (13)	1757 (12)	182 (6)	468 (30)
C(32)	530 (12)	3216 (12)	157 (6)	425 (28)
C(33)	2369 (14)	1829 (14)	-671 (7)	572 (34)
C(34)	3230 (14)	4329 (14)	-269 (7)	585 (34)
C(1)	3581 (13)	445 (13)	2835 (6)	481 (30)
C(2)	-428 (14)	1783 (13)	2814 (6)	476 (30)
C(3)	1014 (14)	-409 (15)	3408 (7)	600 (35)
C(111)	3210 (12)	3932 (12)	3310 (6)	424 (28)
C(112)	2871 (15)	5327 (14)	3325 (7)	645 (37)

Table 2.7 cont'd

C(113)	3874 (17)	6340 (18)	3061 (9)	864 (48)
C(114)	5177 (17)	6044 (17)	2719 (9)	858 (47)
C(115)	5520 (16)	4674 (15)	2711 (8)	711 (40)
C(116)	4574 (14)	3637 (15)	3018 (7)	617 (36)
C(121)	2608 (12)	1631 (12)	4428 (6)	462 (30)
C(122)	3598 (14)	2236 (14)	4720 (7)	650 (38)
C(123)	3974 (16)	1539 (15)	5366 (8)	710 (40)
C(124)	3447 (15)	333 (15)	5691 (8)	688 (39)
C(125)	2535 (15)	-290 (15)	5409 (7)	680 (39)
C(126)	2119 (14)	323 (14)	4764 (7)	608 (35)
C(131)	338 (12)	3470 (12)	3947 (6)	477 (30)
C(132)	-346 (14)	4425 (14)	3468 (8)	686 (39)
C(133)	-1604 (16)	5132 (16)	3672 (8)	793 (44)
C(134)	-2156 (19)	4837 (17)	4357 (9)	920 (51)
C(135)	-1495 (18)	3924 (17)	4832 (10)	919 (50)
C(136)	-212 (14)	3226 (14)	4612 (7)	628 (37)
H(0)	2021	3094	2356	500

Table 2.8. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for $(Cp^*)(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (**3**)

Atom	x/a	y/b	z/c	U(iso)
Os(1)	5787.5(9)	3418.6(6)	1712.3(3)	386
Os(2)	5793.9(9)	3618.9(5)	818.3(3)	384
Os(3)	6437.1(9)	1930.8(6)	1186.3(3)	422

Table 2.8 cont'd

Os(4)	3548.5(7)	3757.8(5)	1268.9(3)	341
O(11)	5209(18)	2118(11)	2419(6)	735
O(12)	8198(18)	3374(14)	2046(6)	835
O(13)	5465(16)	5116(12)	2221(6)	603
O(21)	5114(21)	2688(13)	-23(6)	665
O(22)	8170(17)	3748(15)	463(7)	810
O(23)	5631(16)	5485(11)	466(6)	612
O(31)	4029(17)	1280(13)	1217(10)	928
O(32)	8917(14)	2589(13)	1193(8)	789
O(33)	6775(23)	917(15)	338(6)	876
O(34)	6982(22)	513(16)	1834(7)	1153
O(41)	3058(20)	2499(14)	529(7)	854
O(42)	3103(17)	2388(13)	1938(7)	707
C(11)	5330(23)	2621(17)	2149(8)	503(69)
C(12)	7272(24)	3372(16)	1926(7)	455(64)
C(13)	5489(21)	4493(16)	2031(7)	456(63)
C(21)	5384(23)	3022(17)	288(8)	530(69)
C(22)	7289(28)	3650(18)	595(9)	678(83)
C(23)	5588(19)	4800(15)	607(7)	377(56)
C(31)	4870(23)	1568(17)	1189(8)	545(68)
C(32)	8024(23)	2376(17)	1186(9)	570(72)
C(33)	6655(24)	1319(18)	645(9)	644(76)
C(34)	6792(24)	1057(19)	1577(9)	662(82)
C(41)	3358(23)	2965(17)	793(8)	604(72)
C(42)	3381(27)	2887(20)	1661(9)	771(86)
C(1)	1922(21)	4363(16)	1493(7)	507(67)
C(2)	2790(20)	4922(14)	1651(7)	397(57)
C(3)	3358(17)	5309(13)	1290(7)	388(55)
C(4)	2841(19)	4975(13)	914(6)	321(52)
C(5)	1947(21)	4404(16)	1040(7)	494(66)
C(6)	936(24)	3922(19)	1757(8)	784(88)
C(7)	2932(22)	5199(16)	2120(7)	571(72)
C(8)	4202(19)	6072(14)	1311(7)	470(61)
C(9)	2933(22)	5348(16)	454(7)	575(73)
C(10)	1053(21)	4033(17)	744(8)	627(79)
H(0)	6050	4040	1310	500

Table 2.9. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for $(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}\cdot 1/2(CH_2Cl_2)$ (4-solvate)

Atom	x/a	y/b	z/c	U(iso)
Os(1)	9750.5 (3)	7919.2 (5)	1837.5 (2)	480
Os(2)	8962.7 (4)	7670.3 (7)	613.5 (2)	634
Os(3)	8806.1 (4)	10495.0 (7)	1185.3 (3)	664
Re	10596.8 (3)	8139.7 (6)	3237.0 (2)	510
P(1)	11457 (3)	10483 (5)	3293 (2)	748
P(2)	9422 (2)	9456 (4)	3471 (2)	630
O(11)	11476 (6)	8992 (12)	1747 (5)	800
O(12)	8184 (7)	6603 (13)	2109 (5)	870
O(13)	10473 (8)	4729 (11)	1931 (5)	982
O(21)	10648 (7)	8669 (13)	445 (5)	877
O(22)	7335 (9)	6454 (19)	820 (5)	1119
O(23)	9404 (13)	4445 (16)	395 (7)	1541
O(24)	7964 (9)	8656 (22)	-608 (5)	1164
O(31)	10514 (8)	11623 (12)	1067 (6)	1067
O(32)	7233 (9)	9324 (15)	1480 (8)	1285
O(33)	7749 (12)	12035 (23)	84 (7)	1553
O(34)	8830 (9)	13241 (14)	1958 (7)	1306
O(41)	12057 (8)	6371 (18)	2976 (5)	1043
O(42)	9659 (8)	5065 (11)	3221 (5)	998
O(43)	11426 (8)	7813 (17)	4540 (5)	1063
C(11)	10819 (9)	8636 (14)	1765 (6)	604 (34)
C(12)	8747 (10)	7152 (15)	1984 (6)	683 (37)
C(13)	10217 (9)	5962 (16)	1916 (6)	697 (38)
C(21)	10029 (10)	8358 (15)	527 (6)	694 (39)
C(22)	7939 (13)	6925 (19)	772 (8)	979 (52)
C(23)	9248 (14)	5660 (24)	474 (10)	1235 (68)
C(24)	8345 (13)	8314 (19)	-145 (9)	1057 (57)
C(31)	9892 (11)	11107 (17)	1113 (7)	840 (45)
C(32)	7834 (14)	9669 (21)	1379 (9)	1077 (58)
C(33)	8142 (16)	11411 (24)	469 (11)	1311 (72)
C(34)	8820 (12)	12151 (20)	1666 (8)	959 (51)
C(41)	11527 (11)	7020 (17)	3057 (7)	828 (45)
C(42)	10006 (9)	6228 (16)	3211 (6)	658 (36)
C(43)	11117 (11)	7940 (17)	4023 (8)	894 (47)
C(44)	11157 (13)	11855 (18)	2729 (8)	1210 (65)
C(45)	11566 (21)	11701 (32)	3895 (13)	2330 (145)
C(46)	12564 (15)	10024 (25)	3313 (10)	1660 (91)

Table 2.9 cont'd

C(47)	8982 (15)	11119 (23)	3101 (9)	1540 (85)
C(48)	9692 (13)	9984 (21)	4224 (8)	1340 (73)
C(49)	8512 (13)	8352 (22)	3418 (9)	1390 (77)
CL(1)	5682 (9)	887 (13)	-37 (6)	3042
C(1)	5340 (30)	-340 (48)	310 (19)	1279 (139)
H(110)	4987 (52)	3953 (86)	2515 (34)	278 (233)

Table 2.10. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5)

Atom	x/a	y/b	z/c	U(iso)
Os(1)	6953.5 (6)	850.6 (3)	2018.8 (3)	380
Os(2)	7250.4 (6)	2497.0 (3)	2479.5 (3)	385
Os(3)	5216.2 (6)	2630.9 (4)	1355.0 (3)	464
Re(1)	9002.3 (6)	-1187.3 (3)	2658.2 (3)	372
Re(2)	7292.4 (6)	4354.8 (3)	3083.3 (3)	411
P(1)	11432 (4)	-664 (2)	2060 (2)	513
P(2)	9104 (4)	-1212 (2)	4087 (2)	517
P(3)	4680 (7)	5011 (5)	3184 (4)	495 (14)
P(30)	4621 (7)	4798 (5)	3439 (5)	495 (14)
P(4)	8001 (8)	5479 (5)	1689 (4)	485 (13)
P(40)	7516 (9)	5641 (5)	1770 (4)	485 (13)
O(11)	4615 (11)	124 (7)	3522 (6)	677
O(12)	9447 (12)	1416 (7)	602 (6)	759
O(13)	5726 (12)	-183 (8)	1090 (7)	794
O(21)	5068 (13)	1784 (7)	4051 (6)	748
O(22)	9672 (14)	3201 (9)	1033 (7)	936
O(23)	9602 (11)	1582 (6)	3545 (6)	689
O(31)	2937 (12)	2062 (8)	2915 (7)	866
O(32)	7599 (14)	3206 (8)	-120 (7)	992
O(33)	3706 (15)	4663 (7)	881 (7)	822
O(34)	3749 (16)	1887 (9)	307 (7)	973
O(41)	6041 (11)	-1971 (7)	3368 (7)	685

Table 2.10 cont'd

O(42)	8762 (12)	-1256 (8)	915 (6)	752
O(43)	10562 (12)	-3213 (7)	3027 (8)	798
O(51)	6910 (15)	2866 (8)	4804 (7)	947
O(52)	10605 (12)	3718 (9)	2883 (9)	897
O(53)	7782 (13)	5772 (8)	3913 (7)	835
C(11)	5499 (14)	425 (9)	2954 (8)	469 (32)
C(12)	8504 (16)	1235 (9)	1124 (9)	554 (36)
C(13)	6209 (15)	199 (9)	1454 (8)	529 (35)
C(21)	5824 (16)	2060 (10)	3440 (9)	582 (37)
C(22)	8706 (17)	2909 (10)	1572 (9)	637 (40)
C(23)	8686 (14)	1946 (9)	3136 (8)	449 (31)
C(31)	3835 (18)	2257 (10)	2357 (9)	648 (41)
C(32)	6737 (17)	2956 (11)	478 (9)	666 (42)
C(33)	4349 (18)	3897 (12)	1055 (9)	735 (45)
C(34)	4285 (17)	2165 (11)	713 (9)	682 (42)
C(41)	7133 (15)	-1658 (9)	3106 (8)	504 (34)
C(42)	8842 (15)	-1201 (9)	1568 (8)	528 (35)
C(43)	9945 (17)	-2430 (10)	2897 (9)	631 (39)
C(44)	12026 (17)	-593 (11)	971 (6)	748 (45)
C(45)	11774 (15)	466 (7)	2119 (8)	633 (39)
C(46)	12933 (13)	-1496 (9)	2515 (9)	793 (47)
C(47)	9108 (19)	-2400 (8)	4814 (9)	901 (53)
C(48)	7585 (13)	-528 (9)	4566 (8)	693 (43)
C(49)	10670 (13)	-838 (10)	4310 (9)	723 (44)
C(51)	6980 (16)	3408 (10)	4145 (9)	597 (38)
C(52)	9341 (19)	3936 (11)	2959 (9)	690 (42)
C(53)	7592 (17)	5239 (10)	3583 (9)	629 (39)
C(54)	4089 (17)	5801 (8)	3850 (8)	760 (46)
C(55)	3434 (36)	4119 (22)	3670 (22)	1065 (90)
C(550)	3633 (38)	3916 (22)	4251 (18)	1065 (90)
C(56)	3883 (39)	5794 (22)	2283 (16)	1003 (84)
C(560)	3547 (36)	5096 (26)	2603 (16)	1003 (84)
C(57)	7167 (16)	5460 (10)	829 (6)	753 (45)
C(58)	7496 (36)	6731 (10)	1637 (22)	842 (72)
C(580)	6578 (34)	6806 (13)	1811 (22)	842 (72)
C(59)	9955 (15)	5446 (25)	1349 (23)	952 (81)
C(590)	9381 (19)	5915 (25)	1391 (23)	952 (81)
H(110)	8408	88	2611	500
H(220)	6631	3746	2458	500

Chapter 3. Stepwise C-H Cleavage of Two Methyl Groups of a Pentamethylcyclopentadienyl Ligand on a Tetraosmium Cluster

3.1 Introduction

The pentamethylcyclopentadienyl ligand, $\eta^5\text{-}C_5Me_5$ (Cp*), is a widely used ligand in organometallic chemistry because of its exceptional steric and electronic properties.[5,93] In Chapter 2 the synthesis of $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (**3**) by the addition of $Cp^*Os(CO)_2(H)$ to $Os_3(CO)_{10}(\text{cyclooctene})_2$ was described. The butterfly arrangement of metal atoms and the bonding in **3** have also be discussed.[40]

In the preparation of the precursor $Cp^*Os(CO)_2(H)$,[≠] by the reaction of C_5Me_5H with $Os_3(CO)_{12}$ at 200 °C,[58] a small amount of a crystalline by product was isolated. Subsequent analysis of the compound by X-ray diffraction and NMR spectroscopy revealed it to be $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**) (compounds **11-13** will be mentioned in the next paragragh), that is, a product in which C-H cleavage of two methyl groups of the C_5Me_5 ligand had apparently occurred on a tetranuclear metal unit. The C-H cleavage of a methyl group of a C_5Me_5 ligand in a mononuclear complex is common,[94-97] and there are examples where double C-H activation of this ligand has been observed.[97] Although C-H scissions have been reported in di- and polynuclear compounds without metal-metal bonds such as $[(C_5Me_4CH_2)RuCl_2]_2$[98] and $[Cp^*_3(\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2Ce_2]_2$[99] and in the triosmium cluster $(\mu\text{-}H)Os_3(CO)_8[\overline{C(O\text{-})C(CHMe\text{-})CHCHC}Et]$,[100] to our knowledge, however, there

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[≠] This reaction was carried out by Dr. H. B. Davis.

is only one example of C-H scissions of a C_5Me_5 ligand by a metal cluster, i.e., the compound $Ru_3[\mu_3,\eta^7\text{-}C_5Me_3(CH_2)_2](\mu_3\text{-}O)(\mu_2\text{-}H)(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SO_4)$[101] prepared from the reaction of $[Cp^*Ru(OMe)]_2$ with $KHSO_4$ in $H_2O\text{-}CH_2Cl_2$.

In this chapter a rational synthesis of **14** by the careful pyrolysis of $Cp^*(OC)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3) is reported. Furthermore, intermediates in the pyrolysis, *viz.*, $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**11**) and $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**12**), have been isolated and structurally characterized, thereby providing a unique series of structures that illustrate the stepwise C-H activation of two methyl groups of a C_5Me_5 ligand on a metal cluster. Also isolated, in trace amounts, in the pyrolysis of 3 was $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (13) the structure of which has been determined and is reported here.

3.2 Results and Discussion

$Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (11). Cluster **11** was prepared by the method depicted in eq 3.1. The cluster was isolated as air-stable, orange crystals.

$$\underset{\mathbf{3}}{Cp^*Os_4(\mu\text{-}H)(CO)_{12}} \xrightarrow{50\ ^\circ C} \underset{\mathbf{11}}{Cp^*Os_4(\mu\text{-}H)(CO)_{11}} \tag{3.1}$$

The crystal structure of **11** (Figure 3.1) reveals a tetrahedral metal core, with six metal-metal bonds, as expected from polyhedral skeletal electron pair theory (PSEPT) for a 60-electron metal cluster compound.[3,54,55,102] (As described in Chapter 2, the precursor compound (3) has a butterfly arrangement of metal atoms with five metal-metal bonds.) Some selected bond lengths and angles for **11** are given in Table 3.1. Molecule **11** contains a crystallographic mirror plane

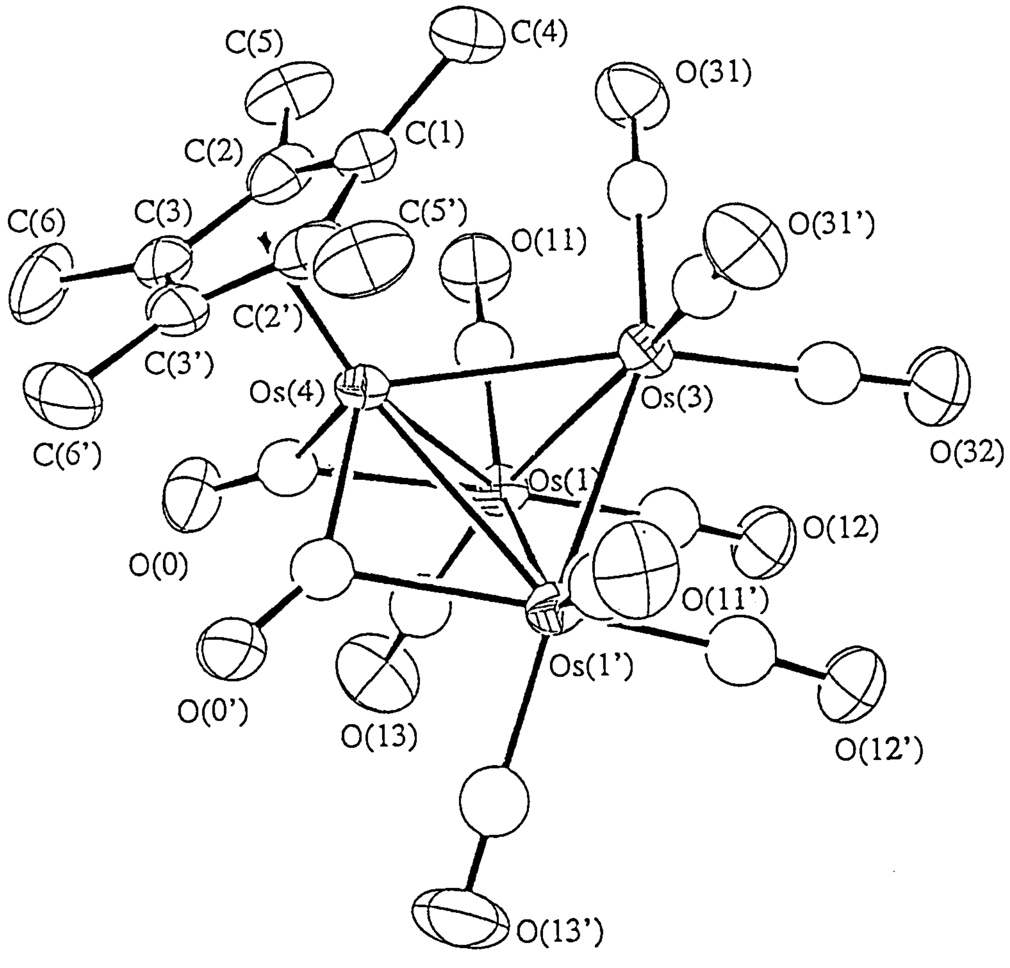

Figure 3.1. The molecular structure of Cp*$Os_4(\mu\text{-}H)(CO)_{11}$ **(11)**

Table 3.1. Selected Bond Lengths (Å) and Angles (°) for $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ **(11)**

Bond Lengths

Os(1) - Os(1')^a	2.938 (1)	Os(3) - C(31)	1.89 (1)
Os(1) - Os(3)	2.776 (1)	Os(3) - C(32)	1.90 (1)
Os(1) - Os(4)	2.875 (1)	Os(4) - C(0)	1.95 (1)
Os(3) - Os(4)	2.808 (1)	Os(1) - H(1'1)	1.69 (7)
Os(1) - C(0)	2.28 (1)		
Os(1) - C(11)	1.90 (1)	(C-O)	1.13 (1) - 1.17 (1)
Os(1) - C(12)	1.90 (1)	$(C\text{-}C)_{ring}$	1.38 (1) - 1.45 (1)
Os(1) - C(13)	1.92 (1)	$(C\text{-}C_{Me})$	1.50 (1) - 1.52 (1)

Bond Angles

Os(3) - Os(1) - Os(1')^a	58.051 (6)	Os(3) - Os(4) - Os(1)	58.46 (1)
Os(4) - Os(1) - Os(1')^a	59.271 (6)	C(11) - Os(1) - Os(1')^a	149.0 (2)
Os(4) - Os(1) - Os(3)	59.57 (1)	C(11) - Os(1) - Os(3)	92.9 (2)
Os(1) - Os(3) - Os(1')^a	63.90 (2)	C(12) - Os(1) - Os(1')^a	93.9 (2)
Os(1) - Os(4) - Os(1')^a	61.46 (1)	C(13) - Os(1) - Os(1')^a	113.4 (2)
Os(4) - Os(3) - Os(1)	61.96 (1)	Os(1) - Os(1')^a - H(1'1)	29 (4)

[a] These are symmetry equivalent atoms by the operation of (x, 0.5-y, z).

that passes through the Os(3) and Os(4) atoms and the midpoint of the Os(1)-Os(1') vector. All the available evidence indicates that the hydride ligand bridges the Os(1)-Os(1') bond. The location of the hydride ligand and the Os-Os lengths in **11** is further discussed in a later section (page 76).

A feature of interest in the structure of **11** is the presence of an asymmetrically bridging carbonyl ligand between Os(4) and Os(1), and between Os(4) and Os(1') (Os(4)-C(0) = 1.95 (1) Å; Os(1)-C(0) = 2.28 (1) Å). Bridging carbonyl ligands are comparatively rare in the carbonyl clusters of osmium.[103] The infrared spectrum of **11** in CH_2Cl_2 exhibits bands at 1814 and 1773 cm^{-1} consistent with the presence of bridging carbonyl ligands. (IR bands attributed to bridging carbonyl ligands are expected in the range of 1850-1650 cm^{-1}.

As mentioned above (page 61), the tetrahedral arrangement of the metal core of **11** is as expected from PSEPT. Electron counts based on the 18-electron rule for the individual osmium atoms in the cluster, however, do not lead to an unambiguous description of the bonding in this cluster, or the clusters **12-14** described below. For example, if all the metal-metal interactions in **11** are regarded as nondative, single bonds the electron count at Os(3) is 17 electrons (eight electrons from Os(3), two electrons from each of the carbonyl ligands attached to Os(3) and one electron from each M-Os(3) bond). An 18-electron configuration could be achieved if the Os(4)-Os(3) bond were a dative bond (i.e. Os(4)→Os(3)), or if the Os(1)-Os(3) and Os(1')-Os(3) bonds had a bond order of 1.5. Both types of metal-metal interactions have been proposed in an attempt to rationalize the bonding in other tetranuclear clusters of osmium.[29,31,33,35,40,71a] If the Os(4)-Os(3) bond were a dative metal-metal bond the semibridging carbonyl ligands between these atoms would be expected to offset the charge build up in the formation of such a bond (i.e., (δ+)Os→Os(δ-)).[104]

$[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (12) and $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (13). These clusters were isolated in low yield from the pyrolysis of **11** above 90 °C (eq 3.2).

$$\mathbf{11} \xrightarrow{>90\ ^\circ C} \underset{\mathbf{12}}{[C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}} + \underset{\mathbf{13}}{[C_5Me_4CH_2]Os_4(CO)_{11}} + \mathbf{14} \qquad (3.2)$$

Furthermore, samples of **12** contained $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**) the final product of the pyrolysis of **11** at these temperatures. For these reasons, the characterization of **12** and **13** relied mainly on X-ray diffraction. (The single crystal used for the X-ray diffraction study of **12** was hand separated under a microscope from a sample containing crystals of both **12** and **14**.)

The structures of **12** (Figure 3.2) and **13** (Figure 3.3) reveal both to contain a $C_5Me_4CH_2$ ligand that is η^5 bound to one osmium atom and η^1 bound to a second osmium atom of a tetrahedral Os_4 skeleton via the CH_2 unit. In other words, **12** and **13** result from the C-H cleavage of a methyl group in the precursor cluster **11**, and are examples of cluster-assisted ligand transformations (page 201 of ref. 4). Both **12** and **13** maintain 60-electron counts: by elimination of CO in **12**, and elimination of H_2 in **13**. The Os-CH_2- bond lengths in **12** (Table 3.2) and **13** (Table 3.3) are equal within the experimental error (2.15 (2) Å in **12**, 2.17 (2) Å in **13**); lengths that, not unexpectedly, are significantly longer than the Os-CO lengths. In $(\mu\text{-H})Os_3(CO)_8[\overline{C(O\text{-})C(CHMe\text{-})CHCHC}Et]$ the Os-C length to the CHMe substituent is 2.194 (14) Å.[100]

The available evidence indicates that the hydrides in **12** bridge the Os(1)-Os(3) and Os(2)-Os(3) bonds (see the Experimental Section and the discussion below). In solution, the $[C_5Me_4CH_2]Os(CO)_2$ moiety probably rocks with respect to the rest of the cluster such that the hydride ligands are rendered chemically equivalent; consistent with this view is that **12** exhibits just one sharp resonance (at δ -16.88) in the hydride region of the ^1H NMR spectrum. The ^1H NMR signal of the CH_2 unit at δ 2.75 consists of an appeared triplet attributed to the overlap of doublets due to a small coupling (J_{HH} = 0.7 Hz) with the two hydride ligands, that is not resolved in the hydride resonance. A small coupling between a bridging hydride ligand and a CH unit in an osmium carbonyl cluster has been

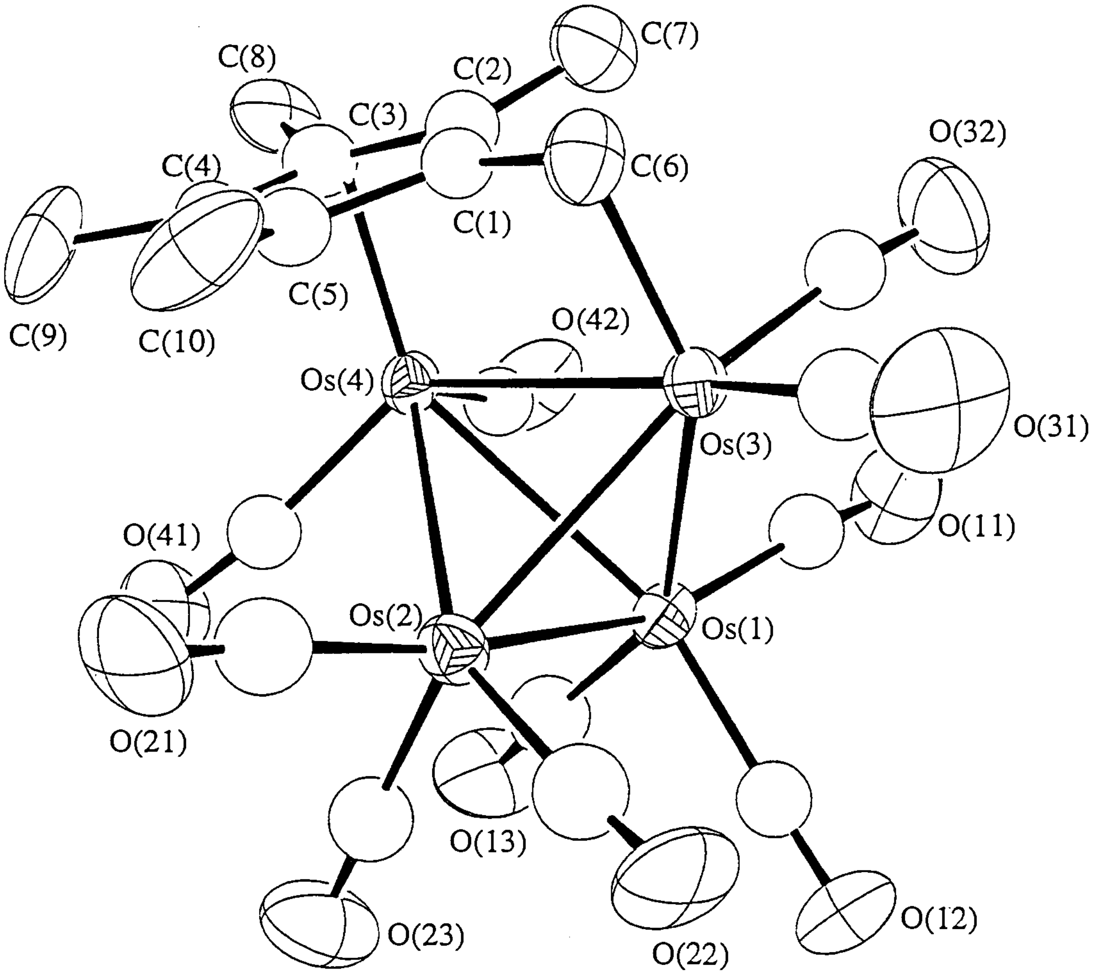

Figure 3.2. The molecular structure of $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ **(12)**

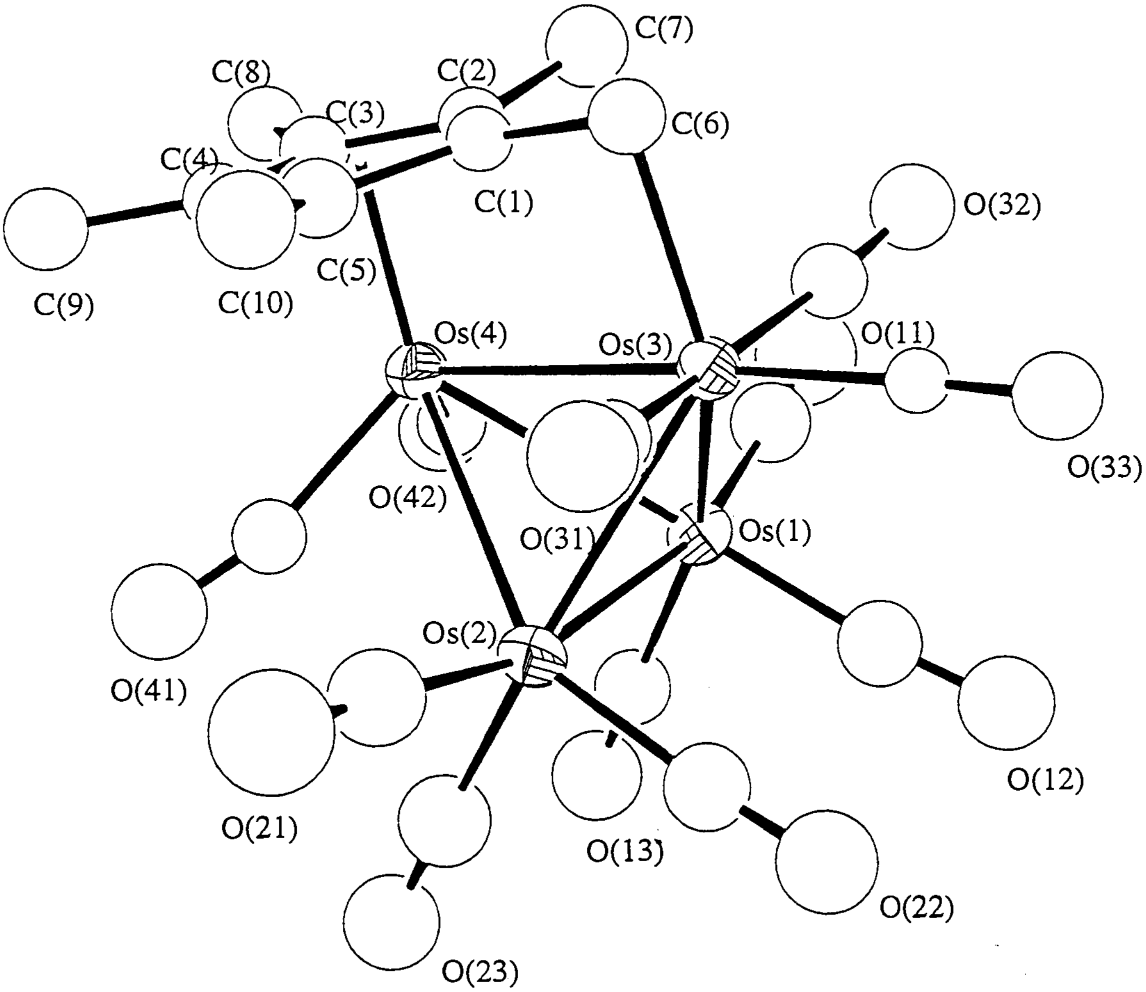

Figure 3.3. The molecular structure of [μ,η^5,η^1-$C_5Me_4CH_2$]$Os_4(CO)_{11}$ **(13)**

Table 3.2. Selected Bond Lengths (Å) and Angles (°) for
$[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ **(12)**

Bond Lengths

Os(1) - Os(2)	2.739 (1)	Os(3) - C(6)	2.15 (1)
Os(1) - Os(3)	2.823 (1)	C(1) - C(6)	1.44 (3)
Os(1) - Os(4)	2.997 (1)	(Os-CO)	1.84 (2) - 1.93 (2)
Os(2) - Os(3)	2.932 (1)	(C-O)	1.13 (3) - 1.18 (3)
Os(2) - Os(4)	2.898 (1)	$(C\text{-}C)_{ring}$	1.41 (3) - 1.47 (3)
Os(3) - Os(4)	2.928 (1)	$(C\text{-}C_{Me})$	1.44 (3) - 1.53 (3)

Bond Angles

Os(3) - Os(1) - Os(2)	63.62 (2)	Os(2) - Os(4) - Os(1)	55.34 (2)
Os(4) - Os(1) - Os(2)	60.48 (2)	Os(3) - Os(4) - Os(1)	56.89 (2)
Os(4) - Os(1) - Os(3)	60.33 (2)	Os(3) - Os(4) - Os(2)	60.44 (2)
Os(3) - Os(2) - Os(1)	59.59 (2)	C(11) - Os(1) - Os(2)	160.3 (5)
Os(4) - Os(2) - Os(1)	64.18 (2)	C(11) - Os(1) - Os(3)	97.0 (5)
Os(4) - Os(2) - Os(3)	60.30 (2)	C(12) - Os(1) - Os(2)	94.6 (4)
Os(2) - Os(3) - Os(1)	56.79 (2)	C(12) - Os(1) - Os(3)	112.8 (4)
Os(4) - Os(3) - Os(1)	62.78 (2)	C(13) - Os(1) - Os(2)	99.3 (5)
Os(4) - Os(3) - Os(2)	59.26 (2)		

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observed previously.[105]

In **12**, the carbonyl ligands of the $[\eta^5\text{-}C_5Me_4CH_2]Os(CO)_2$ unit have only weak semibridging interactions with other Os atoms in the cluster (Os(1)-C(42) = 2.80 (2) Å, Os(2)-C(41) = 2.88 (2) Å). The isolated $[\eta^5\text{-}C_5Me_4CH_2]Os(CO)_2$ unit is a 17-electron fragment and therefore requires but one metal-metal bond for it to have an 18-electron configuration. This suggests that the three metal-metal interactions of the unit with the rest of the cluster are comprised of one nondative and two dative metal-metal bonds, that is, this unit contributes five

Table 3.3. Selected Bond Lengths (Å) and Angles (°) for $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**13**)

Bond Lengths

Os(1) - Os(2)	2.745 (1)	Os(3) - C(6)	2.17 (2)
Os(1) - Os(3)	2.772 (1)	C(1) - C(6)	1.47 (3)
Os(1) - Os(4)	2.927 (1)	(Os-CO)	1.83 (3) - 1.93 (3)
Os(2) - Os(3)	2.764 (1)	(C-O)	1.13 (2) - 1.21 (3)
Os(2) - Os(4)	2.902 (1)	$(C\text{-}C)_{ring}$	1.42 (3) - 1.46 (3)
Os(3) - Os(4)	2.913 (1)	$(C\text{-}C_{Me})$	1.47 (3) - 1.51 (3)

Bond Angles

Os(3) - Os(1) - Os(2)	60.12 (3)	Os(2) - Os(4) - Os(1)	56.17 (3)
Os(4) - Os(1) - Os(2)	61.45 (3)	Os(3) - Os(4) - Os(1)	56.68 (3)
Os(4) - Os(1) - Os(3)	61.39 (3)	Os(3) - Os(4) - Os(2)	56.75 (3)
Os(3) - Os(2) - Os(1)	60.43 (3)	C(11) - Os(1) - Os(2)	166.6 (7)
Os(4) - Os(2) - Os(1)	62.38 (3)	C(11) - Os(1) - Os(3)	113.3 (7)
Os(4) - Os(2) - Os(3)	61.81 (3)	C(12) - Os(1) - Os(2)	96.9 (8)
Os(2) - Os(3) - Os(1)	59.45 (3)	C(13) - Os(1) - Os(2)	91.3 (7)
Os(4) - Os(3) - Os(1)	61.93 (3)	C(13) - Os(1) - C(12)	88.7 (10)
Os(4) - Os(3) - Os(2)	61.43 (3)		

electrons to the metal-metal bonding of the metal skeleton. That some metal-metal bonds in osmium carbonyl clusters should be considered as dative bonds was first suggested by John, Johnson, and Lewis.[70] In Chapter 5 of this thesis the preparation and structure of $Os_5(CO)_{15}(L)$ (L = PMe_3, $CNBu^t$) will be described; in order to account for some of the properties of these clusters it is proposed that there are two dative and two nondative metal-metal bonds from one osmium atom present in these clusters. Previous work by Pomeroy and coworkers has shown that among group 8 elements, only osmium is able to form strong dative metal-metal bonds.[72,77] This ability of osmium to form strong dative (donor-acceptor) metal-metal bonds may, in part, explain why osmium forms so many more high nuclearity metal carbonyl clusters in comparison to iron and ruthenium. For reasons discussed in Chapter 2, the strong donor $[C_5Me_4CH_2]$ ligand would be expected to stabilize the donor-acceptor metal-metal bonds believed present in **12** and **13**.

$[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (14). Cluster **14** was formed in excellent yield by the prolonged pyrolysis of **11** at 115-120 °C, presumably via the intermediate **12** (eq 3.3).

$$\mathbf{11} \xrightarrow[\text{[12]}]{115\text{-}120\ ^\circ C} \underset{\mathbf{14}}{[C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9} \tag{3.3}$$

It was also formed in low yield by the reaction of $Os_3(CO)_{12}$ with a large excess of C_5Me_5H in heptane at 200 °C. Cluster **14** appeared stable under the latter reaction conditions. It was isolated as a yellow-brown, air-stable crystalline solid.

The crystal structure of **14** (Figure 3.4) reveals a $C_5Me_3(CH_2)_2$ ligand that is η^5 bound to one osmium atom of a tetrahedral Os_4 cluster and with adjacent CH_2 units each η^1 bound to other osmium atoms of the cluster (Os(2)-C(10) = 2.22 (2) Å; Os(3)-C(6) = 2.19 (2) Å; Table 3.4). As mentioned in the Introduction, although double C-H bond cleavage of a C_5Me_5 ligand has been reported,[97] we believe this is the only second case where it has taken place on a metal cluster. Bond length data (see below) and calculations with the HYDEX program[37] indicate that the hydride ligands bridge each of the Os-Os bonds of the

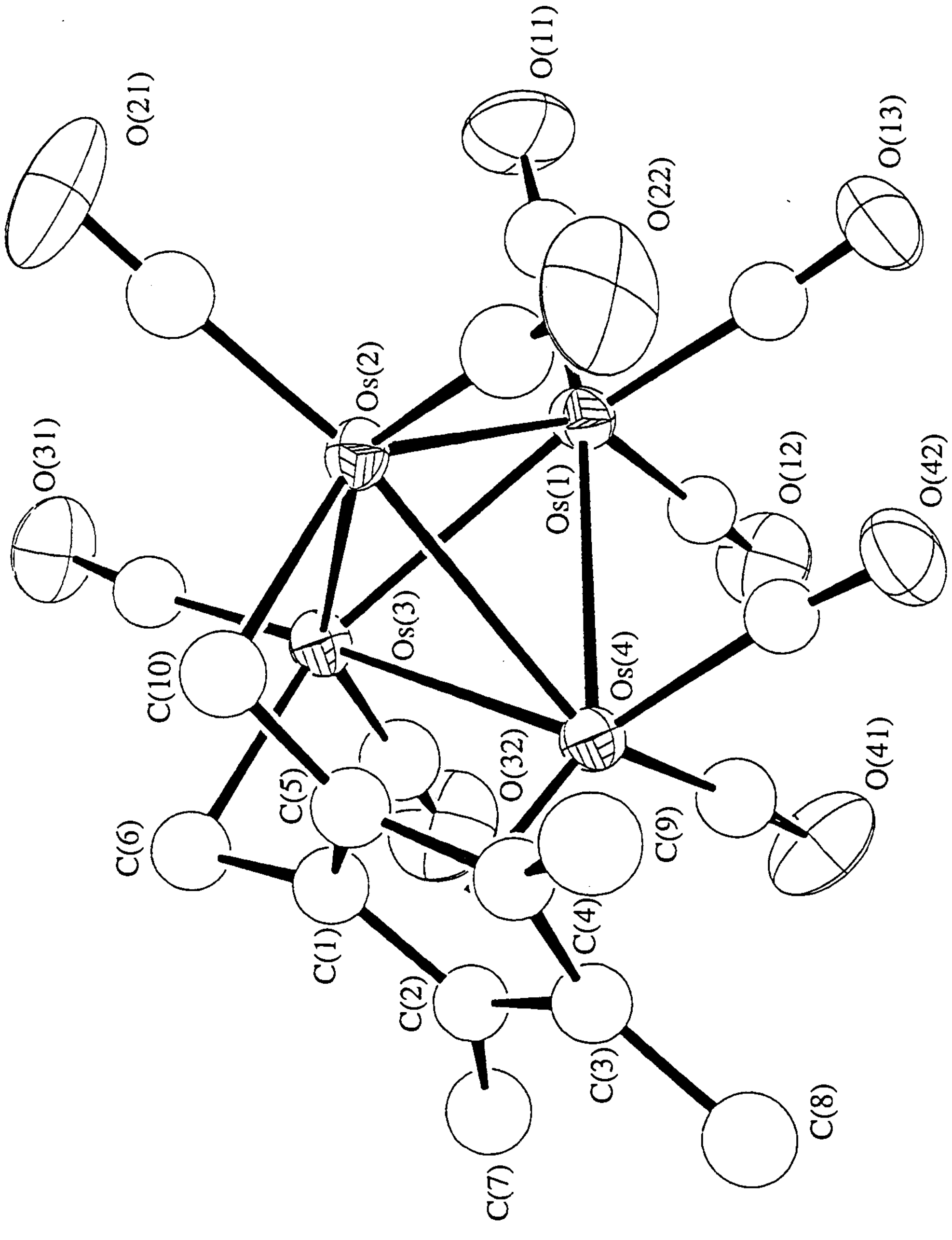


Figure 3.4. The molecular structure of
$[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**)

Table 3.4. Selected Bond Lengths (Å) and Angles (°) for $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**)

Bond Lengths

Os(1) - Os(2)	2.887 (1)	Os(3) - C(6)	2.19 (1)
Os(1) - Os(3)	2.864 (1)	C(1) - C(6)	1.48 (2)
Os(1) - Os(4)	2.997 (1)	C(5) - C(10)	1.45 (2)
Os(2) - Os(3)	2.955 (1)	(Os-CO)	1.85 (2) - 1.95 (2)
Os(2) - Os(4)	2.912 (1)	(C-O)	1.10 (2) - 1.15 (2)
Os(3) - Os(4)	2.934 (1)	$(C\text{-}C)_{ring}$	1.42 (2) - 1.48 (2)
Os(2) - C(10)	2.22 (1)	$(C\text{-}C_{Me})$	1.45 (2) - 1.52 (2)

Bond Angles

Os(3) - Os(1) - Os(2)	61.84 (2)	Os(3) - Os(4) - Os(1)	57.73 (2)
Os(4) - Os(1) - Os(2)	59.29 (2)	Os(3) - Os(4) - Os(2)	60.73 (2)
Os(4) - Os(1) - Os(3)	60.02 (2)	C(11) - Os(1) - Os(2)	115.4 (4)
Os(3) - Os(2) - Os(1)	58.69 (2)	C(12) - Os(1) - Os(4)	92.4 (4)
Os(4) - Os(2) - Os(1)	62.24 (2)	C(13) - Os(1) - Os(2)	98.1 (4)
Os(4) - Os(2) - Os(3)	60.00 (2)	C(13) - Os(1) - Os(4)	98.0 (4)
Os(2) - Os(3) - Os(1)	59.47 (2)	C(21) - Os(2) - Os(1)	125.4 (4)
Os(4) - Os(3) - Os(1)	62.24 (2)	C(21) - Os(2) - Os(3)	116.5 (4)
Os(4) - Os(3) - Os(2)	59.27 (2)	C(22) - Os(2) - Os(1)	100.6 (4)
Os(2) - Os(4) - Os(1)	58.47 (2)	C(22) - Os(2) - Os(4)	95.2 (4)

Os(1)Os(2)Os(3) triangle.

As can be seen from Figure 3.4, cluster **14** has an approximate mirror plane that passes through Os(1), Os(4), and the midpoint of the Os(2)-Os(3) (and C(1)-C(5)) vector. The ^1H (Figure 3.5) and $^{13}C\{^1H\}$ (Figure 3.6) NMR data for **14** indicate that the cluster has the same structure (with a mirror plane) in solution as found in the solid state. Two signals in a 6:3 ratio in the ^1H NMR spectrum at

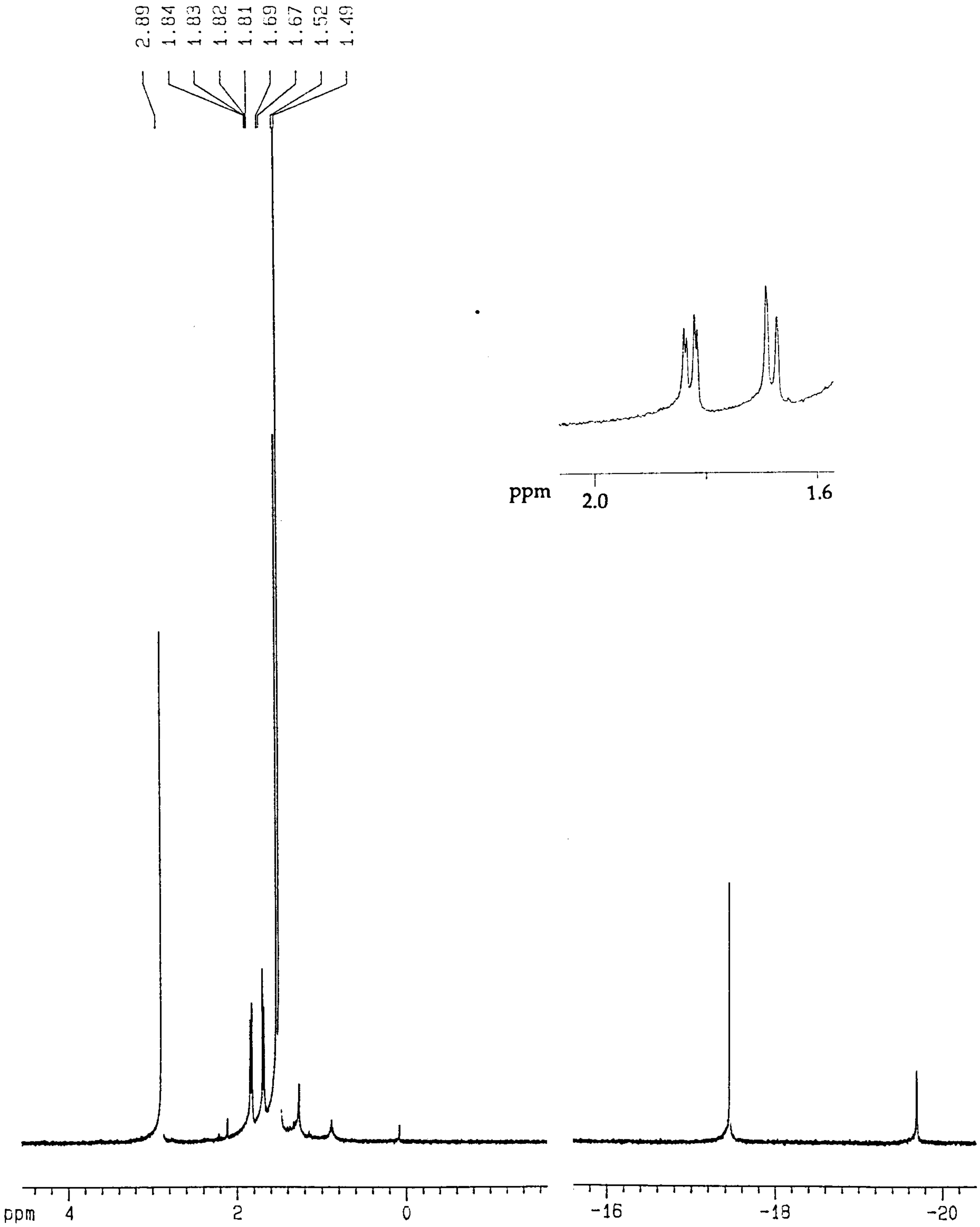


Figure 3.5. ^{1}H NMR spectrum of $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**)
(The signal at δ 1.52 is attributed to the solvent.)

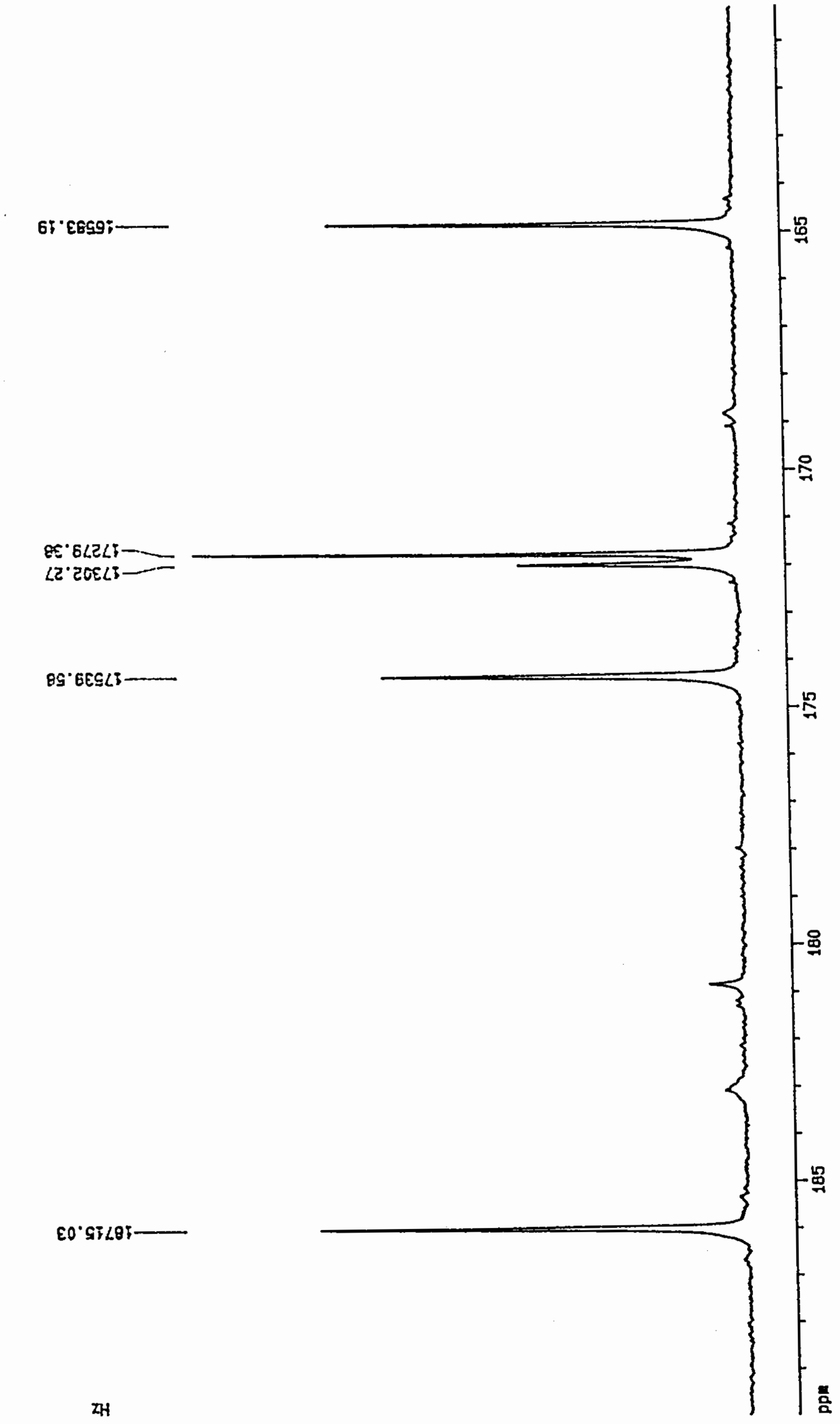


Figure 3.6. $^{13}C\{^{1}H\}$ NMR spectrum of $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ **(14)**

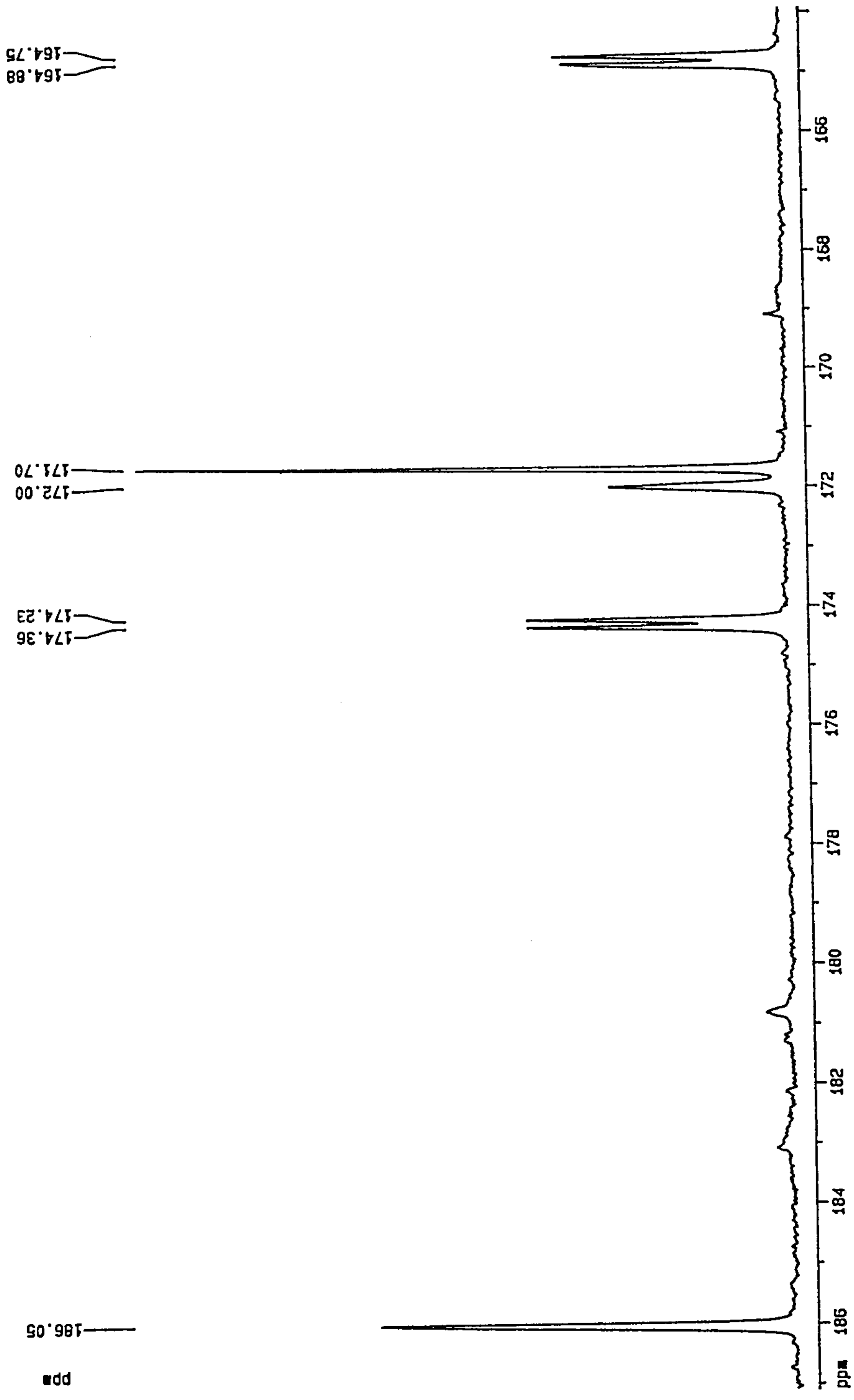


Figure 3.7. ^{13}C NMR spectrum of $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ **(14)**

δ 1.49 and 2.89 are assigned to the chemically different methyl groups; a relatively broad doublet atδ 1.68 and a doublet of doublets at δ 1.82 in a 2:2 ratio are assigned to the chemically different (inner and outer) protons ($J_{H_AH_{A'}}$ = 8 Hz) of the CH_2 groups which also couple probably to the unique hydride ligand H(32) (unresolved for the signal at δ 1.68 and $J_{H_AH_B}$ = 1~2 Hz for the signal at δ 1.82); the two resonances at δ -17.46 and -19.70 are assigned to the chemically different hydride ligands. The $^{13}C\{^1H\}$ NMR spectrum of ^{13}CO-enriched **14** (Figure 3.6) exhibits five signals in the carbonyl region in a 2:2:1:2:2 intensity ratio and, furthermore, two of the signals are split into doublets in the ^1H-coupled ^{13}C NMR spectrum (Figure 3.7, previous page). This data is therefore not only consistent with the solid-state structure, but also with the view that the hydride and carbonyl ligands in **14** are stereochemically rigid in solution on the NMR time scale at room temperature.

Comparison of the Structures of 11, 12, 13, and 14. The important structural transformations described here are summarized in Figure 3.8. As mentioned in the Introduction, we are aware of only one other report of C-H activation of a C_5Me_5 ligand in a cluster compound. The series of structures reported here provides a unique opportunity to compare the metal-metal bond lengths of tetrahedral Os_4, $Os_4(\mu\text{-}H)$, $Os_4(\mu\text{-}H)_2$, and $Os_4(\mu\text{-}H)_3$ units in a closely related series of clusters. These lengths are shown diagrammatically in Chart 3.1 (the solid and dashed lines represent Os-Os bonds that are believed to be unbridged and hydride-bridged, respectively). As can be seen, they may be divided into three groups: unbridged, and hydride-bridged, Os-Os bonds that do not involve Os(4) (to which the cyclopentadienyl ligand is coordinated), and Os-Os bonds that do involve Os(4).

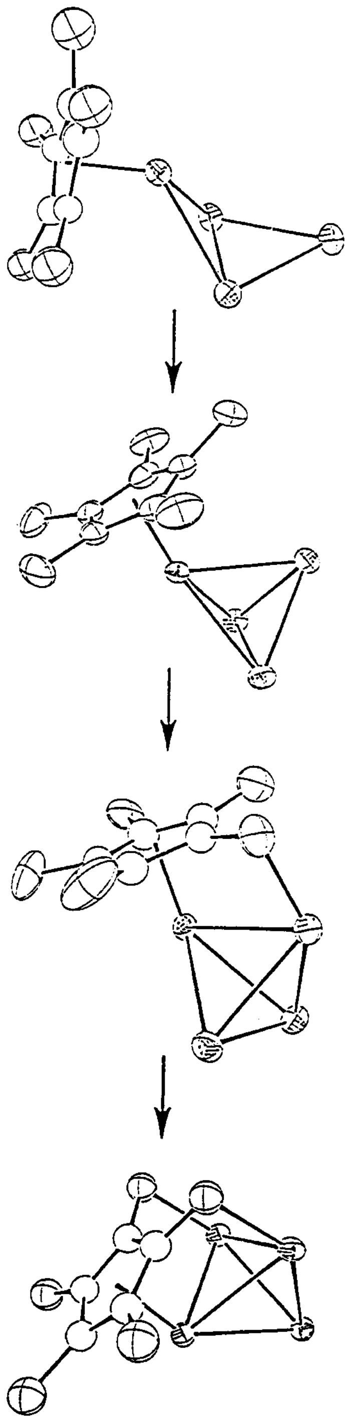


Figure 3.8

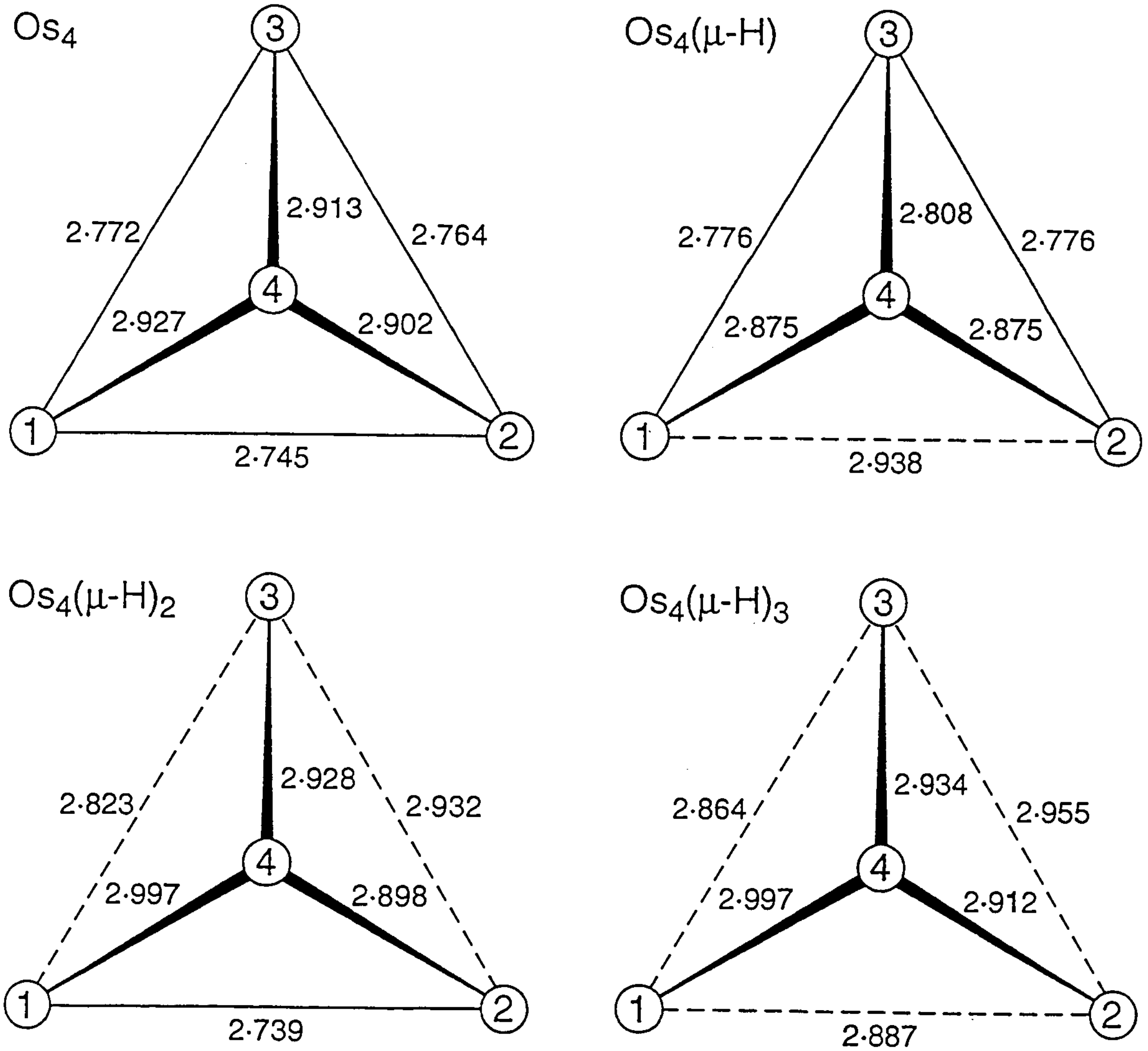

Os4
3
2·772
2·913
2·764
4
2·927
2·902
1
2
2·745
Os4(μ-H)
3
2·776
2·808
2·776
4
2·875
2·875
1
2
2·938
Os4(μ-H)2
3
2·823
2·928
2·932
4
2·997
2·898
1
2
2·739
Os4(μ-H)3
3
2·864
2·934
2·955
4
2·997
2·912
1
2
2·887

Chart 3.1

The six lengths of the first type range from 2.739 to 2.776 Å, which is significantly shorter than 2.88 Å, the average Os-Os length in $Os_3(CO)_{12}$,[36] and which is usually taken as representative of an Os-Os single bond length in osmium carbonyl cluster compounds. It has, however, been found that Os-Os bond lengths in more-condensed, higher-nuclearity clusters of osmium are often shorter than 2.88 Å.[8,39b,106] This can be attributed in part to the fewer terminal ligands on the osmium atoms in such clusters and consequently the fewer steric repulsions between these terminal ligands. The short bonds in clusters **11-14** are consistent with this view.

The six Os-Os vectors in **11-14** believed to be bridged by a hydride ligand range in length from 2.823 (1) to 2.955 (1) Å. As pointed out in Chapter 2, in trinuclear carbonyl clusters of osmium, Os-Os distances of Os(μ-H)Os linkages are usually much longer than 2.88 Å:[38] a distance of 3.00 ± 0.05 Å is typical for such lengths.[39] The Os-Os lengths of the Os(μ-H)Os linkages in **11-14** would therefore not, if each molecule were considered in isolation, be considered significantly lengthened. But as discussed above, the comparable unbridged Os-Os distances in these clusters are some 0.1 Å shorter than 2.88 Å so that the Os-Os distances of the Os(μ-H)Os groups in these tetranuclear clusters do indeed represent a significant lengthening over the comparable unbridged Os-Os bonds.[106]

As can be seen from Chart 3.1, if the Os-Os bonds lengths of **11** are excluded from the discussion, the Os-Os bonds that involve Os(4) range in length from 2.898 (1) to 2.997 (1) Å. This may, in part, be attributed to the higher coordination number of Os(4) (it can be regarded as eight coordinate in these clusters). It may also, as discussed above, be because some of the metal-metal bonds are weak dative bonds. We and others have previously observed a long metal-metal bond, believed to be a dative bond (see Chapter 2), in a cluster compound.[35,40,107] Another possible reason for these long metal-metal bonds is the close interaction between the [$C_5Me_4CH_2$] (and [$C_5Me_3(CH_2)_2$]) ligand and the carbonyls in the other osmium atoms upon the formation of the Os-CH_2- bonds.

Another feature of interest is the displacement of one of the methyl carbon atoms (C(4) in molecule $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**11**)) 0.52 Å out of the plane of the central carbon ring of the C_5Me_5 ligand. The next largest displacement of this type observed in the clusters described here is 0.32 Å (C(10) in molecule [μ,η^5,η^1-$C_5Me_4CH_2$]$Os_4(\mu\text{-}H)_2(CO)_{10}$ (**12**)); the displacements of the other methyl carbons from the carbon ring plane in clusters **11-14** are in the range 0.13 to 0.22 Å. The bending away of C(4) in **11** (and C(10) in **12**) can be attributed to steric interaction of the methyl group with the nearest carbonyls. This closeness of approach of methyl groups to adjacent osmium atoms is no doubt responsible for the facile intramolecular C-H cleavage reactions that **11** undergoes, and which is described below.

The metal-metal bonds in **11** that involve Os(4) are shorter than expected (Os(1)-Os(4) = Os(1')-Os(4) = 2.875 (1) Å, Os(1') ≡ Os(2); Os(3)-Os(4) = 2.808 (1) Å). The considerable steric interaction of one of the methyl groups of the C_5Me_5 ligand (C(4)) and two of the carbonyl ligands on Os(3) might be expected to lengthen the Os(3)-Os(4) bond and yet this is by far the shortest Os-Os bond that involves Os(4) in the molecules **11-14**. The reason for the shortness of this bond is uncertain although it is noted that, of the clusters considered here, **11** is the only cluster in which the cyclopentadienyl ligand is bound solely in the η^5 mode. It may be that the requirements of the μ, η^5, η^1 (or μ_3, η^5, η^1, η^1) mode of bonding of the cyclopentadienyl ligand lengthens the metal-metal bonds that involve

Os(4) in **12, 13** and **14**. The shorter Os-Os bonds to Os(4) in **11** may explain why the carbonyls on Os(4) in this cluster have the strongest bridging interactions with other metal atoms in the cluster.

For the $C_5Me_4CH_2$ ligand, besides the η^5, η^1 mode of coordination (Chart 3.2, structure A) there is the possibility that the coordination should be considered as η^4, η^2, that is, the $C_5Me_4CH_2$ should be considered as a fulvene unit with monoene and diene groups (Chart 3.2, structure B).[108] The distances of the η^2-bound osmium atom to the internal carbon atom of the olefin unit in fulvene formulation are short: the Os(3)-C(1) distance is 2.70 (2) in **12** and 2.71 (2) Å in **13**; in **14** the comparable distances are 2.66 (2) Å (Os(3)-C(1)), and 2.71 (2) Å (Os(2)-C(5)). Although these distances probably indicate some bonding interaction, we nevertheless believe that the η^5,η^1 (or η^5,η^1,η^1) description more accurately describes the bonding of the cyclopentadienyl ligand in these clusters. The C-C ring distances for the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ groups are all equal within experimental error, and the $C\text{-}C_{CH_2}$

(A)

(B)

Chart 3.2

lengths are not significantly shorter than the corresponding $C\text{-}C_{Me}$ distances in these molecules (Tables 3.2-3.4). Both data are consistent with the η^5, η^1 formulation. Furthermore, the H-H coupling of the chemically different (inner and outer) protons of the CH_2 units of **14** of 8 Hz is entirely consistent with *sp*^{3} hybridization at these carbons.[109] The analysis of the bonding of the $C_5Me_4CH_2$, and $C_5Me_3(CH_2)_2$, fragment in these clusters is similar to that previously carried out for $(Cp^*Ti)_2(\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2)\text{-}(\mu\text{-}O)_2$, a molecule that contains a $C_5Me_4CH_2$ bridging two metal atoms and believed to be bonded to these two atoms in an η^5, η^1 fashion.[95,96]

3.3 Experimental Section

The general procedure used for the synthesis and X-ray structure analysis has been described in the Experimental Section of Chapter 2.

3.3.1 Preparation.

Preparation of $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (11). A round-bottom flask fitted with a Teflon valve was charged with $Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (**3**, prepared according to eq 2.1 in Chapter 2) (20 mg, 0.016 mmol) and CH_2Cl_2 (20 mL). The flask and contents were cooled to -196 °C and evacuated; the solution was degassed with three freeze-pump-thaw cycles. The sealed flask was heated at 50 °C for 8 h. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel (1.2 x 20 cm). Elution with hexane/CH_2Cl_2 (3/1) gave an orange band from which **11** (14 mg, 72%) was isolated as air-stable, orange crystals: IR(CH_2Cl_2) ν(CO) 2083 (s), 2056 (vs), 2024 (vs), 2003 (sh), 1995 (m), 1937 (m), 1814 (m, br), 1773 (sh) cm^{-1}; ^{1}H NMR (CD_2Cl_2, room temperature) δ 2.11 (s, 15H), -20.71 (s, 1H). Anal. Calcd for $C_{21}H_{16}O_{11}Os_4$: C, 20.93; H, 1.34. Found: C, 21.05, H, 1.30.

Preparation of $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (12), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (13), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (14). The pyrolysis of **11** always gave **14** as the major product. Below 90 °C, the reaction was slow (as determined by IR spectroscopy); above ~110 °C, the reaction produced mainly **14** (as described below). Because of their similar solubilities, clusters **12** and **14** could not be separated completely by chromatography. For these reasons, the yield of **13** was insufficient to allow for a microanalysis, and samples of **12** which always contained compound **14** were also not microanalyzed. **Method 1:** A flask with **11** (25 mg, 0.021 mmol), CH_2Cl_2 (7 mL), and hexane (20 mL) was cooled to -196 °C and evacuated; the solvent mixture was degassed with three freeze-pump-thaw cycles. The evacuated, sealed flask was heated at 94 °C for 3 d. The solvent was then removed on the vacuum line and the remaining solid chromatographed on silica gel (1.2 x 25 cm). Elution with hexane/CH_2Cl_2 (7/1) gave a yellow band from which 15 mg of a mixture of **12** and **14** was obtained (the ratio **12**/**14** was approximately 1/3 after further recrystallization from CH_2Cl_2/hexane). Further elution of the column with hexane/CH_2Cl_2 (3/1) gave an orange band from which 8 mg of a mixture of **11** and **13** (in an approximate 1/1 ratio based on the IR spectrum) was obtained. Spectroscopic properties and the crystal used in the X-ray study of **12** were obtained from samples hand separated from **14**. **Method 2:** A similar reaction to that described above was carried except that a temperature of 115-120 °C and a reaction time of 42 h were employed. Chromatography as above gave pure **13** (~2 mg, ~10 %) and **14** (14 mg, 82 %).

There was no evidence for **12** in the IR spectrum of the reaction solution. Compound **12**: IR (CH_2Cl_2) ν(CO) 2097 (w), 2079 (s), 2040 (vs), 2012 (vs), 1999 (m), 1967 (sh), 1964 (m), 1937 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.75 (t, J_{HH} = 0.7 Hz, 2H), 2.34 (s, 6H), 1.53 (s, 6H), -16.88 (s, 2H). Compound **13**: IR (CH_2Cl_2) ν(CO) 2078 (s), 2035 (vs) 2003 (vs), 1993 (sh), 1974 (m), 1951 (w,sh), 1904 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.78 (s, 2H), 2.21 (s, 6H), 1.14 (s, 6H). Compound **14**: IR (CH_2Cl_2) ν(CO) 2097 (s), 2053 (vw), 2023 (vs), 2012 (s), 1999 (m), 1966 (vw), 1938 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.89 (s, 3H), 1.82 (dd, $J_{H_AH_{A'}}$ = 8 Hz, $J_{H_AH_B}$ = 1~2 Hz, 2H), 1.68 (d, $J_{H_AH_{A'}}$ = 8 Hz, 2H), 1.49 (s, 6H), -17.46 (s, 2H), -19.70 (s, 1H); ^{13}C/^{13}C{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 4/1) δ 186.0 (2C), 174.4 (2C, J_{CH} = 13 Hz), 172.0 (1C), 171.8 (2C), 164.8 (2C, J_{CH} = 13 Hz). Anal. Calcd for $C_{19}H_{16}O_9Os_4$: C, 19.86; H, 1.41. Found: C, 20.04; H, 1.45.

3.3.2. **X-ray Analysis of Compounds 11, 12, 13, and 14.**

Two intensity standards, measured every one hour (two hours for **13**) of acquisition time, varied up to ±2% (**11**,**13**,**14**) and ±3% (**12**) during the data collection process. The coordinates of carbon atoms with attached hydrogen atoms were linked so that the derived shifts in coordinates included contributions from appropriate derivatives from the atom sites. In each case an extinction parameter was required in the refinement. Crystallographic data are summarized in Table 3.5. Final fractional coordinates for the non-hydrogen atoms and hydride ligands of **11**, **12**, **13** and **14** are given in Tables 3.6, 3.7, 3.8 and 3.9, respectively. Other crystallographic data are included in the supplementary tables of this thesis.

Cp*Os_4(μ-H)(CO)$_{11}$ (11). An azimuth position for which the minimum

Table 3.5. Summary of Crystal Data and Details of Intensity Collection for $Cp^*Os_4(\mu\text{-}H)(CO)_{11}$ (**11**), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (**12**), $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**13**), and $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**).

compound	**11**	**12**
formula	$C_{21}H_{16}O_{11}Os_4$	$C_{20}H_{16}O_{10}Os_4$
fw	1205.1	1177.1
cryst syst	orthorhombic	monoclinic
space group	Pcmn	$P2_1/c$
a, Å	8.852 (1)	9.924 (1)
b, Å	14.821 (2)	17.051 (3)
c, Å	19.054 (2)	15.020 (3)
β, deg		101.81 (1)
V, $Å^3$	2499.8	2487.7
2θ range of unit cell, deg	29-44	29-38
Z	4	4
D_{calc}, g cm^{-3}	3.202	3.143
μ(Mo, Kα), cm^{-1}	203.47	204.38
cryst size, mm	0.016 x 0.25 x 0.27	0.11 x 0.30 x 0.17
transmission coeff range[a]	0.054-0.73	0.076-0.19
scan method	ω-2θ	ω-2θ
scan range (2θ), deg	3-45	3-48
scan width (ω), deg	1.0 + 0.35tanθ	0.90 + 0.35tanθ
scan rate (ω), deg min^{-1}	0.92-5.5	0.82-5.5
no. of unique rflns	2290	3889
no. of obsd rflns[b]	1813	2934
no. of variables	149	234
R[c]	0.019	0.031
Rw[d]	0.021	0.039
k[d]	0.00005	0.00006
GOF[e]	1.2	2.1
extinction (g)	0.41 (2)	0.106 (12)
F000	2135.12	2079.13

Table 3.5 cont'd

compound	**13**	**14**
formula	$C_{21}H_{14}O_{11}Os_4$	$C_{19}H_{16}O_9Os_4$
fw	1203.1	1149.1
cryst syst	orthorhombic	monoclinic
space group	Pbca	$P2_1/n$
a, Å	14.254 (2)	9.655 (1)
b, Å	16.214 (2)	16.380 (2)
c, Å	21.735 (3)	14.842 (1)
β, deg		92.66 (1)
V, $Å^3$	5023	2344.7
2θ range of unit cell, deg	28-38	31-48
Z	8	4
D_{calc}, g cm^{-3}	3.182	3.255
μ(Mo, Kα), cm^{-1}	202.51	216.79
cryst size, mm	0.048 x 0.11 x 0.11	0.13 x 0.27 x 0.28
transmission coeff range[a]	0.087-0.40	0.019-0.12
scan method	ω-2θ	ω-2θ
scan range (2θ), deg	3-45	3-48
scan width (ω), deg	0.85 + 0.35tanθ	0.95 + 0.35tanθ
scan rate (ω), deg min^{-1}	0.78-5.5	0.87-5.5
no. of unique rflns	3264	3633
no. of obsd rflns[b]	2197	2822
no. of variables	167	189
R[c]	0.038	0.030
Rw[d]	0.047	0.041
k[d]	0.0016	0.00006
GOF[e]	0.92	2.4
extinction (g)	0.79 (7)	0.316 (16)
F000	4254.25	2023.14

---

[a] Absorption corrections. [b] Io > 2.5(Io). [c] $R = \Sigma \| Fo| - |Fc\| / \Sigma |Fo|$.
[d] $Rw = (\Sigma w(|Fo| - |Fc|)^2 / \Sigma w |Fo|^2)^{1/2}$, $w = [\sigma^2(Fo) + k(Fo)^2]^{-1}$.
[e] $GOF = (\Sigma w(|Fo| - |Fc|)^2 / (\text{ degrees of freedom }))^{1/2}$.

absorption was determined from the shape and mounting of the crystal was used in the intensity data collection because of the crystal shape (an extremely thin plate) of **11**. The final least-squares refinement included an extinction parameter, coordinates for all non-hydrogen atoms and the hydride ligand, anisotropic thermal parameters for the osmium, oxygen atoms and carbon atoms of the Cp* ligand, isotropic thermal parameters for the carbonyl carbon atoms and the hydride ligand, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to carbon atoms.

$[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ (12). The final least-squares refinement included an extinction parameter, coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium, oxygen atoms and the outer-ring carbon atoms of the Cp* ligand, isotropic thermal parameters for the ring and carbonyl carbon atoms, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to carbon atoms.

$[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (13). A similar method for the intensity data collection, i.e., using an azimuth position like that in **11**, was applied to **13**. The final least-squares refinement included an extinction parameter, coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium atoms, isotropic thermal parameters for the oxygen and carbon atoms, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to the carbon atoms.

$[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (14). The final least-squares refinement included an extinction parameter, coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium and oxygen atoms, one thermal parameter for the inner-ring carbon atoms, one for C(6) and C(10), one for C(7) and C(9), isotropic thermal parameters for all other carbon atoms, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to the carbon atoms.

Placement of the Hydride Ligands. Compound 11: Immediately before the final refinement a low angle ($0 < (\sin\theta)/\lambda \leq 0.35$ Å^{-1}) difference map revealed the largest peak with electron density 0.35 (7) eÅ^{-3} was on the mirror-symmetry plane 1.7 Å from Os(1) and Os(1'). The hydride ligand was therefore placed in that position and the coordinates and isotropic thermal parameter were refined. The relatively long Os(1)-Os(1') distance (2.938 (1) Å) and large Os(1')-Os(1)-C(13) angle (113.4 (2)°) also supported the view that the hydride ligand bridged Os(1) and Os(1'). Calculations for the hydride ligand in different bridging modes with the HYDEX[37] program indicated that a hydride ligand bridging Os(1) and Os(1') had the minimum "site energy" in agreement with the refined position. **Compound 12:** The singlet at δ -16.88 with intensity 2 in the ^{1}H NMR spectrum of **12** suggested the existence of two equivalent hydride ligands. The low angle difference map revealed two largest peaks with electron densities 0.67 (13) eÅ^{-3} (1.6 Å from Os(2) and 2.0 Å from Os(3)) and 0.53 (13) eÅ^{-3} (1.3 Å from Os(1) and 1.8 Å from Os(3)). The HYDEX calculations also showed two sites with a minimum "site energy" arrangement that were near the indicated positions but had more reasonable distances from the appropriate Os atoms. After a consideration of the evidence, the two hydride ligands were placed in the positions calculated with the HYDEX program and included as fixed contributions in the final refinements. **Compound 14:** The ^{1}H NMR spectrum showed two peaks at δ -17.46 (2H) and -19.70 (1H). No clear evidence, however, was obtained from the low angle difference map for the hydride positions. The ^{13}C NMR spectra revealed two doublets at δ 174.35 (2C) and 164.84 (2C). This evidence suggested that the two equivalent hydride ligands, H(12) and H(13), bridge Os(1)-Os(2) and Os(1)-Os(3), respectively (with H(12) coupling to C(12) and H(13) coupling to C(13)) and the other hydride ligand, H(23), bridges Os(2)-Os(3) (and couples to C(22) and C(32)). Calculations with the HYDEX program showed that hydride ligands bridging Os(1)-Os(2), Os(1)-Os(3), and Os(2)-Os(3) was the minimum "site energy" arrangement. Prior to their inclusion in the refinement, a Fourier difference map revealed that the electron densities at the proposed sites were 0.6 (3), 0.2 (3) and 0.3 (3) eÅ^{-3}, respectively (compared to a peak of 1.7 (3) eÅ^{-3} at a distance of 1.1 Å from Os(2)). The three hydride ligands were therefore placed in the positions calculated with the HYDEX program and included as fixed contributions in the final refinements.

Table 3.6. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for **(11)**

Atom	x	y	z	U(iso)
Os(1)	2728.0 (3)	3491.2 (2)	238.6 (1)	297
Os(3)	484.1 (4)	2500	-426.0 (2)	313
Os(4)	3386.1 (4)	2500	-1021.8 (2)	264
O(0)	5837 (5)	3753 (4)	-537 (3)	491
O(11)	1711 (6)	5251 (3)	-438 (3)	548
O(12)	335 (6)	3650 (4)	1375 (3)	528
O(13)	5205 (6)	4295 (4)	1162 (3)	636
O(31)	-851 (5)	4094 (3)	-1208 (3)	494
O(32)	-2165 (8)	2500	581 (4)	586
C(0)	4676 (7)	3370 (4)	-539 (4)	350 (15)
C(11)	2101 (8)	4588 (5)	-184 (4)	411 (17)
C(12)	1187 (8)	3579 (5)	927 (4)	455 (17)
C(13)	4292 (8)	4004 (5)	807 (4)	448 (18)
C(31)	-357 (7)	3491 (4)	-915 (4)	376 (15)
C(32)	-1178 (12)	2500	203 (6)	437 (24)
C(1)	2086 (10)	2500	-2099 (5)	309
C(2)	3024 (8)	3279 (4)	-2038 (4)	364
C(3)	4570 (7)	2964 (5)	-2015 (3)	357
C(4)	507 (11)	2500	-2386 (6)	438
C(5)	2538 (8)	4238 (4)	-2137 (4)	513
C(6)	5958 (8)	3560 (6)	-2077 (4)	556
H(1'1)	3293 (152)	2500	596 (74)	1165 (501)

Table 3.7. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for **(12)**

Atom	x	y	z	U(iso)
Os(1)	3759.1 (5)	5483.2 (3)	1549.2 (4)	342
Os(2)	2875.3 (5)	4974.3 (3)	3061.9 (4)	363
Os(3)	3976.3 (5)	6564.4 (3)	2995.0 (4)	318
Os(4)	1202.2 (5)	6173.0 (3)	1999.7 (3)	284
O(11)	4856 (12)	6553 (8)	219 (9)	738
O(12)	6184 (11)	4384 (7)	1813 (9)	691
O(13)	2125 (13)	4377 (7)	117 (9)	657
O(21)	1331 (15)	4491 (8)	4546 (10)	828
O(22)	5592 (12)	4353 (7)	4124 (9)	678
O(23)	2079 (13)	3448 (7)	2043 (9)	735
O(31)	6440 (12)	6723 (9)	4539 (9)	734
O(32)	5048 (13)	7846 (8)	1963 (10)	854
O(41)	-398 (11)	4666 (7)	1617 (9)	675
O(42)	1195 (11)	6478 (8)	12 (7)	577
C(11)	4381 (15)	6169 (10)	714 (10)	487 (39)
C(12)	5247 (14)	4789 (9)	1697 (10)	436 (36)
C(13)	2707 (16)	4788 (10)	656 (11)	575 (44)
C(21)	1918 (17)	4705 (11)	3984 (12)	624 (46)
C(22)	4523 (17)	4559 (10)	3710 (11)	589 (44)
C(23)	2379 (15)	4044 (10)	2415 (11)	525 (41)
C(31)	5521 (16)	6659 (10)	3952 (11)	541 (41)
C(32)	4580 (15)	7382 (9)	2376 (10)	484 (39)
C(41)	316 (14)	5211 (9)	1787 (10)	439 (36)
C(42)	1350 (14)	6291 (9)	773 (10)	418 (35)
C(1)	1522 (13)	7215 (8)	3063 (9)	369 (32)
C(2)	959 (14)	7492 (9)	2179 (10)	434 (36)
C(3)	-335 (14)	7129 (9)	1829 (10)	448 (37)
C(4)	-638 (13)	6625 (8)	2513 (9)	382 (33)
C(5)	523 (14)	6639 (9)	3262 (10)	435 (35)
C(6)	2823 (14)	7362 (9)	3664 (10)	470
C(7)	1564 (15)	8137 (9)	1715 (11)	549
C(8)	-1383 (15)	7363 (9)	1003 (10)	515
C(9)	-1955 (15)	6215 (12)	2494 (13)	715
C(10)	470 (19)	6326 (13)	4208 (11)	724
H(31)	5015	5961	2420	500
H(32)	3316	5867	3698	500

Table 3.8. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for **(13)**

Atom	x	y	z	U(iso)
Os(1)	4285.9(6)	4037.3(5)	1909.6(3)	312
Os(2)	5283.1(6)	2668.3(5)	1557.4(3)	331
Os(3)	3363.1(6)	2555.5(5)	1713.1(3)	293
Os(4)	4081.4(5)	3439.6(5)	645.9(3)	286
O(11)	2962(16)	5511(14)	1979(9)	939(61)
O(12)	4429(13)	3807(11)	3291(7)	676(48)
O(13)	6028(14)	5113(11)	1922(7)	717(48)
O(21)	6089(16)	1145(14)	919(9)	952(63)
O(22)	5566(13)	2052(11)	2851(7)	662(47)
O(23)	7163(13)	3514(11)	1462(7)	681(47)
O(31)	4077(13)	791(12)	1505(7)	694(48)
O(32)	1932(12)	3823(10)	2141(7)	583(42)
O(33)	2738(11)	1785(9)	2894(6)	487(37)
O(41)	6021(14)	3199(11)	147(7)	697(48)
O(42)	4416(12)	5278(11)	687(7)	622(44)
C(11)	3470(17)	4945(15)	1970(10)	569(62)
C(12)	4425(18)	3898(16)	2747(11)	581(65)
C(13)	5373(17)	4679(15)	1912(9)	483(56)
C(21)	5763(18)	1757(16)	1156(11)	602(66)
C(22)	5502(17)	2297(15)	2352(10)	515(61)
C(23)	6436(20)	3230(16)	1495(10)	617(66)
C(31)	3946(15)	1522(13)	1537(8)	387(49)
C(32)	2571(16)	3456(13)	1967(8)	428(50)
C(33)	2959(13)	2090(11)	2432(7)	278(43)
C(41)	5343(16)	3257(13)	413(9)	422(52)
C(42)	4319(15)	4569(13)	770(9)	394(50)
C(1)	2690(14)	2714(11)	554(8)	308(45)
C(2)	2555(15)	3583(12)	414(8)	351(47)
C(3)	3106(14)	3754(13)	-128(9)	389(50)
C(4)	3622(15)	3045(13)	-303(8)	371(48)
C(5)	3393(16)	2388(14)	132(9)	443(54)
C(6)	2267(15)	2238(12)	1059(8)	394(50)
C(7)	1806(17)	4129(15)	657(10)	563(62)
C(8)	3049(16)	4564(14)	-467(10)	499(57)
C(9)	4208(16)	2948(15)	-853(9)	509(60)
C(10)	3674(18)	1514(16)	39(10)	616(67)

Table 3.9. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for **(14)**

Atom	x	y	z	U(iso)
Os(1)	876.9 (5)	9653.0 (3)	2450.3 (3)	280
Os(2)	805.5 (5)	7891.5 (3)	2407.6 (3)	270
Os(3)	-1029.8 (5)	8832.4 (3)	3561.8 (3)	287
Os(4)	-1566.2 (5)	8767.2 (3)	1601.4 (3)	267
O(11)	3293 (13)	10360 (7)	3550 (8)	674
O(12)	-618 (13)	11276 (6)	2435 (7)	607
O(13)	2503 (12)	9938 (6)	786 (6)	560
O(21)	2880 (15)	6759 (7)	3310 (7)	676
O(22)	2103 (15)	7550 (8)	614 (7)	593
O(31)	-381 (13)	8704 (6)	5556 (6)	570
O(32)	-3068 (15)	10175 (7)	3864 (8)	730
O(41)	-2857 (13)	10439 (6)	1368 (7)	533
O(42)	48 (11)	8974 (6)	-92 (6)	469
C(11)	2367 (17)	10111 (9)	3129 (10)	465 (36)
C(12)	-60 (14)	10655 (8)	2411 (8)	353 (30)
C(13)	1876 (16)	9825 (8)	1379 (9)	396 (32)
C(21)	2084 (16)	7205 (9)	2996 (9)	433 (34)
C(22)	1670 (17)	7682 (9)	1268 (9)	467 (36)
C(31)	-702 (15)	8749 (8)	4806 (9)	396 (32)
C(32)	-2296 (18)	9661 (10)	3737 (10)	528 (40)
C(41)	-2312 (16)	9829 (9)	1491 (9)	437 (35)
C(42)	-469 (14)	8918 (7)	564 (8)	327 (29)
C(1)	-2695 (15)	7878 (7)	2545 (8)	368 (14)
C(2)	-3684 (14)	8308 (8)	1973 (8)	368 (14)
C(3)	-3395 (14)	8105 (8)	1025 (8)	368 (14)
C(4)	-2254 (14)	7556 (8)	1053 (8)	368 (14)
C(5)	-1824 (15)	7404 (8)	1962 (8)	368 (14)
C(6)	-2591 (15)	7863 (8)	3541 (8)	418 (23)
C(7)	-4870 (16)	8795 (8)	2273 (9)	513 (22)
C(8)	-4362 (16)	8323 (9)	221 (9)	513 (22)
C(9)	-1718 (16)	7133 (8)	250 (9)	513 (22)
C(10)	-710 (14)	6875 (8)	2287 (9)	418 (23)
H(32)	74	7912	3537	500
H(21)	2019	8749	2611	500
H(31)	325	9625	3631	500

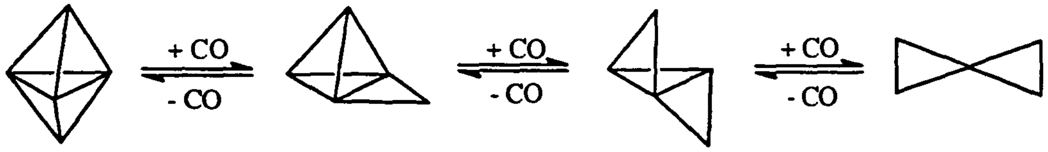
Chapter 4. Pentaosmium Binary Carbonyl Clusters

4.1 Introduction

Osmium forms more binary carbonyls than any other element; compounds with one to eight metal atoms are known.[8,32] Carbonyl-containing clusters of osmium of still higher nuclearity are also common.[8,110] The study of osmium carbonyl clusters and their derivatives therefore occupies a central place in cluster science.

Systematic buildup of metal clusters has been a goal of research in this laboratory for some time.[32] Previous work in this laboratory has shown that $Os_4(CO)_{15}$[29] can be synthesized from the reaction of a triosmium cluster with $Os(CO)_5$. Subsequent decarbonylation or carbonylation of $Os_4(CO)_{15}$ gives $Os_4(CO)_{14}$[31] or $Os_4(CO)_{16}$,[30] respectively. It is our aim to build osmium clusters with higher nuclearity (e.g. pentaosmium clusters) from those with lower nuclearity.

More than 15 years ago, the synthesis and single crystal structure of the first pentaosmium binary carbonyl cluster, $Os_5(CO)_{16}$ (**17**) (compounds **15** and **16** will be mentioned soon after), were reported by Johnson, Lewis and Sheldrick.[10,46] It was a minor product from the pyrolysis of $Os_3(CO)_{12}$.[10] The molecule has a trigonal pyramidal arrangement of metal atoms with an osmium atom in the equatorial plane having four carbonyl groups.[46] During 1981 to 1982, the synthesis and single crystal structure of $Os_5(CO)_{19}$ (**15**), were reported.[47] This compound was made from the reaction of $Os_6(CO)_{18}$ with CO at 160 °C and 90 atm for *ca.* 1 h. The molecule has a bow-tie arrangement of metal atoms. Based mainly on the structures of **15** and **17**, a possible pathway of conversion among Os_5 clusters (with two postulated intermediates) had been proposed by Lewis and co-workers (Chart 4.1).[47b]



17 $[Os_5(CO)_{17}]^a$ $[Os_5(CO)_{18}]^a$ **15**

Chart 4.1. A pathway of conversion among pentaosmium clusters.
^{a} Postulated intermediate.

In Chapter 5 the study on $Os_5(CO)_n(PMe_3)$ (n = 18, 17, 15) clusters will be reported. It was the synthesis and crystal structure of $Os_5(CO)_{17}(PMe_3)$ that encouraged the investigation of $Os_5(CO)_{18}$. In this chapter we describe the systematic syntheses of $Os_5(CO)_{19}$, $Os_5(CO)_{18}$ (**16**) a hitherto missing member of the pentanuclear binary carbonyls of osmium, and $Os_5(CO)_{16}$, at easily controlled and milder conditions. The single crystal structure of **16** will also be described.

4.2 Results and Discussion

$Os_5(CO)_{19}$ (15). The reaction (eq 4.1) of $Os_4(CO)_{14}$[31] and $Os(CO)_5$[111] in CH_2Cl_2/hexane at 40 °C for 24 h afforded the known $Os_5(CO)_{19}$[47] (checked by IR) in 63% yield after chromatography. The compound was isolated as red, air-

$$Os_4(CO)_{14} + Os(CO)_5 \xrightarrow{40\ ^\circ\mathrm{C}} \underset{\mathbf{15}}{Os_5(CO)_{19}} \qquad (4.1)$$

stable solids. Clearly, the cleavage of metal-metal bonds in $Os_4(CO)_{14}$ and the formation of new metal-metal bonds between $Os_4(CO)_{14}$ and $Os(CO)_5$ occurred during the reaction to give $Os_5(CO)_{19}$ (**15**).

The ^{13}C NMR spectrum of **15** (Figure 4.1) revealed eight signals with the approximate intensity ratio 2:4:4:2:1:2:2:2; suggesting that the corresponding carbonyls in the two adjacent triangular parts are equivalent on the NMR time scale (see Fig 5.1, page 112, for a similar arrangement of the carbonyl ligands by replacing PMe_3 with CO(44)). This probably means that the two parts flip up and down relative to each other in solution.

$Os_5(CO)_{18}$ (16). Pyrolysis of **15** in CH_2Cl_2 contained in a sealed, evacuated flask at 50-55 °C for 3 days gave **16** (eq 4.2). The cluster was isolated in 78% yield after chromatography and recrystallisation as deep-red, air-stable crystals.

$$Os_5(CO)_{19} \xrightarrow{50\text{-}55\ ^\circ C} \underset{\mathbf{16}}{Os_5(CO)_{18}} \qquad (4.2)$$

The molecular structure of **16** is shown in Figure 4.2. As can be seen from the figure, **16** has a planar, raft-like arrangement of osmium atoms. It therefore resembles $Os_6(CO)_{17}[P(OMe)_3]_4$[112] and $Os_3Pt_2(CO)_{14}$.[113] (A similar crystal structure of $Os_5(CO)_{18}$ was published by Coughling, Lewis and Moss[114] soon after our publication. That sample was obtained from the decomposition of an unstable compound, tentatively formulated as a hexaosmium adduct.) This raft-like skeleton of metal atoms in $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$ (see Chapter 5) hence represents the first example of such an arrangement of metal atoms in pentaosmium clusters. The seven Os-Os bond lengths in **16** range from 2.847 (1) to 2.892 (1) Å (Table 4.1), consistent with Os-Os single bonds. An unusual

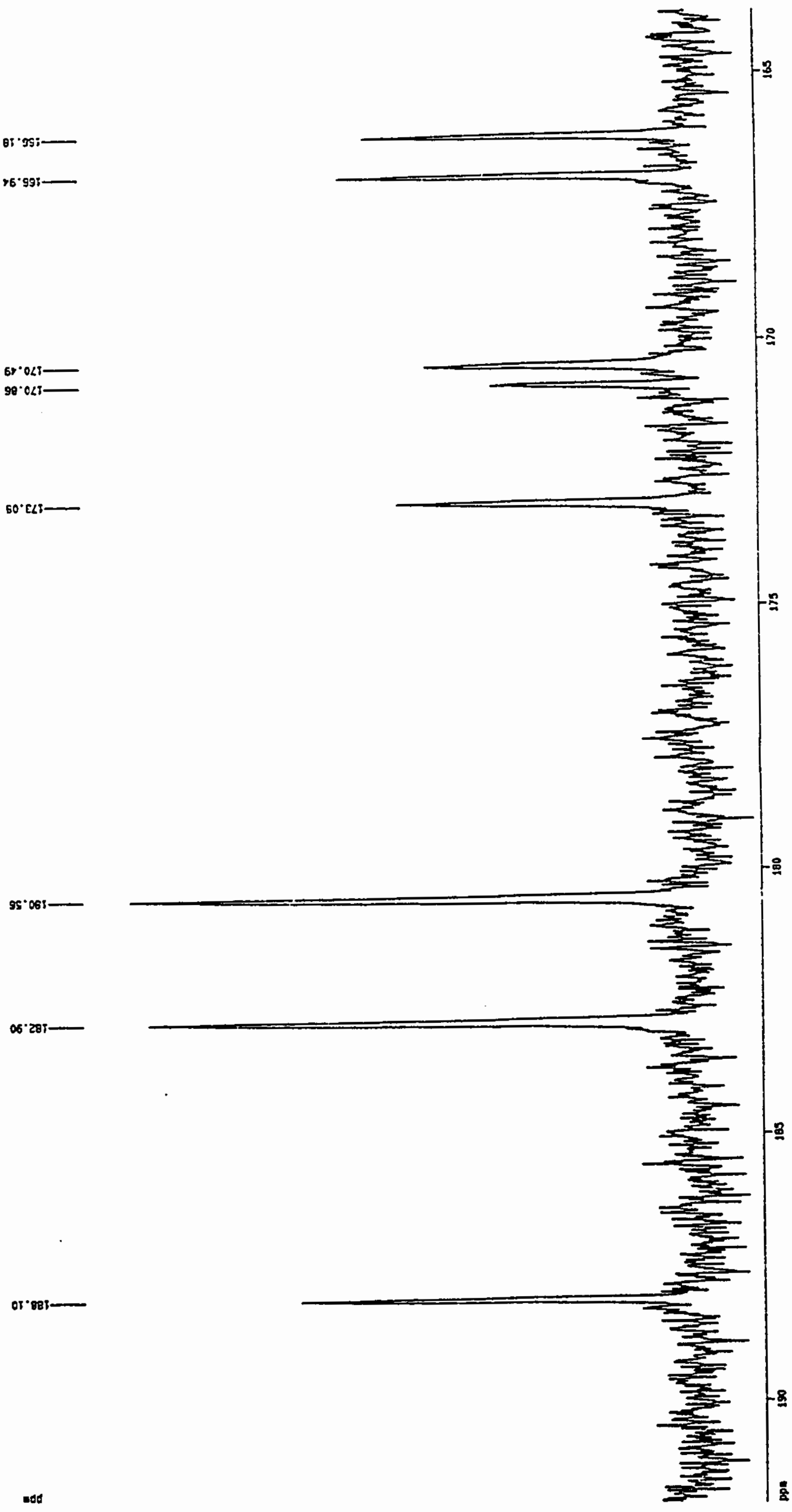


Figure 4.1. The ^{13}C NMR spectrum of $Os_5(CO)_{19}$

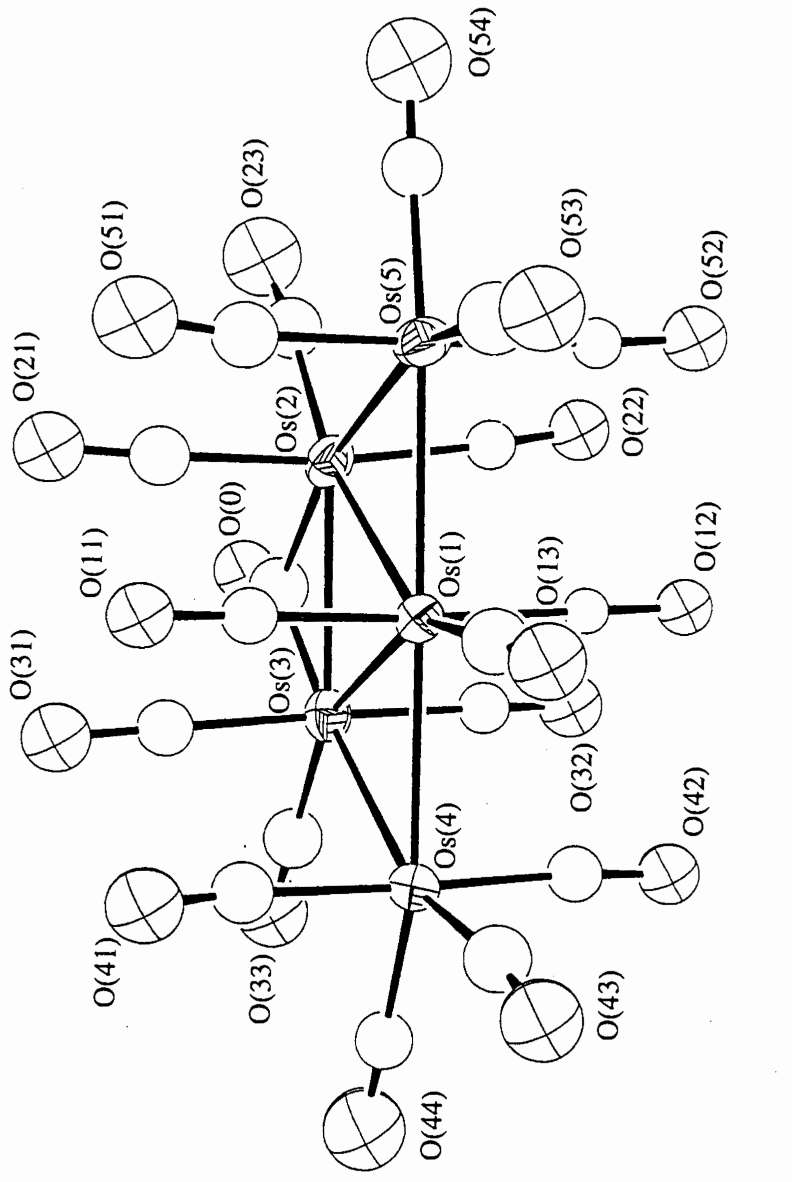


Figure 4.2. The molecular structure of $Os_5(CO)_{18}$ **(16)**

Table 4.1. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{18}$ (**16**)

Bond Lengths

Os(1) - Os(2)	2.860 (1)	Os(3) - Os(4)	2.892 (1)
Os(1) - Os(3)	2.860 (1)	Os(2) - C(0)	2.23 (3)
Os(1) - Os(4)	2.850 (1)	Os(3) - C(0)	1.99 (3)
Os(1) - Os(5)	2.878 (1)		
Os(2) - Os(3)	2.847 (1)	$(Os\text{-}CO_{term})$	1.87 (3) - 1.96 (3)
Os(2) - Os(5)	2.853 (1)	$(C\text{-}O)_{term}$	1.10 (3) - 1.19 (3)

Bond Angles

Os(3) - Os(1) - Os(2)	59.70 (3)	Os(4) - Os(3) - Os(1)	59.41 (3)
Os(4) - Os(1) - Os(3)	60.86 (4)	Os(3) - Os(4) - Os(1)	59.73 (3)
Os(5) - Os(1) - Os(2)	59.64 (4)	Os(2) - Os(5) - Os(1)	59.87 (3)
Os(3) - Os(2) - Os(1)	60.14 (3)	Os(3) - C(0) - Os(2)	84.8 (10)
Os(5) - Os(2) - Os(1)	60.49 (3)	O(0) - C(0) - Os(2)	131.4 (19)
Os(2) - Os(3) - Os(1)	60.16 (3)	O(0) - C(0) - Os(3)	143.9 (21)

feature of the structure of **16** is the presence of a bridging carbonyl (Os(2)-C(0) = 2.23 (3) Å; Os(3)-C(0) = 1.99 (3) Å), so that in the solid state the molecule has approximate C_{2v} symmetry.

The ^{13}C NMR spectrum of **16** in CD_2Cl_2/CH_2Cl_2 at room temperature (Figure 4.3) showed eight signals with the approximate intensity ratio 2:4:4:1:1:2:2:2, as would be expected for the solid-state molecular structure. This is consistent with a rigid structure in solution at room temperature on the NMR time scale identical to that in the solid state. A partial assignment of the resonances in the spectrum is possible. The resonance to lowest field at δ 192.51 with intensity 2 is assigned to the axial carbon atoms on the Os(1) atom. The

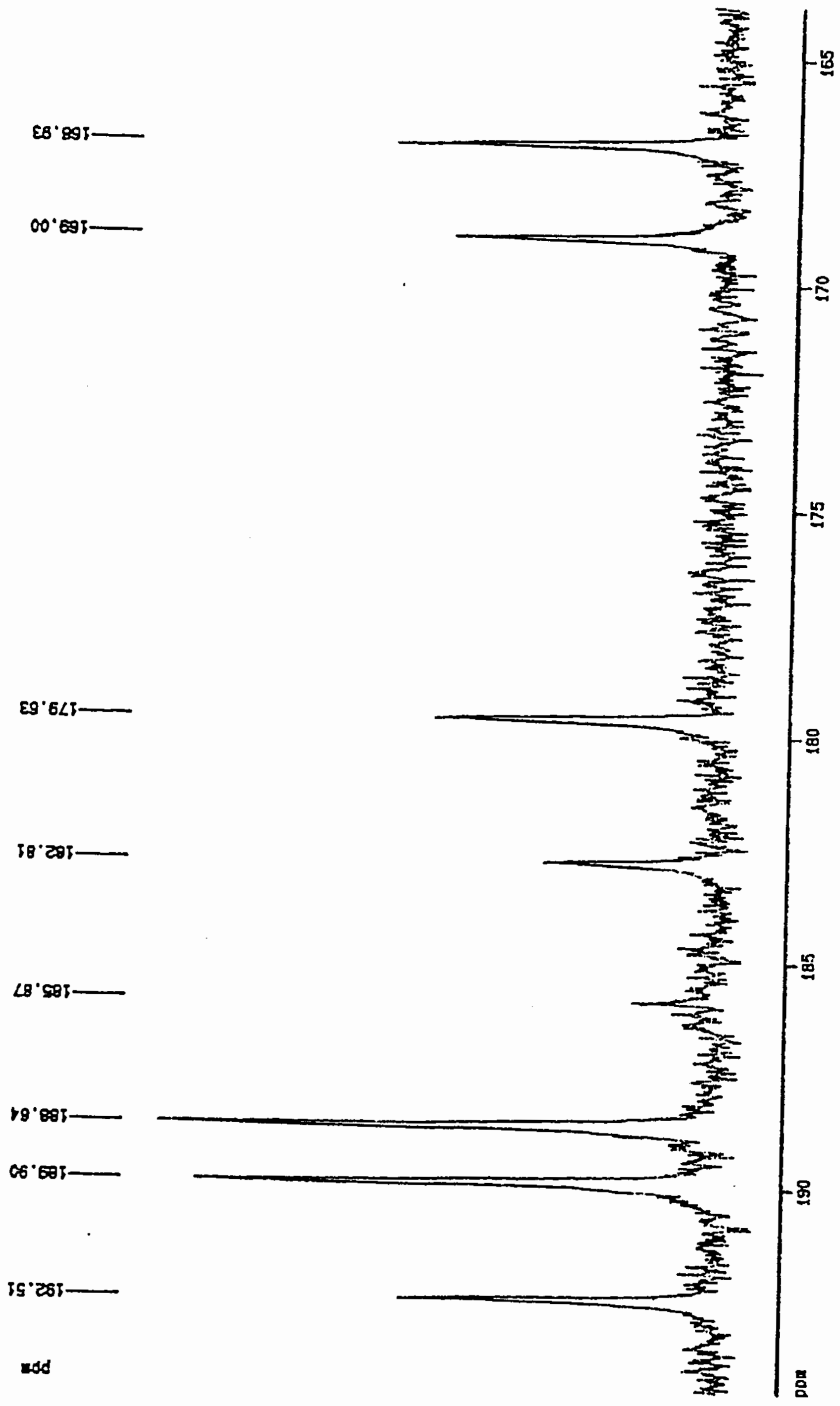


Figure 4.3. The ^{13}C NMR spectrum of $Os_5(CO)_{18}$

signals at δ 189.90 and 188.64 are attributed to all the other eight axial carbonyls since they are in the region associated with axial carbonyls of $Os(CO)_4$ groupings,[64,65] and both have an intensity of 4. The signals at δ 169.00 and 166.93 with intensity 2 remained relatively unchanged in terms of positions and intensities compared to that of $Os_5(CO)_{19}$ (Figure 4.1). They are therefore assigned to the equatorial carbonyls on the Os(4) and Os(5) atoms. Consequently, the signal of intensity 2 at δ 179.63 is attributed to CO(23) and CO(33). The remaining resonances of intensity 1 at δ 185.87 and 182.81 are due to CO(0) and CO(13).

After the Os atoms were refined anisotropically and all light atoms isotropically, the difference map revealed two extended peaks, one (2.3 (3) $eÅ^{-3}$) at 2.9 Å from Os(2) and Os(5), and the second (2.0 (3) $eÅ^{-3}$) at 2.8 Å from Os(3) and Os(4). A contour map (Figure 4.4) in the plane of the five osmium atoms was calculated, after the removal of all the equatorial carbonyls and a cycle of structure factor calculation, to demonstrate more clearly this phenomenon. The average e.s.d. (σ) of the map is 0.66 $eÅ^{-3}$ and the solid contour line are drawn at 1.1 $eÅ^{-3}$ (1.7σ) intervals. (The σ was calculated as $(1/V)x(\Sigma(|Fo|-|Fc|)^2)^{1/2}$; V was the volume of the unit cell; the summation was over all reflections within the limiting sphere.) The dashed lines in the map represent the zero level of electron density. Furthermore, there was greater thermal motion for all the equatorial carbonyl ligands compared to their axial counterparts; this can also be seen from Figure 4.4. Much effort has been put to interpret these results. Although no satisfactory solutions to these two peaks have been found, and there is no other convincing evidence to support the view that a minor isomer exists, these results are interpreted in terms of a possible small amount (<10%) of a second form of **16** with bridging carbonyls across these Os-Os bonds. In CH_2Cl_2, a solvent in which it is only sparingly soluble, **16** exhibits only a very weak infrared absorption in the region expected for a bridging CO ligand. In

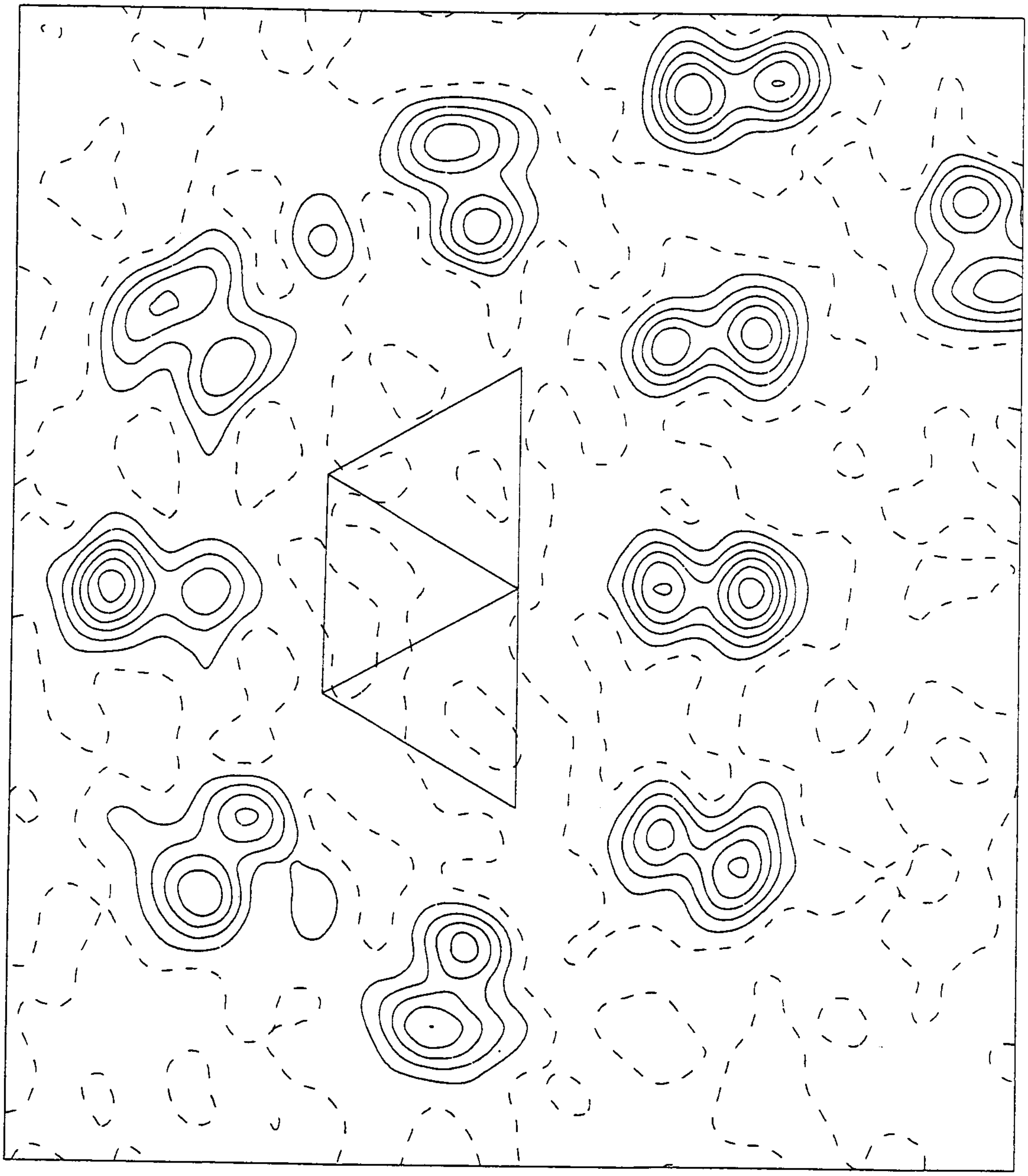


Figure 4.4. The contour map of $Os_5(CO)_{18}$ in the equatorial plane of the five metal atoms

this respect, it resembles its more famous relative $Fe_3(CO)_{12}$.[115]

$Os_5(CO)_{16}$ (17). Heating **16** in CH_2Cl_2 in a closed, evacuated flask above 70 °C caused its conversion to $Os_5(CO)_{16}$ with no evidence by infrared spectroscopy for $Os_5(CO)_{17}$ (eq 4.3).

$$Os_5(CO)_{18} \xrightarrow{\geq 70\ ^{\circ}C} \underset{\mathbf{17}}{Os_5(CO)_{16}} \tag{4.3}$$

It had previously been assumed that $Os_5(CO)_{18}$ would have a nonplanar metal geometry,[47b] but as we have shown it has a planar Os_5 arrangement. A planar structure would not have been predicted by PSEPT theory.[102]

While $Os_5(\mu\text{-}H)_2(CO)_{16}$ has an edge-bridged tetrahedral arrangement of metal atoms,[116] it does not necessarily follow that $Os_5(CO)_{17}$, if it could be prepared, will have the same arrangement. We have shown that $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ has a nonplanar butterfly configuration of osmium atoms whereas in $Os_4(CO)_{14}(PMe_3)$ the metal atoms are essentially planar.[62f]

Both $Os(CO)_5$[111] and $Os_4(CO)_{14}$[31] are prepared from $Os_3(CO)_{12}$. The reactions shown in eq. 4.1-4.3 therefore represent the systematic synthesis of the pentanuclear carbonyl clusters of osmium, and builds on our earlier studies on the synthesis of the tetranuclear congeners $Os_4(CO)_n(L)$ (n = 13, 14, 15).[32]

4.3 Experimental Section

In this chapter the preparations of $Os_4(CO)_{14}$[31] and $Os(CO)_5$[111] were carried out by literature procedures. The ^{13}CO-enriched compound $Os_5(CO)_{19}$ (**15**) was prepared from the reaction of $Os_5(CO)_{18}$ (**16**) with ^{13}CO (16 psi) at 50 °C for about a week. The pyrolysis of ^{13}CO-enriched (15) then gave ^{13}CO-enriched (16), a procedure similar to the preparation of **16** described below.

Preparation of $Os_5(CO)_{19}$ (15). A solution of $Os_4(CO)_{14}$ (94 mg, 0.082 mmol) in CH_2Cl_2 (30 mL) was placed in a round-bottom flask fitted with a Teflon valve. $Os(CO)_5$ in hexane was added to this flask (molar ratio $Os(CO)_5/Os_4(CO)_{14}$ = ~1:1). The vessel and solution were degassed with 3 freeze-pump-thaw cycles. The flask and contents were then heated in the dark at 40 °C for 1 day. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel (1.5 x 25 cm). Elution with CH_2Cl_2/hexane (1/4) afforded an orange-red band that yielded **15** (76 mg, 63 %) as red, air-stable solids: IR (CH_2Cl_2) ν(CO) 2100 (s), 2075 (s), 2042 (s, br), 2029 (sh), 2005 (m), 1982 (w), 1932 (w) cm^{-1}; (hexane) ν(CO) 2099 (m), 2075 (s), 2044 (s), 2036 (sh), 2031 (sh), 2007 (w) cm^{-1}. IR data in the literature:[47] (heptane) ν(CO) 2099 (m), 2073 (s), 2068 (w, sh), 2040 (s, br), 2035 (m, sh), 2027 (w, sh), 2000 (w, br), 1980 (w, br). ^{13}C NMR ($CDCl_3$, room temperature) δ 188.10 (2C), 182.90 (4C), 180.56 (4C), 173.08 (2C), 170.86 (1C), 170.49 (2C), 166.94 (2C), 166.18 (2C).

Preparation of $Os_5(CO)_{18}$ (16). A solution of **15** (51 mg, 0.034 mmol) in CH_2Cl_2 (60 mL) was placed in a round-bottom flask fitted with a Teflon valve. The vessel and solution were degassed with 3 freeze-pump-thaw cycles. The flask and contents were heated at 50-55 °C for 3 days and degassed at low temperature twice more during the reaction period to remove the released CO. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel (2.5 x 20 cm). Elution with CH_2Cl_2 afforded a red band that yielded **16** (39 mg, 59% yield). Recrystallisation from CH_2Cl_2 gave deep-red, air-stable crystals: IR (CH_2Cl_2) ν(CO) 2097 (s), 2075 (m), 2073 (m), 2046 (s), 2027 (m), 2002 (w), 1936 (w), 1832 (w, br); ^{13}C NMR (CD_2Cl_2/CH_2Cl_2, room temperature) δ 192.51 (2C), 189.90 (4C), 188.64 (4C), 185.87 (1C), 182.81 (1C), 179.63 (2C), 169.00 (2C), 166.93 (2C). Anal. Calcd for $C_{18}O_{18}Os_5$: C, 14.86. Found: C, 15.02. m/z (FAB) 1455.6 (vw, M^+).

Preparation of $Os_5(CO)_{16}$ (17). A solution of **16** in CH_2Cl_2 was placed in a round-bottom flask fitted with a Teflon valve. The vessel and solution were degassed with 3 freeze-pump-thaw cycles. The flask and contents were heated at 70 °C (or higher) for 1 day. The color of the solution changed from red to light amber. Only $Os_5(CO)_{16}$ was detected by IR spectroscopy: IR (CH_2Cl_2) ν(CO) 2065 (vs), 2051 (s), 2041 (s), 1991 (m, br) cm^{-1}; (cyclohexane) ν(CO) 2064 (vs), 2049 (s), 2042 (s), 1992 (m, br) cm^{-1}. IR data in the literature:[10] (cyclohexane) ν(CO) 2067 (vs), 2060 (m, sh), 2053 (s), 2045 (s), 1996 (m, br) cm^{-1}.

X-ray Analysis of 16. Several attempts to grow crystals of **16** suited for an X-ray diffraction study failed. In the end, the best samples we could get were in the form of extremely thin plates obtained by the very slow evaporation of a solution of **16** in CH_2Cl_2 at room temperature. Intensity data were collected with the use of an azimuth position, a method similar to that used for compound **11** (page 84). Two intensity standards, measured every hour of acquisition time, varied randomly (±2%) during the data collection process. Unit weights were employed in the refinement. The final least-squares refinement included coordinates for all atoms, anisotropic thermal parameters for the osmium atoms, and isotropic thermal parameters for all oxygen and carbon atoms. Crystallographic data are summarized in Table 4.2. Final fractional coordinates for the atoms of **16** are given in Table 4.3.

Table 4.2. Summary of Crystal Data and Details of Intensity Collection for **16**.

formula	$C_{18}O_{18}Os_5$
fw	1455.2
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	8.866 (2)
b, Å	10.311 (2)
c, Å	15.527 (3)
α, deg	73.71 (1)
β, deg	83.99 (2)
γ, deg	71.06 (1)
V, $Å^3$	1288.4
2θ range of unit cell, deg	26-38
Z	2
D_{calc}, g cm^{-3}	3.751
μ(Mo, K_α), cm^{-1}	246.78
cryst size, mm	0.20x0.18x0.007
transmission coeff range[a]	0.10-0.84
scan method	ω-2θ
scan range (2θ), deg	3-46
scan width (ω), deg	1.0 + 0.35tanθ
scan rate (ω), deg min^{-1}	0.92-5.5
No. of unique rflns	3572
No. of obsd rflns[b]	2474
No. of variables	191
R[c]	0.039
Rw[d]	0.039
G.O.F.[e]	0.49
extinction (g)	0.102(16)

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[a] Absorption corrections. [b] $Io > 2.5(Io)$. [c] $R = \sum||Fo| - |Fc||/\sum|Fo|$.
[d] $Rw = (\sum w(|Fo| - |Fc|)^2/\sum w|Fo|^2)^{1/2}$, $w = [\sigma^2(Fo) + k(Fo)^2]^{-1}$.
[e] $GOF = (\sum w(|Fo| - |Fc|)^2/(\text{degrees of freedom}))^{1/2}$.

Table 4.3. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for $Os_5(CO)_{18}$ **(16)**

Atom	x/a	y/b	z/c	U(iso)
Os(1)	9266 (1)	4934.7 (9)	2174.2 (6)	272
Os(2)	5940 (1)	6407.2 (9)	2302.7 (6)	326
Os(3)	7152 (1)	3463.6 (9)	3187.0 (6)	329
Os(4)	10527 (1)	2000.5 (9)	3079.1 (6)	317
Os(5)	8014 (1)	7910.4 (9)	1287.4 (6)	340
O(0)	3582 (21)	4796 (18)	3385 (12)	523 (45)
O(11)	9807 (18)	5867 (16)	3798 (11)	450 (40)
O(12)	8764 (17)	4178 (15)	472 (10)	376 (37)
O(13)	12635 (21)	4944 (17)	1497 (11)	580 (45)
O(21)	6008 (21)	7365 (18)	4014 (12)	593 (48)
O(22)	5207 (19)	5938 (17)	533 (11)	494 (42)
O(23)	2752 (34)	8667 (29)	2105 (18)	837 (79)
O(31)	7630 (21)	4128 (18)	4934 (12)	582 (48)
O(32)	6466 (21)	2621 (18)	1548 (12)	567 (46)
O(33)	6574 (26)	812 (23)	4372 (15)	730 (61)
O(41)	11329 (22)	2863 (19)	4673 (13)	616 (48)
O(42)	9908 (19)	1131 (16)	1451 (11)	465 (40)
O(43)	14056 (25)	1259 (22)	2600 (14)	676 (57)
O(44)	10756 (28)	-948 (25)	4275 (16)	839 (69)
O(51)	8324 (23)	8931 (20)	2911 (13)	699 (54)
O(52)	7635 (19)	7176 (17)	-445 (11)	495 (42)
O(53)	11140 (21)	8438 (18)	520 (12)	673 (48)
O(54)	5769 (27)	10844 (24)	480 (15)	814 (64)
C(0)	4920 (32)	4747 (27)	3147 (17)	496 (66)
C(11)	9556 (25)	5516 (22)	3187 (14)	340 (52)
C(12)	8892 (23)	4451 (20)	1119 (13)	245 (45)
C(13)	11349 (28)	4970 (23)	1753 (15)	451 (57)
C(21)	6134 (28)	6982 (24)	3359 (16)	436 (59)
C(22)	5526 (25)	6068 (21)	1182 (14)	318 (49)
C(23)	3978 (39)	7855 (34)	2133 (21)	497 (80)
C(31)	7497 (27)	3892 (23)	4247 (15)	394 (56)
C(32)	6757 (26)	2949 (22)	2137 (15)	353 (52)
C(33)	6767 (32)	1820 (29)	3918 (18)	491 (69)
C(41)	10942 (28)	2606 (24)	4105 (16)	418 (57)
C(42)	10128 (26)	1518 (23)	2051 (15)	381 (54)
C(43)	12678 (33)	1608 (28)	2717 (18)	481 (68)

Table 4.3 cont'd

C(44)	10690 (29)	157 (26)	3815 (16)	401 (61)
C(51)	8255 (29)	8471 (25)	2338 (17)	465 (61)
C(52)	7745 (24)	7396 (21)	200 (14)	290 (48)
C(53)	9972 (30)	8274 (25)	799 (16)	528 (62)
C(54)	6591 (29)	9715 (26)	802 (16)	411 (58)

Chapter 5. Derivatives of $Os_5(CO)_n$ (n = 19, 18, 16)

5.1 Introduction

A fundamental aspect of metal carbonyl cluster chemistry is the structure, or structures, adopted by a cluster of a given nuclearity and electron count.[2,3,6,55] Another question of importance is the isomer or isomers that are observed when a carbonyl ligand in a metal carbonyl cluster is replaced by some other two-electron donor ligand, such as phosphine and isocyanide.[71b,117]

Organophosphine (PR_3)[118] and isocyanide (CNR)[119,120] ligands are ubiquitous ligands in metal carbonyl chemistry. Although both classes of ligands are believed to be better σ-donors and poorer π-acceptors than carbonyl itself,[76a,121,122] they have different site preferences in binuclear and trinuclear metal carbonyl complexes. In binuclear compounds phosphines are usually, but not always, found in the sites trans to the metal-metal bond (the axial sites).[65c,123] Isocyanide ligands, on the other hand, invariably adopt sites that are cis to the metal-metal bonds (i.e., in radial or equatorial sites).[65b,124] Similarly, in trinuclear metal carbonyl clusters phosphines occupy positions trans to the metal-metal bonds,[62a,125] whereas isocyanides occupy positions cis to the metal-metal bonds.[67,126] The recent report of the structure of $Os_3(CO)_{10}(CNPr)(PPh_3)$ illustrates the latter observations.[127]

This difference in site preference can undoubtedly be attributed to the different steric requirements of the two classes of ligands. The sterically-undemanding isocyanide ligands[128] can enter electronically-preferred coordination sites that are sterically inaccesible to bulky phosphine ligands.[76b,129]

There are a significantly larger number of chemically-different coordination sites in the pentanuclear binary carbonyls of osmium (i.e.,

$Os_5(CO)_{19}$,[47] $Os_5(CO)_{18}$ (Chapter 4) and $Os_5(CO)_{16}$[10,46]) than the two sites in $Os_3(CO)_{12}$.[36] It was therefore of interest to investigate the site preference of the PMe_3 and $CNBu^t$ ligands in clusters of formula $Os_5(CO)_n(L)$ (L = PMe_3, $CNBu^t$; n = 18, 17, 15).

In this chapter further studies, on the systematic synthesis of osmium carbonyl clusters, namely, the preparation of $Os_5(CO)_n(PMe_3)$ (n = 18; **18**; n = 17; **19**), $Os_5(CO)_{15}(L)$ (L = *ax*-PMe_3 on an apical osmium atom; **20**; L = *eq*-PMe_3 on an equatorial osmium atom; **21**), and $Os_5(CO)_n(CNBu^t)$ (n = 18; **22**; n = 17; **23**; n = 15; **24**) are discussed. $Os_5(CO)_{15}(PMe_3)$ has been isolated in two isomeric forms (i.e., **20** and **21**). The structures of **18**·CH_2Cl_2, **19-22** and **24** are described.

5.2 Results and Discussion

5.2.1 $Os_5(CO)_n(PMe_3)$ (n = 18, 17, 15)

$Os_5(CO)_{18}(PMe_3)$ (18). Addition of $Os(CO)_4(PMe_3)$[130] to $Os_4(CO)_{14}$ in CH_2Cl_2 at room temperature afforded $Os_5(CO)_{18}(PMe_3)$ (**18**) in good yield after 24 h (eq 5.1). The product was isolated as red, air-stable crystals.

$$Os_4(CO)_{14} + Os(CO)_4(PMe_3) \longrightarrow \underset{\textbf{18}}{Os_5(CO)_{18}(PMe_3)} \qquad (5.1)$$

We have exploited the nucleophilic properties of $Os(CO)_4(L)$ (L = two-electron donor ligand) compounds in the synthesis of a number of novel bimetallic and cluster complexes.[29,33,65b-c] Nevertheless, the ease with which the reaction depicted in eq 5.1 occurs is surprising given that the fourteen carbonyl ligands in $Os_4(CO)_{14}$ are expected to sterically hinder access to the osmium atoms. Steric crowding between the carbonyl ligands in such clusters is believed to be large.[131]

The structure* of **18** (Figure 5.1) has a bow-tie arrangement of osmium atoms and thus resembles the parent binary carbonyl $Os_5(CO)_{19}$.[47] The Os-Os lengths (Table 5.1) from the four outer osmium atoms in **18** to the central osmium atom are 2.941 (1), 2.938 (1), 2.941 (1) and 2.903 (1) Å; these are somewhat long for Os-Os single bonds (2.88 Å is the average Os-Os distance in $Os_3(CO)_{12}$).[36] On the other hand, the two Os-Os vectors that involve only peripheral osmium atoms are shorter than 2.88 Å (2.859 (1), 2.854 (1) Å). A similar pattern is observed for $Os_5(CO)_{19}$.[47] Hoffmann has pointed out that the latter cluster is an isolobal analogue to $Os(CO)_3(\eta^2\text{-}C_2H_4)_2$.[132] The Os-Os bond lengths in these bow-tie clusters are consistent with this view.

The Os-Os bond trans to the PMe_3 ligand is significantly longer than the corresponding bond trans to a carbonyl ligand (2.941 (1) versus 2.903 (1) Å, respectively). It is usually found in osmium carbonyl cluster compounds that phosphorus-donor ligands cause a lengthening of the trans Os-Os bond.[62a,125e,133] This lengthening is observed in the other clusters reported in this thesis (except in the case of $Os_5(CO)_{17}(PMe_3)$ (**19**) in which the Os-Os bond (2.896 (2) Å) trans to the phosphine ligand was marginally shorter than the cis Os-Os bond (2.904 (2) Å).

The trimethylphosphine ligand in **18** occupies one of the sterically least hindered sites in the molecule, namely, an equatorial site on an outer osmium atom. It is invariably found in trinuclear carbonyl clusters of the group 8 elements that phosphorus ligands occupy the less hindered equatorial sites rather than axial positions.[62a,125,133]

The NMR properties of **18** are consistent with the presence of two isomers

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* Initial determination by Mr. C.-Y. Lu and Dr. V. J. Johnston.

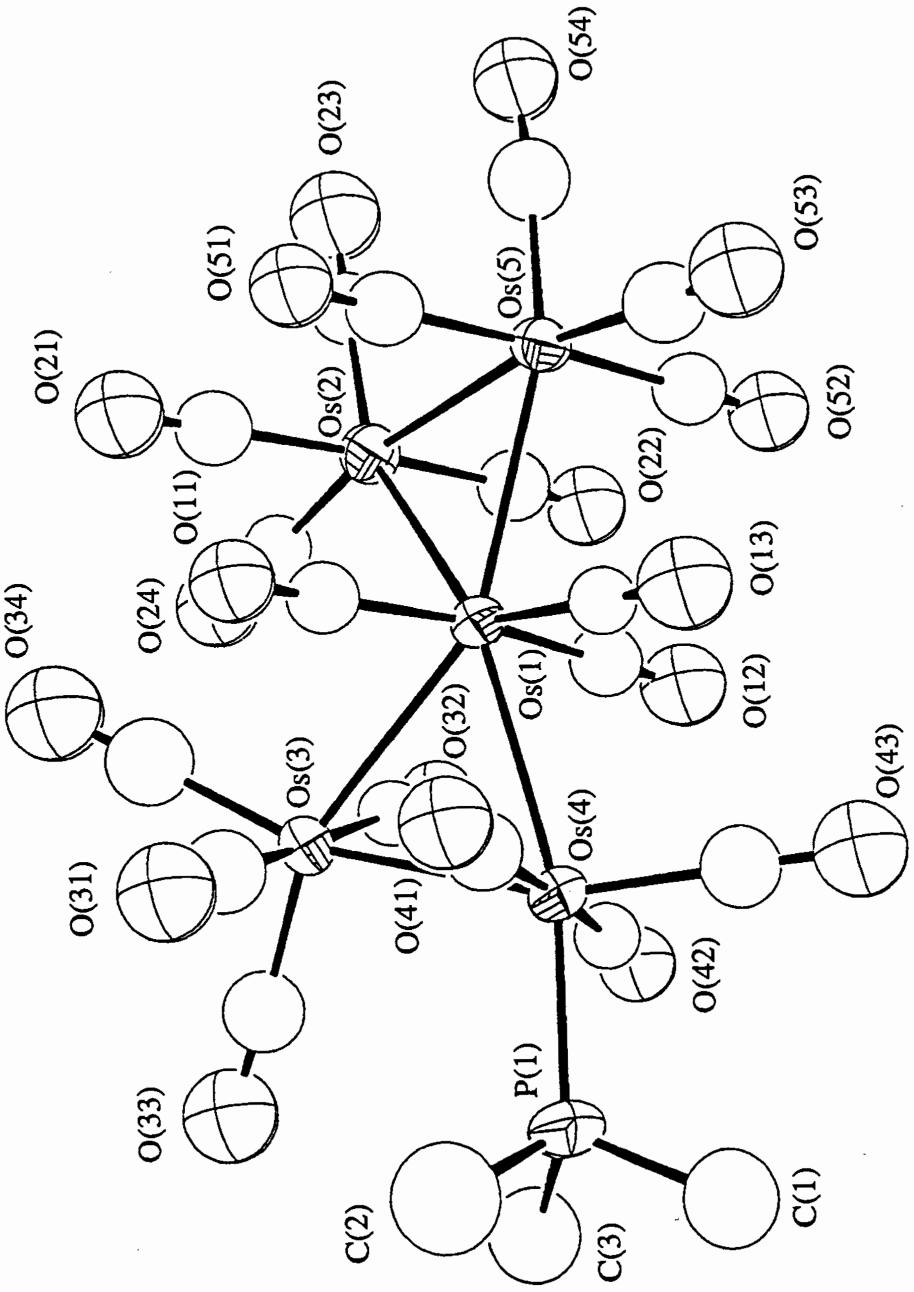

Figure 5.1. The molecular structure of $Os_5(CO)_{18}(PMe_3)$ **(18)**

Table 5.1. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{18}(PMe_3)\cdot CH_2Cl_2$ (**18**$\cdot CH_2Cl_2$)

Bond Lengths

Os(1) - Os(2)	2.941 (1)	Os(3) - Os(4)	2.854 (1)
Os(1) - Os(3)	2.938 (1)	Os(4) - P(1)	2.327 (6)
Os(1) - Os(4)	2.941 (1)		
Os(1) - Os(5)	2.903 (1)	(Os-CO)	1.84 (3) - 2.01 (3)
Os(2) - Os(5)	2.859 (1)	(C-O)	1.08 (3) - 1.21 (3)

Bond Angles

Os(4) - Os(1) - Os(3)	58.08 (3)	C(11) - Os(1) - Os(2)	92.3 (7)
Os(5) - Os(1) - Os(2)	58.57 (3)	C(11) - Os(1) - Os(3)	74.9 (7)
Os(5) - Os(2) - Os(1)	60.06 (3)	C(11) - Os(1) - Os(4)	99.1 (7)
Os(4) - Os(3) - Os(1)	61.03 (3)	C(11) - Os(1) - Os(5)	93.2 (7)
Os(3) - Os(1) - Os(2)	98.35 (4)	C(12) - Os(1) - C(11)	171.7 (10)
Os(5) - Os(1) - Os(4)	147.70 (4)	C(13) - Os(1) - Os(4)	74.1 (7)
P(1) - Os(4) - Os(1)	166.2 (2)	C(13) - Os(1) - Os(5)	75.7 (7)

in solution. Both the ^1H and $^{31}P\{^1H\}$ NMR spectra of **18** in $CDCl_3$ (Figure 5.2) exhibit two resonances (the ^1H NMR resonances are doublets due to P-H coupling). We believe the two isomers are the one found in the solid state plus the isomer with the phosphine ligand either in the other equatorial site on Os(4) (i.e., the position occupied by CO(43), Figure 5.1) or in an equatorial site on Os(3) (i.e., CO(33) or CO(34), Figure 5.1). The former type of isomerism, in which the second isomer has the phosphine ligand in the position of CO(43), has been observed previously for clusters of the type $(OC)_5M[Os(CO)_3(PR_3)]_2$ (M = Cr, Mo, W)[28] and $Os_3(CO)_{12-x}(PR_3)_x$ (x = 2, 4).[64d,79a] Isomerism of this nature cannot be

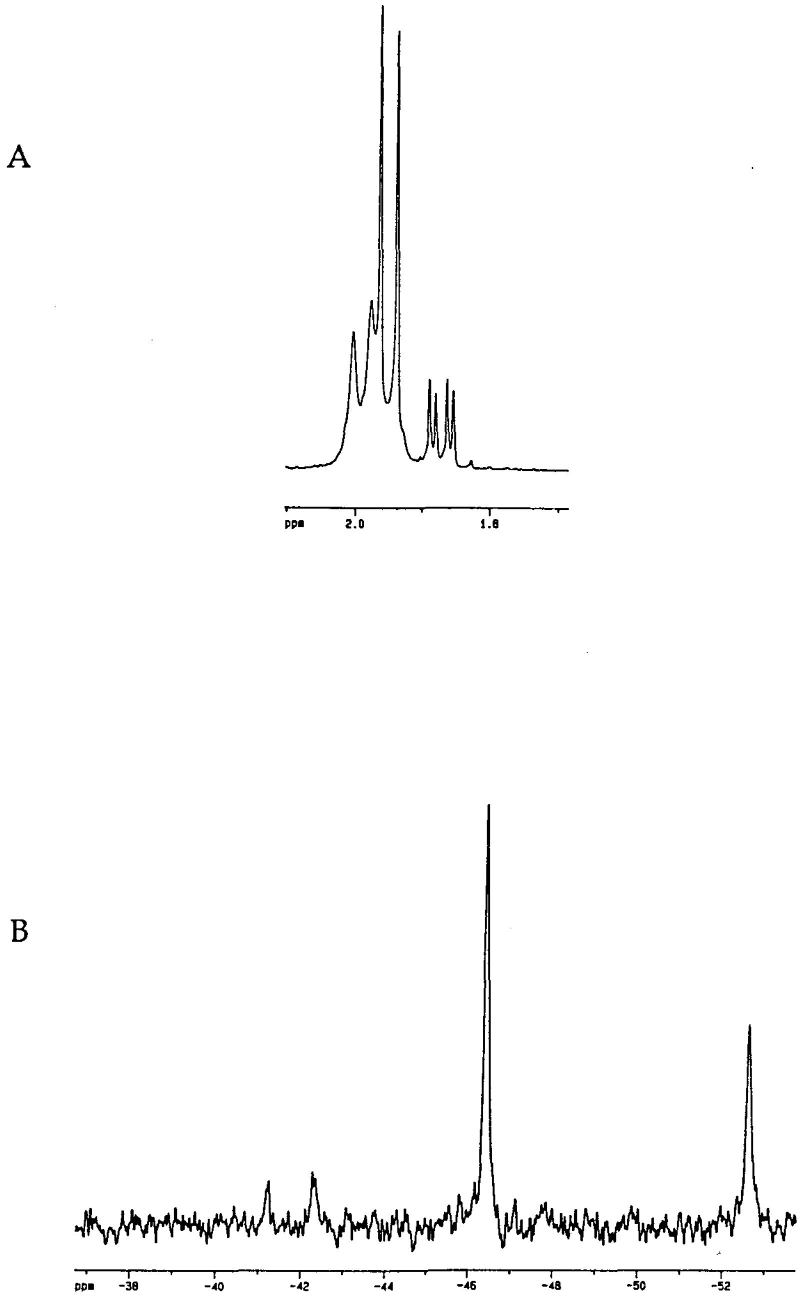

Figure 5.2. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of $(CO)_{18}(PMe_3)$ **(18)** (with a small amount of $Os_5(CO)_{17}(PMe_3)$ **(19)**)
^{1}H -- (A) $^{31}P\{^{1}H\}$ -- (B)

distinguished for the monosubstituted $Os_3(CO)_{11}(PR_3)$ clusters. The latter type of isomerism, in which the second isomer has the phosphine ligand in an equatorial site on Os(3), could result from slow rotation of the $Os_2(CO)_7(PMe_3)$ moiety about the central osmium atom, as discussed above. It cannot, however, be ruled out that the second isomer of the latter type of isomerism may have been formed directly from the reaction of $Os_4(CO)_{14}$ with $Os(CO)_5(PMe_3)$.

$Os_5(CO)_{17}(PMe_3)$ (19). Careful pyrolysis of **18** at 40-45 °C (in CH_2Cl_2) in an evacuated sealed flask gave **19** in 60% yield after 2 days (eq 5.2). Cluster **19** is a dark red, air-stable, crystalline solid.

$$\mathbf{18} \xrightarrow{43\ ^\circ C} \underset{\mathbf{19}}{Os_5(CO)_{17}(PMe_3)} + CO \qquad (5.2)$$

After much effort, crystals suitable for the X-ray structure determination were obtained by the slow evaporation of solvent from a solution of **19** in chlorobenzene. The structure of **19** (Figure 5.3) reveals it to have a raft (bi-edge-bridged triangular) arrangement of osmium atoms. The Os_5 unit is essentially planar: the dihedral angle between the Os(1)Os(2)Os(5) and Os(1)Os(3)Os(4) planes is 0.72 (4)°. $Os_5(CO)_{18}$ and **19** are believed to be the first pentaosmium clusters with a planar raft Os_5 skeleton. The mixed metal cluster $Os_3Pt_2(CO)_{14}$[113] and the hexaosmium cluster $Os_6(CO)_{17}[P(OMe)_3]_4$[112] also have raft-like skeletons.

An unusual feature of both the structures of $Os_5(CO)_{18}$ and **19** is the presence of a bridging carbonyl ligand (such ligands are uncommon in osmium carbonyl cluster compounds).[39] However, whereas the bridge is somewhat asymmetric in $Os_5(CO)_{18}$, it is symmetric in **19** (Table 5.2). The infrared spectrum

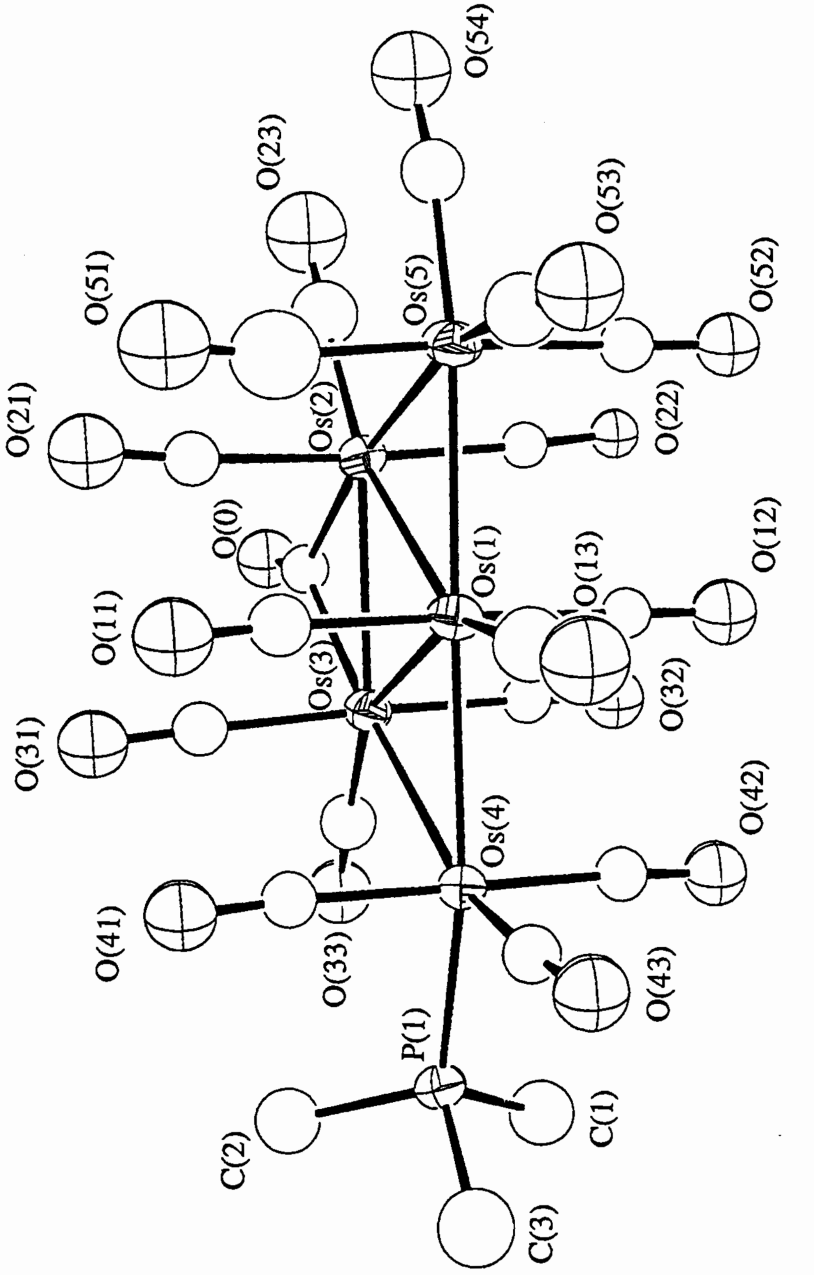

Figure 5.3. The molecular structure of $Os_5(CO)_{17}(PMe_3)$ **(19)**

Table 5.2. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{17}(PMe_3)$ (**19**)

Bond Lengths

Os(1) - Os(2)	2.862 (2)	Os(4) - P(1)	2.337 (6)
Os(1) - Os(3)	2.857 (2)	Os(2) - C(0)	2.12 (2)
Os(1) - Os(4)	2.896 (2)	Os(3) - C(0)	2.11 (2)
Os(1) - Os(5)	2.843 (2)	O(0) - C(0)	1.17 (3)
Os(2) - Os(3)	2.827 (2)		
Os(2) - Os(5)	2.876 (2)	(Os-CO)	1.84 (3) - 1.95 (3)[a]
Os(3) - Os(4)	2.904 (2)	(C-O)	1.12 (4) - 1.20 (4)[a]

Bond Angles

Os(3) - Os(1) - Os(2)	59.26 (4)	P(1) - Os(4) - Os(3)	109.5 (2)
Os(4) - Os(1) - Os(3)	60.62 (5)	C(12) - Os(1) - C(11)	177.0 (11)
Os(5) - Os(1) - Os(2)	60.54 (5)	C(22) - Os(2) - C(21)	176.8 (10)
Os(3) - Os(2) - Os(1)	60.30 (4)	C(32) - Os(3) - C(31)	173.6 (10)
Os(5) - Os(2) - Os(1)	59.41 (4)	C(42) - Os(4) - C(41)	176.7 (10)
Os(4) - Os(3) - Os(1)	60.35 (4)	C(52) - Os(5) - C(51)	175.1 (13)
Os(5) - Os(1) - Os(4)	179.19 (6)	O(0) - C(0) - Os(2)	138.9 (19)
Os(3) - C(0) - Os(2)	83.7 (9)	O(0) - C(0) - Os(3)	137.3 (19)
P(1) - Os(4) - Os(1)	168.2 (2)		

[a] terminal carbonyls.

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of **19** in CH_2Cl_2 exhibits a broad, weak absorption at 1811 cm^{-1} consistent with the presence of a bridging carbonyl in solution as well as in the solid state.

The PMe_3 ligand in **19** is in a site that is expected from the position of this ligand in the precursor cluster $Os_5(CO)_{18}(PMe_3)$ (**18**), namely, in an equatorial site on one of the outer osmium atoms. As found for **18**, the Os-Os length (Os(1)-Os(4) = 2.896 (1) Å) trans to the phosphine substituent in **19** is significantly longer than the corresponding bond that is trans to a carbonyl ligand (Os(1)-Os(5) = 2.843 (2) Å). The Os-Os bonds trans to the bridging carbonyl are also longer than the Os-Os bonds within the central Os_3 triangle (2.876 (2), 2.904 (2) Å versus 2.827 (2), 2.857 (2), 2.862 (2) Å, respectively).

The ^1H and $^{31}P\{^1H\}$ NMR spectra of $Os_5(CO)_{17}(PMe_3)$ show the presence of two isomers in solution (Figure 5.4). They are believed to be the one found in the solid state plus the isomer with the phosphine ligand in the other equatorial position (i.e., CO(43), Figure 5.3). This is consistent with the evidence that two isomers were observed for the compound $Os_5(CO)_{18}(PMe_3)$ (18) in solution.

$Os_5(CO)_{15}$(*ax*-PMe_3) (20). Careful pyrolysis of **19** at ~63 °C in CH_2Cl_2 under vacuum for 2 days gave $Os_5(CO)_{15}(PMe_3)$ (eq 5.3).

$$\mathbf{19} \xrightarrow{\Delta} \underset{\mathbf{20}}{Os_5(CO)_{15}(\textit{ax}\text{-}PMe_3)} + \underset{\mathbf{21}}{Os_5(CO)_{15}(\textit{eq}\text{-}PMe_3)} \qquad (5.3)$$

There was no evidence by infrared spectroscopy for $Os_5(CO)_{16}(PMe_3)$. This is similar to the pyrolysis of $Os_5(CO)_{18}$ to yield $Os_5(CO)_{16}$ where there was no evidence for $Os_5(CO)_{17}$.[51] The $Os_5(CO)_{15}(PMe_3)$ obtained by the method shown in eq 5.3 consisted of a mixture of isomers. The major isomer was purified by chromatography and recrystallization; it was obtained as a deep red, air-stable crystalline solid. (The isolation and purification of the second isomer is described on page 122.)

As found for the parent binary carbonyl, $Os_5(CO)_{16}$,[46] the molecular structure of **20** (Figure 5.5) shows it to contain a somewhat irregular trigonal bipyramidal arrangement of osmium atoms. As also observed for $Os_5(CO)_{16}$,

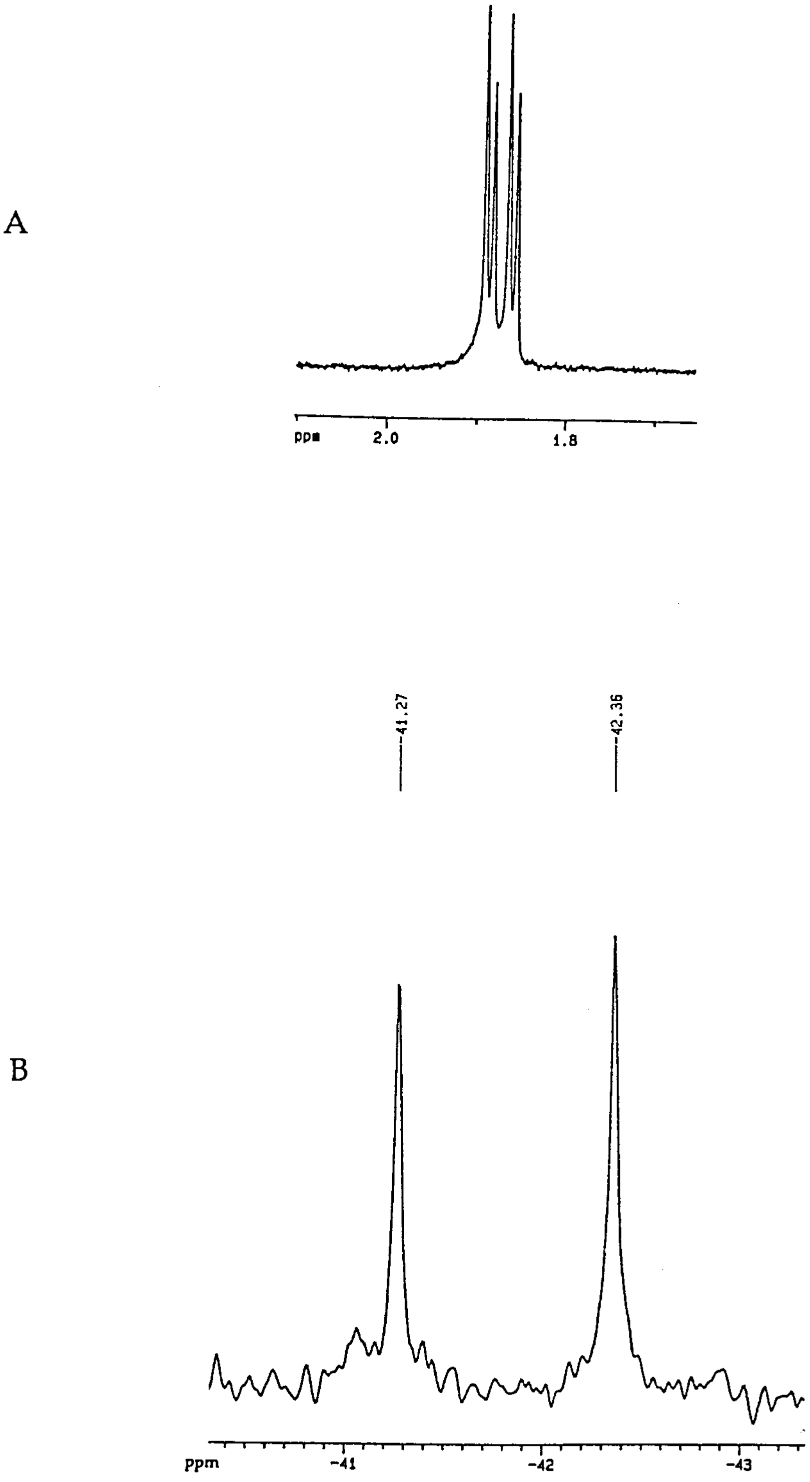

Figure 5.4. ^{1}H and ^{31}P{^{1}H} NMR spectra of $Os_5(CO)_{17}(PMe_3)$ (19)
^{1}H -- (A) ^{31}P{^{1}H} -- (B)

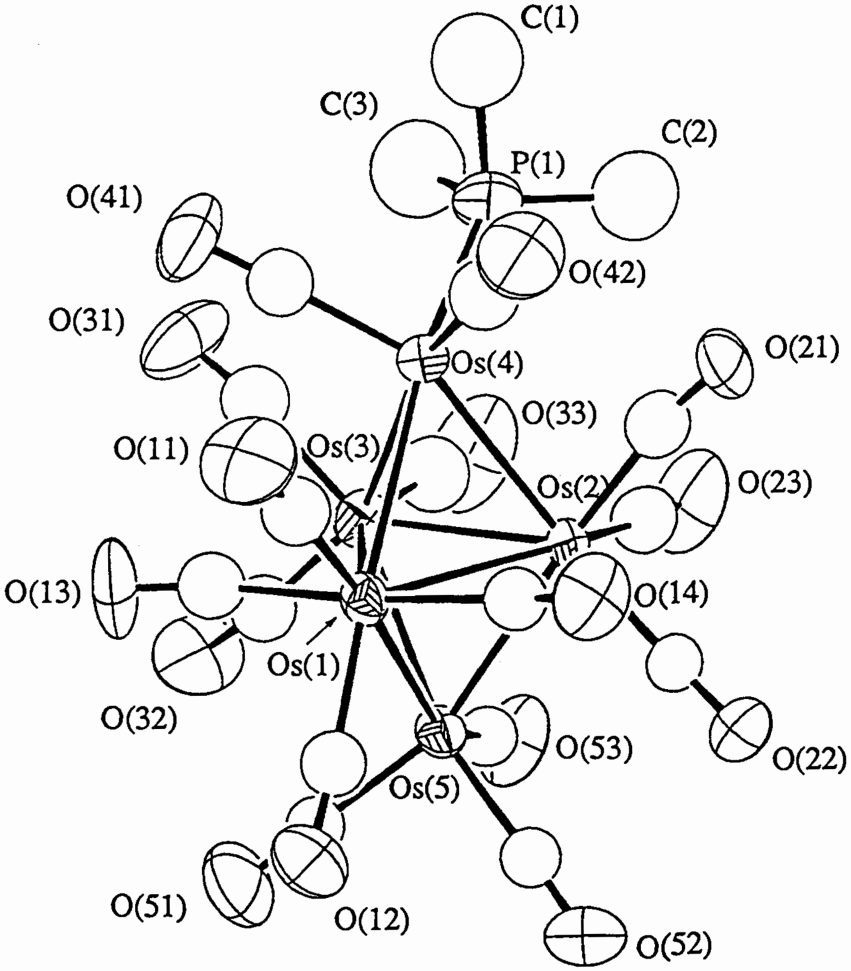

Figure 5.5. The molecular structure of $Os_5(CO)_{15}$(*ax*-PMe_3) **(20)**

Table 5.3. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}$(*ax*-PMe_3) (**20**)

Bond Lengths

Os(1) - Os(2)	2.854 (1)	Os(3) - Os(5)	2.769 (1)
Os(1) - Os(3)	2.869 (1)	Os(4) - P(1)	2.318 (4)
Os(1) - Os(4)	2.919 (1)	Os(1) - C(13)	1.97 (2)
Os(1) - Os(5)	2.896 (1)	Os(1) - C(14)	1.96 (2)
Os(2) - Os(3)	2.773 (1)	Os(2) - C(14)	2.63 (2)
Os(2) - Os(4)	2.823 (1)	Os(3) - C(13)	2.63 (2)
Os(2) - Os(5)	2.775 (1)	(Os-CO)	1.87 (2) - 1.93 (2)[a]
Os(3) - Os(4)	2.785 (1)	(C-O)	1.13 (3) - 1.20 (3)[a]

Bond Angles

Os(3) - Os(1) - Os(2)	57.97 (2)	C(12) - Os(1) - Os(5)	73.9 (5)
Os(3) - Os(2) - Os(1)	61.28 (2)	C(12) - Os(1) - C(11)	102.8 (7)
Os(5) - Os(1) - Os(4)	104.88 (3)	C(13) - Os(1) - Os(3)	62.6 (5)
Os(5) - Os(2) - Os(4)	110.89 (3)	O(13) - C(13) - Os(1)	163.3 (16)
Os(5) - Os(3) - Os(4)	112.24 (3)	C(14) - Os(1) - Os(2)	63.0 (4)
P(1) - Os(4) - Os(2)	107.7 (1)	C(14) - Os(1) - C(13)	173.5 (7)
P(1) - Os(4) - Os(3)	107.7 (1)	O(14) - C(14) - Os(1)	163.1 (14)
C(11) - Os(1) - Os(4)	78.7 (5)		

[a] terminal carbonyls.

---

there is an $Os(CO)_4$ grouping in the equatorial plane of the molecule, and two of the carbonyls of this group have a semibridging interaction (Table 5.3) with the adjacent osmium atoms in the equatorial plane (for **20**: Os(2)-C(13) = 2.63 (2) Å, Os(3)-C(12) = 2.63 (2) Å). In $Os_5(CO)_{16}$ there are two additional weaker interactions ($Os\cdots C$ = 2.89 (4) Å) that were not observed in **20** (between Os(4) and CO(21), and Os(5) and CO(32)).[46]

The two longest Os-Os distances in **20** (2.919 (1), 2.896 (1) Å) link the osmium atom of the $Os(CO)_4$ unit to the two apical osmium atoms; the longest Os-Os bond is in the pseudo-trans position to the phosphine ligand. The third and fourth longest Os-Os lengths in **20** (2.869 (1), 2.854 (1) Å) are from the osmium atom of the $Os(CO)_4$ unit to the osmium atoms in the equatorial plane. The remaining Os-Os distances in **20** range from 2.823 (1) – 2.769 (1) Å and as such are significantly shorter than 2.88 Å, the average Os-Os length in $Os_3(CO)_{12}$.[36] A similar pattern in the lengths of the Os-Os bonds was observed for $Os_5(CO)_{16}$.[46]

The trimethylphosphine ligand in **20** occupies the site on one of the axial osmium atoms that is also anti to the $Os(CO)_4$ grouping, that is, the least sterically-hindered site in the molecule. This is as expected from observations on trinuclear phosphine-substituted clusters,[125] and the position of the phosphine ligand in the precursor **19**. In other words, it might be expected that **20** would be both the kinetic and thermodynamic product from the thermolysis of **19**. A surprising aspect of this study was the isolation of a second isomer of $Os_5(CO)_{15}(PMe_3)$ of comparable thermodynamic stability to **20**.

$Os_5(CO)_{15}$(*eq*-PMe_3) (21). When the pyrolysis of **19** in CH_2Cl_2/hexane was carried out in a sealed evacuated flask at ~110 °C the second isomer of $Os_5(CO)_{15}(PMe_3)$ (**21**) became the predominant product. It was isolated pure following chromatography and recrystallization and like **20** is an air-stable, red crystalline solid.

The X-ray structure determination of **21** (Figure 5.6) reveals a trigonal bipyramidal arrangement of osmium atoms similar to that of **20**. The trimethylphosphine ligand is coordinated to the equatorial osmium atom in the

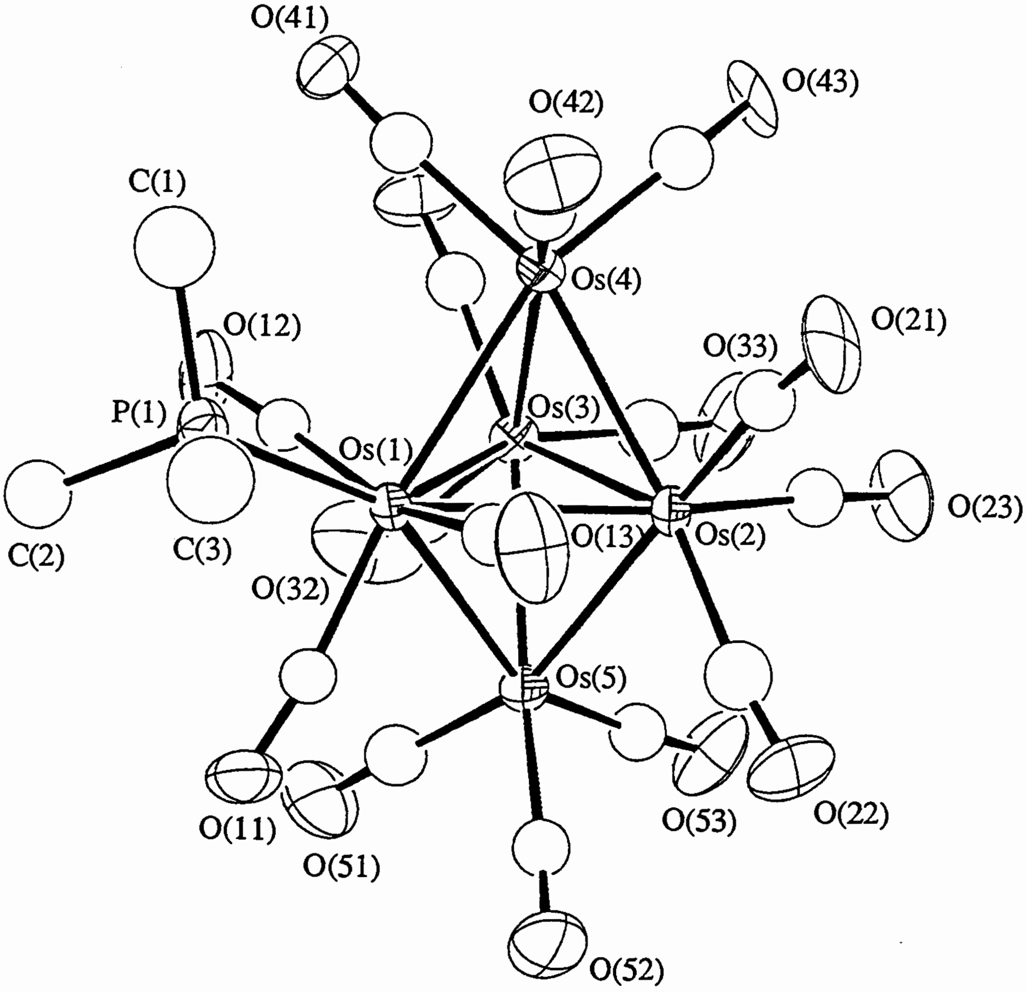

Figure 5.6. The Molecular Structure of $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**)

Table 5.4. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}(\textit{eq}\text{-}PMe_3)$ **(21)**

Bond Lengths

Os(1) - Os(2)	2.860 (1)	Os(1) - P(1)	2.396 (4)
Os(1) - Os(3)	2.867 (1)	Os(2) - C(13)	2.68 (2)
Os(1) - Os(4)	2.853 (1)	Os(3) - C(12)	2.65 (2)
Os(1) - Os(5)	2.908 (1)	Os(4) - C(21)	2.90 (2)
Os(2) - Os(3)	2.781 (1)	Os(4) - C(31)	2.91 (2)
Os(2) - Os(4)	2.793 (1)	Os(5) - C(11)	2.79 (2)
Os(2) - Os(5)	2.770 (1)		
Os(3) - Os(4)	2.778 (1)	(Os-CO)	1.85 (2) - 1.98 (2)
Os(3) - Os(5)	2.755 (1)	(C-O)	1.08 (2) - 1.20 (2)

Bond Angles

Os(3) - Os(1) - Os(2)	58.10 (2)	C(11) - Os(1) - P(1)	87.2 (5)
Os(3) - Os(2) - Os(1)	61.08 (2)	C(12) - Os(1) - Os(3)	63.5 (5)
Os(5) - Os(1) - Os(4)	104.76 (3)	C(13) - Os(1) - Os(2)	64.7 (5)
Os(5) - Os(2) - Os(4)	110.25 (3)	C(13) - Os(1) - C(12)	160.5 (7)
Os(5) - Os(3) - Os(4)	111.13 (3)	O(11) - C(11) - Os(1)	168.5 (14)
P(1) - Os(1) - Os(4)	100.7 (1)	O(12) - C(12) - Os(1)	166.0 (14)
C(11) - Os(1) - Os(5)	67.3 (5)	O(13) - C(13) - Os(1)	166.6 (16)

---

cluster that has four ligands attached to it and occupies a pseudo-axial position. This molecular structure of **21** is similar to that of $Os_5(CO)_{15}\{P(OMe)_3\}$ (**25**, $P(OMe)_3$ in the pseudo-axial position)[50] in terms of the arrangement of metal atoms and the position of the phosphorus atom. The variation of the Os-Os lengths in **21** (Table 5.4) is also similar in pattern to that in **20** and **25**, with the exception that one of the Os-Os vectors from an apical Os atom to the Os atom of the $Os(CO)_3(PMe_3)$ grouping is marginally shorter than the two equatorial Os-Os bonds that involve the Os atom of the $Os(CO)_4(PMe_3)$ unit. As expected, the longest Os-Os distance is that which is approximately trans to the PMe_3 ligand. Like the parent compound $Os_5(CO)_{16}$ and **20**, there are weak semi-bridging carbonyls present in **21**.

Interestingly, the trimethylphosphine ligand is coordinated to the one osmium atom in the cluster that has four ligands attached to it. Furthermore, this osmium atom occupies an equatorial position within the trigonal bipyramidal metal framework. The bulky phosphine ligand, therefore, is in a site that is arguably the most sterically crowded site in the molecule. Consistent with this view is that the Os-P bond length in **21** (2.396 (4) Å) is significantly longer than that in **18**, **19** or **20** (2.327 (6), 2.337 (6), and 2.318 (4) Å, respectively). A reason for the site preference, that is apparently electronic in origin, is presented in the next section.

Comparison of 20 and 21. A preliminary investigation of the interconversion of **20** and **21** has been carried out. A mixture of **20** and **21** in an approximate 4:1 ratio was heated in hexane at 80 °C. The composition of the mixture was periodically assessed by ^1H NMR spectroscopy (Figure 5.7; $CDCl_3$ was used as the solvent for the spectra). Over four days the composition of the mixture slowly changed until an apparent equilibrium was reached in which the ratio of **20**:**21** was approximately 10:7. This equilibrium mixture was heated for a further day at 100 °C whereupon the **20**:**21** ratio changed to 6:10, that is, **21** was the predominant form in solution at this temperature. There was no detectable decomposition of the solution (based on the ^1H NMR spectra) during this treatment.

The mechanism by which **20** and **21** interconvert is of special interest.

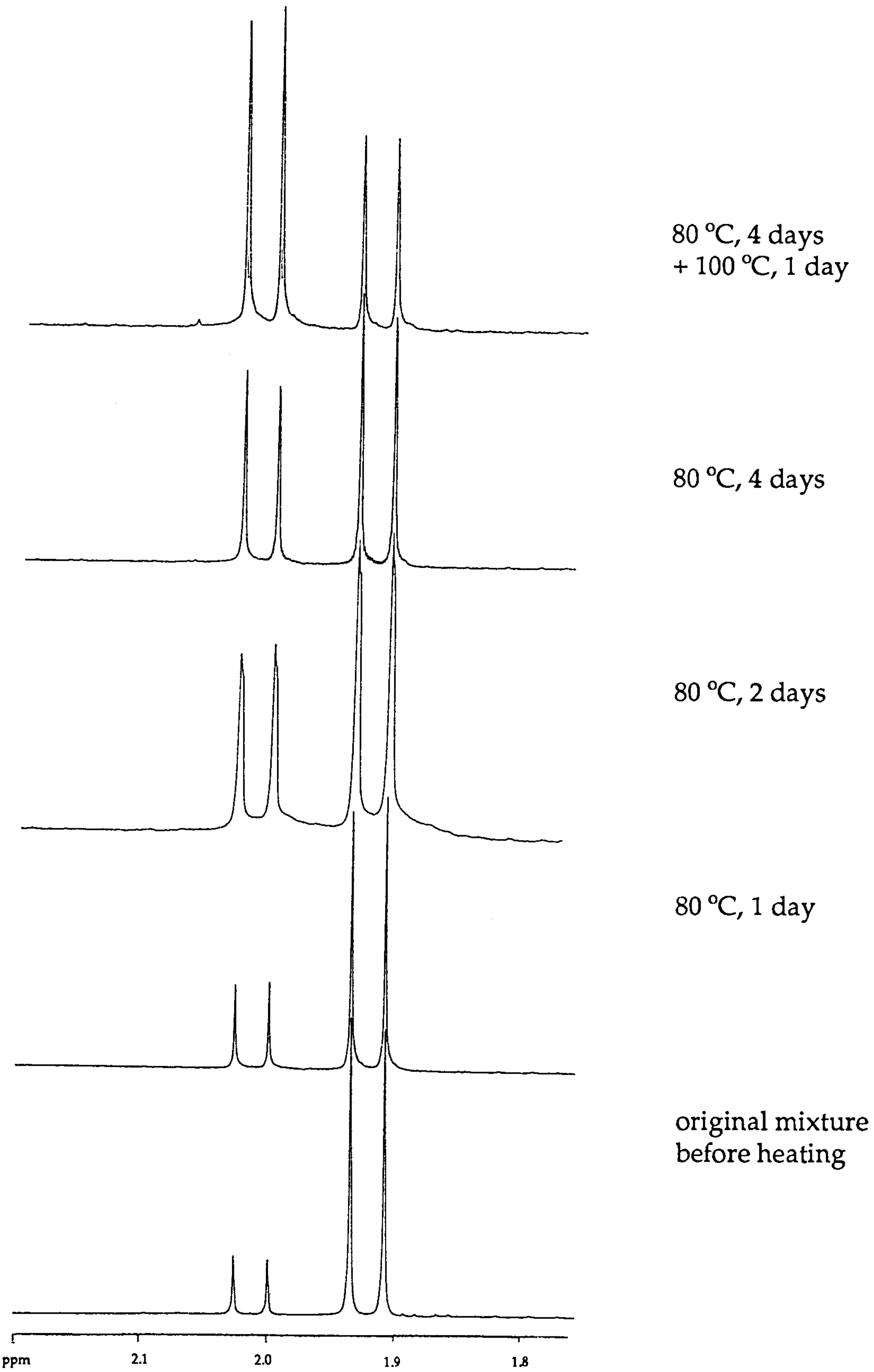

Figure 5.7. ^{1}H NMR spectra for $Os_5(CO)_{15}(ax\text{-}PMe_3) \rightleftharpoons Os_5(CO)_{15}(eq\text{-}PMe_3)$

Reasonable mechanisms include phosphine migration and skeletal rearrangement. Non-dissociative migration of a phosphine ligand from one metal atom to another in a cluster compound is extremely rare, and we are aware of only one example in the literature where this has been proposed.[134] Metal skeletal rearrangements in metal carbonyl cluster compounds where the number of ligands remains constant are also uncommon.[135] The mechanism is therefore as yet uncertain.

From the study described above, it appears that **21** is of comparable thermodynamic stability to **20**; this is contrary to expectations based on steric arguments. A possible explanation for the stability of **21** based on electronic reasons is as follows. A simple view of the metal-metal bonding in $Os_5(CO)_{15}(L)$ ($L = CO$ or PR_3) is depicted in Chart 5.1. In this view of the bonding, there are two dative metal-metal bonds from the osmium atom of the 16-electron $Os(CO)_3(L)$ grouping to the apical $Os(CO)_3$ units, which are 14-electron

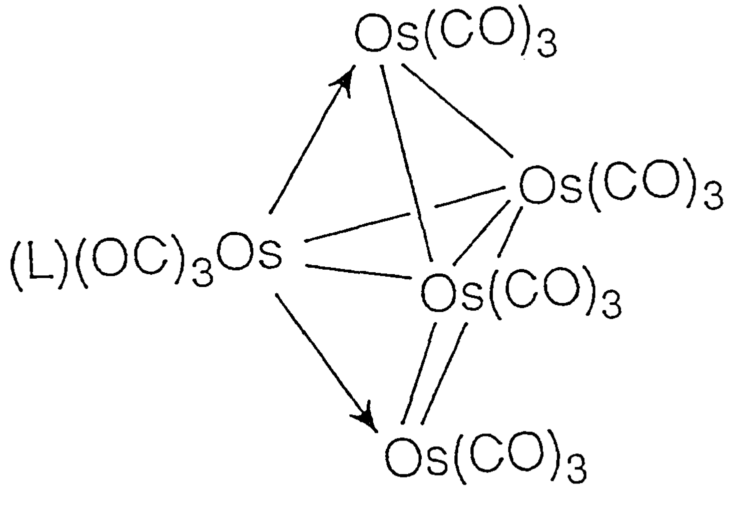

Chart 5.1

fragments. In this way, each osmium atom in the cluster achieves an 18-electron configuration, with the other metal-metal bonds being regarded as nondative.

That some of the metal-metal bonds in certain metal carbonyl clusters should be considered as dative bonds was first proposed in 1979.[70] Furthermore, work from this laboratory has also demonstrated that $Os(CO)_4(L)$ molecules readily add to 16-electron organometallic entities to yield complexes with unbridged dative metal-metal bonds (e.g., $(Me_3P)(OC)_4OsM(CO)_5$ M = Cr, Mo, W).[65c] As expected, complexes with the $Os(CO)_4(PMe_3)$ molecule as the donor unit are much more stable than those in which $Os(CO)_5$ acts as the donor moiety. Indeed, apparent migration of a good donor ligand from the acceptor to the donor metal atom (with simultaneous migration of CO in the opposite direction) has been observed by us,[65b,72] and other workers,[74] in complexes of this type.

If the $Os(CO)_3(L)$ unit is a net electron donating group compared to the $Os(CO)_3$ (or $Os(CO)_2(L)$) units in the $Os_5(CO)_{15}(L)$ cluster, then it would be expected that the cluster would be more stable when L is a good donor ligand such as PMe_3 rather than a CO ligand. The electron releasing nature of a strong donor ligand would offset the charge separation that is associated with the formation of dative bonds (i.e., $\delta(+)M \rightarrow M(\delta-)$).

5.2.2 $Os_5(CO)_n(CNBu^t)$ (n = 18, 17, 15)

$Os_5(CO)_{18}(CNBu^t)$ (22). Addition of $Os(CO)_4(CNBu^t)$[65b] to $Os_4(CO)_{14}$ in CH_2Cl_2 at room temperature afforded $Os_5(CO)_{18}(CNBu^t)$ (**22**) in good yield after 24 h (eq 5.4). The product was isolated after chromatography as red, air stable crystals.

$$Os_4(CO)_{14} + Os(CO)_4(CNBu^t) \longrightarrow \underset{\mathbf{22}}{Os_5(CO)_{18}(CNBu^t)} \tag{5.4}$$

The structure of **23** (Figure 5.8) also has the bow-tie arrangement of metal atoms. The pattern of the Os–Os lengths (Table 5.5) is similar to that of $Os_5(CO)_{19}$ (**16**) and $Os_5(CO)_{18}(PMe_3)$ (**18**): the two peripheral metal-metal bonds are somewhat shorter and the Os–Os bonds that involve the central (Os(1)) atom are somewhat longer than the average Os–Os length of 2.88 Å.[36]

The isocyanide ligand in **22** occupies an axial site on an outer osmium atom (i.e., Os(4)). This is different from **18** where the phosphine ligand is in the equatorial site on Os(4) occupied by CO(43) in **22**. These observations are not unexpected, however, given the different site preferences, as mentioned in the Introduction, of phosphorus-donor and isocyanide ligands in trinuclear metal carbonyl clusters.

In $Os_3(CO)_{12}$ the three axial sites are chemically equivalent, but in $Os_5(CO)_{19}$, if the Os_5 unit is planar, there are three chemically nonequivalent axial sites. In other words, there are three possible isomers for $Os_5(CO)_{18}(L)$ if the ligand L adopts an axial position. The single sharp resonance in the ^1H NMR spectrum of **22** in $CDCl_3$ at room temperature probably indicates there is only

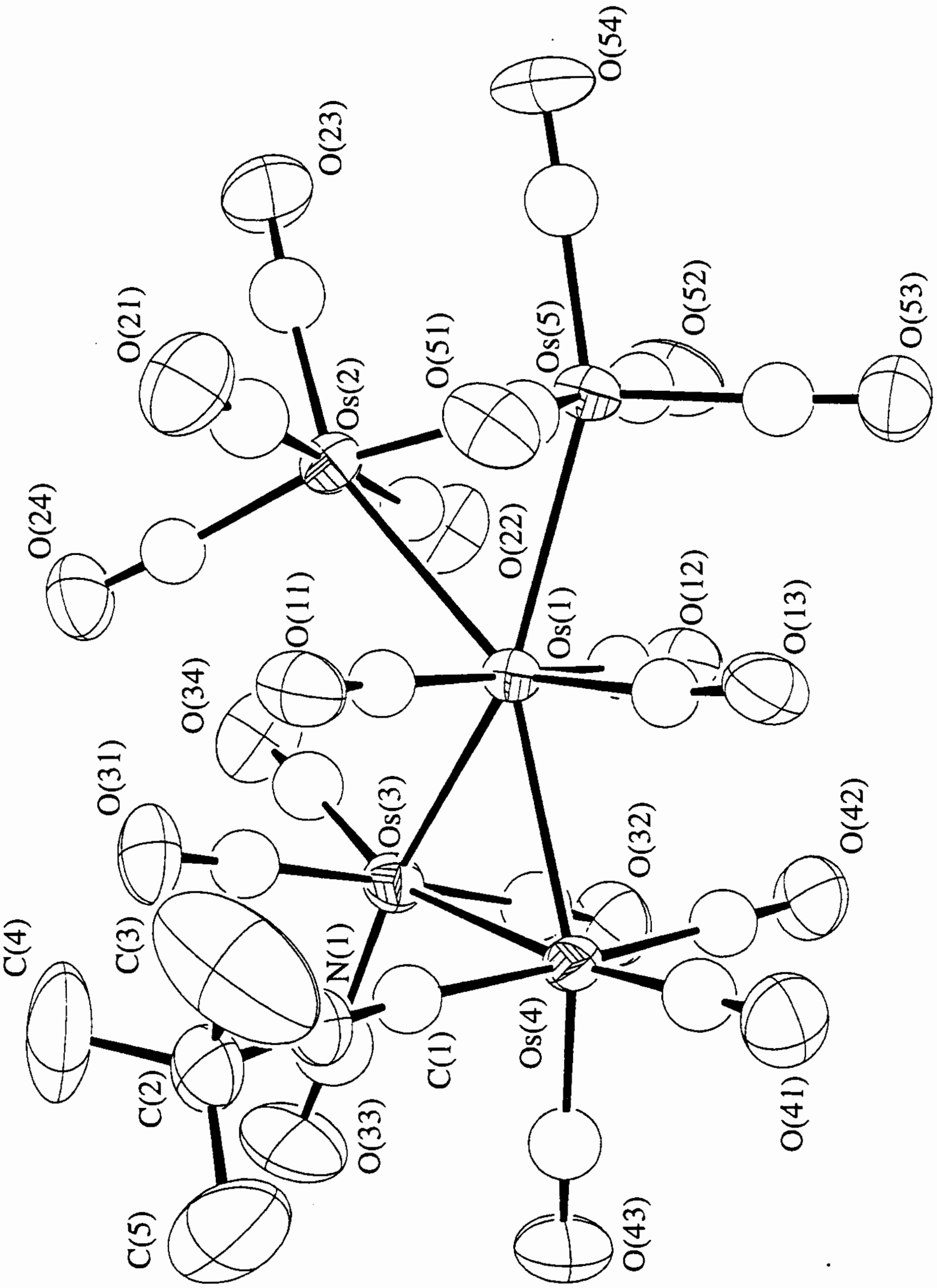

Figure 5.8. The molecular structure of $Os_5(CO)_{18}(CNBu^t)$ (22)

Table 5.5. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{18}(CNBu^t)$ (**22**)

Bond Lengths

Os(1) - Os(2)	2.929 (1)	Os(3) - Os(4)	2.839 (1)
Os(1) - Os(3)	2.938 (1)	Os(4) - C(1)	2.05 (1)
Os(1) - Os(4)	2.940 (1)		
Os(1) - Os(5)	2.900 (1)	(Os-CO)	1.87 (1) - 1.96 (1)
Os(2) - Os(5)	2.844 (1)	(C-O)	1.12 (2) - 1.17 (2)

Bond Angles

Os(4) - Os(1) - Os(3)	57.76 (2)	Os(3) - Os(1) - Os(2)	98.42 (2)
Os(5) - Os(1) - Os(2)	58.40 (2)	Os(5) - Os(1) - Os(4)	149.14 (2)
Os(5) - Os(2) - Os(1)	60.28 (2)	N(1) - C(1) - Os(4)	173.2 (8)
Os(4) - Os(3) - Os(1)	61.16 (2)		

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one isomer of **22** present in solution, although rapid exchange between two or more isomers cannot be completely ruled out.

The bond lengths and angles of the $CNBu^t$ ligand in **22** (and **24**, reported below) are similar to those found in other osmium carbonyl clusters with this ligand (e.g., the isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$,[67,136] $Os_4(CO)_{15}(CNBu^t)$[71a] and $Os_6(CO)_{16}(CNBu^t)_2$[137]).

$Os_5(CO)_{17}(CNBu^t)$ (23). Pyrolysis of **22** in CH_2Cl_2 at 44 - 47 °C (in an evacuated, sealed flask) for 3 days gave **23** in virtually quantitative yield (eq 5.5). Like **22**, **23** is an air-stable, red crystalline solid. Although several attempts were made, crystals of **23** suitable for X-ray crystallography could not be obtained. It

$$\underset{\textbf{22}}{Os_5(CO)_{18}(CNBu^t)} \xrightarrow{44 - 47\ ^\circ C} \underset{\textbf{23}}{Os_5(CO)_{17}(CNBu^t)} \qquad (5.5)$$

would be expected to have a planar, raft-like arrangement of metal atoms similar to that in $Os_5(CO)_{18}$[51,114] (16) and $Os_5(CO)_{17}(PMe_3)$[52] (19). By analogy to the structures of $Os_5(CO)_n(PMe_3)$ (n = 18, 17),[52] the isocyanide ligand in **23** remains in essentially the same position it adopts in **22**. The weak band in the infrared spectrum of **23** at 1821 cm^{-1}, is consistent with a bridging carbonyl ligand as found for $Os_5(CO)_{17}(L)$ (L = CO, PMe_3).

$Os_5(CO)_{15}(CNBu^t)$ (24). This cluster was synthesized by the thermolysis of **23** in CH_2Cl_2 at 65 - 70 °C (in a sealed, evacuated vessel) over 5 days (eq 5.6); the yield was essentially quantitative. Like **22** and **23**, **24** is also a red, air-stable crystalline solid.

$$\underset{\textbf{23}}{Os_5(CO)_{17}(CNBu^t)} \xrightarrow{65 - 70\ ^\circ C} \underset{\textbf{24}}{Os_5(CO)_{15}(CNBu^t)} \qquad (5.6)$$

In one synthesis, the reaction was monitored by infrared spectroscopy. There was no evidence by this technique for an intermediate product in the conversion of **23** to **24**. In other words, there was no evidence for $Os_5(CO)_{16}(CNBu^t)$. This observation is similar to that observed in the pyrolysis of $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$, to yield $Os_5(CO)_{16}$ and $Os_5(CO)_{15}(PMe_3)$, respectively.[51,52] Furthermore, there was no evidence for a second isomer of **24**.

The structure (Figure 5.9) of **24** reveals a trigonal bipyramidal arrangement of osmium atoms and in this respect it resembles the structures of the other clusters of formula $Os_5(CO)_{15}(L)$ (L = CO,[10,46] PMe_3[52]). The pattern of

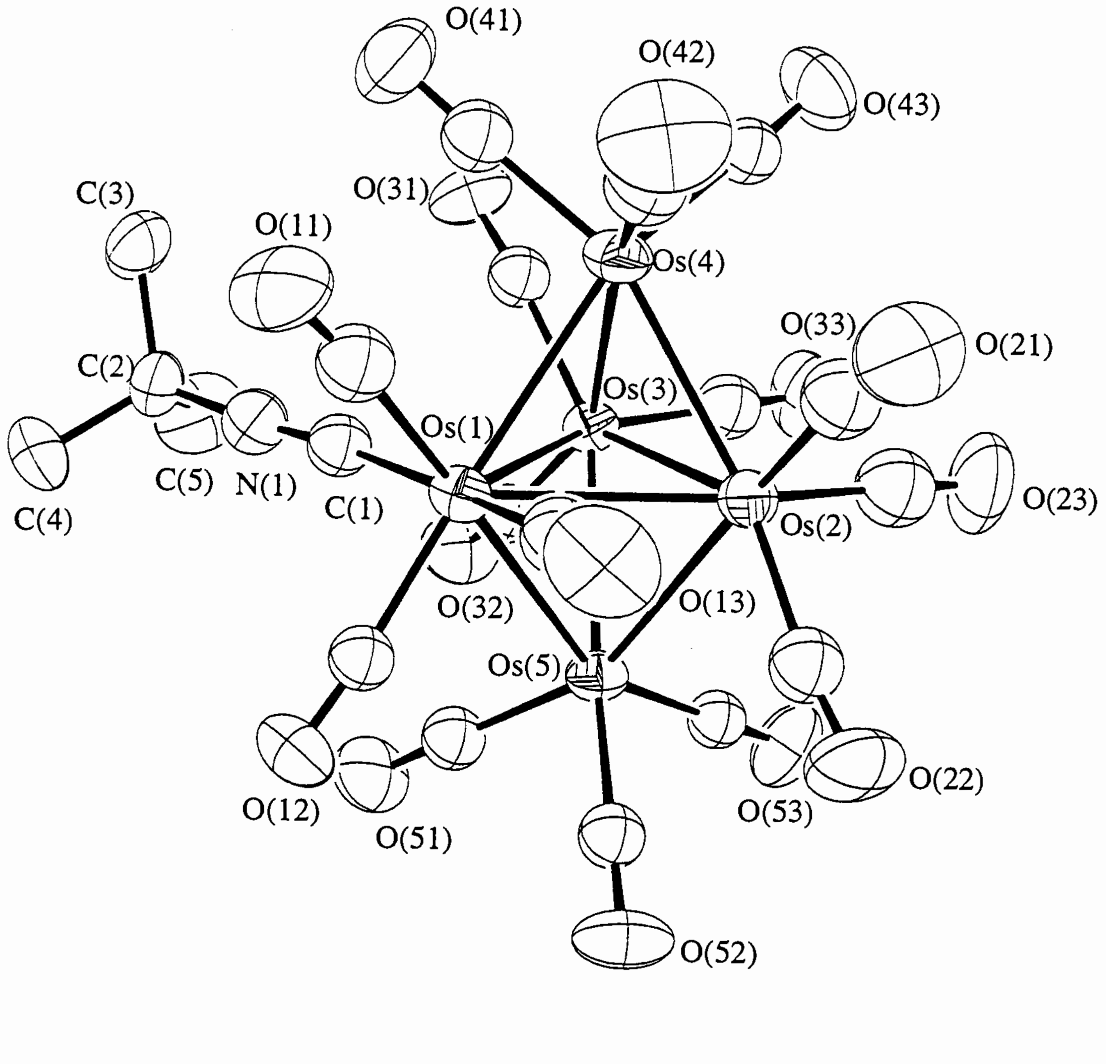

Figure 5.9. The Molecular Structure of $Os_5(CO)_{15}(CNBu^t)$ **(24)**

Table 5.6. Selected Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}(CNBu^t)$ (**24**)

Bond Lengths

Os(1) - Os(2)	2.882 (1)	Os(2) - Os(5)	2.771 (1)
Os(1) - Os(3)	2.897 (1)	Os(3) - Os(4)	2.748 (1)
Os(1) - Os(4)	2.903 (1)	Os(3) - Os(5)	2.755 (1)
Os(1) - Os(5)	2.915 (1)	Os(1) - C(1)	2.03 (1)
Os(2) - Os(3)	2.756 (1)	(Os-CO)	1.88 (1) - 1.93 (1)
Os(2) - Os(4)	2.789 (1)	(C-O)	1.13 (2) - 1.17 (2)

Bond Angles

Os(3) - Os(1) - Os(2)	56.96 (1)	Os(4) - Os(3) - Os(1)	61.83 (2)
Os(4) - Os(1) - Os(2)	57.65 (1)	Os(4) - Os(3) - Os(2)	60.89 (2)
Os(4) - Os(1) - Os(3)	56.57 (1)	Os(5) - Os(3) - Os(1)	62.04 (2)
Os(5) - Os(1) - Os(2)	57.11 (1)	Os(5) - Os(3) - Os(2)	60.38 (2)
Os(5) - Os(1) - Os(3)	56.60 (1)	Os(5) - Os(3) - Os(4)	112.07 (2)
Os(5) - Os(1) - Os(4)	103.36 (2)	C(11) - Os(1) - Os(4)	77.4 (4)
Os(3) - Os(2) - Os(1)	61.78 (1)	C(12) - Os(1) - Os(5)	74.7 (3)
Os(4) - Os(2) - Os(1)	61.54 (2)	C(13) - Os(1) - Os(2)	65.5 (4)
Os(4) - Os(2) - Os(3)	59.42 (2)	C(1) - Os(1) - Os(3)	67.2 (3)
Os(5) - Os(2) - Os(1)	62.04 (2)	C(12) - Os(1) - C(11)	104.6 (5)
Os(5) - Os(2) - Os(3)	59.80 (2)	C(1) - Os(1) - C(13)	169.7 (5)
Os(5) - Os(2) - Os(4)	110.35 (2)		

Os–Os lengths (Table 5.6) in all these clusters is similar. The two longest Os–Os bonds involve the osmium atom that has four terminal ligands coordinated to it (i.e., Os(1)) and the apical Os atoms Os(4) and Os(5). (An exception involves the Os(1)-Os(4) length in **21**, a bond between an apical Os atom and the Os atom of the $Os(CO)_3(PMe_3)$ grouping, which is marginally shorter than the two equatorial Os-Os bonds that involve the Os atom of the $Os(CO)_4(PMe_3)$ unit). In

24, these lengths (Table 5.6) are 2.903 (1) and 2.915 (1) Å. The next two longest Os–Os lengths involve Os(1) and the remaining osmium atoms (Os(2), Os(3)) in the equatorial plane (for **24**, these distances are 2.882 (1) and 2.897 (1) Å). The remaining five Os–Os vectors are all significantly shorter than 2.88 Å, the average Os–Os distance in $Os_3(CO)_{12}$. For **24**, these vectors range in length from 2.748 (1) to 2.789 (1) Å. It is usually found that, compared to the Os–Os distance in $Os_3(CO)_{12}$, Os–Os bonds are somewhat shorter in more condensed, higher nuclearity clusters of osmium.[8,54,106] As can be seen from Figure 5.9, the isocyanide ligand in **24** occupies a site that is arguably the sterically most crowded site in the molecule; it is coordinated to the osmium that has four terminal ligands (similar to $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**) and $Os_5(CO)_{15}\{P(OMe)_3\}$ (**25**)) and, furthermore, it is adjacent to one of the shorter Os–Os bonds that involves this osmium atom. Given the known mobility of both carbonyl and isocyanide ligands in multinuclear complexes and the temperature at which **24** was synthesized, it is probable that the isomer observed for **24** is the most thermodynamically stable isomer.

5.2.3 Comparison

As shown in Chart 5.1 (page 127), the stability of **21** was rationalized by electronic arguments: the dative metal-metal bonds thought present in **21** would be stabilized by having the better donor ligand coordinated to the osmium that has four terminal ligands.[52] A similar reasoning may be applied to **24**.

The difference between the site of occupancy of the noncarbonyl ligand in **21** and **24** can be rationalized by using arguments previously used to explain the site preference of phosphine and isocyanide ligands in bi- and trinuclear metal carbonyl compounds: In Table 5.7 are listed the nearest nonbonded contacts for

Table 5.7. Nearest Nonbonded Contacts (Å) for C(11) and C(13) in **24**

C···C Contacts

C(11)···C(1)	2.63 (2)	C(13)···C(11)	2.66 (2)
C(11)···C(13)	2.66 (2)	C(13)···C(12)	2.73 (2)
C(11)···C(12)	3.05 (2)	C(13)···C(22)	2.98 (2)
C(11)···C(41)	3.05 (2)	C(13)···C(21)	3.06 (2)
C(11)···C(42)	3.31 (2)	C(13)···C(42)	3.49 (2)
		C(13)···C(52)	3.89 (2)

C···Os Contacts

C(11)···Os(4)	3.11 (2)	C(13)···Os(2)	2.72 (2)
C(11)···Os(3)	4.23 (2)	C(13)···Os(4)	3.47 (2)
C(11)···Os(2)	4.30 (2)	C(13)···Os(5)	3.67 (2)

C(11) (in a site denoted as *eq,ax*) and C(13) (in a site denoted as *eq,eq*) of **24**. As can be seen, the carbon-carbon nonbonded contacts for C(11) and C(13) that are less than *ca.* 3.5 Å are comparable. The carbon to neighboring osmium atom distances are, however, significantly different: C(11)···Os(4) = 3.11 (2) Å whereas C(13)···Os(2) = 2.72 (2) Å. For the carbonyl and isocyanide ligands these interactions with neighboring osmium atoms may be attractive, but for the trimethylphosphine ligand this contact would almost certainly be repulsive. (In **24** the Os(4)Os(1)C(11) angle is 77.4 (4)° whereas in **21** the corresponding Os(4)Os(1)P angle is 100.7 (1)°.) For this reason, we believe that for a phosphine ligand the *eq,ax* positions in Os$_5$(CO)$_{15}$(L) clusters are less hindered than the *eq,eq* positions; this explains why the bulky PMe$_3$ grouping is found in the *eq,ax* positions. On the other hand, it would be expected that the *eq,eq* sites would be the electronically preferred sites for a ligand that is a poorer π-acceptor than the carbonyl ligand. This is because the resulting pseudo-facial configuration of the $Os(CO)_3(L)(X)_2$ ($X = Os_2(CO)_6$) unit avoids as much as possible the strong π-acceptor ligands competing for the same electron density on the central osmium atom. The reason that the *eq,eq* sites would be the electronically preferred sites for a ligand that is a poorer π-acceptor than the carbonyl ligand could also be described in a different way. For example, from Table 5.6 the *eq,eq* site in **24** is in a pseudo-trans position of C(13) (C(1)-Os(1)-C(13) = 169.7 (5)°). With the isocyanide ligand in the *eq,eq* position the competition between two good π-acceptor ligands (e.g., two CO ligands) for the electron density on the Os(1) atom would be avoided.

The consequence of these different site preferences is that the $CNBu^t$ ligand makes more acute angles with the Os–Os vectors of the Os_5 unit than does the PMe_3 ligand. In **24**, the C(1)Os(1)Os angles are in the range 67.2 (3)° to 124.2 (3)° whereas in **21** the POs(1)Os angles are in the range 100.7 (1)° to 154.4 (1)°. In other words, the $CNBu^t$ and PMe_3 groups are, as far as the geometry of the cluster allows, in cis and trans positions, respectively, to the metal-metal bonds in the cluster. In this respect the site preferences resemble those observed in bi and trinuclear carbonyl complexes.

Two isomers of $Os_5(CO)_{15}[P(OMe)_3]$ were synthesized.[50] One, **25**, was structurally characterized and found to have the $P(OMe)_3$ ligand in a pseudo-axial site on the osmium atom with four ligands (i.e., the *eq,ax* isomer). The other isomer **25a** was not characterized by X-ray crystallography. On the basis of the similarity of IR spectra of **25** and **25a**, it was proposed that in **25a** the $P(OMe)_3$ ligand occupied a pseudo equatorial site on the unique osmium atom (i.e., the *eq,eq* isomer). The isomerization from **25** to **25a** is irreversible and, therefore, the latter isomer is the thermodynamically more stable product. The equatorial position that the phosphite ligand was proposed to occupy in **25a** was thought to be the most favorable position for bulky, strong σ-donor ligands.[50] The results described above (and in Chapter 6) suggest that the *eq,ax* positions in $Os_5(CO)_{15}(L)$ clusters are much less hindered than the *eq,eq* positions and bulky ligands would therefore not coordinate in the *eq,eq* positions. The infrared spectra of $Os_5(CO)_{15}(ax\text{-}PMe_3)$ (**20**), $Os_5(CO)_{15}(eq\text{-}PMe_3)$ (**21**) and $Os_5(CO)_{15}(CNBu^t)$ (**24**) in the carbonyl stretching region are shown in Figure 5.10. As can be seen, all three isomers (i.e., the *ax, eq,ax* and *eq,eq* isomers) have similar IR spectra in this region. The IR pattern of **25a** (ν(CO) 2089w, 2043s, 2034vs, 2013sh, 1976m cm^{-1})[50] is closest to that of **20**. We believe that the phosphite ligand in the thermodynamically more stable isomer **25a** occupies a position on an apical osmium atom analogous to that of the phosphine ligand in **20**. Since $P(OMe)_3$ is a much weaker σ-donor ligand than PMe_3 it might be expected that there would be much less of an electronic preference for the $P(OMe)_3$ ligand to occupy the *eq,ax* position and hence the *ax* isomer is the preferred form. It would be a worthwhile study to investigate the stability of the two isomers of $Os_5(CO)_{15}(PR_3)$ as the steric and electronic properties of the P-donor ligands are varied.

5.2.4 **Conclusion.**

In conclusion, the use of PMe_3 and $CNBu^t$ as ligands has provided new geometric isomers of the binary pentanuclear carbonyl clusters $Os_5(CO)_n$ (n = 19, 18, 16). As expected from observations on trinuclear metal carbonyl clusters,[125]

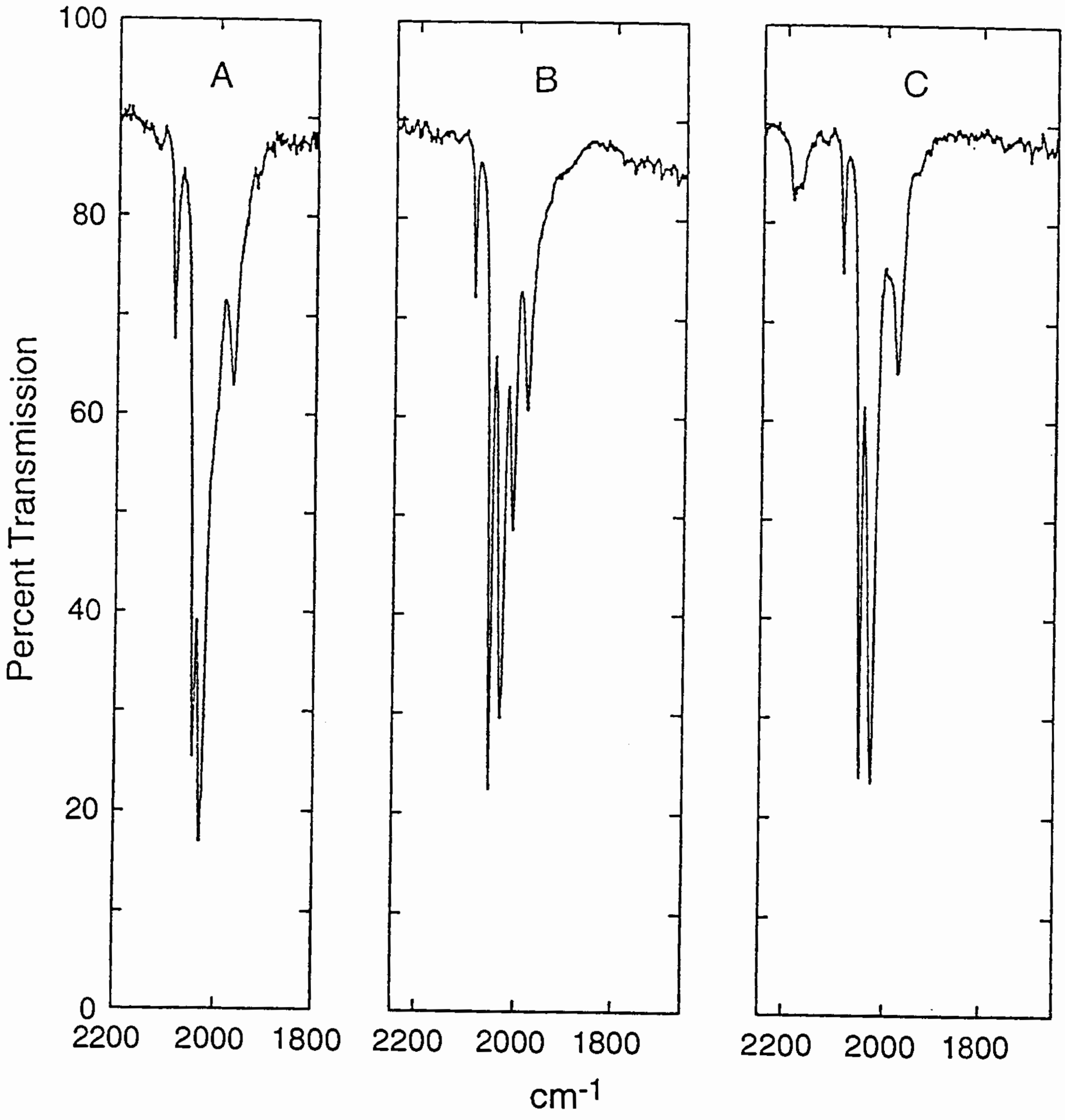

Figure 5.10. The infrared spectra of $Os_5(CO)_{15}$(*ax*-PMe_3) (A), $Os_5(CO)_{15}$(*eq*-PMe_3) (B) and $Os_5(CO)_{15}(CNBu^t)$ (C)

the trimethylphosphine ligand in **18**, **19** and **20** occupies a sterically unhindered site and the isocyanide ligand occupies a sterically hindered, but electronically preferred, site in the molecules. The different site preference of the PMe_3 and $CNBu^t$ ligands in the pentanuclear carbonyl clusters resembles that previously observed in trinuclear clusters. The difference in site preference is consistent with the view that the PMe_3 ligand adopts, for the most part, the site that is least sterically crowded, but the $CNBu^t$ ligand adopts the site that is electronically preferred in the clusters. An unexpected result of this study was the isolation of **21**, in which the PMe_3 ligand is in a sterically crowded site. The unexpected stability of **21** appears to indicate that electronic factors are overriding the normal steric requirements of the phosphine ligand. We believe this stability illustrates the importance of dative metal-metal bonds in metal carbonyl clusters. That the presence of the strong σ-donor ligand, PMe_3, on the osmium atom with four ligands stabilizes the dative metal-metal bonds from this osmium atom to the apical osmium atoms in the cluster is consistent with the changeover in the structures of $Os_4(CO)_{15}(L)$ (L = CO, P-donor ligand, $CNBu^t$) clusters.[71a] This changeover from a puckered-square arrangement of metal atoms with no dative metal-metal bonds to a spiked triangular geometry with one dative and three non-dative metal-metal bonds (i.e., $(L)(OC)_4Os{\rightarrow}Os_3(CO)_{11}$) occurs as the σ-donor properties of L increase.

In this study the metal skeletal transformations have been established for $Os_5(CO)_n(PMe_3)$ (shown in Chart 5.2) and $Os_5(CO)_n(CNBu^t)$ (n = 18, 17, 15). Several different attempts were made to prepare a cluster of the formula $Os_5(CO)_{16}(L)$ (or $Os_5(CO)_{15}(PMe_3)(L)$), but so far these have been unsuccessful. As we have previously pointed out (page 103),[51] while $Os_5(\mu\text{-}H)_2(CO)_{16}$ has an edge-bridged tetrahedral arrangement of metal atoms,[116] it does not necessarily follow that $Os_5(CO)_{17}$, if it could be prepared, will have the same arrangement. From polyhedral skeletal electron pair theory (PSEPT),[102] $Os_5(CO)_{17}$ should have a nido octahedral skeleton, that is, a square-based pyramidal arrangement of osmium atoms.

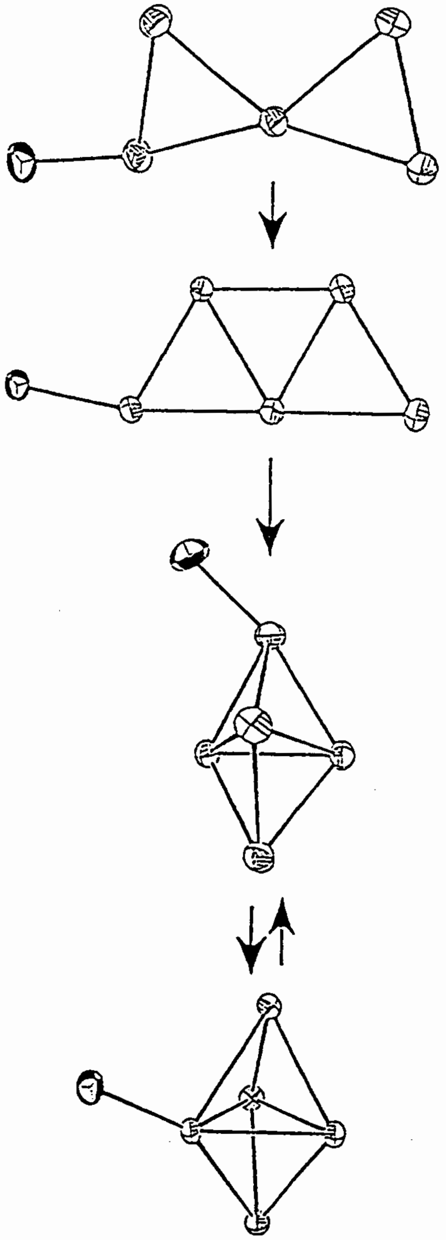

Chart 5.2

5.3 Preliminary Study of Hexaosmium Clusters

Some preliminary attempts have been conducted to synthesize hexanuclear clusters of osmium from precursors of lower nuclearities. Cluster $Os_6(CO)_{20}(PMe_3)$ (**26**) was prepared from the reaction of $Os_5(CO)_{18}$ with $Os(CO)_4(PMe_3)$ (eq 5.7). Compound **26** is an air-stable, blue crystalline solid.

$$\underset{\mathbf{16}}{Os_5(CO)_{18}} + Os(CO)_4(PMe_3) \longrightarrow Os_3(CO)_{12} + Os_3(CO)_{11}(PMe_3) + Os_5(CO)_{16} + Os_5(CO)_{19} + \underset{\mathbf{26}}{Os_6(CO)_{20}(PMe_3)} \quad (5.7)$$

The products were identified by their IR data.[10,17,47,138,140]

A blue compound was also separated from the reaction of $Os_5(CO)_{18}$ with $Os(CO)_4(CNBu^t)$. The comparison of its IR data with that of $Os_6(CO)_{20}(PMe_3)$ suggests that it is probably $Os_6(CO)_{20}(CNBu^t)$ (**27**).

5.4 Experimental Section

The general procedure used for the synthesis and X-ray structure analysis has been described in the Experimental Section of Chapter 2. The preparation of $Os(CO)_4(PMe_3)$[130] and $Os(CO)_4(CNBu^t)$[65b] were carried out by literature procedures.

5.4.1 Synthesis

Preparation of $Os_5(CO)_{18}(PMe_3)$ (18). A solution of $Os_4(CO)_{14}$ (33 mg, 0.029 mmol) and $Os(CO)_4(PMe_3)$ (11 mg, 0.029 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 25 h. The solvent was removed on the vacuum line and the remaining solid subjected to chromatography on a silica gel column (2.5 x 20 cm). Elution with CH_2Cl_2/hexane (1/2) gave an orange band from which red crystals of **18** (35 mg, 80%) were isolated: IR (hexane) ν(CO) 2119 (m), 2084 (s), 2066 (s), 2042 (sh), 2035 (vs), 2017 (m), 2005 (w), 1987 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (d, J_{PH} = 10.2 Hz), 1.99 (d, J_{PH} = 10.4 Hz), ratio of signals: 3.0:1.0; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -46.48, -52.66 (ratio: 2.1:1.0). Anal. Calcd for $C_{22}H_{11}O_{18}Cl_2Os_5P$: C, 16.35; H, 0.69. Found: C, 16.33, H, 0.64.

Preparation of $Os_5(CO)_{17}(PMe_3)$ (19). A solution of **18** (33 mg, 0.022 mmol) in CH_2Cl_2 (20 mL) was placed in a round-bottom flask fitted with a Teflon valve. The vessel was cooled to -196 °C and evacuated; the solution was degassed with 3 freeze-pump-thaw cycles. The flask and contents were heated at 40-45 °C for 2 days. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel (2.5 x 20 cm). Elution with CH_2Cl_2/hexane (1/1) afforded a red band that yielded **19** (19 mg, 59% yield) as deep red, air-stable crystals: IR (CH_2Cl_2) ν(CO) 2120 (m), 2078 (m), 2074 (m), 2062 (w), 2034 (s), 2013 (m), 1811 (w, br); ^1H NMR ($CDCl_3$) δ 1.88 (d, J_{PH} = 10.5 Hz), 1.87 (d, J_{PH} = 10.6 Hz) ratio of signals: 1.3:1.0; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -42.36, -41.27 (ratio, 1.1:1.0). Anal. Calcd for $C_{20}H_9O_{17}Os_5P$: C, 15.98; H, 0.60. Found: C, 16.19; H = 0.66.

Preparation of $Os_5(CO)_{15}$(*ax*-PMe_3) (20). A solution of $Os_5(CO)_{17}(PMe_3)$ (44 mg, 0.030 mmol) in CH_2Cl_2/hexane (1/3) was placed in a round bottom flask fitted with a Teflon valve; the flask was cooled to -196 °C and degassed with 3 freeze-pump-thaw cycles. The vessel was sealed under vacuum and heated at 63 °C for 2 days. The solvent was then removed on the vacuum line and the residue chromatographed on silica gel (2.5 x 20 cm). Elution with CH_2Cl_2/hexane (1/4) gave a red-brown band from which **20** (15 mg), with small amounts of $Os_5(CO)_{15}$(*eq*-PMe_3), was obtained. A second band yielded unreacted **19** (27 mg). Pure **20** was obtained by recrystallization from CH_2Cl_2 as deep red, air-stable crystals: IR (CH_2Cl_2) ν(CO) 2117 (vw), 2086 (m), 2045 (s), 2028 (vs), 2004 (sh), 1968 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (d, J_{PH} = 10.8 Hz); $^{31}P\{^1H\}$ ($CDCl_3$) δ -28.65. Anal. Calcd for $C_{18}H_9O_{15}Os_5P$: C, 14.94; H, 0.63. Found: C, 15.56; H, 0.69.

Preparation of $Os_5(CO)_{15}$(*eq*-PMe_3) (21). The pyrolysis of **20** was carried out in a similar manner to that used to prepare **20** except that a temperature of 110 °C and a reaction period of 24 h was employed. The desired cluster **21** was also isolated in a similar manner; the yield of **21** was not determined but appeared excellent. Compound **21** was isolated as deep red, air-stable crystals: IR (CH_2Cl_2) ν(CO) 2089 (m), 2053 (vs), 2030 (s), 2007 (m), 1979 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (d, J_{PH} = 10.6 Hz); $^{31}P\{^1H\}$ NMR δ -34.81. Anal. Calcd for $C_{18}H_9O_{15}Os_5P$: C, 14.94; 0.63. Found: C, 15.06; H, 0.69.

Preparation of $Os_5(CO)_{18}(CNBu^t)$ (22). A solution of $Os_4(CO)_{14}$ (26 mg, 0.023 mmol) and $Os(CO)_4(CNBu^t)$ (9 mg, 0.02 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 24 h. The solvent was removed on the vacuum line and the remaining solid subjected to chromatography on a silica gel column (1.2 x 20 cm). Elution with CH_2Cl_2/hexane (1/7) gave a red band from which red, air-stable crystals of **22** (26 mg, 78%) were obtained: IR(hexane) ν(CN) 2190 (w); ν(CO) 2116 (m), 2081 (s), 2066 (s), 2054 (m), 2034 (s), 2031 (sh), 2015 (m), 1977 (m), 1978 (vw), 1930 (vw) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (s). Anal. Calcd for $C_{23}H_9NO_{18}Os_5$: C, 17.96%, H, 0.59%, N, 0.91%. Found: C, 18.19%, H, 0.63%, N, 0.99%.

Preparation of $Os_5(CO)_{17}(CNBu^t)$ (23). A solution of **22** (30 mg, 0.020 mmol) in CH_2Cl_2 (35 mL) was placed in a round-bottom flask fitted with a Teflon valve. The vessel and contents were cooled to -196 °C and the vessel evacuated; the solution was degassed with 3 freeze-pump-thaw cycles. The flask was sealed under vacuum and heated at 44 - 47 °C for 3 days. Isolation by a similar procedure given for **22** gave a virtually quantitative yield of **23**: IR(CH_2Cl_2) ν(CN) 2194 (w); ν(CO) 2116 (m), 2076 (s), 2061 (m), 2033 (vs), 2020 (sh), 1998 (sh), 1958 (sh), 1821 (w,br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (s). Anal. Calcd for $C_{22}H_9NO_{17}Os_5$: C, 17.50%; H, 0.60%, N, 0.93%. Found: C, 17.69%; H, 0.65%; N, 1.10%.

Preparation of $Os_5(CO)_{15}(CNBu^t)$ (24). A solution of **23** (23 mg, 0.015 mmol) in CH_2Cl_2 (50 mL) was placed in a round bottom flask, cooled to -196 °C and degassed with 3 freeze-pump-thaw cycles. The vessel containing the solution was sealed under vacuum and heated at 65-70 °C for 5 days. Chromatography in a manner similar to that described for **22** afforded unreacted **23** (2 mg), and **24** (20 mg, 90%) as red, air-stable crystals: IR(CH_2Cl_2) ν(CN) 2189 (w, br); ν(CO) 2088 (m), 2055 (s), 2032 (s), 1981 (m), 1942 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (s). Anal. Calcd for $C_{20}H_9NO_{15}Os_5$: C, 16.52%; H, 0.62%; N, 0.96%. Found: C, 16.60%; H, 0.61%; N, 1.01%.

Preparation of $Os_6(CO)_{20}(PMe_3)$ (26). A solution of $Os_5(CO)_{18}$ (8 mg, 0.005 mmol) and $Os(CO)_4(PMe_3)$ (3 mg, 0.008 mmol) in CH_2Cl_2 (30 mL) was placed in a round bottom flask, cooled to -196 °C and degassed with 3 freeze-pump-thaw cycles. The flask was sealed under vacuum and heated at 40 °C for 18 h. The solvent was removed on the vacuum line and the remaining solid subjected to chromatography on a silica gel column (1.2 x 20 cm). Elution with CH_2Cl_2/hexane (1/1.5) gave a blue band from which air-stable solids of **26** were obtained. Isolation of $Os_3(CO)_{12}$, $Os_3(CO)_{11}(PMe_3)$, $Os_5(CO)_{16}$ and $Os_5(CO)_{19}$ from the reaction mixture was also achieved by chromatography and recrystallization; these four clusters were identified by their IR data. The yields, not measured, appeared to be low. Compound **26**: IR (CH_2Cl_2) ν(CO) 2125 (w), 2090 (s), 2067 (m), 2040 (vs), 2018 (m), 1997 (m) cm^{-1}.

Preparation of $Os_6(CO)_{20}(CNBu^t)$ (27). A reaction of $Os_5(CO)_{18}$ with $Os(CO)_4(CNBu^t)$ was conducted under similar conditions to that for the reaction of $Os_5(CO)_{18}$ with $Os(CO)_4(PMe_3)$ described above. Chromatography with CH_2Cl_2/hexane (1/3) gave a blue band from which solids of **27** were obtained. IR (CH_2Cl_2) ν(CN) 2198 (w, br); ν(CO) 2123 (w), 2090 (m), 2081 (sh), 2068 (s), 2051 (sh), 2031 (vs, br), 1997 (sh), 1966 (sh) cm^{-1}.

5.5.2 X-ray Structure Determinations for Compounds $18{\cdot}CH_2Cl_2$, 19-22 and 24

Two intensity standards, measured every hour (and 1.5 h for **22** and 3 h for **24**) of acquisition time, decreased by 11%, 9%, 5%, and 6% for **$18{\cdot}CH_2Cl_2$**, **21**, **22**, and **24**, respectively, and varied up to ±2% for **19** and ±1% for **20** during the data collection process.

The coordinates (and thermal parameters as well for **$18{\cdot}CH_2Cl_2$** and **19-21**) of carbon atoms with attached hydrogen atoms were linked so that the derived shifts in coordinates (and thermal parameters as well for **$18{\cdot}CH_2Cl_2$** and **19-21**) included contributions from appropriate derivatives from the atom sites. Crystallographic data are summarized in Table 5.8. The final fractional coordinates for the non-hydrogen atoms of **$18{\cdot}CH_2Cl_2$**, **19-22** and **24** are given in Table 5.9-5.14, respectively.

Table 5.8. Summary of Crystal Data and Details of Intensity Collection for **$18 \cdot CH_2Cl_2$, 19-22 and 24**

compound	$18 \cdot CH_2Cl_2$	19	20
fw	1616.2	1503.2	1447.2
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	15.204 (2)	9.019 (5)	9.112 (1)
b, Å	9.612 (1)	12.264 (3)	12.361 (2)
c, Å	23.942 (3)	26.479 (5)	12.548 (2)
α, deg			94.04 (1)
β, deg	91.23 (1)	91.00 (3)	98.34 (1)
γ, deg			91.96 (1)
V, $Å^3$	3498	2928.4	1393.5
2θ range of unit cell, deg	27-35	30-45	30-41
Z	4	4	2
D_{calc}, g cm^{-3}	3.069	3.410	3.449
μ(Mo, K_α), cm^{-1}	183.87	217.70	228.63
cryst size, mm	0.07x0.16x0.23	0.083x0.10x0.16	0.070x0.21x0.22
transmission coeff range[a]	0.18-0.46	0.13-0.23	0.10-0.35
scan method	ω-2θ	ω	ω-2θ
scan width (ω), deg	$0.83 + 0.35\tan\theta$	$1.1 + 0.35\tan\theta$	$1.0 + 0.35\tan\theta$
scan rate (ω), deg min^{-1}	0.75-5.5	1.1-5.5	0.92-5.5
scan range (2θ), deg	2.5-45	4-44	2.5-45
no. of unique rflns	4569	3570	3612
no. of obsd rflns[b]	2730	2187	2768
no. of variables	236	203	262
R[c]	0.035	0.040	0.031
Rw[d]	0.047	0.047	0.038
k[d]	0.0008	0.00035	0.0003
G.O.F.[e]	1.2	1.4	1.5
F000	2862.91	2638.92	1263.48

Table 5.8 cont'd

compound	**21**	**22**	**24**
fw	1447.2	1538.3	1482.3
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	10.799 (1)	9.079 (1)	9.048 (1)
b, Å	17.555 (2)	12.065 (2)	18.389 (2)
c, Å	14.504 (2)	15.757 (2)	17.759 (2)
α, deg		76.36 (1)	
β, deg	93.68 (1)	76.63 (1)	102.65 (1)
γ, deg		77.86 (1)	
V, Å^3	2744.0	1609.4	2883.1
2θ range of unit cell, deg	28-37	30-44	30-36
Z	4	2	4
D_{calc}, g cm^{-3}	3.503	3.174	3.350
μ(Mo, Kα), cm^{-1}	232.21	197.64	220.50
cryst size, mm	0.062x0.11x0.23	0.020x0.19x0.16	0.047x0.057x0.22
transmission coeff range[a]	0.098-0.32	0.14-0.68	0.28-0.39
scan method	ω-2θ	ω-2θ	ω-2θ
scan width (ω), deg	0.80 + 0.35tanθ	0.90 + 0.35tanθ	0.90 + 0.35tanθ
scan rate (ω), deg min^{-1}	0.75-5.5	0.82-5.5	0.82-5.5
scan range (2θ), deg	2.5-50	4-45	4-48
no. of unique rflns	4810	4173	4507
no. of obsd rflns[b]	3578	3355	3240
no. of variables	263	330	291
R[c]	0.033	0.021	0.025
Rw[d]	0.046	0.025	0.025
k[d]	0.0001	0.0001	0.0001
G.O.F.[e]	2.2	1.2	1.6
extinction (g)	0.110 (14)		0.329 (16)
F000	2526.93	1355.44	2542.90

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[a] Absorption corrections. [b] $I_o > 2.5(I_o)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[d] $Rw = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + k(F_o)^2]^{-1}$.

[e] $GOF = (\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom}))^{1/2}$.

Table 5.9. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $Os_5(CO)_{18}(PMe_3)\cdot CH_2Cl_2$ (**18**$\cdot CH_2Cl_2$)

Atom	x	y	z	U(iso)
Os(1)	7511.3 (6)	1620.3 (8)	1357.4 (4)	348
Os(2)	9178.1 (6)	2678.4 (9)	923.5 (4)	420
Os(3)	6396.2 (6)	4029.8 (9)	1080.4 (4)	428
Os(4)	5585.6 (6)	1391.0 (9)	1252.8 (4)	400
Os(5)	9174.6 (6)	257.9 (9)	1617.2 (4)	412
P(1)	4073 (4)	1765 (7)	1240 (3)	524
O(11)	7599 (11)	3385 (17)	2424 (7)	663 (48)
O(12)	7266 (13)	56 (20)	249 (8)	838 (58)
O(13)	7028 (13)	-870 (20)	2056 (8)	822 (57)
O(21)	9266 (13)	4645 (20)	1941 (8)	836 (57)
O(22)	9012 (12)	885 (20)	-142 (8)	837 (57)
O(23)	11139 (15)	2627 (22)	828 (9)	1007 (69)
O(24)	8773 (13)	5205 (21)	205 (8)	866 (59)
O(31)	5776 (13)	4672 (21)	2266 (9)	909 (61)
O(32)	7041 (12)	3260 (18)	-95 (8)	746 (53)
O(33)	4871 (14)	5711 (22)	582 (9)	982 (66)
O(34)	7691 (16)	6454 (24)	1235 (9)	1070 (72)
O(41)	5652 (12)	1653 (18)	2548 (8)	747 (54)
O(42)	5474 (11)	1310 (17)	-16 (7)	667 (49)
O(43)	5376 (14)	-1770 (21)	1316 (8)	890 (61)
O(51)	9321 (11)	2128 (18)	2645 (7)	670 (49)
O(52)	8916 (12)	-1636 (19)	586 (8)	767 (55)
O(53)	8775 (13)	-2142 (20)	2402 (8)	850 (58)
O(54)	11160 (13)	-44 (20)	1603 (8)	805 (56)
C(11)	7589 (15)	2788 (24)	1993 (10)	526 (64)
C(12)	7376 (17)	672 (26)	655 (11)	603 (70)
C(13)	7203 (15)	79 (23)	1783 (9)	459 (60)
C(21)	9219 (17)	3901 (28)	1604 (11)	631 (73)
C(22)	9050 (17)	1483 (27)	297 (11)	646 (73)
C(23)	10379 (19)	2667 (27)	855 (11)	662 (75)
C(24)	8945 (16)	4208 (26)	466 (10)	565 (67)
C(31)	6020 (18)	4420 (29)	1815 (12)	688 (78)
C(32)	6812 (15)	3528 (24)	348 (10)	508 (62)
C(33)	5459 (20)	5012 (28)	784 (12)	737 (81)
C(34)	7207 (22)	5533 (33)	1168 (13)	885 (95)

Table 5.9 cont'd

C(41)	5636 (17)	1624 (25)	2072 (11)	583 (69)
C(42)	5542 (15)	1351 (23)	451 (10)	485 (61)
C(43)	5449 (17)	-540 (28)	1321 (11)	666 (75)
C(51)	9286 (16)	1473 (25)	2243 (10)	571 (67)
C(52)	9011 (17)	-950 (27)	943 (11)	602 (70)
C(53)	8920 (18)	-1267 (27)	2072 (11)	650 (73)
C(54)	10391 (20)	23 (28)	1607 (11)	741 (82)
C(1)	3417 (19)	249 (29)	1283 (12)	864 (92)
C(2)	3674 (21)	2777 (33)	1781 (13)	1074 (115)
C(3)	3630 (20)	2645 (30)	626 (12)	906 (96)
Cl(1)[a]	741 (8)	6485 (11)	1021 (4)	1091 (39)
Cl(2)[a]	1481 (49)	6136 (69)	1021 (26)	1091 (39)
Cl(3)[a]	2297 (25)	5533 (36)	1629 (10)	1091 (39)
Cl(4)[a]	2719 (39)	6173 (59)	1478 (21)	1091 (39)
Cl(5)[a]	1871 (57)	4974 (82)	1639 (25)	1091 (39)
Cl(6)[a]	1887 (24)	6951 (38)	1230 (15)	1091 (39)

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[a] The occupancies of Cl(1) to Cl(6) are 0.91 (2), 0.16 (2), 0.51 (3), 0.21 (2), 0.17 (3), 0.29 (2).

$Os_5(CO)_{18}(PMe_3)\cdot CH_2Cl_2$ ($18\cdot CH_2Cl_2$). Red crystals that contained molecules of solvent were obtained by recrystallization from CH_2Cl_2/hexane. The electron density difference peaks in a confined region were consistent with several disordered orientations of a methylene chloride molecule. While no further attempt was made to interpret these peaks, they were modeled by six partial occupancy chlorine atoms, one of which showed high occupancy (0.91 (2)). In total, approximately one molecule of CH_2Cl_2 was indicated. The loss of solvent may well have occurred during the data collection since the standards decreased in intensity. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium and

Table 5.10. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for $Os_5(CO)_{17}(PMe_3)$ (**19**)

Atom	x	y	z	U(iso)
Os(1)	7895 (1)	7153.0 (8)	1151.3 (4)	293
Os(2)	4960 (1)	7706.6 (8)	813.4 (3)	292
Os(3)	5679 (1)	7757.9 (8)	1856.7 (3)	266
Os(4)	8638 (1)	7196.7 (8)	2219.5 (3)	269
Os(5)	7177 (1)	7078.5 (8)	102.2 (4)	331
P(1)	8780 (8)	7429 (5)	3095 (2)	334
O(0)	2521 (20)	8482 (13)	1546 (6)	480 (48)
O(11)	8882 (23)	9537 (16)	1034 (7)	646 (57)
O(12)	7210 (20)	4723 (14)	1298 (7)	501 (50)
O(13)	11017 (26)	6401 (17)	935 (8)	782 (66)
O(21)	5638 (23)	10133 (16)	650 (7)	661 (59)
O(22)	3985 (17)	5302 (12)	888 (6)	311 (40)
O(23)	2281 (28)	7997 (18)	77 (9)	879 (70)
O(31)	6374 (22)	10218 (15)	1838 (7)	577 (53)
O(32)	4659 (19)	5389 (14)	2028 (6)	506 (52)
O(33)	4438 (21)	7992 (14)	2903 (7)	555 (52)
O(41)	9491 (20)	9597 (15)	2116 (7)	538 (52)
O(42)	7654 (20)	4841 (13)	2407 (7)	489 (48)
O(43)	11771 (22)	6450 (15)	2167 (7)	586 (54)
O(51)	8134 (27)	9483 (18)	-46 (9)	835 (69)
O(52)	6570 (19)	4632 (14)	234 (6)	471 (49)
O(53)	10012 (25)	6320 (16)	-384 (8)	738 (63)
O(54)	5081 (23)	7222 (16)	-818 (8)	716 (61)
C(0)	3722 (27)	8181 (18)	1452 (8)	309 (63)
C(11)	8463 (30)	8656 (21)	1065 (10)	422 (73)
C(12)	7427 (27)	5622 (18)	1249 (9)	290 (60)
C(13)	9841 (36)	6710 (23)	1021 (11)	582 (84)
C(21)	5474 (28)	9228 (20)	722 (9)	352 (64)
C(22)	4429 (26)	6187 (18)	864 (8)	269 (59)
C(23)	3306 (34)	7910 (24)	347 (11)	589 (82)
C(31)	6147 (28)	9279 (20)	1829 (9)	362 (65)
C(32)	5053 (27)	6247 (19)	1945 (9)	312 (62)
C(33)	4935 (29)	7923 (20)	2493 (10)	414 (65)
C(41)	9164 (27)	8695 (20)	2133 (9)	340 (65)
C(42)	8010 (27)	5736 (19)	2322 (9)	333 (63)

Table 5.10 cont'd

C(43)	10587 (29)	6801 (19)	2197 (9)	356 (65)
C(51)	7761 (42)	8587 (31)	51 (14)	859 (117)
C(52)	6721 (27)	5538 (19)	198 (9)	337 (64)
C(53)	8909 (34)	6667 (23)	-197 (11)	558 (81)
C(54)	5924 (30)	7116 (21)	-481 (10)	450 (69)
C(1)	7757 (31)	6434 (20)	3459 (10)	532 (78)
C(2)	8196 (31)	8735 (20)	3316 (10)	514 (77)
C(3)	10627 (32)	7307 (23)	3377 (11)	658 (88)

phosphorus atoms, isotropic thermal parameters for all oxygen and carbon atoms, and occupancies and one thermal parameter for all chlorine atoms.

$Os_5(CO)_{17}(PMe_3)$ (19). Dark red crystals were obtained by the slow (over a month, at room temperature) evaporation of solvent from a solution of **19** in chlorobenzene. Static background measurements were made for **19** at positions on each edge of the scan width. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium and phosphorus atoms, and isotropic thermal parameters for all oxygen and carbon atoms.

$Os_5(CO)_{15}$(*ax*-PMe_3) (20). Dark red crystals were obtained by recrystallization from CH_2Cl_2. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium, phosphorus and oxygen atoms, and isotropic thermal parameters for carbon atoms.

$Os_5(CO)_{15}$(*eq*-PMe_3) (21). Dark red crystals were obtained by recrystallization from CH_2Cl_2/hexane. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal

Table 5.11. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $Os_5(CO)_{15}$(ax-PMe_3) (**20**)

Atom	x/a	y/b	z/c	U(iso)
Os(1)	1918.2 (6)	3800.5 (4)	3546.6 (5)	343
Os(2)	4241.1 (6)	2463.2 (5)	3017.3 (5)	344
Os(3)	1331.6 (7)	1639.1 (5)	2547.8 (5)	411
Os(4)	2287.0 (7)	3229.2 (5)	1306.7 (5)	388
Os(5)	2719.1 (7)	1889.2 (5)	4669.8 (5)	392
P(1)	2801 (6)	2371 (4)	-291 (4)	619
O(11)	831 (17)	5877 (10)	2521 (12)	795
O(12)	1662 (15)	4455 (11)	5908 (11)	772
O(13)	-1408 (14)	3159 (13)	3249 (14)	791
O(14)	4896 (14)	5121 (9)	3784 (10)	637
O(21)	6179 (14)	3704 (15)	1661 (12)	743
O(22)	6716 (13)	2988 (10)	4925 (10)	623
O(23)	5604 (17)	339 (12)	2478 (14)	843
O(31)	-1247 (17)	1584 (12)	690 (13)	854
O(32)	-973 (18)	481 (13)	3679 (14)	851
O(33)	2419 (20)	-485 (12)	1701 (17)	1010
O(41)	-646 (14)	3940 (11)	181 (12)	736
O(42)	3747 (16)	5342 (11)	829 (12)	809
O(51)	184 (16)	1801 (13)	6021 (13)	912
O(52)	4905 (16)	2521 (11)	6698 (10)	759
O(53)	3363 (15)	-486 (9)	4661 (13)	765
C(11)	1245 (20)	5064 (15)	2872 (15)	597 (46)
C(12)	1794 (19)	4172 (13)	5038 (15)	549 (44)
C(13)	-159 (22)	3241 (14)	3285 (15)	599 (46)
C(14)	3920 (19)	4490 (13)	3701 (13)	488 (40)
C(21)	5338 (21)	3224 (14)	2080 (15)	607 (47)
C(22)	5772 (18)	2763 (12)	4247 (14)	464 (39)
C(23)	5072 (22)	1138 (15)	2692 (16)	687 (52)
C(31)	-209 (23)	1696 (15)	1339 (17)	709 (53)
C(32)	-25 (22)	951 (15)	3293 (16)	686 (51)
C(33)	2028 (26)	339 (20)	1990 (19)	932 (69)
C(41)	479 (21)	3687 (14)	595 (15)	599 (46)
C(42)	3220 (21)	4542 (15)	994 (15)	622 (47)
C(51)	1138 (19)	1819 (13)	5499 (14)	510 (41)
C(52)	4099 (19)	2316 (13)	5931 (15)	512 (42)

Table 5.11 cont'd

C(53)	3121 (19)	415 (14)	4654 (14)	570 (45)
C(1)	2656 (30)	3263 (20)	-1393 (21)	1176 (87)
C(2)	4674 (27)	1957 (20)	-313 (21)	1146 (85)
C(3)	1624 (33)	1282 (23)	-881 (24)	1442 (108)

parameters for the osmium, phosphorus and oxygen atoms, and isotropic thermal parameters for all carbon atoms.

$Os_5(CO)_{18}(CNBu^t)$ (22) and $Os_5(CO)_{15}(CNBu^t)$ (24). The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium, oxygen, nitrogen atoms and carbon atoms of the *t*-butyl group, isotropic thermal parameters for all other carbon atoms, and one variable for the shifts of the thermal parameters of all hydrogen atoms attached to carbon atoms. An extinction parameter was included in the refinement of **24**.

Table 5.12. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**)

Atom	x	y	z	U(iso)
Os(1)	4579.6 (5)	3879.1 (4)	2634.8 (4)	217
Os(2)	3730.2 (5)	2359.5 (4)	2921.1 (4)	228
Os(3)	2574.3 (6)	3225.0 (4)	1509.0 (4)	270
Os(4)	4972.6 (6)	2693.9 (4)	1339.8 (4)	263
Os(5)	2166.7 (6)	3548.1 (4)	3323.1 (5)	285
P(1)	6409 (4)	4631 (3)	2490 (3)	320
O(11)	4039 (12)	5074 (8)	4106 (8)	459
O(12)	3936 (14)	4849 (8)	899 (9)	449
O(13)	6382 (12)	3035 (8)	3987 (11)	568
O(21)	5862 (12)	1205 (7)	2959 (11)	416
O(22)	3697 (16)	2076 (10)	5005 (9)	580
O(23)	1967 (13)	1042 (8)	2605 (11)	508
O(31)	2959 (13)	3436 (9)	-549 (8)	511
O(32)	622 (17)	4422 (13)	1172 (13)	833
O(33)	718 (15)	1966 (10)	1085 (11)	642
O(41)	5844 (13)	3560 (8)	-314 (9)	508
O(42)	7636 (11)	2378 (9)	1985 (10)	548
O(43)	4424 (16)	1239 (7)	236 (10)	271
O(51)	790 (15)	5052 (9)	3235 (12)	695
O(52)	2592 (15)	3727 (9)	5397 (9)	582
O(53)	-245 (12)	2647 (10)	3366 (10)	573
C(11)	4115 (14)	4593 (10)	3531 (12)	316 (38)
C(12)	4030 (14)	4443 (10)	1523 (11)	307 (37)
C(13)	5609 (16)	3278 (11)	3492 (12)	366 (41)
C(21)	5094 (16)	1643 (11)	2886 (12)	374 (42)
C(22)	3674 (17)	2230 (12)	4241 (14)	487 (50)
C(23)	2625 (16)	1542 (11)	2689 (12)	383 (43)
C(31)	2894 (16)	3327 (11)	220 (13)	412 (44)
C(32)	1352 (17)	3978 (11)	1387 (13)	416 (45)
C(33)	1428 (18)	2451 (12)	1268 (14)	492 (50)
C(41)	5523 (16)	3271 (11)	296 (13)	390 (42)
C(42)	6666 (16)	2510 (10)	1742 (12)	358 (41)
C(43)	4654 (16)	1737 (12)	648 (13)	435 (45)
C(51)	1332 (17)	4475 (12)	3249 (13)	447 (46)
C(52)	2425 (15)	3649 (11)	4638 (13)	353 (40)

Table 5.12 cont'd

C(53)	684 (16)	3020 (11)	3368 (12)	402 (44)
C(1)	7270 (19)	4481 (14)	1500 (15)	642 (61)
C(2)	6078 (17)	5664 (11)	2447 (13)	463 (48)
C(3)	7588 (19)	4496 (14)	3407 (15)	665 (63)

Table 5.13. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors ($Å^2$ x 10^4) for $Os_5(CO)_{18}(CNBu^t)$ (**22**)

Atom	x	y	z	U(iso)
Os(1)	-6029.8 (4)	-2797.0 (3)	-2572.3 (2)	324
Os(2)	-7955.5 (4)	-4604.7 (3)	-1933.6 (2)	406
Os(3)	-6954.6 (4)	-1673.5 (3)	-1023.2 (2)	411
Os(4)	-5428.3 (4)	-469.6 (3)	-2652.1 (2)	364
Os(5)	-5358.6 (4)	-4861.8 (3)	-3325.6 (2)	380
O(11)	-8798 (8)	-1605 (5)	-3462 (4)	556
O(12)	-3396 (8)	-4021 (5)	-1592 (4)	604
O(13)	-3831 (9)	-2144 (5)	-4299 (4)	601
O(21)	-10002 (10)	-3848 (7)	-3337 (5)	809
O(22)	-5953 (9)	-5383 (6)	-496 (4)	685
O(23)	-8603 (10)	-7068 (6)	-1610 (6)	832
O(24)	-10668 (8)	-3671 (6)	-600 (4)	669
O(31)	-10058 (8)	-1005 (7)	-1649 (5)	640
O(32)	-3864 (9)	-2187 (7)	-395 (5)	744
O(33)	-7941 (12)	317 (8)	-29 (7)	1017
O(34)	-8180 (9)	-3551 (7)	471 (5)	774
O(41)	-3903 (9)	575 (6)	-4528 (5)	724
O(42)	-2242 (8)	-1753 (6)	-2355 (5)	675
O(43)	-5249 (10)	1465 (6)	-1771 (6)	787
O(51)	-7095 (8)	-3241 (5)	-4730 (4)	583
O(52)	-3578 (10)	-6390 (6)	-1903 (5)	741
O(53)	-2286 (8)	-4663 (6)	-4591 (5)	714
O(54)	-5989 (9)	-7034 (6)	-3738 (5)	673

Table 5.13 cont'd

N(1)	-8579 (9)	862 (6)	-3229 (5)	501
C(11)	-7774 (11)	-2066 (7)	-3102 (6)	433 (22)
C(12)	-4406 (11)	-3577 (8)	-1931 (6)	450 (22)
C(13)	-4675 (11)	-2325 (7)	-3622 (6)	458 (22)
C(21)	-9180 (13)	-4089 (9)	-2852 (7)	606 (27)
C(22)	-6644 (11)	-5055 (8)	-1064 (6)	492 (23)
C(23)	-8398 (12)	-6122 (9)	-1721 (7)	616 (27)
C(24)	-9645 (11)	-3992 (8)	-1096 (6)	474 (23)
C(31)	-8894 (12)	-1246 (8)	-1455 (6)	498 (23)
C(32)	-4977 (13)	-2020 (9)	-645 (7)	585 (26)
C(33)	-7543 (14)	-444 (10)	-395 (8)	755 (32)
C(34)	-7719 (12)	-2873 (9)	-92 (7)	577 (26)
C(41)	-4510 (11)	171 (8)	-3839 (6)	491 (23)
C(42)	-3428 (12)	-1282 (8)	-2425 (6)	485 (23)
C(43)	-5340 (11)	754 (8)	-2116 (6)	526 (24)
C(51)	-6502 (11)	-3828 (8)	-4182 (6)	457 (22)
C(52)	-4265 (12)	-5797 (9)	-2399 (7)	567 (26)
C(53)	-3444 (12)	-4705 (8)	-4126 (6)	528 (24)
C(54)	-5737 (11)	-6224 (8)	-3586 (6)	519 (24)
C(1)	-7498 (11)	338 (7)	-2978 (6)	439 (22)
C(2)	-9882 (11)	1562 (8)	-3591 (8)	573
C(3)	-9811 (21)	1217 (14)	-4479 (10)	1279
C(4)	-11315 (14)	1287 (11)	-3005 (11)	939
C(5)	-9720 (16)	2797 (10)	-3773 (13)	1013

Table 5.14. Fractional Atomic Coordinates (x 10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 x 10^4) for $Os_5(CO)_{15}(CNBu^t)$ (24)

Atom	x	y	z	U(iso)
Os(1)	2911.4 (4)	1673.8 (2)	2277.4 (2)	354[a]
Os(2)	3165.4 (5)	182.6 (2)	2789.8 (2)	388[a]
Os(3)	5057.4 (4)	659.4 (2)	1869.6 (2)	324[a]

Table 5.14 cont'd

Os(4)	5546.1 (5)	1131.7 (2)	3372.1 (2)	401
Os(5)	2025.5 (4)	448.4 (2)	1234.9 (2)	357
O(11)	3886 (11)	3042 (5)	3236 (5)	783
O(12)	125 (9)	2235 (4)	1119 (5)	624
O(13)	863 (10)	1399 (6)	3417 (5)	757
O(21)	3292 (14)	76 (7)	4520 (5)	906
O(22)	-78 (10)	-379 (6)	2593 (5)	783
O(23)	4338 (11)	-1353 (5)	2796 (7)	866
O(31)	8084 (8)	1447 (5)	2111 (5)	608
O(32)	4949 (9)	802 (5)	146 (4)	617
O(33)	6546 (10)	-801 (4)	1851 (6)	709
O(41)	7617 (11)	2439 (5)	3453 (6)	787
O(42)	4877 (12)	1574 (6)	4913 (5)	858
O(43)	8099 (10)	92 (5)	4038 (5)	710
O(51)	1554 (10)	1270 (5)	-279 (4)	671
O(52)	-1387 (8)	307 (5)	1005 (4)	561
O(53)	2364 (10)	-1067 (4)	623 (5)	653
N(1)	4749 (10)	2502 (5)	1213 (5)	494
C(11)	3566 (14)	2513 (7)	2908 (7)	622 (32)
C(12)	1143 (12)	2000 (6)	1537 (6)	448 (26)
C(13)	1662 (14)	1427 (7)	2988 (7)	590 (31)
C(21)	3371 (14)	150 (7)	3886 (7)	653 (34)
C(22)	1138 (14)	-145 (7)	2622 (7)	594 (32)
C(23)	3907 (15)	-773 (8)	2797 (7)	707 (37)
C(31)	6959 (12)	1145 (6)	2071 (6)	467 (26)
C(32)	4874 (12)	735 (6)	774 (6)	448 (26)
C(33)	5989 (13)	-262 (6)	1861 (6)	540 (29)
C(41)	6805 (13)	1953 (7)	3421 (7)	559 (30)
C(42)	5107 (14)	1412 (7)	4339 (8)	657 (34)
C(43)	7122 (13)	472 (6)	3799 (6)	481 (27)
C(51)	1738 (12)	959 (6)	284 (6)	489 (28)
C(52)	-105 (13)	375 (6)	1109 (6)	463 (26)
C(53)	2241 (12)	-489 (6)	855 (6)	420 (25)
C(1)	4176 (12)	2123 (6)	1583 (6)	456 (26)
C(2)	5568 (13)	2975 (6)	798 (7)	532
C(3)	6924 (12)	3283 (6)	1372 (8)	618
C(4)	4478 (15)	3583 (7)	436 (8)	721
C(5)	6113 (17)	2521 (8)	188 (7)	825

Chapter 6 Estimation of Steric Interactions at Coordination Sites of Metal Carbonyl Compounds

6.1 Introduction

The steric properties of ligands can greatly affect the reactivities and formation of organometallic compounds.[140] Tolman first discussed the steric effects of phosphorus in terms of their cone angles in mononuclear complexes.[76b-c] The cone angle concept has been modified when it is applied to cluster compounds and a cluster cone angle concept has been introduced.[131b] Recently, Brown and co-workers reported a more quantitative means of evaluating the steric repulsive interactions for a ligand coordinated to a metal center in a series of mononuclear complexes.[140,141] The method is based on molecular mechanics techniques and computes the gradient of the van der Waals repulsive energy between a ligand and the rest of the molecule to which it is attached as found in structures determined by X-ray crystallography.

In Chapter 5 three different isomers of formula $Os_5(CO)_{15}(L)$ were described. In the *eq,ax* and *eq,eq* isomers it was not apparent in which isomer the noncarbonyl ligand, L, occupied the more sterically crowded site. This prompted a more thorough investigation into the steric effects experienced at a given coordination site in a metal carbonyl complex. In this respect it is complementary to the treatments of Tolman and Brown that estimate the steric effect exerted by a ligand in a metal carbonyl compound.

The method used is based on the HYDEX program.[37] The HYDEX program, created by Orpen, uses X-ray structural coordinates to compute optimized positions for hydride ligands bonded to one, two, or three metal atoms. An optimized position is the position with the minimum potential energy compared to other positions that the same hydride ligand might occupy when it is bonded to the same metal atom(s) subject to appropriate bond length constraints. The potential energy of a particular position is given by the sum of terms $V(r)$ (defined in eq 6.1) over all intramolecular nonbonded interactions involving the hydride in question.[37]

$$V(r) = \frac{a \exp(-br)}{r^d} - \frac{c}{r^6} \tag{6.1}$$

The parameters[142] a, b, c and d are coefficients of the van der Waals potentials and dependent on the atomic type of an atom other than the hydride ligand calculated, and only serve to place the interactions of the hydride with various atomic types on a common (if arbitrary) scale. The potential energies calculated using these parameters are, therefore, relative potential energies (called site energies). Large site energies represent large steric interactions to which the hydride ligand is exposed.

In the current treatment, in order to probe the steric interactions imposed on different coordination sites from the coordinates of a structure determined by X-ray crystallography, the ligands of the compound were replaced one at a time by an atom and the site energy experienced by that atom was calculated with the HYDEX program.[≠] Initially the ligand was replaced by a hydrogen atom, but very small or negative numbers for the site energies were obtained. This was to

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[≠] The author greatly appreciates the assistance of Dr. Jacek Styszynski of this department with this aspect of the study.

be expected since the small hydrogen atom was in a coordination site previously occupied by a carbonyl ligand or an even larger ligand such as a phosphine. An iodine atom was therefore chosen to replace the ligand in a compound. A set of parameters *a-d* for the I···X (instead of H···X) interactions were chosen accordingly. This gave site energies experienced at coordination sites that were in agreement with the expected ideas concerning these interactions in simple metal carbonyl complexes. A metal-iodine distance of 2.00 ± 0.01 Å was chosen so as to be close to M-CO bond lengths; this also gave site energies in a convenient range (2.4 in $Ni(CO)_4$ to 45.2 in $Os_5(CO)_{15}$(*eq*-PMe_3)). This is an artificially short Os-I distance (e.g., the Os-I length in $Os_3(CO)_{12}(I)_2$[143] is 2.8 Å), but variation in the M-I lengths did not change the general relative differences in steric interactions (Table 6.6, page 170), although the differences did not change uniformly. The outputs of the calculations are denoted as "*I numbers*" for the coordination sites. These I numbers are believed to give an indication of the relative size of steric interactions at different coordination sites in mono-, and polynuclear carbonyl compounds. As stated above, the I number magnitudes agree with the expected views of steric interactions at sites in simple metal carbonyl compounds. This does give insight into the steric interactions in more complicated compounds where it is less obvious which the most sterically crowded site is.

6.2 Results and Discussion

6.2.1 Mononuclear Complexes

The results of calculation for some mononuclear species are shown in

Table 6.1 I Numbers for Some Mononuclear Complexes

Complex	I Number
$Ni(CO)_4$	2.5-2.4
$[Fe(CO)_4]^{2-}$	2.6
$[Mn(CO)_5]^-$	22.0-22.5[a]
	13.6-15.7[b]
$Fe(CO)_5$	22.4[a]
	14.7-15.9[b]
$V(CO)_6$	15.1-15.9
$[Nb(CO)_6]^-$	11.5
$[Ta(CO)_6]^-$	11.7
$Cr(CO)_6$	20.5-21.3

[a] Axial positions. [b] Equatorial positions.

Table 6.1. As can be seen, the calculations gave approximately equal values for all coordination sites on each of the tetrahedral species $Ni(CO)_4$[144] and $[Fe(CO)_4]^{2-}$[145] as expected from the symmetry of the species. Similar results were obtained for the six-coordinate species $V(CO)_6$,[146] $[Nb(CO)_6]^-$,[147] $[Ta(CO)_6]^-$,[147] and $Cr(CO)_6$.[148] As expected the I number increases with an increase in the coordination number.

For the five-coordinate trigonal bipyramidal species $[Mn(CO)_5]^-$ [149] and $Fe(CO)_5$[144] the axial sites have larger I numbers (22.0 - 22.5) than that of the equatorial sites (13.6 - 15.9). This is consistent with the one of the basic ideas of VSEPR theory:[150] that lone pairs occupy equatorial positions since these positions are less sterically crowded and there are therefore less electron pair, electron pair repulsions.

Table 6.2 I Numbers for $Os_3(CO)_{12}$

Compound	I Number	
	ax-position	*eq*-position
$Os_3(CO)_{12}$	19.5-21.4	8.2-9.9

6.2.2 Trinuclear Compounds

Table 6.2 shows the results of calculation for the trinuclear compound $Os_3(CO)_{12}$.[36] It is clear that the axial positions have much larger I numbers than the equatorial positions. This is consistent with the observation that bulky phosphorus-donor ligands invariably occupy the equatorial positions in trinuclear clusters even though the axial positions are believed to be the electronically more preferred positions for good σ-donor ligands such as phosphorus-donor ligands.[62a,125]

6.2.3 Pentanuclear Compounds

Previous discussions in this chapter have shown the consistency between the results of calculation using the HYDEX program and the expected view of steric interactions at sites in mononuclear complexes and in $Os_3(CO)_{12}$. In this section the application of the method on pentaosmium clusters is reported.

In $Os_5(CO)_{19}$ (i.e., with the bow-tie configuration) the corresponding carbonyls in the two triangular parts are equal in solution on the NMR time scale. There are, therefore, three axial sites, CO(11), CO(21) and CO(31), and five equatorial sites, CO(13), CO(23), CO(24), CO(33) and CO(34) (see Fig 6.1 for the labeling of these positions). The results of calculation for $Os_5(CO)_{19}$[47] and

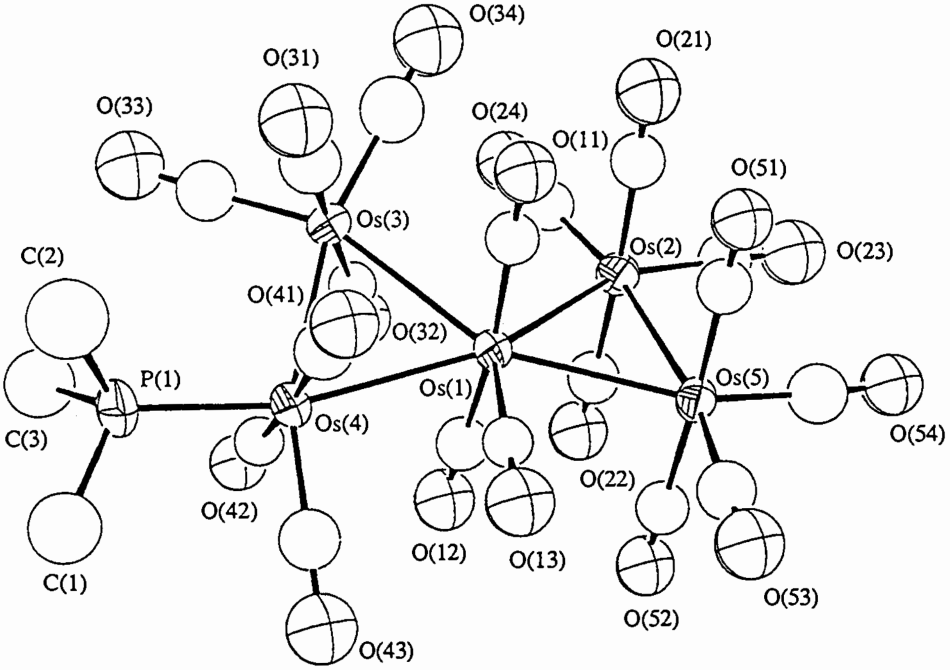

Figure 6.1. The labeling scheme for $Os_5(CO)_{18}(PMe_3)$

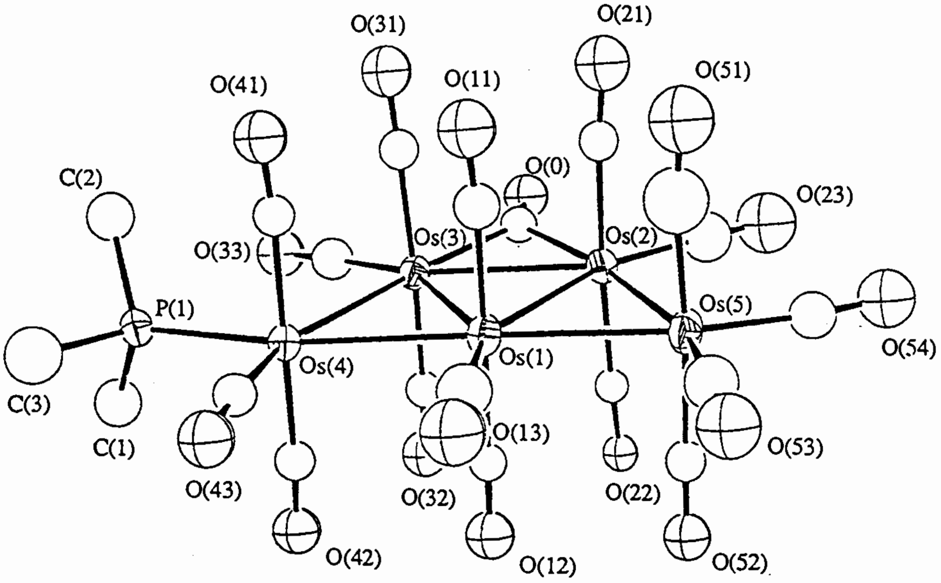

Figure 6.2. The labeling scheme for $Os_5(CO)_{17}(PMe_3)$

Table 6.3 I Numbers[a] for $Os_5(CO)_{19}$ and $Os_5(CO)_{18}(PMe_3)$

Position		I Numbers	
		$Os_5(CO)_{19}$	$Os_5(CO)_{18}(PMe_3)$
Axial	CO(11)	24.2	26.8
	CO(12)	26.9	26.0
	CO(21)	15.6	20.3
	CO(22)	23.1	24.9
	CO(31)	20.7	25.1
	CO(32)	18.4	19.1
	CO(41)	18.0	22.9
	CO(42)	22.6	22.3
	CO(51)	21.1	21.1
	CO(52)	17.0	20.7
Equatorial	CO(13)	29.3	34.4
	CO(23)	10.7	11.3
	CO(24)	12.7	11.1
	CO(33)	9.4	10.7
	CO(34)	10.1	11.6
	CO(43)	15.5	14.3
	P/CO(44)	10.3	11.5
	CO(53)	14.3	14.1
	CO(54)	9.94	12.2

[a] See Figure 6.1 (previous page) for the labeling of the atoms in $Os_5(CO)_{18}(PMe_3)$. The labeling for $Os_5(CO)_{19}$ is similar to that of $Os_5(CO)_{18}(PMe_3)$ except CO(44) occupies the position of the phosphorus atom in $Os_5(CO)_{18}(PMe_3)$.

$Os_5(CO)_{18}(PMe_3)$ are given in Table 6.3. The difference in the I numbers between the axial and equatorial positions is clearly shown. The relatively small value for CO(21) is caused by the twist of the two metal triangles with each other in the solid state and the largest value for CO(13) is apparently due to the presence of

Os(4) and Os(5) (Fig 6.1).

Similarly, in the raft-like $Os_5(CO)_{18}$ there are three axial sites and five equatorial sites (Figure 6.2; replacing PMe_3 with CO(44)). The I numbers for the axial positions in $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$ (Table 6.4) are in the range of 19.4-26.6 and 20.2-29.5, respectively, while those for the equatorial positions are in the range of 10.0-14.2 and 9.33-14.8, respectively. The difference of the values between the axial and equatorial positions is approximately a factor of two; which again is consistent with the view that an axial position in such compounds experiences more steric interactions than that of an equatorial position.

Both the positions of the bridging carbonyls in $Os_5(CO)_{17}(L)$ (L = CO, PMe_3) gave large values for the I numbers. This is rationalized by the steric effects experienced by the iodine atom from ligands on *both* the Os(2) and Os(3) atoms.

The results of calculation for the trigonal bipyramidal $Os_5(CO)_{16}$, $Os_5(CO)_{15}$(*ax*-PMe_3) (20), $Os_5(CO)_{15}$(*eq*-PMe_3) and $Os_5(CO)_{15}(CNBu^t)$ are shown in Table 6.5. In $Os_5(CO)_{16}$ there are six chemically different sites, CO(11), CO(13), CO(21), CO(23), CO(41) and P/CO(43) (see Fig 6.3 for the labeling of these positions; CO(43) occupies the position of the phosphorus atom). The positions corresponding to the P/CO(43) site in all four molecules gave the lowest values. The I numbers confirm that these positions are sterically the least hindered positions in the clusters consistent with the experimental result that the bulky phosphine ligand occupies the position in question in $Os_5(CO)_{15}$(*ax*-PMe_3) (20).

The I numbers for the positions CO(11) (the *eq,eq* position on the Os atom

Table 6.4 I Numbers[a] for $Os_5(CO)_{18}$ and $Os_5(CO)_{17}(PMe_3)$

Position		I Numbers	
		$Os_5(CO)_{18}$	$Os_5(CO)_{17}(PMe_3)$
Axial	CO(11)	26.6	26.7
	CO(12)	25.1	28.4
	CO(21)	23.0	20.9
	CO(22)	22.6	20.2
	CO(31)	23.7	21.0
	CO(32)	23.4	29.5
	CO(41)	19.4	22.9
	CO(42)	22.4	21.6
	CO(51)	20.8	21.3
	CO(52)	23.6	24.9
Equatorial	CO(13)	13.1	14.4
	CO(23)	14.2	12.3
	CO(33)	14.1	14.8
	CO(43)	12.8	13.3
	P/CO(44)	10.0	13.3
	CO(53)	12.1	12.0
	CO(54)	10.9	9.3
Bridging[b]	CO(0)	23.4	23.6

[a] See Figure 6.2 for the labeling of the atoms in $Os_5(CO)_{17}(PMe_3)$. The labeling for $Os_5(CO)_{18}$ is similar to that of $Os_5(CO)_{17}(PMe_3)$ except CO(44) occupies the position of the phosphorus atom in $Os_5(CO)_{17}(PMe_3)$.

[b] The distances from the iodine atom to both the osmium atoms are 2.00 Å.

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with four ligands) and CO(13) (the *eq,ax* position on the same atom) in $Os_5(CO)_{16}$ are 18.6 and 37.2, respectively. The same trend exists in the other $Os_5(CO)_{15}(L)$ molecules. This shows the steric effect at the CO(11) site is actually much smaller compared to that at the CO(13) site. It was the results of these

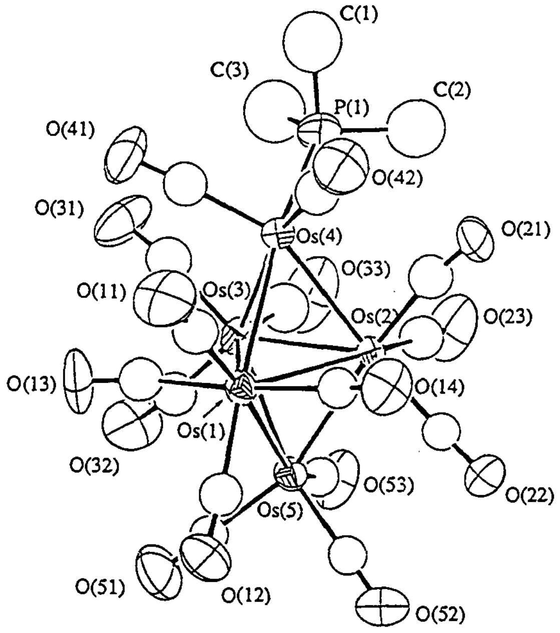

Figure 6.3 The labeling scheme for $Os_5(CO)_{15}$(*ax*-PMe_3).

calculations that made us into a more closer examination of the nonbonded contacts in $Os_5(CO)_{15}(CNBu^t)$ as discussed in Chapter 5 (page 136). The consistency of the examination of the nonbonded contacts and the calculations is expected since they are mainly based on the X-ray results. It also suggests that the HYDEX program can be used to clusters of high nuclearity to indicate qualitatively the differences of steric interactions at the various sites.

Table 6.6 shows the change of the I numbers as the osmium-iodine distances are changed for a pair of similar positions (C(41) and C(42) in $Os_5(CO)_{15}$(*ax*-PMe_3) (20) shown in Fig 6.3) and a pair of different sites (C(12) and C(13) shown in Fig 6.3) in $Os_5(CO)_{15}$(*eq*-PMe_3). As can be seen, the variation in the M-I lengths did not change the general relative differences in the I numbers although the differences did not change uniformly.

Table 6.5 I Numbers[a] for $Os_5(CO)_{16}$ (**17**), $Os_5(CO)_{15}$(*ax*-PMe_3) (**20**), $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**) and $Os_5(CO)_{15}$($CNBu^t$) (**24**)

Position	I Numbers			
	Compound			
	17	**20**	**21**	**24**
CO(11)	18.6	16.8	26.3[b]	19.1
CO(12)	18.6	14.5	29.8	15.8
CO(13)	37.2	39.2	45.2	39.6[c]
CO(14)	37.2	41.0	44.4	33.2
CO(21)	24.8	26.7	27.4	24.9
CO(22)	26.1	23.0	19.4	23.3
CO(23)	14.4	12.6	15.2	13.8
CO(31)	26.1	27.8	28.1	24.1
CO(32)	24.8	23.7	22.3	25.9
CO(33)	14.4	12.2	14.1	13.4
CO(41)	17.7	15.7	14.6	14.4
CO(42)	14.9	15.9	12.1	13.9
P	5.2[d]	4.73	4.1[d]	5.1[d]
CO(51)	14.9	11.9	15.2	15.0
CO(52)	17.7	12.4	14.5	14.1
CO(53)	5.2	7.48	8.0	6.3

[a] See Figure 6.3 (previous page) for the labeling of the atoms in compound **20**. The labeling for compounds **17**, **21** and **24** is similar to that of **20** except those positions specified in the footnotes b-d.

[b] Position occupied by the phosphine ligand.

[c] Position occupied by the isocyanide ligand. [d] Position occupied by CO(43).

Table 6.6 I Numbers for Positions CO(12), CO(13), CO(41) and CO(42) (shown in Fig 6.3) for $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**)

M-I (Å)	I Numbers			
	CO(12)	CO(13)	CO(41)	CO(42)
2.00	29.8	45.2	14.6	12.1
2.20	19.7	31.6	7.9	6.1
2.40	12.4	21.6	3.7	2.3
2.6	7.2	14.5	0.8	0.2

6.2.4 **Errors in I Numbers**

The errors in the I numbers are not clear. An approach to this problem is to compare the I numbers of chemically equivalent sites in a molecule. The maximium variation of the values for the chemically equivalent sites in the four-coordinate and six-coordinate species $Ni(CO)_4$, $[Fe(CO)_4]^{2-}$, $V(CO)_6$, $[Nb(CO)_6]^-$, $[Ta(CO)_6]^-$ and $Cr(CO)_6$ (Table 6.1) is 0.1, 0, 0.8, 0, 0 and 0.8, respectively. The maximum variation of the I numbers in the five-coordinate compounds $[Mn(CO)_5]^-$ and $Fe(CO)_5$ is 0.5 and 0, respectively, for the axial sites, and 2.1 and 1.2, respectively, for the equatorial sites. In other words, the variation in the mononuclear species is in the range of 0-2.1. Similar analysis of data for $Os_3(CO)_{12}$ (Table 6.2) showed maximum variations 1.9 and 1.7 for the axial and equatorial sites, respectively.

In $Os_5(CO)_{18}$ there are eight chemically different sites. The maximum variation of the I numbers (Table 6.4) among chemically equivalent sites is 1.4, 0, 1.1, 0.1, 0, 4.2, 0.7 and 0.9 for CO(11) (CO(12)), CO(13), CO(21) (CO(22), CO(31), CO(32)), CO(23) (CO(33)), CO(0), CO(41) (CO(42), CO(51), CO(52)), CO(43) (CO(53)) and CO(44) (CO(54)), respectively, a range of 0-4.2.

The results obtained from mono, tri and pentanuclear compounds suggest that the errors for the I numbers are approximately ± 2.1. In other words, I numbers for two sites that differ by more than 5.4 (2.58σ, confidence level 99%) clearly indicate greater steric interactions at the site with the larger I number.

6.2.5 Conclusion

The results presented here are preliminary results. They do, however, show that the I numbers calculated by the HYDEX program have significant potential in the discussion of steric interactions in metal carbonyl compounds, and indeed metal complexes in general.

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Table A.1. Uij ($Å^2$ x 10^4) for $[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ **(2)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	358(3)	312(3)	323(3)	-38(2)	-53(2)	2(2)
Os(2)	329(3)	317(3)	327(3)	-43(2)	-51(2)	4(2)
Os(3)	340(3)	375(3)	316(3)	-35(2)	-19(2)	18(2)
Re(1)	465(3)	371(3)	280(3)	-30(2)	-68(2)	7(2)
P(1)	555(19)	401(17)	315(17)	-45(14)	-130(15)	59(15)
O(11)	382(50)	709(63)	812(71)	2(53)	-85(48)	-19(45)
O(12)	521(55)	715(65)	750(67)	-157(54)	-101(49)	192(49)
O(13)	972(76)	480(58)	879(77)	-18(54)	-80(63)	-164(53)
O(21)	488(53)	531(54)	903(71)	-103(50)	-206(51)	187(44)
O(22)	371(49)	735(65)	890(74)	-184(55)	-109(49)	84(45)
O(23)	1260(90)	757(73)	558(63)	226(55)	-111(64)	-376(66)
O(24)	620(55)	614(58)	617(58)	-322(50)	-152(47)	15(45)
O(31)	382(50)	778(67)	887(75)	-176(56)	0(49)	201(46)
O(32)	404(48)	443(50)	793(65)	-79(47)	-133(45)	42(39)
O(33)	796(68)	1222(91)	561(61)	-496(62)	-44(54)	-65(62)
O(34)	714(66)	605(66)	1099(93)	272(62)	61(63)	-163(54)
O(1)	633(58)	616(60)	809(69)	-131(51)	-355(53)	219(48)
O(2)	541(58)	945(77)	708(67)	-220(58)	14(50)	-11(52)
O(3)	1595(111)	616(67)	626(68)	243(57)	-154(72)	-455(71)

Table A.2. Additional Bond Lengths (Å) and Angles (°) for $[(Ph_3P)(OC)_3Re](\mu\text{-}H)Os_3(CO)_{11}$ (**2**)

Bond Lengths

Os(1) - C(11)	1.93 (1)
Os(1) - C(12)	1.94 (1)
Os(1) - C(13)	1.86 (1)
Os(2) - C(21)	1.98 (1)
Os(2) - C(22)	1.97 (1)
Os(2) - C(23)	1.92 (1)
Os(2) - C(24)	1.93 (1)
Os(3) - C(31)	1.97 (1)
Os(3) - C(32)	1.94 (1)
Os(3) - C(33)	1.91 (1)
Os(3) - C(34)	1.90 (1)
Re(1) - C(1)	1.98 (1)
Re(1) - C(2)	1.98 (1)
Re(1) - C(3)	1.91 (1)
P(1) - C(111)	1.81(1)
P(1) - C(121)	1.83(1)
P(1) - C(131)	1.84(1)
O(11) - C(11)	1.14(1)
O(12) - C(12)	1.13(1)
O(13) - C(13)	1.18(1)
O(21) - C(21)	1.11(1)
O(22) - C(22)	1.13(1)
O(23) - C(23)	1.12(1)
O(24) - C(24)	1.11(1)
O(31) - C(31)	1.13(1)
O(32) - C(32)	1.14(1)
O(33) - C(33)	1.13(2)
O(34) - C(34)	1.14(1)
O(1) - C(1)	1.13(1)
O(2) - C(2)	1.14(1)
O(3) - C(3)	1.15(1)
C(111) - C(112)	1.38(2)
C(111) - C(116)	1.39(2)
C(112) - C(113)	1.38(2)
C(113) - C(114)	1.38(2)
C(114) - C(115)	1.36(2)
C(115) - C(116)	1.38(2)
C(121) - C(122)	1.39(2)
C(121) - C(126)	1.39(2)
C(122) - C(123)	1.41(2)
C(123) - C(124)	1.31(2)
C(124) - C(125)	1.33(2)
C(125) - C(126)	1.41(2)
C(131) - C(132)	1.39(2)
C(131) - C(136)	1.34(2)
C(132) - C(133)	1.40(2)
C(133) - C(134)	1.38(2)
C(134) - C(135)	1.36(2)
C(135) - C(136)	1.42(2)

Bond Angles

C(11) - Os(1) - Os(2)	89.5(3)
C(11) - Os(1) - Os(3)	89.6(4)
C(11) - Os(1) - Re(1)	85.7(4)
C(12) - Os(1) - Os(2)	95.6(3)
C(12) - Os(1) - Os(3)	96.3(3)
C(12) - Os(1) - Re(1)	93.0(3)
C(12) - Os(1) - C(11)	173.5(5)
C(13) - Os(1) - Os(2)	167.2(4)
C(13) - Os(1) - C(11)	89.5(5)
C(13) - Os(1) - C(12)	86.4(5)
C(21) - Os(2) - Os(1)	91.0(3)
C(21) - Os(2) - Os(3)	90.1(3)
C(21) - Os(2) - Re(1)	86.9(3)
C(22) - Os(2) - Os(1)	84.4(3)
C(22) - Os(2) - Os(3)	90.4(4)
C(22) - Os(2) - Re(1)	87.7(3)

Table A.2 cont'd

C(22) - Os(2) - C(21)	174.3(5)	O(24) - C(24) - Os(2)	175.2(11)
C(23) - Os(2) - Os(1)	133.5(4)	O(31) - C(31) - Os(3)	177.4(11)
C(23) - Os(2) - Os(3)	169.0(4)	O(32) - C(32) - Os(3)	174.0(10)
C(23) - Os(2) - C(21)	91.0(5)	O(33) - C(33) - Os(3)	174.9(12)
C(23) - Os(2) - C(22)	89.6(5)	O(34) - C(34) - Os(3)	176.5(13)
C(24) - Os(2) - Os(1)	132.1(3)	O(1) - C(1) - Re(1)	172.7(11)
C(24) - Os(2) - Re(1)	169.2(3)	O(2) - C(2) - Re(1)	174.7(11)
C(24) - Os(2) - C(21)	92.0(5)	O(3) - C(3) - Re(1)	175.7(13)
C(24) - Os(2) - C(22)	93.6(5)	C(111) - P(1) - Re(1)	112.4(4)
C(24) - Os(2) - C(23)	94.2(5)	C(121) - P(1) - Re(1)	119.5(4)
C(31) - Os(3) - Os(1)	92.4(3)	C(121) - P(1) - C(111)	102.6(5)
C(31) - Os(3) - Os(2)	89.3(4)	C(131) - P(1) - Re(1)	114.3(4)
C(32) - Os(3) - Os(1)	85.2(3)	C(131) - P(1) - C(111)	103.8(5)
C(32) - Os(3) - Os(2)	87.0(3)	C(131) - P(1) - C(121)	102.4(6)
C(32) - Os(3) - C(31)	176.2(5)	C(112) - C(111) - P(1)	122.8(9)
C(33) - Os(3) - Os(1)	170.4(4)	C(116) - C(111) - P(1)	120.7(9)
C(33) - Os(3) - C(31)	91.2(5)	C(116) - C(111) - C(112)	116.5(12)
C(33) - Os(3) - C(32)	90.7(5)	C(113) - C(112) - C(111)	120.0(14)
C(34) - Os(3) - Os(2)	150.0(4)	C(114) - C(113) - C(112)	122.5(16)
C(34) - Os(3) - C(31)	89.5(5)	C(115) - C(114) - C(113)	117.3(16)
C(34) - Os(3) - C(32)	93.4(5)	C(116) - C(115) - C(114)	120.8(15)
C(34) - Os(3) - C(33)	99.7(6)	C(115) - C(116) - C(111)	122.5(13)
C(1) - Re(1) - Os(1)	95.8(4)	C(122) - C(121) - P(1)	121.0(10)
C(1) - Re(1) - Os(2)	91.7(4)	C(126) - C(121) - P(1)	121.1(9)
C(1) - Re(1) - P(1)	89.1(4)	C(126) - C(121) - C(122)	118.0(12)
C(2) - Re(1) - Os(1)	92.5(4)	C(123) - C(122) - C(121)	118.6(13)
C(2) - Re(1) - Os(2)	89.2(4)	C(124) - C(123) - C(122)	122.3(14)
C(2) - Re(1) - P(1)	92.8(4)	C(125) - C(124) - C(123)	120.1(15)
C(2) - Re(1) - C(1)	170.6(5)	C(126) - C(125) - C(124)	121.3(14)
C(3) - Re(1) - Os(1)	158.8(4)	C(125) - C(126) - C(121)	119.5(12)
C(3) - Re(1) - C(1)	85.8(5)	C(132) - C(131) - P(1)	117.8(10)
C(3) - Re(1) - C(2)	84.9(5)	C(136) - C(131) - P(1)	122.5(10)
O(11) - C(11) - Os(1)	173.1(11)	C(136) - C(131) - C(132)	119.7(13)
O(12) - C(12) - Os(1)	175.1(10)	C(133) - C(132) - C(131)	120.7(15)
O(13) - C(13) - Os(1)	179.4(12)	C(134) - C(133) - C(132)	118.2(16)
O(21) - C(21) - Os(2)	174.6(11)	C(135) - C(134) - C(133)	122.0(18)
O(22) - C(22) - Os(2)	174.1(11)	C(136) - C(135) - C(134)	118.7(18)
O(23) - C(23) - Os(2)	172.2(12)	C(135) - C(136) - C(131)	120.8(14)

Table B.1. Uij ($Å^2 \times 10^4$) for $(Cp^*)(CO)_2OsOs_3(\mu\text{-}H)(CO)_{10}$ (3)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	447(6)	335(5)	389(6)	-10(4)	-44(5)	10(5)
Os(2)	414(6)	357(5)	389(6)	41(4)	27(5)	25(5)
Os(3)	490(6)	324(5)	491(6)	-4(4)	-24(6)	72(5)
Os(4)	350(5)	294(4)	387(5)	-8(4)	7(6)	-20(4)
O(11)	952(176)	566(115)	965(151)	329(115)	-14(124)	138(119)
O(12)	657(155)	1049(160)	1098(161)	-322(136)	-282(124)	250(129)
O(13)	731(146)	669(123)	960(143)	-559(113)	-243(118)	175(108)
O(21)	1354(215)	961(150)	315(102)	-269(101)	-122(112)	239(142)
O(22)	532(141)	1316(192)	1144(172)	619(147)	225(122)	242(136)
O(23)	808(143)	452(104)	1033(148)	266(100)	485(123)	102(110)
O(31)	512(132)	592(128)	3003(351)	-51(181)	427(198)	-20(112)
O(32)	419(113)	684(127)	1723(214)	25(135)	-48(159)	12(101)
O(33)	1929(272)	1063(165)	516(121)	-338(121)	-99(144)	617(179)
O(34)	1383(228)	1091(187)	1269(196)	374(166)	-398(172)	49(178)
O(41)	877(217)	1047(173)	1423(195)	-832(157)	-141(156)	-132(139)
O(42)	644(175)	808(140)	1203(165)	541(128)	167(129)	-162(115)

Table B.2. Additional Bond Lengths (Å) and Angles (°) for
$Cp^*Os_4(\mu\text{-}H)(CO)_{12}$ (**3**)

Bond lengths

Os(1) - C(11)	1.89(3)	O(33) - C(33)	1.14(3)
Os(1) - C(12)	1.88(3)	O(34) - C(34)	1.16(3)
Os(1) - C(13)	1.93(2)	O(41) - C(41)	1.13(3)
Os(2) - C(21)	1.94(3)	O(42) - C(42)	1.19(3)
Os(2) - C(22)	1.90(3)	C(1) - C(2)	1.41(3)
Os(2) - C(23)	1.91(2)	C(1) - C(5)	1.41(3)
Os(3) - C(31)	1.93(3)	C(2) - C(3)	1.43(3)
Os(3) - C(32)	1.99(3)	C(3) - C(4)	1.41(3)
Os(3) - C(33)	1.93(3)	C(4) - C(5)	1.42(3)
Os(3) - C(34)	1.84(3)	C(1) - C(6)	1.57(3)
Os(4) - C(41)	1.91(3)	C(2) - C(7)	1.52(3)
Os(4) - C(42)	1.80(3)	C(3) - C(8)	1.52(3)
O(11) - C(11)	1.14(3)	C(4) - C(9)	1.54(3)
O(12) - C(12)	1.15(3)	C(5) - C(10)	1.51(3)
O(13) - C(13)	1.11(2)	Os(4) - C(1)	2.24(2)
O(21) - C(21)	1.13(3)	Os(4) - C(2)	2.30(2)
O(22) - C(22)	1.13(3)	Os(4) - C(3)	2.34(2)
O(23) - C(23)	1.12(2)	Os(4) - C(4)	2.29(2)
O(31) - C(31)	1.09(3)	Os(4) - C(5)	2.24(2)
O(32) - C(32)	1.10(3)		

Bond Angles

C(11) - Os(1) - Os(3)	89.4(7)	C(23) - Os(2) - C(21)	96.1(9)
C(11) - Os(1) - Os(4)	100.6(8)	C(23) - Os(2) - C(22)	88.3(11)
C(12) - Os(1) - Os(3)	85.6(7)	C(31) - Os(3) - Os(1)	87.8(7)
C(12) - Os(1) - Os(4)	169.9(7)	C(31) - Os(3) - Os(2)	89.9(7)
C(13) - Os(1) - Os(3)	173.3(7)	C(32) - Os(3) - Os(1)	89.4(8)
C(13) - Os(1) - Os(4)	86.2(7)	C(32) - Os(3) - Os(2)	87.2(7)
C(12) - Os(1) - C(11)	89.4(11)	C(32) - Os(3) - C(31)	176.7(10)
C(13) - Os(1) - C(11)	96.3(10)	C(33) - Os(3) - Os(1)	154.1(8)
C(13) - Os(1) - C(12)	91.1(10)	C(33) - Os(3) - Os(2)	96.3(8)
C(21) - Os(2) - Os(3)	89.7(7)	C(33) - Os(3) - C(31)	89.8(11)
C(21) - Os(2) - Os(4)	102.0(8)	C(33) - Os(3) - C(32)	92.0(11)
C(22) - Os(2) - Os(3)	85.5(8)	C(34) - Os(3) - Os(1)	104.0(8)
C(22) - Os(2) - Os(4)	171.6(8)	C(34) - Os(3) - Os(2)	162.0(8)
C(22) - Os(2) - C(21)	86.1(12)	C(34) - Os(3) - C(31)	90.8(11)
C(23) - Os(2) - Os(3)	171.2(7)	C(34) - Os(3) - C(32)	91.5(11)
C(23) - Os(2) - Os(4)	89.0(7)	C(34) - Os(3) - C(33)	101.8(11)

Table B.2 cont'd

C(41) - Os(4) - Os(1)	110.5(8)
C(41) - Os(4) - Os(2)	72.6(8)
C(42) - Os(4) - Os(1)	70.4(10)
C(42) - Os(4) - Os(2)	111.2(10)
C(42) - Os(4) - C(41)	93.2(12)
C(1) - Os(4) - Os(1)	132.6(6)
C(1) - Os(4) - Os(2)	158.6(6)
C(1) - Os(4) - C(41)	113.2(10)
C(1) - Os(4) - C(42)	89.5(12)
C(2) - Os(4) - Os(1)	103.5(6)
C(2) - Os(4) - Os(2)	129.6(6)
C(2) - Os(4) - C(41)	146.0(10)
C(2) - Os(4) - C(42)	99.4(11)
C(2) - Os(4) - C(1)	36.3(8)
C(3) - Os(4) - Os(1)	103.8(5)
C(3) - Os(4) - Os(2)	99.6(5)
C(3) - Os(4) - C(41)	129.1(9)
C(3) - Os(4) - C(42)	134.0(10)
C(3) - Os(4) - C(1)	60.3(8)
C(3) - Os(4) - C(2)	35.9(7)
C(4) - Os(4) - Os(1)	132.2(5)
C(4) - Os(4) - Os(2)	98.8(5)
C(4) - Os(4) - C(41)	94.7(9)
C(4) - Os(4) - C(42)	150.0(12)
C(4) - Os(4) - C(1)	60.8(8)
C(4) - Os(4) - C(2)	59.9(7)
C(5) - Os(4) - Os(1)	162.7(6)
C(5) - Os(4) - Os(2)	128.8(6)
C(5) - Os(4) - C(41)	85.7(10)
C(5) - Os(4) - C(42)	116.0(12)
C(5) - Os(4) - C(1)	36.7(7)
C(5) - Os(4) - C(2)	60.3(8)
C(4) - Os(4) - C(3)	35.4(6)
C(5) - Os(4) - C(3)	59.8(8)
C(5) - Os(4) - C(4)	36.3(7)
O(11) - C(11) - Os(1)	170.5(25)
O(12) - C(12) - Os(1)	177.0(24)
O(13) - C(13) - Os(1)	170.9(23)
O(21) - C(21) - Os(2)	177.8(24)
O(22) - C(22) - Os(2)	173.9(27)
O(23) - C(23) - Os(2)	169.7(22)
O(31) - C(31) - Os(3)	171.6(26)
O(32) - C(32) - Os(3)	176.9(25)
O(33) - C(33) - Os(3)	176.3(24)
O(34) - C(34) - Os(3)	177.4(27)
O(41) - C(41) - Os(4)	168.5(26)
O(42) - C(42) - Os(4)	168.6(27)
C(2) - C(1) - Os(4)	74.2(14)
C(5) - C(1) - Os(4)	71.9(15)
C(5) - C(1) - C(2)	107.7(22)
C(6) - C(1) - Os(4)	128.9(17)
C(6) - C(1) - C(2)	127.4(21)
C(6) - C(1) - C(5)	123.8(23)
C(1) - C(2) - Os(4)	69.5(13)
C(3) - C(2) - Os(4)	73.8(12)
C(3) - C(2) - C(1)	108.0(19)
C(7) - C(2) - Os(4)	131.2(16)
C(7) - C(2) - C(1)	125.0(21)
C(7) - C(2) - C(3)	126.0(20)
C(2) - C(3) - Os(4)	70.3(12)
C(4) - C(3) - Os(4)	70.4(11)
C(4) - C(3) - C(2)	107.6(18)
C(8) - C(3) - Os(4)	133.6(14)
C(8) - C(3) - C(2)	125.4(19)
C(8) - C(3) - C(4)	126.0(19)
C(3) - C(4) - Os(4)	74.2(11)
C(5) - C(4) - Os(4)	69.8(13)
C(5) - C(4) - C(3)	108.0(18)
C(9) - C(4) - Os(4)	135.4(15)
C(9) - C(4) - C(3)	127.5(19)
C(9) - C(4) - C(5)	122.0(19)
C(1) - C(5) - Os(4)	71.4(15)
C(4) - C(5) - Os(4)	73.8(13)
C(4) - C(5) - C(1)	108.6(21)
C(10) - C(5) - Os(4)	128.6(17)
C(10) - C(5) - C(1)	125.3(23)
C(10) - C(5) - C(4)	125.3(21)

Table C.1. Uij ($Å^2 \times 10^4$) for $(Me_3P)_2(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$ (**4**)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	466 (3)	547 (3)	427 (3)	21 (2)	124 (2)	-36 (2)
Os(2)	770 (5)	936 (4)	434 (3)	-14 (3)	147 (3)	-386 (3)
Os(3)	564 (4)	768 (4)	696 (4)	240 (3)	95 (3)	13 (3)
Re(1)	436 (3)	757 (4)	419 (3)	23 (3)	140 (2)	106 (3)
P(1)	622 (28)	1212 (34)	582 (25)	-110 (23)	156 (21)	-240 (24)
P(2)	559 (25)	845 (25)	623 (24)	-76 (19)	269 (20)	64 (19)
O(11)	454 (62)	1297 (85)	957 (80)	91 (65)	196 (56)	-209 (58)
O(12)	695 (75)	1403 (89)	793 (75)	237 (66)	294 (61)	-93 (65)
O(13)	1134 (99)	623 (62)	1461 (111)	16 (62)	418 (84)	228 (61)
O(21)	843 (83)	1423 (90)	803 (74)	-247 (68)	425 (66)	-408 (70)
O(22)	1150 (112)	2796 (175)	866 (89)	7 (102)	345 (83)	-1169 (119)
O(23)	3180 (245)	1092 (107)	1754 (153)	-451 (97)	1484 (170)	-420 (125)
O(24)	1025 (107)	3337 (207)	669 (81)	543 (111)	-87 (76)	-972 (123)
O(31)	1146 (105)	909 (75)	1415 (115)	64 (71)	551 (89)	-241 (69)
O(32)	827 (97)	1441 (115)	2891 (213)	579 (118)	974 (120)	220 (81)
O(33)	1565 (164)	3133 (233)	1383 (143)	1452 (157)	-37 (119)	234 (148)
O(34)	1238 (119)	1048 (90)	2144 (164)	-267 (93)	812 (116)	-1 (77)
O(41)	932 (98)	2365 (148)	999 (93)	-214 (96)	247 (77)	945 (102)
O(42)	1555 (117)	658 (63)	1058 (91)	152 (59)	455 (85)	-74 (68)
O(43)	854 (93)	2457 (152)	622 (74)	34 (86)	82 (66)	581 (94)
CL(1)	3044 (167)	3045 (132)	3497 (167)	705 (120)	1337 (141)	-64 (116)

Table C.2. Additional Bond Lengths (Å) and Angles (°) for $(OC)_3(Me_3P)_2Re(\mu\text{-}H)Os_3(CO)_{11}$ (**4**)

Bond Lengths

Os(1) - C(11)	1.93 (1)	P(2) - C(48)	1.80 (2)
Os(1) - C(12)	1.92 (2)	P(2) - C(49)	1.76 (2)
Os(1) - C(13)	1.86 (1)	O(11) - C(11)	1.14 (1)
Os(2) - C(21)	1.93 (2)	O(12) - C(12)	1.17 (2)
Os(2) - C(22)	1.96 (2)	O(13) - C(13)	1.16 (1)
Os(2) - C(23)	1.88 (2)	O(21) - C(21)	1.13 (2)
Os(2) - C(24)	1.89 (2)	O(22) - C(22)	1.12 (2)
Os(3) - C(31)	1.93 (2)	O(23) - C(23)	1.13 (2)
Os(3) - C(32)	1.95 (2)	O(24) - C(24)	1.14 (2)
Os(3) - C(33)	1.92 (3)	O(31) - C(31)	1.16 (2)
Os(3) - C(34)	1.86 (2)	O(32) - C(32)	1.13 (2)
Re(1) - C(41)	1.98 (2)	O(33) - C(33)	1.10 (2)
Re(1) - C(42)	1.93 (1)	O(34) - C(34)	1.19 (2)
Re(1) - C(43)	1.84 (2)	O(41) - C(41)	1.11 (2)
P(1) - C(44)	1.77 (2)	O(42) - C(42)	1.17 (2)
P(1) - C(45)	1.77 (3)	O(43) - C(43)	1.20 (2)
P(1) - C(46)	1.85 (2)	CL(1) - C(1)	1.58 (4)
P(2) - C(47)	1.75 (2)		

Bond Angles

C(11) - Os(1) - Os(2)	93.3 (4)	C(24) - Os(2) - Os(3)	96.4 (5)
C(11) - Os(1) - Os(3)	92.5 (4)	C(31) - Os(3) - Os(1)	85.0 (5)
C(11) - Os(1) - Re(1)	88.5 (4)	C(31) - Os(3) - Os(2)	88.1 (5)
C(12) - Os(1) - Os(2)	91.9 (4)	C(32) - Os(3) - Os(1)	85.4 (6)
C(12) - Os(1) - Os(3)	91.7 (4)	C(32) - Os(3) - Os(2)	90.2 (5)
C(12) - Os(1) - Re(1)	86.3 (4)	C(33) - Os(3) - Os(1)	150.9 (6)
C(13) - Os(1) - Os(2)	94.2 (4)	C(34) - Os(3) - Os(2)	170.3 (6)
C(13) - Os(1) - Os(3)	154.4 (4)	C(41) - Re(1) - Os(1)	81.1 (5)
C(13) - Os(1) - Re(1)	85.4 (4)	C(41) - Re(1) - P(1)	87.4 (4)
C(21) - Os(2) - Os(1)	87.7 (4)	C(41) - Re(1) - P(2)	178.2 (4)
C(21) - Os(2) - Os(3)	90.5 (4)	C(42) - Re(1) - Os(1)	82.5 (4)
C(22) - Os(2) - Os(1)	87.5 (5)	C(42) - Re(1) - P(1)	175.7 (4)
C(22) - Os(2) - Os(3)	88.7 (5)	C(42) - Re(1) - P(2)	89.3 (4)
C(23) - Os(2) - Os(1)	101.7 (7)	C(43) - Re(1) - Os(1)	170.8 (5)
C(23) - Os(2) - Os(3)	162.5 (7)	C(43) - Re(1) - P(1)	87.2 (5)
C(24) - Os(2) - Os(1)	157.2 (5)	C(43) - Re(1) - P(2)	87.0 (5)

Table C.2 cont'd

C(12) - Os(1) - C(11)	174.5 (6)	C(46) - P(1) - C(44)	101.4 (10)
C(13) - Os(1) - C(11)	87.1 (6)	C(46) - P(1) - C(45)	105.5 (14)
C(13) - Os(1) - C(12)	90.6 (6)	C(47) - P(2) - Re(1)	120.0 (7)
C(22) - Os(2) - C(21)	174.9 (7)	C(48) - P(2) - Re(1)	113.2 (7)
C(23) - Os(2) - C(21)	89.1 (8)	C(48) - P(2) - C(47)	103.8 (9)
C(23) - Os(2) - C(22)	90.2 (8)	C(49) - P(2) - Re(1)	116.1 (7)
C(24) - Os(2) - C(21)	91.6 (7)	C(49) - P(2) - C(47)	102.5 (10)
C(24) - Os(2) - C(22)	93.5 (8)	C(49) - P(2) - C(48)	98.4 (9)
C(24) - Os(2) - C(23)	101.1 (9)	O(11) - C(11) - Os(1)	175.7 (12)
C(32) - Os(3) - C(31)	169.6 (7)	O(12) - C(12) - Os(1)	174.1 (13)
C(33) - Os(3) - C(31)	94.6 (8)	O(13) - C(13) - Os(1)	175.7 (13)
C(33) - Os(3) - C(32)	95.7 (9)	O(21) - C(21) - Os(2)	174.5 (13)
C(34) - Os(3) - C(31)	90.8 (7)	O(22) - C(22) - Os(2)	174.5 (17)
C(34) - Os(3) - C(32)	89.1 (8)	O(23) - C(23) - Os(2)	178.5 (21)
C(34) - Os(3) - C(33)	97.7 (8)	O(24) - C(24) - Os(2)	177.8 (17)
C(42) - Re(1) - C(41)	88.9 (6)	O(31) - C(31) - Os(3)	173.1 (14)
C(43) - Re(1) - C(41)	92.5 (7)	O(32) - C(32) - Os(3)	173.4 (17)
C(43) - Re(1) - C(42)	90.9 (6)	O(33) - C(33) - Os(3)	174.1 (23)
C(44) - P(1) - Re(1)	120.4 (7)	O(34) - C(34) - Os(3)	177.7 (17)
C(45) - P(1) - Re(1)	116.9 (10)	O(41) - C(41) - Re(1)	177.4 (15)
C(45) - P(1) - C(44)	99.2 (12)	O(42) - C(42) - Re(1)	177.2 (12)
C(46) - P(1) - Re(1)	111.3 (7)	O(43) - C(43) - Re(1)	177.4 (16)

Table D.1. Uij ($Å^2 \times 10^4$) for $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	428 (3)	325 (3)	383 (3)	-100 (2)	-70 (2)	-15 (2)
Os(2)	445 (3)	320 (3)	391 (3)	-90 (2)	-75 (2)	-41 (2)
Os(3)	522 (4)	378 (3)	530 (3)	-67 (2)	-210 (3)	-4 (3)
Re(1)	394 (3)	321 (3)	403 (3)	-93 (2)	-79 (2)	-36 (2)
Re(2)	448 (3)	351 (3)	460 (3)	-123 (2)	-112 (3)	-34 (2)
P(1)	434 (22)	492 (20)	584 (22)	-113 (17)	-48 (18)	-51 (17)
P(2)	724 (27)	480 (20)	400 (19)	-46 (16)	-130 (19)	-151 (19)
O(11)	587 (67)	657 (62)	811 (70)	-260 (54)	90 (57)	-71 (53)
O(12)	935 (86)	697 (67)	636 (65)	-43 (54)	170 (63)	-171 (63)
O(13)	766 (80)	952 (79)	1098 (87)	-554 (71)	-250 (67)	-166 (65)
O(21)	1091 (92)	761 (71)	602 (63)	-245 (54)	208 (63)	-361 (68)
O(22)	980 (95)	1252 (102)	767 (76)	-280 (71)	175 (69)	-467 (82)
O(23)	839 (78)	591 (59)	722 (65)	-50 (52)	-350 (60)	-40 (56)
O(31)	692 (78)	973 (85)	850 (79)	-136 (66)	9 (66)	17 (66)
O(32)	956 (96)	998 (89)	920 (86)	57 (72)	-152 (76)	-129 (77)
O(33)	1494 (118)	593 (65)	1012 (86)	-329 (61)	-726 (85)	274 (73)
O(34)	1664 (136)	1034 (91)	925 (87)	-189 (72)	-639 (89)	-471 (93)
O(41)	455 (63)	666 (64)	1176 (87)	-221 (61)	-148 (61)	-166 (53)
O(42)	851 (83)	1188 (90)	585 (64)	-500 (62)	-71 (58)	-59 (70)
O(43)	690 (77)	529 (62)	1491 (107)	-323 (67)	-245 (74)	127 (57)
O(51)	1575 (124)	798 (75)	647 (71)	-112 (62)	-174 (77)	-214 (81)
O(52)	422 (70)	1062 (90)	1782 (133)	-494 (91)	-269 (77)	10 (63)
O(53)	1051 (97)	885 (79)	1017 (87)	-579 (71)	-144 (73)	-203 (72)

Table D.2. Additional Bond Lengths (Å) and Angles (°) for $[(Me_3P)_2(OC)_3Re(\mu\text{-}H)]_2Os_3(CO)_{10}$ (5)

Bond Lengths

Os(1) - C(11)	1.91 (1)	P(3) - C(54)	1.837 (8)
Os(1) - C(12)	1.91 (1)	P(3) - C(55)	1.82 (1)
Os(1) - C(13)	1.88 (1)	P(3) - C(56)	1.82 (1)
Os(2) - C(21)	1.92 (1)	P(30) - C(54)	1.802 (8)
Os(2) - C(22)	1.88 (2)	P(30) - C(550)	1.81 (1)
Os(2) - C(23)	1.84 (1)	P(30) - C(560)	1.82 (1)
Os(3) - C(31)	1.93 (2)	P(4) - C(57)	1.821 (8)
Os(3) - C(32)	1.86 (2)	P(4) - C(58)	1.82 (1)
Os(3) - C(33)	1.86 (2)	P(4) - C(59)	1.81 (1)
Os(3) - C(34)	1.90 (2)	P(40) - C(57)	1.827 (8)
Re(1) - P(1)	2.470 (4)	P(40) - C(580)	1.81 (1)
Re(1) - P(2)	2.469 (3)	P(40) - C(590)	1.82 (1)
Re(2) - P(3)	2.466 (6)	O(11) - C(11)	1.17 (1)
Re(2) - P(30)	2.481 (6)	O(12) - C(12)	1.13 (2)
Re(2) - P(4)	2.488 (6)	O(13) - C(13)	1.17 (2)
Re(2) - P(40)	2.449 (6)	O(21) - C(21)	1.14 (2)
Re(1) - C(41)	1.94 (1)	O(22) - C(22)	1.19 (2)
Re(1) - C(42)	1.92 (1)	O(23) - C(23)	1.17 (1)
Re(1) - C(43)	1.85 (2)	O(31) - C(31)	1.14 (2)
Re(2) - C(51)	1.92 (1)	O(32) - C(32)	1.18 (2)
Re(2) - C(52)	1.90 (2)	O(33) - C(33)	1.16 (2)
Re(2) - C(53)	1.88 (2)	O(34) - C(34)	1.15 (2)
P(1) - C(44)	1.818 (8)	O(41) - C(41)	1.16 (1)
P(1) - C(45)	1.813 (8)	O(42) - C(42)	1.17 (1)
P(1) - C(46)	1.823 (8)	O(43) - C(43)	1.18 (2)
P(2) - C(47)	1.810 (8)	O(51) - C(51)	1.16 (1)
P(2) - C(48)	1.812 (8)	O(52) - C(52)	1.17 (2)
P(2) - C(49)	1.820 (8)	O(53) - C(53)	1.17 (2)

Bond Angles

P(1) - Re(1) - Os(1)	99.16 (8)	P(4) - Re(2) - P(30)	105.2 (3)
P(2) - Re(1) - Os(1)	100.70 (9)	P(40) - Re(2) - Os(2)	102.6 (2)
P(3) - Re(2) - Os(2)	100.7 (2)	P(40) - Re(2) - P(3)	83.7 (3)
P(30) - Re(2) - Os(2)	99.3 (2)	P(40) - Re(2) - P(30)	94.2 (3)
P(4) - Re(2) - Os(2)	97.6 (2)	C(11) - Os(1) - Os(2)	93.6 (4)

Table D.2 cont'd

C(11) - Os(1) - Os(3)	93.9 (4)
C(11) - Os(1) - Re(1)	88.8 (4)
C(12) - Os(1) - Os(2)	86.1 (4)
C(12) - Os(1) - Os(3)	89.1 (4)
C(12) - Os(1) - Re(1)	88.2 (4)
C(12) - Os(1) - C(11)	176.4 (5)
C(13) - Os(1) - Os(2)	155.0 (4)
C(13) - Os(1) - Os(3)	93.8 (4)
C(13) - Os(1) - Re(1)	83.9 (4)
C(13) - Os(1) - C(11)	88.7 (5)
C(13) - Os(1) - C(12)	93.1 (6)
C(21) - Os(2) - Os(1)	86.9 (4)
C(21) - Os(2) - Os(3)	91.8 (4)
C(21) - Os(2) - Re(2)	88.7 (4)
C(22) - Os(2) - Os(1)	93.9 (4)
C(22) - Os(2) - Os(3)	90.7 (4)
C(22) - Os(2) - Re(2)	90.6 (4)
C(22) - Os(2) - C(21)	177.5 (6)
C(23) - Os(2) - Os(1)	98.7 (4)
C(23) - Os(2) - Os(3)	157.6 (4)
C(23) - Os(2) - Re(2)	83.6 (4)
C(23) - Os(2) - C(21)	88.4 (6)
C(23) - Os(2) - C(22)	89.1 (6)
C(31) - Os(3) - Os(1)	86.0 (4)
C(31) - Os(3) - Os(2)	84.9 (4)
C(32) - Os(3) - Os(1)	89.2 (5)
C(32) - Os(3) - Os(2)	87.7 (5)
C(32) - Os(3) - C(31)	172.4 (6)
C(33) - Os(3) - Os(1)	166.2 (5)
C(33) - Os(3) - Os(2)	106.5 (5)
C(33) - Os(3) - C(31)	94.2 (7)
C(33) - Os(3) - C(32)	89.1 (7)
C(34) - Os(3) - Os(1)	95.4 (5)
C(34) - Os(3) - Os(2)	155.2 (5)
C(34) - Os(3) - C(31)	95.0 (6)
C(34) - Os(3) - C(32)	91.3 (6)
C(34) - Os(3) - C(33)	98.3 (7)
C(41) - Re(1) - Os(1)	83.1 (4)
C(41) - Re(1) - P(1)	176.9 (4)
C(41) - Re(1) - P(2)	86.2 (4)
C(42) - Re(1) - Os(1)	79.4 (4)
C(42) - Re(1) - P(1)	87.2 (4)
C(42) - Re(1) - P(2)	177.3 (4)
C(42) - Re(1) - C(41)	91.1 (6)
C(43) - Re(1) - Os(1)	168.0 (5)
C(43) - Re(1) - P(1)	87.2 (5)
C(43) - Re(1) - P(2)	88.7 (5)
C(43) - Re(1) - C(41)	90.2 (6)
C(43) - Re(1) - C(42)	90.8 (6)
C(51) - Re(2) - Os(2)	80.1 (4)
C(51) - Re(2) - P(3)	92.1 (5)
C(51) - Re(2) - P(30)	81.7 (5)
C(51) - Re(2) - P(4)	173.1 (5)
C(51) - Re(2) - P(40)	175.4 (5)
C(52) - Re(2) - Os(2)	81.9 (5)
C(52) - Re(2) - P(3)	175.9 (5)
C(52) - Re(2) - P(30)	172.6 (5)
C(52) - Re(2) - P(4)	81.8 (5)
C(52) - Re(2) - P(40)	92.7 (5)
C(52) - Re(2) - C(51)	91.4 (6)
C(53) - Re(2) - Os(2)	167.5 (4)
C(53) - Re(2) - P(3)	88.6 (5)
C(53) - Re(2) - P(30)	88.3 (5)
C(53) - Re(2) - P(4)	89.9 (4)
C(53) - Re(2) - P(40)	86.5 (4)
C(53) - Re(2) - C(51)	91.3 (6)
C(53) - Re(2) - C(52)	89.3 (7)
C(44) - P(1) - Re(1)	115.4 (5)
C(45) - P(1) - Re(1)	118.9 (5)
C(46) - P(1) - Re(1)	113.8 (5)
C(45) - P(1) - C(44)	103.6 (6)
C(46) - P(1) - C(44)	100.2 (7)
C(46) - P(1) - C(45)	102.6 (7)
C(47) - P(2) - Re(1)	112.6 (6)
C(48) - P(2) - Re(1)	116.2 (5)
C(49) - P(2) - Re(1)	120.0 (5)
C(48) - P(2) - C(47)	102.8 (7)
C(49) - P(2) - C(47)	100.7 (7)
C(49) - P(2) - C(48)	102.0 (7)
C(54) - P(3) - Re(2)	115.0 (6)
C(55) - P(3) - Re(2)	114.4 (13)
C(55) - P(3) - C(54)	100.6 (14)

Table D.2 cont'd

C(56) - P(3) - Re(2)	122.0 (13)	O(31) - C(31) - Os(3)	174.9 (14)
C(56) - P(3) - C(54)	97.4 (14)	O(32) - C(32) - Os(3)	173.8 (14)
C(56) - P(3) - C(55)	104.2 (17)	O(33) - C(33) - Os(3)	174.8 (15)
C(54) - P(30) - Re(2)	115.7 (6)	O(34) - C(34) - Os(3)	178.3 (15)
C(55) - P(30) - Re(2)	126.0 (16)	O(41) - C(41) - Re(1)	177.4 (12)
C(550) - P(30) - Re(2)	116.9 (13)	O(42) - C(42) - Re(1)	176.8 (12)
C(550) - P(30) - C(54)	99.7 (14)	O(43) - C(43) - Re(1)	178.2 (13)
C(560) - P(30) - Re(2)	116.6 (13)	O(51) - C(51) - Re(2)	173.1 (13)
C(560) - P(30) - C(54)	103.4 (13)	O(52) - C(52) - Re(2)	177.1 (14)
C(560) - P(30) - C(550)	102.0 (17)	O(53) - C(53) - Re(2)	178.3 (12)
C(57) - P(4) - Re(2)	118.1 (6)	P(30) - C(54) - P(3)	14.2 (4)
C(58) - P(4) - Re(2)	114.0 (12)	P(30) - C(55) - P(3)	12.4 (4)
C(58) - P(4) - C(57)	99.6 (13)	C(550) - C(55) - P(3)	100.2 (21)
C(59) - P(4) - Re(2)	114.5 (12)	C(550) - C(55) - P(30)	88.0 (22)
C(59) - P(4) - C(57)	107.9 (14)	C(55) - C(550) - P(30)	58.9 (11)
C(59) - P(4) - C(58)	100.4 (16)	C(560) - C(56) - P(3)	59.1 (10)
C(57) - P(40) - Re(2)	119.8 (6)	P(30) - C(560) - P(3)	12.8 (4)
C(580) - P(40) - Re(2)	115.7 (11)	C(56) - C(560) - P(3)	84.6 (18)
C(580) - P(40) - C(57)	107.2 (13)	C(56) - C(560) - P(30)	96.5 (18)
C(590) - P(40) - Re(2)	112.9 (12)	P(40) - C(57) - P(4)	15.5 (4)
C(590) - P(40) - C(57)	97.6 (14)	P(40) - C(58) - P(4)	14.3 (5)
C(590) - P(40) - C(580)	100.5 (16)	C(580) - C(58) - P(4)	106.6 (23)
O(11) - C(11) - Os(1)	177.0 (11)	C(580) - C(58) - P(40)	92.3 (24)
O(12) - C(12) - Os(1)	176.6 (13)	C(58) - C(580) - P(40)	59.6 (13)
O(13) - C(13) - Os(1)	178.2 (12)	C(590) - C(59) - P(4)	53.9 (16)
O(21) - C(21) - Os(2)	174.2 (13)	P(40) - C(590) - P(4)	12.6 (5)
O(22) - C(22) - Os(2)	174.9 (13)	C(59) - C(590) - P(4)	99.8 (30)
O(23) - C(23) - Os(2)	178.6 (12)	C(59) - C(590) - P(40)	112.4 (29)

Table E.1. Uij ($Å^2 \times 10^4$) for (η^5-C_5Me_5)Os_4(μ-H)$(CO)_{11}$ (**11**)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	342(1)	270(1)	290(1)	-33(1)	-24(1)	-1(1)
Os(3)	255(2)	332(2)	365(2)	0	-28(2)	0
Os(4)	269(2)	284(2)	244(2)	0	-31(1)	0
O(0)	461(29)	686(33)	468(32)	-124(28)	29(24)	-224(28)
O(11)	617(32)	366(26)	761(42)	74(28)	-31(31)	68(26)
O(12)	552(31)	805(38)	375(30)	-62(28)	141(26)	36(30)
O(13)	720(38)	736(38)	721(42)	-161(33)	-263(34)	-223(32)
O(31)	474(29)	418(27)	691(39)	116(26)	-91(27)	80(24)
O(32)	495(45)	960(62)	492(50)	0	183(42)	0
C(1)	367(47)	340(46)	238(48)	0	-15(41)	0
C(2)	490(38)	366(35)	285(35)	27(30)	-37(32)	-88(31)
C(3)	350(32)	651(42)	213(32)	9(33)	-32(29)	-106(33)
C(4)	406(55)	529(61)	443(69)	0	-146(50)	0
C(5)	864(62)	446(42)	358(44)	43(35)	-53(42)	-52(42)
C(6)	510(46)	1205(73)	418(49)	71(55)	-3(39)	-445(51)

Table E.2. Additional Bond Lengths (Å) and Angles (°) for $(\eta^5\text{-}C_5Me_5)Os_4(\mu\text{-}H)(CO)_{11}$ (**11**)

Bond Lengths

Os(4) - C(1)	2.352(9)	O(32) - C(32)	1.13(1)
Os(4) - C(2)	2.278(7)	C(1) - C(2)	1.427(8)
Os(4) - C(3)	2.269(7)	C(1) - C(4)	1.50(1)
O(0) - C(0)	1.174(7)	C(2) - C(3)	1.447(9)
O(11) - C(11)	1.148(8)	C(2) - C(5)	1.497(9)
O(12) - C(12)	1.145(8)	C(3) - C(3')[a]	1.38(1)
O(13) - C(13)	1.139(8)	C(3) - C(6)	1.518(9)
O(31) - C(31)	1.141(8)		

Bond Angles

C(0) - Os(1) - Os(1')[a]	85.5(2)	C(32) - Os(3) - C(31)	90.4(3)
C(0) - Os(1) - Os(3)	101.7(2)	C(32) - Os(3) - Os(1)	105.5(3)
C(0) - Os(1) - Os(4)	42.6(2)	C(32) - Os(3) - Os(4)	164.7(3)
C(0) - Os(4) - Os(1)	52.2(2)	C(1) - Os(4) - Os(1)	129.0(2)
C(0) - Os(4) - Os(1')[a]	93.6(2)	C(1) - Os(4) - Os(3)	84.5(2)
C(0) - Os(4) - Os(3)	110.1(2)	C(1) - Os(4) - C(0)	134.2(2)
C(0) - Os(4) - C(0')[a]	82.7(4)	C(2) - Os(4) - Os(1)	115.0(2)
C(11) - Os(1) - Os(4)	98.2(2)	C(2) - Os(4) - Os(1')[a]	160.2(2)
C(11) - Os(1) - C(0)	90.7(3)	C(2) - Os(4) - Os(3)	102.4(2)
C(12) - Os(1) - Os(3)	80.6(2)	C(2) - Os(4) - C(0)	98.5(2)
C(12) - Os(1) - Os(4)	139.3(2)	C(2) - Os(4) - C(0')[a]	144.9(3)
C(12) - Os(1) - C(0)	176.8(3)	C(3) - Os(4) - Os(1)	129.4(2)
C(12) - Os(1) - C(11)	91.4(3)	C(3) - Os(4) - Os(1')[a]	160.9(2)
C(13) - Os(1) - Os(3)	170.1(2)	C(3) - Os(4) - Os(3)	139.4(2)
C(13) - Os(1) - Os(4)	121.9(2)	C(3) - Os(4) - C(0)	85.6(2)
C(13) - Os(1) - C(0)	81.5(3)	C(3) - Os(4) - C(0')[a]	108.8(2)
C(13) - Os(1) - C(11)	96.4(3)	C(2) - Os(4) - C(1)	35.9(2)
C(13) - Os(1) - C(12)	95.8(3)	C(2) - Os(4) - C(2')[a]	60.9(3)
C(31) - Os(3) - Os(1)	95.5(2)	C(3) - Os(4) - C(1)	59.9(2)
C(31) - Os(3) - Os(1')[a]	156.5(2)	C(3) - Os(4) - C(2)	37.1(2)
C(31) - Os(3) - Os(4)	99.3(2)	C(3) - Os(4) - C(2')[a]	60.6(2)
C(31) - Os(3) - C(31')[a]	101.8(4)	C(3) - Os(4) - C(3')[a]	35.3(3)
C(32) - Os(3) - Os(1)	105.5(3)	Os(4) - C(0) - Os(1)	85.2(2)
C(32) - Os(3) - Os(4)	164.7(3)	O(0) - C(0) - Os(1)	128.5(5)

Table E.2 cont'd

O(0) - C(0) - Os(4)	146.3(6)	C(5) - C(2) - C(1)	126.2(6)
O(11) - C(11) - Os(1)	179.5(6)	C(5) - C(2) - C(3)	125.6(6)
O(12) - C(12) - Os(1)	175.1(7)	C(2) - C(3) - Os(4)	71.8(4)
O(13) - C(13) - Os(1)	178.0(7)	C(3) - C(3') - Os(4)	72.4(2)
O(31) - C(31) - Os(3)	179.3(6)	C(3')[a] - C(3) - C(2)	108.8(4)
O(32) - C(32) - Os(3)	179.7(10)	C(6) - C(3) - Os(4)	128.0(5)
C(2) - C(1) - Os(4)	69.2(4)	C(6) - C(3) - C(2)	125.1(7)
C(2) - C(1) - C(2)	108.0(8)	C(6) - C(3) - C(3')[a]	125.6(5)
C(4) - C(1) - Os(4)	140.7(7)	Os(3) - Os(1) - H(1'1)	86(4)
C(4) - C(1) - C(2)	124.8(4)	Os(4) - Os(1) - H(1'1)	80(4)
C(1) - C(2) - Os(4)	74.9(4)	C(0) - Os(1) - H(1'1)	88(5)
C(3) - C(2) - Os(4)	71.1(4)	C(11) - Os(1) - H(1'1)	178(4)
C(3) - C(2) - C(1)	107.0(6)	C(12) - Os(1) - H(1'1)	89(5)
C(5) - C(2) - Os(4)	129.0(5)	C(13) - Os(1) - H(1'1)	84(4)

[a] These are symmetry equivalent atoms by the operation of (x, 0.5-y, z).

Table F.1. Uij (Å^2 x 10^4) for [η^5,η^1-$C_5Me_4CH_2$]$Os_4(\mu$-$H)_2(CO)_{10}$ **(12)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	296(3)	393(4)	347(3)	-35(3)	59(2)	26(2)
Os(2)	362(3)	340(3)	383(3)	50(3)	39(2)	-11(2)
Os(3)	250(3)	353(3)	362(3)	-46(3)	-18(2)	-35(2)
Os(4)	224(2)	324(3)	306(3)	-12(2)	18(2)	-14(2)
O(11)	684(77)	966(106)	789(94)	379(79)	219(68)	95(71)
O(12)	559(69)	676(89)	1089(108)	21(73)	155(68)	271(63)
O(13)	881(91)	746(97)	844(94)	-515(77)	-249(74)	-12(72)
O(21)	1342(127)	732(101)	1066(113)	300(84)	669(99)	-109(86)
O(22)	619(75)	826(99)	874(94)	160(73)	-171(66)	322(67)
O(23)	860(90)	495(80)	956(100)	-78(70)	-189(77)	-44(65)
O(31)	666(82)	1383(142)	911(104)	-231(94)	-564(77)	92(87)
O(32)	796(90)	814(104)	1274(126)	346(93)	245(85)	-200(77)
O(41)	464(65)	679(87)	1195(111)	-166(80)	-105(68)	-213(63)
O(42)	735(77)	1024(101)	386(63)	287(65)	92(56)	387(70)
C(6)	453(84)	602(111)	391(89)	-19(77)	59(69)	-111(76)
C(7)	475(89)	554(111)	627(111)	-17(88)	-109(81)	-5(79)
C(8)	522(94)	458(103)	613(108)	-91(84)	-138(81)	-46(77)
C(9)	309(85)	1237(192)	1118(169)	-51(147)	239(96)	56(100)
C(10)	959(147)	1291(195)	540(117)	253(121)	346(106)	599(137)

Table F.2. Additional Bond Lengths (Å) and Angles (°) for $[\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(\mu\text{-}H)_2(CO)_{10}$ **(12)**

Bond Lengths

Os(1) - C(11)	1.91 (2)	O(13) - C(13)	1.13 (2)
Os(1) - C(12)	1.87 (1)	O(21) - C(21)	1.18 (2)
Os(1) - C(13)	1.93 (2)	O(22) - C(22)	1.17 (2)
Os(2) - C(21)	1.89 (2)	O(23) - C(23)	1.17 (2)
Os(2) - C(22)	1.86 (2)	O(31) - C(31)	1.14 (2)
Os(2) - C(23)	1.87 (2)	O(32) - C(32)	1.16 (2)
Os(3) - C(31)	1.88 (2)	O(41) - C(41)	1.17 (2)
Os(3) - C(32)	1.84 (2)	O(42) - C(42)	1.17 (2)
Os(4) - C(41)	1.86 (2)	C(1) - C(2)	1.41 (2)
Os(4) - C(42)	1.89 (1)	C(1) - C(5)	1.47 (2)
Os(4) - C(1)	2.37 (1)	C(2) - C(3)	1.43 (2)
Os(4) - C(2)	2.28 (1)	C(2) - C(7)	1.49 (2)
Os(4) - C(3)	2.21 (1)	C(3) - C(4)	1.42 (2)
Os(4) - C(4)	2.26 (1)	C(3) - C(8)	1.50 (2)
Os(4) - C(5)	2.28 (1)	C(4) - C(5)	1.44 (2)
O(11) - C(11)	1.16 (2)	C(4) - C(9)	1.48 (2)
O(12) - C(12)	1.14 (2)	C(5) - C(10)	1.53 (2)

Bond Angles

C(11) - Os(1) - Os(4)	108.1 (5)	C(23) - Os(2) - C(22)	93.4 (7)
C(12) - Os(1) - Os(4)	155.0 (4)	C(31) - Os(3) - Os(1)	124.5 (5)
C(12) - Os(1) - C(11)	96.5 (6)	C(31) - Os(3) - Os(2)	107.7 (5)
C(13) - Os(1) - Os(3)	151.8 (5)	C(31) - Os(3) - Os(4)	160.6 (5)
C(13) - Os(1) - Os(4)	92.0 (5)	C(32) - Os(3) - Os(1)	95.0 (5)
C(13) - Os(1) - C(11)	97.0 (7)	C(32) - Os(3) - Os(2)	151.5 (5)
C(13) - Os(1) - C(12)	89.7 (6)	C(32) - Os(3) - Os(4)	106.5 (4)
C(21) - Os(2) - Os(1)	168.4 (5)	C(32) - Os(3) - C(31)	91.3 (7)
C(21) - Os(2) - Os(3)	119.8 (5)	C(6) - Os(3) - Os(1)	143.8 (4)
C(21) - Os(2) - Os(4)	104.9 (5)	C(6) - Os(3) - Os(2)	109.3 (4)
C(22) - Os(2) - Os(1)	99.1 (5)	C(6) - Os(3) - Os(4)	81.3 (4)
C(22) - Os(2) - Os(3)	94.3 (5)	C(6) - Os(3) - C(31)	91.0 (6)
C(22) - Os(2) - Os(4)	154.0 (5)	C(6) - Os(3) - C(32)	90.9 (6)
C(22) - Os(2) - C(21)	92.5 (7)	C(41) - Os(4) - Os(1)	90.4 (4)
C(23) - Os(2) - Os(1)	86.2 (5)	C(41) - Os(4) - Os(2)	70.7 (4)
C(23) - Os(2) - Os(3)	145.7 (5)	C(41) - Os(4) - Os(3)	130.7 (4)
C(23) - Os(2) - Os(4)	104.6 (5)	C(42) - Os(4) - Os(1)	65.4 (4)
C(23) - Os(2) - C(21)	93.2 (7)	C(42) - Os(4) - Os(2)	117.5 (4)

Table F.2 cont'd

C(42) - Os(4) - Os(3)	102.8 (4)
C(42) - Os(4) - C(41)	93.1 (6)
C(1) - Os(4) - Os(1)	116.4 (3)
C(1) - Os(4) - Os(2)	100.1 (3)
C(1) - Os(4) - Os(3)	60.1 (3)
C(1) - Os(4) - C(41)	140.6 (6)
C(1) - Os(4) - C(42)	123.5 (6)
C(2) - Os(4) - Os(1)	121.9 (3)
C(2) - Os(4) - Os(2)	133.8 (3)
C(2) - Os(4) - Os(3)	80.0 (3)
C(2) - Os(4) - C(41)	146.3 (6)
C(2) - Os(4) - C(42)	92.4 (6)
C(2) - Os(4) - C(1)	35.3 (5)
C(3) - Os(4) - Os(1)	149.2 (4)
C(3) - Os(4) - Os(2)	152.6 (4)
C(3) - Os(4) - Os(3)	116.4 (4)
C(3) - Os(4) - C(41)	109.9 (6)
C(3) - Os(4) - C(42)	89.9 (6)
C(3) - Os(4) - C(1)	61.2 (5)
C(3) - Os(4) - C(2)	36.9 (5)
C(4) - Os(4) - Os(1)	172.8 (3)
C(4) - Os(4) - Os(2)	117.7 (3)
C(4) - Os(4) - Os(3)	119.3 (3)
C(4) - Os(4) - C(41)	88.4 (6)
C(4) - Os(4) - C(42)	121.8 (5)
C(4) - Os(4) - C(1)	61.3 (5)
C(4) - Os(4) - C(2)	60.7 (5)
C(4) - Os(4) - C(3)	37.0 (5)
C(5) - Os(4) - Os(1)	137.1 (3)
C(5) - Os(4) - Os(2)	91.2 (4)
C(5) - Os(4) - Os(3)	84.4 (3)
C(5) - Os(4) - C(41)	103.9 (6)
C(5) - Os(4) - C(42)	150.3 (6)
C(5) - Os(4) - C(1)	36.8 (5)
C(5) - Os(4) - C(2)	60.1 (5)
C(5) - Os(4) - C(3)	61.6 (5)
C(5) - Os(4) - C(4)	36.9 (5)
O(11) - C(11) - Os(1)	174.6 (14)
O(12) - C(12) - Os(1)	177.4 (14)
O(13) - C(13) - Os(1)	177.7 (16)
O(21) - C(21) - Os(2)	176.0 (17)
O(22) - C(22) - Os(2)	175.2 (16)
O(23) - C(23) - Os(2)	177.4 (15)
O(31) - C(31) - Os(3)	178.8 (15)
O(32) - C(32) - Os(3)	173.4 (15)
O(41) - C(41) - Os(4)	171.0 (13)
O(42) - C(42) - Os(4)	164.6 (13)
C(2) - C(1) - Os(4)	69.1 (8)
C(5) - C(1) - Os(4)	68.5 (8)
C(5) - C(1) - C(2)	105.1 (12)
C(6) - C(1) - Os(4)	122.3 (10)
C(6) - C(1) - C(2)	131.6 (13)
C(6) - C(1) - C(5)	123.0 (12)
C(1) - C(2) - Os(4)	75.6 (8)
C(3) - C(2) - Os(4)	68.8 (8)
C(3) - C(2) - C(1)	110.8 (13)
C(7) - C(2) - Os(4)	127.5 (11)
C(7) - C(2) - C(1)	124.5 (13)
C(7) - C(2) - C(3)	124.4 (13)
C(2) - C(3) - Os(4)	74.3 (8)
C(4) - C(3) - Os(4)	73.3 (8)
C(4) - C(3) - C(2)	107.7 (12)
C(8) - C(3) - Os(4)	129.5 (11)
C(8) - C(3) - C(2)	127.6 (14)
C(8) - C(3) - C(4)	123.1 (13)
C(3) - C(4) - Os(4)	69.7 (8)
C(5) - C(4) - Os(4)	72.4 (8)
C(5) - C(4) - C(3)	107.6 (12)
C(9) - C(4) - Os(4)	127.3 (11)
C(9) - C(4) - C(3)	126.3 (13)
C(9) - C(4) - C(5)	125.9 (14)
C(1) - C(5) - Os(4)	74.8 (8)
C(4) - C(5) - Os(4)	70.7 (8)
C(4) - C(5) - C(1)	108.6 (12)
C(10) - C(5) - Os(4)	136.3 (11)
C(10) - C(5) - C(1)	125.2 (14)
C(10) - C(5) - C(4)	123.2 (14)
C(1) - C(6) - Os(3)	95.3 (9)

Table G.1. Uij ($Å^2$ x 10^4) for [μ,η^5,η^1-$C_5Me_4CH_2$]$Os_4(CO)_{11}$ **(13)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	352(5)	272(5)	320(4)	-10(3)	-26(3)	-18(4)
Os(2)	265(5)	404(5)	351(4)	15(4)	-8(4)	55(4)
Os(3)	280(5)	317(5)	297(4)	11(3)	4(3)	-60(4)
Os(4)	268(4)	330(5)	268(4)	10(3)	-10(3)	-31(4)

Table G.2. Additional Bond Lengths (Å) and Angles (°) for $[\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2]Os_4(CO)_{11}$ (**13**)

Bond Lengths

Os(1) - C(11)	1.88(3)	O(13) - C(13)	1.17(3)
Os(1) - C(12)	1.85(2)	O(21) - C(21)	1.21(3)
Os(1) - C(13)	1.87(2)	O(22) - C(22)	1.16(2)
Os(2) - C(21)	1.85(3)	O(23) - C(23)	1.14(3)
Os(2) - C(22)	1.85(2)	O(31) - C(31)	1.20(3)
Os(2) - C(23)	1.88(3)	O(32) - C(32)	1.15(2)
Os(3) - C(31)	1.91(2)	O(33) - C(33)	1.16(2)
Os(3) - C(32)	1.93(2)	O(41) - C(41)	1.13(2)
Os(3) - C(33)	1.83(2)	O(42) - C(42)	1.17(3)
Os(4) - C(41)	1.89(2)	C(1) - C(2)	1.45(3)
Os(4) - C(42)	1.88(2)	C(1) - C(5)	1.46(3)
Os(4) - C(1)	2.31(2)	C(2) - C(3)	1.44(3)
Os(4) - C(2)	2.25(2)	C(2) - C(7)	1.48(3)
Os(4) - C(3)	2.24(2)	C(3) - C(4)	1.42(3)
Os(4) - C(4)	2.26(2)	C(3) - C(8)	1.51(3)
Os(4) - C(5)	2.26(2)	C(4) - C(5)	1.46(3)
O(11) - C(11)	1.17(3)	C(4) - C(9)	1.47(3)
O(12) - C(12)	1.19(3)	C(5) - C(10)	1.49(3)

Bond Angles

C(11) - Os(1) - Os(4)	105.3(7)	C(22) - Os(2) - C(21)	96.8(10)
C(12) - Os(1) - Os(3)	95.6(8)	C(23) - Os(2) - Os(1)	94.6(8)
C(12) - Os(1) - Os(4)	153.6(8)	C(23) - Os(2) - Os(3)	154.8(8)
C(12) - Os(1) - C(11)	95.3(10)	C(23) - Os(2) - Os(4)	104.9(8)
C(13) - Os(1) - Os(3)	151.4(7)	C(23) - Os(2) - C(21)	91.7(11)
C(13) - Os(1) - Os(4)	105.6(6)	C(23) - Os(2) - C(22)	94.4(10)
C(13) - Os(1) - C(11)	94.4(10)	C(31) - Os(3) - Os(1)	125.8(6)
C(21) - Os(2) - Os(1)	166.0(7)	C(31) - Os(3) - Os(2)	66.6(6)
C(21) - Os(2) - Os(3)	111.8(8)	C(31) - Os(3) - Os(4)	96.9(6)
C(21) - Os(2) - Os(4)	103.9(7)	C(32) - Os(3) - Os(1)	65.0(7)
C(22) - Os(2) - Os(1)	95.2(7)	C(32) - Os(3) - Os(2)	124.4(7)
C(22) - Os(2) - Os(3)	91.8(7)	C(32) - Os(3) - Os(4)	93.5(6)
C(22) - Os(2) - Os(4)	151.0(7)	C(32) - Os(3) - C(31)	167.9(9)

Table G.2 cont'd

C(33) - Os(3) - Os(1)	112.1(6)
C(33) - Os(3) - Os(2)	116.4(6)
C(33) - Os(3) - Os(4)	174.0(6)
C(33) - Os(3) - C(31)	86.9(8)
C(33) - Os(3) - C(32)	83.3(8)
C(6) - Os(3) - Os(1)	130.3(5)
C(6) - Os(3) - Os(2)	130.3(5)
C(6) - Os(3) - Os(4)	81.3(5)
C(6) - Os(3) - C(31)	88.5(8)
C(6) - Os(3) - C(32)	86.9(8)
C(6) - Os(3) - C(33)	103.5(8)
C(41) - Os(4) - Os(1)	102.0(6)
C(41) - Os(4) - Os(2)	63.6(6)
C(41) - Os(4) - Os(3)	118.1(6)
C(42) - Os(4) - Os(1)	61.6(6)
C(42) - Os(4) - Os(2)	102.4(6)
C(42) - Os(4) - Os(3)	115.3(6)
C(42) - Os(4) - C(41)	91.1(9)
C(1) - Os(4) - Os(1)	109.6(4)
C(1) - Os(4) - Os(2)	110.2(4)
C(1) - Os(4) - Os(3)	61.2(4)
C(1) - Os(4) - C(41)	135.4(8)
C(1) - Os(4) - C(42)	131.4(8)
C(2) - Os(4) - Os(1)	105.8(4)
C(2) - Os(4) - Os(2)	140.3(5)
C(2) - Os(4) - Os(3)	83.6(5)
C(2) - Os(4) - C(41)	151.3(7)
C(2) - Os(4) - C(42)	96.1(8)
C(2) - Os(4) - C(1)	37.2(7)
C(3) - Os(4) - Os(1)	133.7(5)
C(3) - Os(4) - Os(2)	167.6(5)
C(3) - Os(4) - Os(3)	119.5(5)
C(3) - Os(4) - C(41)	115.1(8)
C(3) - Os(4) - C(42)	89.9(8)
C(3) - Os(4) - C(1)	61.3(7)
C(4) - Os(4) - Os(1)	168.6(5)
C(4) - Os(4) - Os(2)	132.3(5)
C(4) - Os(4) - Os(3)	119.1(5)
C(4) - Os(4) - C(41)	89.3(8)
C(4) - Os(4) - C(42)	117.4(8)
C(4) - Os(4) - C(1)	61.8(7)
C(5) - Os(4) - Os(1)	139.1(5)
C(5) - Os(4) - Os(2)	105.5(5)
C(5) - Os(4) - Os(3)	82.5(5)
C(5) - Os(4) - C(41)	99.3(8)
C(5) - Os(4) - C(42)	152.0(8)
C(5) - Os(4) - C(1)	37.1(7)
C(3) - Os(4) - C(2)	37.5(6)
C(4) - Os(4) - C(2)	62.8(7)
C(4) - Os(4) - C(3)	36.7(7)
C(5) - Os(4) - C(2)	63.1(7)
C(5) - Os(4) - C(3)	62.1(8)
C(5) - Os(4) - C(4)	37.8(7)
O(11) - C(11) - Os(1)	176.8(20)
O(12) - C(12) - Os(1)	174.1(23)
O(13) - C(13) - Os(1)	176.8(21)
O(21) - C(21) - Os(2)	177.0(21)
O(22) - C(22) - Os(2)	174.8(22)
O(23) - C(23) - Os(2)	174.9(24)
O(31) - C(31) - Os(3)	160.9(19)
O(32) - C(32) - Os(3)	161.6(19)
O(33) - C(33) - Os(3)	177.3(17)
O(41) - C(41) - Os(4)	164.4(19)
O(42) - C(42) - Os(4)	162.4(17)
C(2) - C(1) - Os(4)	68.9(11)
C(5) - C(1) - Os(4)	69.5(11)
C(5) - C(1) - C(2)	108.2(16)
C(6) - C(1) - Os(4)	123.6(12)
C(6) - C(1) - C(2)	127.6(17)
C(6) - C(1) - C(5)	124.0(17)
C(1) - C(2) - Os(4)	74.0(11)
C(3) - C(2) - Os(4)	71.1(11)
C(3) - C(2) - C(1)	106.6(16)
C(7) - C(2) - Os(4)	132.8(14)
C(7) - C(2) - C(1)	126.8(18)
C(7) - C(2) - C(3)	124.6(18)
C(2) - C(3) - Os(4)	71.4(11)
C(4) - C(3) - Os(4)	72.2(11)
C(4) - C(3) - C(2)	110.2(17)
C(8) - C(3) - Os(4)	126.8(15)
C(8) - C(3) - C(2)	122.5(19)
C(8) - C(3) - C(4)	127.1(17)
C(3) - C(4) - Os(4)	71.1(11)
C(5) - C(4) - Os(4)	71.3(11)

Table G.2 cont'd

C(5) - C(4) - C(3)	107.7(17)
C(9) - C(4) - Os(4)	127.6(15)
C(9) - C(4) - C(3)	127.0(18)
C(9) - C(4) - C(5)	125.1(19)
C(1) - C(5) - Os(4)	73.4(11)
C(4) - C(5) - Os(4)	70.9(12)
C(4) - C(5) - C(1)	107.1(18)
C(10) - C(5) - Os(4)	132.1(16)
C(10) - C(5) - C(1)	128.1(19)
C(10) - C(5) - C(4)	123.2(19)
C(1) - C(6) - Os(3)	93.9(12)

Table H.1. Uij ($Å^2$ x 10^4) for $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ **(14)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	283 (3)	230 (3)	338 (3)	3 (2)	14 (2)	-18 (2)
Os(2)	314 (3)	233 (3)	278 (3)	4 (2)	24 (2)	43 (2)
Os(3)	326 (3)	280 (3)	267 (3)	-15 (2)	48 (2)	6 (2)
Os(4)	267 (3)	257 (3)	277 (3)	7 (2)	5 (2)	-4 (2)
O(11)	525 (80)	890 (88)	882 (85)	-104 (69)	-230 (71)	-221 (68)
O(12)	700 (84)	402 (65)	879 (82)	-9 (53)	52 (68)	160 (57)
O(13)	552 (73)	790 (80)	498 (63)	125 (54)	153 (58)	-140 (62)
O(21)	1213 (122)	694 (80)	609 (71)	60 (58)	-168 (78)	528 (80)
O(22)	1193 (122)	1059 (99)	393 (61)	-56 (58)	441 (72)	387 (89)
O(31)	923 (93)	724 (79)	292 (52)	-89 (48)	-66 (56)	9 (67)
O(32)	866 (104)	743 (87)	1039 (99)	-98 (72)	190 (85)	469 (79)
O(41)	730 (87)	466 (63)	797 (76)	-82 (55)	-182 (68)	373 (60)
O(42)	517 (66)	591 (64)	389 (53)	26 (46)	151 (49)	-64 (53)

Table H.2. Additional Bond Lengths (Å) and Angles (°) for $[\mu_3,\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2]Os_4(\mu\text{-}H)_3(CO)_9$ (**14**)

Bond Lengths

Os(1) - C(11)	1.87 (1)	O(13) - C(13)	1.11 (2)
Os(1) - C(12)	1.87 (1)	O(21) - C(21)	1.14 (2)
Os(1) - C(13)	1.92 (2)	O(22) - C(22)	1.10 (2)
Os(2) - C(21)	1.86 (1)	O(31) - C(31)	1.14 (1)
Os(2) - C(22)	1.95 (2)	O(32) - C(32)	1.15 (2)
Os(3) - C(31)	1.86 (1)	O(41) - C(41)	1.14 (2)
Os(3) - C(32)	1.85 (2)	O(42) - C(42)	1.12 (1)
Os(4) - C(41)	1.89 (1)	C(1) - C(2)	1.43 (2)
Os(4) - C(42)	1.93 (1)	C(1) - C(5)	1.46 (2)
Os(4) - C(1)	2.33 (1)	C(2) - C(3)	1.48 (2)
Os(4) - C(2)	2.27 (1)	C(2) - C(7)	1.48 (2)
Os(4) - C(3)	2.21 (1)	C(3) - C(4)	1.42 (2)
Os(4) - C(4)	2.23 (1)	C(3) - C(8)	1.52 (2)
Os(4) - C(5)	2.31 (1)	C(4) - C(5)	1.42 (2)
O(11) - C(11)	1.14 (2)	C(4) - C(9)	1.49 (2)
O(12) - C(12)	1.15 (1)		

Bond Angles

C(11) - Os(1) - Os(3)	112.1 (5)	C(31) - Os(3) - Os(2)	117.2 (4)
C(11) - Os(1) - Os(4)	171.6 (4)	C(31) - Os(3) - Os(4)	173.7 (4)
C(12) - Os(1) - Os(2)	149.8 (4)	C(32) - Os(3) - Os(1)	100.5 (5)
C(12) - Os(1) - Os(3)	96.1 (4)	C(32) - Os(3) - Os(2)	151.7 (5)
C(12) - Os(1) - C(11)	91.4 (6)	C(32) - Os(3) - Os(4)	94.5 (4)
C(13) - Os(1) - Os(3)	155.2 (4)	C(32) - Os(3) - C(31)	89.9 (6)
C(13) - Os(1) - C(11)	89.1 (6)	C(6) - Os(3) - Os(1)	142.5 (3)
C(13) - Os(1) - C(12)	96.1 (6)	C(6) - Os(3) - Os(2)	92.6 (4)
C(21) - Os(2) - Os(4)	169.8 (5)	C(6) - Os(3) - Os(4)	82.5 (3)
C(22) - Os(2) - Os(3)	152.4 (4)	C(6) - Os(3) - C(31)	92.6 (5)
C(22) - Os(2) - C(21)	90.0 (6)	C(6) - Os(3) - C(32)	94.3 (6)
C(10) - Os(2) - Os(1)	140.1 (4)	C(41) - Os(4) - Os(1)	83.1 (4)
C(10) - Os(2) - Os(3)	91.5 (4)	C(41) - Os(4) - Os(2)	141.2 (4)
C(10) - Os(2) - Os(4)	80.4 (3)	C(41) - Os(4) - Os(3)	95.8 (4)
C(10) - Os(2) - C(21)	90.3 (6)	C(42) - Os(4) - Os(1)	79.8 (4)
C(10) - Os(2) - C(22)	96.1 (6)	C(42) - Os(4) - Os(2)	86.6 (4)
C(31) - Os(3) - Os(1)	121.4 (4)	C(42) - Os(4) - Os(3)	135.3 (4)

Table H.2 cont'd

C(42) - Os(4) - C(41)	92.0 (6)
C(1) - Os(4) - Os(1)	115.6 (3)
C(1) - Os(4) - Os(2)	79.9 (3)
C(1) - Os(4) - Os(3)	59.4 (3)
C(1) - Os(4) - C(41)	116.2 (6)
C(1) - Os(4) - C(42)	148.5 (5)
C(2) - Os(4) - Os(1)	139.3 (3)
C(2) - Os(4) - Os(2)	115.9 (3)
C(2) - Os(4) - Os(3)	83.7 (3)
C(2) - Os(4) - C(41)	88.9 (6)
C(2) - Os(4) - C(42)	140.5 (5)
C(2) - Os(4) - C(1)	36.3 (4)
C(3) - Os(4) - Os(1)	177.9 (3)
C(3) - Os(4) - Os(2)	121.1 (3)
C(3) - Os(4) - Os(3)	120.2 (3)
C(3) - Os(4) - C(41)	97.1 (5)
C(3) - Os(4) - C(42)	102.3 (5)
C(3) - Os(4) - C(1)	62.5 (5)
C(4) - Os(4) - Os(1)	143.0 (3)
C(4) - Os(4) - Os(2)	85.8 (3)
C(4) - Os(4) - Os(3)	115.4 (3)
C(4) - Os(4) - C(41)	132.9 (5)
C(4) - Os(4) - C(42)	89.3 (5)
C(4) - Os(4) - C(1)	61.6 (5)
C(5) - Os(4) - Os(1)	117.5 (3)
C(5) - Os(4) - Os(2)	61.3 (3)
C(5) - Os(4) - Os(3)	79.7 (3)
C(5) - Os(4) - C(41)	149.9 (6)
C(5) - Os(4) - C(42)	112.3 (5)
C(5) - Os(4) - C(1)	36.6 (5)
C(3) - Os(4) - C(2)	38.7 (4)
C(4) - Os(4) - C(2)	62.5 (5)
C(4) - Os(4) - C(3)	37.3 (5)
C(5) - Os(4) - C(2)	61.1 (5)
C(5) - Os(4) - C(3)	61.5 (5)
C(5) - Os(4) - C(4)	36.2 (4)
O(11) - C(11) - Os(1)	177.4 (13)
O(12) - C(12) - Os(1)	176.3 (11)
O(13) - C(13) - Os(1)	176.7 (13)
O(21) - C(21) - Os(2)	175.9 (13)
O(22) - C(22) - Os(2)	176.9 (15)
O(31) - C(31) - Os(3)	174.1 (14)
O(32) - C(32) - Os(3)	178.6 (14)
O(41) - C(41) - Os(4)	173.3 (12)
O(42) - C(42) - Os(4)	172.5 (12)
C(2) - C(1) - Os(4)	69.7 (7)
C(5) - C(1) - Os(4)	71.1 (8)
C(5) - C(1) - C(2)	107.2 (11)
C(6) - C(1) - Os(4)	127.0 (9)
C(6) - C(1) - C(2)	127.9 (13)
C(6) - C(1) - C(5)	124.8 (12)
C(1) - C(2) - Os(4)	74.0 (8)
C(3) - C(2) - Os(4)	68.5 (8)
C(3) - C(2) - C(1)	107.6 (12)
C(7) - C(2) - Os(4)	127.8 (10)
C(7) - C(2) - C(1)	126.1 (12)
C(7) - C(2) - C(3)	126.0 (11)
C(2) - C(3) - Os(4)	72.8 (7)
C(4) - C(3) - Os(4)	72.2 (8)
C(4) - C(3) - C(2)	107.1 (11)
C(8) - C(3) - Os(4)	129.6 (9)
C(8) - C(3) - C(2)	123.7 (12)
C(8) - C(3) - C(4)	128.2 (12)
C(3) - C(4) - Os(4)	70.5 (7)
C(5) - C(4) - Os(4)	74.9 (7)
C(5) - C(4) - C(3)	109.4 (12)
C(9) - C(4) - Os(4)	126.5 (10)
C(9) - C(4) - C(3)	124.6 (11)
C(9) - C(4) - C(5)	125.6 (12)
C(1) - C(5) - Os(4)	72.2 (7)
C(4) - C(5) - Os(4)	68.9 (7)
C(4) - C(5) - C(1)	108.7 (11)
C(10) - C(5) - Os(4)	124.7 (9)
C(10) - C(5) - C(1)	124.1 (11)
C(10) - C(5) - C(4)	127.2 (13)
C(1) - C(6) - Os(3)	90.9 (8)
C(5) - C(10) - Os(2)	93.1 (8)

Table I.1. Uij ($\AA^2$ x10^4) for $Os_5(CO)_{18}$ **(16)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	263(5)	264(4)	291(5)	-88(3)	-0(4)	-71(4)
Os(2)	276(5)	354(5)	381(6)	-164(4)	-18(4)	-38(4)
Os(3)	342(6)	363(5)	309(5)	-103(4)	27(4)	-131(4)
Os(4)	339(5)	285(5)	296(5)	-55(4)	-22(4)	-56(4)
Os(5)	402(6)	254(5)	392(5)	-89(4)	-45(4)	-85(4)

Table I.2. Additional Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{18}$ **(16)**

Bond Lengths

Os(1) - C(11) 1.90 (2)
Os(1) - C(12) 1.93 (2)
Os(1) - C(13) 1.90 (2)
Os(2) - C(21) 1.93 (2)
Os(2) - C(22) 1.96 (2)
Os(2) - C(23) 1.87 (3)
Os(3) - C(31) 1.90 (2)
Os(3) - C(32) 1.95 (2)
Os(3) - C(33) 1.87 (3)
Os(4) - C(41) 1.97 (2)
Os(4) - C(42) 1.90 (2)
Os(4) - C(43) 1.88 (3)
Os(4) - C(44) 1.89 (2)
Os(5) - C(51) 1.93 (3)
Os(5) - C(52) 1.96 (2)
Os(5) - C(53) 1.93 (3)
Os(5) - C(54) 1.87 (2)
O(0) - C(0) 1.19 (3)

O(11) - C(11) 1.17 (2)
O(12) - C(12) 1.14 (2)
O(13) - C(13) 1.16 (2)
O(21) - C(21) 1.17 (3)
O(22) - C(22) 1.13 (2)
O(23) - C(23) 1.13 (4)
O(31) - C(31) 1.18 (3)
O(32) - C(32) 1.14 (2)
O(33) - C(33) 1.13 (3)
O(41) - C(41) 1.10 (3)
O(42) - C(42) 1.17 (2)
O(43) - C(43) 1.17 (3)
O(44) - C(44) 1.15 (3)
O(51) - C(51) 1.13 (3)
O(52) - C(52) 1.11 (2)
O(53) - C(53) 1.13 (3)
O(54) - C(54) 1.16 (3)

Bond Angles

Os(3) - Os(1) - Os(2) 59.70 (3)
Os(4) - Os(1) - Os(2) 120.55 (4)
Os(4) - Os(1) - Os(3) 60.86 (4)
Os(5) - Os(1) - Os(2) 59.64 (4)
Os(5) - Os(1) - Os(3) 119.34 (4)
Os(5) - Os(1) - Os(4) 178.92 (5)
C(11) - Os(1) - Os(2) 87.4 (6)
C(11) - Os(1) - Os(3) 90.8 (6)
C(11) - Os(1) - Os(4) 92.4 (6)
C(11) - Os(1) - Os(5) 86.5 (6)
C(12) - Os(1) - Os(2) 90.2 (6)
C(12) - Os(1) - Os(3) 89.9 (6)
C(12) - Os(1) - Os(4) 90.7 (6)
C(12) - Os(1) - Os(5) 90.4 (6)
C(12) - Os(1) - C(11) 176.8 (9)

C(13) - Os(1) - Os(2) 149.4 (7)
C(13) - Os(1) - Os(3) 150.9 (7)
C(13) - Os(1) - Os(4) 90.0 (7)
C(13) - Os(1) - Os(5) 89.8 (7)
C(13) - Os(1) - C(11) 89.6 (9)
C(13) - Os(1) - C(12) 91.3 (9)
Os(3) - Os(2) - Os(1) 60.14 (3)
Os(5) - Os(2) - Os(1) 60.49 (3)
Os(5) - Os(2) - Os(3) 120.63 (4)
C(0) - Os(2) - Os(1) 104.2 (7)
C(0) - Os(2) - Os(3) 44.0 (7)
C(0) - Os(2) - Os(5) 164.7 (7)
C(21) - Os(2) - Os(1) 94.8 (7)
C(21) - Os(2) - Os(3) 92.9 (7)
C(21) - Os(2) - Os(5) 91.8 (7)

Table I.2 cont'd

C(21) - Os(2) - C(0) 89.9 (9)
C(22) - Os(2) - Os(1) 91.3 (6)
C(22) - Os(2) - Os(3) 93.9 (6)
C(22) - Os(2) - Os(5) 87.4 (6)
C(22) - Os(2) - C(0) 92.9 (9)
C(22) - Os(2) - C(21) 172.4 (9)
C(23) - Os(2) - Os(1) 161.1 (10)
C(23) - Os(2) - Os(3) 138.7 (10)
C(23) - Os(2) - Os(5) 100.7 (10)
C(23) - Os(2) - C(0) 94.6 (12)
C(23) - Os(2) - C(21) 86.2 (12)
C(23) - Os(2) - C(22) 86.6 (11)
Os(2) - Os(3) - Os(1) 60.16 (3)
Os(4) - Os(3) - Os(1) 59.41 (3)
Os(4) - Os(3) - Os(2) 119.56 (4)
C(0) - Os(3) - Os(1) 111.3 (7)
C(0) - Os(3) - Os(2) 51.2 (7)
C(0) - Os(3) - Os(4) 170.7 (7)
C(31) - Os(3) - Os(1) 91.5 (7)
C(31) - Os(3) - Os(2) 91.0 (7)
C(31) - Os(3) - Os(4) 89.5 (7)
C(31) - Os(3) - C(0) 90.2 (10)
C(32) - Os(3) - Os(1) 91.2 (6)
C(32) - Os(3) - Os(2) 91.1 (6)
C(32) - Os(3) - Os(4) 91.1 (6)
C(32) - Os(3) - C(0) 89.6 (10)
C(32) - Os(3) - C(31) 177.1 (9)
C(33) - Os(3) - Os(1) 151.3 (8)
C(33) - Os(3) - Os(2) 148.6 (8)
C(33) - Os(3) - Os(4) 91.8 (8)
C(33) - Os(3) - C(0) 97.4 (11)
C(33) - Os(3) - C(31) 87.8 (11)
C(33) - Os(3) - C(32) 89.3 (10)
Os(3) - Os(4) - Os(1) 59.73 (3)
C(41) - Os(4) - Os(1) 87.6 (7)
C(41) - Os(4) - Os(3) 91.1 (7)
C(42) - Os(4) - Os(1) 89.5 (7)
C(42) - Os(4) - Os(3) 88.5 (7)
C(42) - Os(4) - C(41) 176.8 (10)
C(43) - Os(4) - Os(1) 101.6 (8)
C(43) - Os(4) - Os(3) 161.1 (8)
C(43) - Os(4) - C(41) 91.4 (10)

C(43) - Os(4) - C(42) 88.0 (10)
C(44) - Os(4) - Os(1) 161.8 (7)
C(44) - Os(4) - Os(3) 102.2 (7)
C(44) - Os(4) - C(41) 91.4 (10)
C(44) - Os(4) - C(42) 91.7 (10)
C(44) - Os(4) - C(43) 96.5 (11)
Os(2) - Os(5) - Os(1) 59.87 (3)
C(51) - Os(5) - Os(1) 92.6 (7)
C(51) - Os(5) - Os(2) 89.0 (7)
C(52) - Os(5) - Os(1) 89.0 (6)
C(52) - Os(5) - Os(2) 91.9 (6)
C(52) - Os(5) - C(51) 178.4 (9)
C(53) - Os(5) - Os(1) 99.4 (7)
C(53) - Os(5) - Os(2) 159.1 (7)
C(53) - Os(5) - C(51) 89.5 (10)
C(53) - Os(5) - C(52) 90.2 (9)
C(54) - Os(5) - Os(1) 161.8 (7)
C(54) - Os(5) - Os(2) 102.3 (7)
C(54) - Os(5) - C(51) 90.5 (10)
C(54) - Os(5) - C(52) 87.9 (9)
C(54) - Os(5) - C(53) 98.5 (10)
Os(3) - C(0) - Os(2) 84.8 (10)
O(0) - C(0) Os(2) 131.4 (19)
O(0) C(0) Os(3) 143.9 (21)
O(11) - C(11) - Os(1) 176.9 (19)
O(12) - C(12) - Os(1) 175.5 (17)
O(13) - C(13) - Os(1) 177.7 (19)
O(21) - C(21) - Os(2) 169.9 (21)
O(22) - C(22) - Os(2) 175.9 (19)
O(23) - C(23) - Os(2) 173.7 (30)
O(31) - C(31) - Os(3) 175.6 (20)
O(32) - C(32) - Os(3) 176.5 (20)
O(33) - C(33) - Os(3) 178.1 (25)
O(41) - C(41) - Os(4) 172.9 (21)
O(42) - C(42) - Os(4) 175.6 (19)
O(43) - C(43) - Os(4) 171.6 (24)
O(44) - C(44) - Os(4) 178.2 (24)
O(51) - C(51) - Os(5) 173.4 (22)
O(52) - C(52) - Os(5) 175.3 (19)
O(53) - C(53) - Os(5) 177.6 (21)
O(54) - C(54) - Os(5) 176.9 (23)

Table J.1. Uij ($Å^2 \times 10^4$) for $Os_5(CO)_{18}(PMe_3)$ (**18**)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	287(5)	331(5)	443(6)	2(4)	-10(4)	-16(4)
Os(2)	380(6)	375(5)	545(7)	52(5)	54(5)	-51(4)
Os(3)	403(6)	332(5)	598(7)	-20(5)	-49(5)	30(4)
Os(4)	290(5)	411(5)	548(6)	-44(5)	-15(4)	-35(4)
Os(5)	328(5)	374(5)	582(7)	64(5)	-20(4)	15(4)
P(1)	279(35)	658(46)	796(54)	-88(38)	24(34)	3(32)

Table J.2. Additional Bond Lengths (Å) and angles (°) for $Os_5(CO)_{18}(PMe_3)$ **(18)**

Bond Lengths

Os(1) - C(11)	1.89 (2)	O(24) - C(24)	1.17 (3)
Os(1) - C(12)	1.92 (3)	O(31) - C(31)	1.17 (3)
Os(1) - C(13)	1.86 (2)	O(32) - C(32)	1.15 (3)
Os(2) - C(21)	2.01 (3)	O(33) - C(33)	1.21 (3)
Os(2) - C(22)	1.90 (3)	O(34) - C(34)	1.16 (3)
Os(2) - C(23)	1.84 (3)	O(41) - C(41)	1.14 (3)
Os(2) - C(24)	1.86 (2)	O(42) - C(42)	1.12 (2)
Os(3) - C(31)	1.90 (3)	O(43) - C(43)	1.19 (3)
Os(3) - C(32)	1.94 (2)	O(51) - C(51)	1.15 (3)
Os(3) - C(33)	1.84 (3)	O(52) - C(52)	1.09 (3)
Os(3) - C(34)	1.91 (3)	O(53) - C(53)	1.18 (3)
Os(4) - C(41)	1.97 (3)	O(54) - C(54)	1.17 (3)
Os(4) - C(42)	1.92 (2)	Cl(1) - Cl(2)	1.17 (7)
Os(4) - C(43)	1.88 (3)	Cl(1) - Cl(3)	2.90 (3)
Os(5) - C(51)	1.91 (3)	Cl(1) - Cl(5)	2.67 (6)
Os(5) - C(52)	2.00 (3)	Cl(1) - Cl(6)	1.86 (4)
Os(5) - C(53)	1.87 (3)	Cl(2) - Cl(3)	1.98 (7)
Os(5) - C(54)	1.86 (3)	Cl(2) - Cl(4)	2.16 (9)
P(1) - C(1)	1.77 (3)	Cl(2) - Cl(5)	1.94 (8)
P(1) - C(2)	1.74 (3)	Cl(2) - Cl(6)	1.11 (6)
P(1) - C(3)	1.81 (3)	Cl(3) - Cl(4)	0.96 (5)
O(11) - C(11)	1.18 (3)	Cl(3) - Cl(5)	0.84 (7)
O(12) - C(12)	1.15 (3)	Cl(3) - Cl(6)	1.77 (4)
O(13) - C(13)	1.16 (2)	Cl(4) - Cl(5)	1.8 (1)
O(21) - C(21)	1.08 (3)	Cl(4) - Cl(6)	1.57 (5)
O(22) - C(22)	1.20 (3)	Cl(5) - Cl(6)	2.14 (8)
O(23) - C(23)	1.16 (3)		

Bond Angles

Os(3) - Os(4) - Os(1)	60.89 (3)	C(12) - Os(1) - Os(3)	97.2 (7)
Os(2) - Os(5) - Os(1)	61.37 (3)	C(12) - Os(1) - Os(4)	78.6 (8)
Os(4) - Os(1) - Os(2)	149.27 (4)	C(12) - Os(1) - Os(5)	92.9 (7)
Os(5) - Os(1) - Os(3)	154.13 (4)	C(13) - Os(1) - Os(2)	134.2 (7)
P(1) - Os(4) - Os(3)	106.9 (2)	C(13) - Os(1) - Os(3)	126.8 (7)
C(12) - Os(1) - Os(2)	86.1 (8)	C(13) - Os(1) - C(11)	92.5 (10)

Table J.2 cont'd

C(13) - Os(1) - C(12)	94.5 (10)	C(43) - Os(4) - C(41)	91.6 (11)
Os(5) - Os(2) - Os(1)	60.06 (3)	C(43) - Os(4) - C(42)	93.8 (11)
C(21) - Os(2) - Os(1)	85.9 (8)	Os(2) - Os(5) - Os(1)	61.37 (3)
C(21) - Os(2) - Os(5)	90.3 (7)	C(51) - Os(5) - Os(1)	87.4 (7)
C(22) - Os(2) - Os(1)	89.7 (8)	C(51) - Os(5) - Os(2)	87.5 (7)
C(22) - Os(2) - Os(5)	88.0 (8)	C(52) - Os(5) - Os(1)	89.8 (7)
C(22) - Os(2) - C(21)	175.5 (11)	C(52) - Os(5) - Os(2)	90.3 (7)
C(23) - Os(2) - Os(1)	153.6 (8)	C(52) - Os(5) - C(51)	177.0 (10)
C(23) - Os(2) - Os(5)	93.5 (8)	C(53) - Os(5) - Os(1)	106.8 (8)
C(23) - Os(2) - C(21)	93.6 (11)	C(53) - Os(5) - Os(2)	168.1 (8)
C(23) - Os(2) - C(22)	90.6 (11)	C(53) - Os(5) - C(51)	92.2 (11)
C(24) - Os(2) - Os(1)	109.0 (8)	C(53) - Os(5) - C(52)	89.5 (11)
C(24) - Os(2) - Os(5)	168.9 (8)	C(54) - Os(5) - Os(1)	155.8 (8)
C(24) - Os(2) - C(21)	91.0 (10)	C(54) - Os(5) - Os(2)	94.4 (8)
C(24) - Os(2) - C(22)	89.9 (11)	C(54) - Os(5) - C(51)	90.7 (11)
C(24) - Os(2) - C(23)	97.4 (11)	C(54) - Os(5) - C(52)	91.5 (11)
Os(4) - Os(3) - Os(1)	61.03 (3)	C(54) - Os(5) - C(53)	97.5 (12)
C(31) - Os(3) - Os(1)	97.5 (8)	C(1) - P(1) - Os(4)	115.4 (10)
C(31) - Os(3) - Os(4)	84.4 (8)	C(2) - P(1) - Os(4)	116.0 (11)
C(32) - Os(3) - Os(1)	79.0 (7)	C(2) - P(1) - C(1)	102.2 (15)
C(32) - Os(3) - Os(4)	93.4 (7)	C(3) - P(1) - Os(4)	115.6 (10)
C(32) - Os(3) - C(31)	176.5 (11)	C(3) - P(1) - C(1)	103.3 (13)
C(33) - Os(3) - Os(1)	158.5 (8)	C(3) - P(1) - C(2)	102.3 (15)
C(33) - Os(3) - Os(4)	100.3 (9)	O(11) - C(11) - Os(1)	172.1 (21)
C(33) - Os(3) - C(31)	90.6 (12)	O(12) - C(12) - Os(1)	176.3 (23)
C(33) - Os(3) - C(32)	92.5 (11)	O(13) - C(13) - Os(1)	178.4 (21)
C(34) - Os(3) - Os(1)	101.7 (9)	O(21) - C(21) - Os(2)	173.9 (25)
C(34) - Os(3) - Os(4)	159.6 (9)	O(22) - C(22) - Os(2)	170.7 (23)
C(34) - Os(3) - C(31)	87.5 (12)	O(23) - C(23) - Os(2)	177.4 (25)
C(34) - Os(3) - C(32)	93.8 (12)	O(24) - C(24) - Os(2)	176.0 (23)
C(34) - Os(3) - C(33)	98.5 (13)	O(31) - C(31) - Os(3)	179.0 (24)
Os(3) - Os(4) - Os(1)	60.89 (3)	O(32) - C(32) - Os(3)	177.8 (21)
C(41) - Os(4) - Os(1)	83.7 (7)	O(33) - C(33) - Os(3)	176.8 (25)
C(41) - Os(4) - Os(3)	92.0 (7)	O(34) - C(34) - Os(3)	178.2 (29)
C(41) - Os(4) - P(1)	90.7 (8)	O(41) - C(41) - Os(4)	174.8 (22)
C(42) - Os(4) - Os(1)	95.7 (7)	O(42) - C(42) - Os(4)	176.5 (21)
C(42) - Os(4) - Os(3)	83.1 (7)	O(43) - C(43) - Os(4)	174.4 (25)
C(42) - Os(4) - P(1)	88.7 (7)	O(51) - C(51) - Os(5)	174.6 (22)
C(42) - Os(4) - C(41)	174.6 (10)	O(52) - C(52) - Os(5)	178.0 (24)
C(43) - Os(4) - Os(1)	100.3 (8)	O(53) - C(53) - Os(5)	173.5 (24)
C(43) - Os(4) - Os(3)	160.3 (8)	O(54) - C(54) - Os(5)	176.2 (25)
C(43) - Os(4) - P(1)	92.5 (8)		

Table K.1. Uij ($\mathring{A}^2 \times 10^4$) for $Os_5(CO)_{17}(PMe_3)$ **(19)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	286(6)	365(6)	241(5)	-23(5)	3(4)	-5(6)
Os(2)	335(6)	288(6)	267(6)	15(5)	-52(5)	-5(5)
Os(3)	285(6)	281(5)	237(6)	-16(5)	-2(5)	2(5)
Os(4)	292(6)	279(5)	244(5)	-10(5)	-41(4)	1(5)
Os(5)	436(7)	393(6)	219(6)	-16(5)	15(5)	-73(6)
P(1)	461(44)	326(38)	272(36)	-14(30)	-87(33)	69(34)

Table K.2. Additional Bond Lengths (Å) and angles (°) for $Os_5(CO)_{17}(PMe_3)$ (**19**)

Bond Lengths

Os(4) - P(1)	2.337 (6)	P(1) - C(2)	1.79 (2)
Os(1) - C(11)	1.93 (3)	P(1) - C(3)	1.82 (3)
Os(1) - C(12)	1.94 (2)	O(11) - C(11)	1.15 (3)
Os(1) - C(13)	1.88 (3)	O(12) - C(12)	1.13 (2)
Os(2) - C(21)	1.94 (2)	O(13) - C(13)	1.15 (3)
Os(2) - C(22)	1.93 (2)	O(21) - C(21)	1.14 (3)
Os(2) - C(23)	1.94 (3)	O(22) - C(22)	1.16 (2)
Os(3) - C(31)	1.91 (2)	O(23) - C(23)	1.16 (3)
Os(3) - C(32)	1.95 (2)	O(31) - C(31)	1.17 (3)
Os(3) - C(33)	1.84 (3)	O(32) - C(32)	1.13 (2)
Os(4) - C(41)	1.91 (2)	O(33) - C(33)	1.18 (3)
Os(4) - C(42)	1.90 (2)	O(41) - C(41)	1.15 (2)
Os(4) - C(43)	1.83 (3)	O(42) - C(42)	1.17 (3)
Os(5) - C(51)	1.93 (4)	O(43) - C(43)	1.16 (3)
Os(5) - C(52)	1.95 (2)	O(51) - C(51)	1.18 (4)
Os(5) - C(53)	1.84 (3)	O(52) - C(52)	1.12 (2)
Os(5) - C(54)	1.90 (3)	O(53) - C(53)	1.20 (3)
P(1) - C(1)	1.82 (3)	O(54) - C(54)	1.17 (3)

Bond Angles

Os(4) - Os(1) - Os(2)	119.87 (5)	C(12) - Os(1) - Os(5)	93.0 (7)
Os(5) - Os(1) - Os(3)	119.80 (6)	C(13) - Os(1) - Os(2)	151.1 (9)
Os(5) - Os(1) - Os(4)	179.19 (6)	C(13) - Os(1) - Os(3)	149.7 (9)
Os(5) - Os(2) - Os(3)	119.70 (5)	C(13) - Os(1) - Os(4)	89.0 (9)
Os(4) - Os(3) - Os(2)	120.79 (5)	C(13) - Os(1) - Os(5)	90.5 (9)
P(1) - Os(4) - Os(1)	168.2 (2)	C(12) - Os(1) - C(11)	177.0 (11)
P(1) - Os(4) - Os(3)	109.5 (2)	C(13) - Os(1) - C(11)	90.2 (12)
C(11) - Os(1) - Os(2)	89.0 (8)	C(13) - Os(1) - C(12)	87.2 (11)
C(11) - Os(1) - Os(3)	91.1 (8)	C(0) - Os(2) - Os(1)	108.2 (6)
C(11) - Os(1) - Os(4)	92.3 (8)	C(0) - Os(2) - Os(3)	48.0 (6)
C(11) - Os(1) - Os(5)	88.4 (8)	C(0) - Os(2) - Os(5)	167.4 (6)
C(12) - Os(1) - Os(2)	94.0 (7)	C(21) - Os(2) - Os(1)	92.6 (7)
C(12) - Os(1) - Os(3)	90.4 (7)	C(21) - Os(2) - Os(3)	92.8 (7)
C(12) - Os(1) - Os(4)	86.3 (7)	C(21) - Os(2) - Os(5)	90.3 (7)

Table K.2 cont'd

C(21) - Os(2) - C(0)	88.0 (9)	C(43) - Os(4) - C(41)	90.6 (10)
C(22) - Os(2) - Os(1)	88.8 (7)	C(43) - Os(4) - C(42)	92.5 (10)
C(22) - Os(2) - Os(3)	90.4 (7)	C(51) - Os(5) - Os(1)	88.9 (11)
C(22) - Os(2) - Os(5)	87.9 (7)	C(51) - Os(5) - Os(2)	89.0 (11)
C(22) - Os(2) - C(0)	94.3 (9)	C(52) - Os(5) - Os(1)	87.1 (7)
C(23) - Os(2) - Os(1)	158.2 (9)	C(52) - Os(5) - Os(2)	91.4 (7)
C(23) - Os(2) - Os(3)	141.4 (9)	C(53) - Os(5) - Os(1)	104.4 (9)
C(23) - Os(2) - Os(5)	98.8 (9)	C(53) - Os(5) - Os(2)	164.5 (9)
C(23) - Os(2) - C(0)	93.6 (11)	C(53) - Os(5) - C(51)	89.9 (14)
C(22) - Os(2) - C(21)	176.8 (10)	C(53) - Os(5) - C(52)	88.4 (11)
C(23) - Os(2) - C(21)	88.8 (11)	C(54) - Os(5) - Os(1)	156.4 (8)
C(23) - Os(2) - C(22)	88.8 (11)	C(54) - Os(5) - Os(2)	96.6 (8)
C(0) - Os(3) - Os(1)	108.7 (6)	C(52) - Os(5) - C(51)	175.1 (13)
C(0) - Os(3) - Os(2)	48.3 (6)	C(54) - Os(5) - C(51)	94.5 (13)
C(0) - Os(3) - Os(4)	168.7 (6)	C(54) - Os(5) - C(52)	90.3 (11)
C(31) - Os(3) - Os(1)	94.1 (7)	C(54) - Os(5) - C(53)	98.9 (12)
C(31) - Os(3) - Os(2)	91.8 (7)	C(1) - P(1) - Os(4)	115.1 (9)
C(31) - Os(3) - Os(4)	92.4 (8)	C(2) - P(1) - Os(4)	115.0 (9)
C(31) - Os(3) - C(0)	85.7 (10)	C(2) - P(1) - C(1)	105.8 (12)
C(32) - Os(3) - Os(1)	92.2 (7)	C(3) - P(1) - Os(4)	115.6 (10)
C(32) - Os(3) - Os(2)	92.0 (7)	C(3) - P(1) - C(1)	101.3 (13)
C(32) - Os(3) - Os(4)	90.1 (7)	C(3) - P(1) - C(2)	102.2 (13)
C(32) - Os(3) - C(0)	93.1 (9)	O(0) - C(0) - Os(2)	138.9 (19)
C(33) - Os(3) - Os(1)	154.1 (8)	O(0) - C(0) - Os(3)	137.3 (19)
C(33) - Os(3) - Os(2)	144.9 (8)	O(11) - C(11) - Os(1)	175.4 (24)
C(33) - Os(3) - Os(4)	94.1 (8)	O(12) - C(12) - Os(1)	177.2 (22)
C(33) - Os(3) - C(0)	97.0 (10)	O(13) - C(13) - Os(1)	177.5 (27)
C(32) - Os(3) - C(31)	173.6 (10)	O(21) - C(21) - Os(2)	173.3 (24)
C(33) - Os(3) - C(31)	90.7 (10)	O(22) - C(22) - Os(2)	174.1 (20)
C(33) - Os(3) - C(32)	83.3 (10)	O(23) - C(23) - Os(2)	177.1 (28)
C(41) - Os(4) - Os(1)	87.4 (7)	O(31) - C(31) - Os(3)	175.7 (22)
C(41) - Os(4) - Os(3)	87.8 (7)	O(32) - C(32) - Os(3)	175.4 (21)
C(41) - Os(4) - P(1)	89.6 (7)	O(33) - C(33) - Os(3)	177.7 (22)
C(42) - Os(4) - Os(1)	93.3 (7)	O(41) - C(41) - Os(4)	175.3 (22)
C(42) - Os(4) - Os(3)	89.8 (7)	O(42) - C(42) - Os(4)	176.9 (21)
C(42) - Os(4) - P(1)	89.1 (7)	O(43) - C(43) - Os(4)	173.2 (22)
C(43) - Os(4) - Os(1)	99.8 (8)	O(51) - C(51) - Os(5)	171.4 (32)
C(43) - Os(4) - Os(3)	158.8 (8)	O(52) - C(52) - Os(5)	174.1 (22)
C(43) - Os(4) - P(1)	91.7 (8)	O(53) - C(53) - Os(5)	175.2 (25)
C(42) - Os(4) - C(41)	176.7 (10)	O(54) - C(54) - Os(5)	173.5 (24)

Table L.1. Uij ($Å^2 \times 10^4$) for $Os_5(CO)_{15}$(*ax*-PMe_3) **(20)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	344(3)	336(3)	384(4)	26(3)	92(3)	79(3)
Os(2)	286(3)	428(3)	356(4)	16(3)	68(3)	72(3)
Os(3)	409(4)	345(3)	507(4)	36(3)	7(3)	-83(3)
Os(4)	390(4)	460(4)	327(4)	47(3)	44(3)	23(3)
Os(5)	410(4)	400(3)	422(4)	122(3)	108(3)	58(3)
P(1)	711(34)	888(36)	386(28)	-116(25)	51(25)	52(28)
O(11)	1214(125)	670(86)	966(112)	341(76)	163(94)	442(87)
O(12)	854(100)	1075(109)	679(94)	-173(80)	250(78)	296(84)
O(13)	315(73)	1265(127)	1416(146)	25(105)	227(81)	117(78)
O(14)	670(82)	466(66)	898(100)	59(63)	19(72)	-172(62)
O(21)	448(79)	1932(165)	861(107)	742(109)	241(76)	37(93)
O(22)	525(75)	842(86)	540(76)	9(63)	-44(64)	-71(64)
O(23)	1030(120)	843(100)	1548(160)	-494(104)	-138(109)	611(93)
O(31)	880(109)	1098(114)	953(116)	239(90)	-442(96)	-368(90)
O(32)	1064(126)	1275(132)	1107(130)	518(103)	185(104)	-639(105)
O(33)	1362(153)	706(98)	2039(202)	-755(120)	-337(140)	384(102)
O(41)	498(80)	940(99)	1122(121)	451(84)	-137(78)	89(73)
O(42)	866(104)	765(92)	1004(113)	351(78)	114(86)	-148(79)
O(51)	737(101)	1361(135)	1105(129)	381(103)	448(97)	29(94)
O(52)	932(104)	977(99)	476(81)	27(69)	86(77)	38(82)
O(53)	820(101)	450(74)	1390(139)	211(77)	-115(94)	143(69)

Table L.2. Additional Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}(ax\text{-}PMe_3)$ (**20**)

Bond Lengths

Os(1) - C(11)	1.91 (2)	O(11) - C(11)	1.18(2)
Os(1) - C(12)	1.92 (2)	O(12) - C(12)	1.15(2)
Os(2) - C(21)	1.92 (2)	O(13) - C(13)	1.13(2)
Os(2) - C(22)	1.93 (2)	O(14) - C(14)	1.15(2)
Os(2) - C(23)	1.87 (2)	O(21) - C(21)	1.16(2)
Os(3) - C(31)	1.92 (2)	O(22) - C(22)	1.13(2)
Os(3) - C(32)	1.87 (2)	O(23) - C(23)	1.15(2)
Os(3) - C(33)	1.87 (2)	O(31) - C(31)	1.15(2)
Os(4) - C(41)	1.88 (2)	O(32) - C(32)	1.20(2)
Os(4) - C(42)	1.90 (2)	O(33) - C(33)	1.14(2)
Os(5) - C(51)	1.90 (2)	O(41) - C(41)	1.14(2)
Os(5) - C(52)	1.90 (2)	O(42) - C(42)	1.13(2)
Os(5) - C(53)	1.87 (2)	O(51) - C(51)	1.16(2)
P(1) - C(1)	1.82(3)	O(52) - C(52)	1.13(2)
P(1) - C(2)	1.80(2)	O(53) - C(53)	1.14(2)
P(1) - C(3)	1.74(3)		

Bond Angles

Os(4) - Os(1) - Os(2)	58.52(2)	Os(2) - Os(5) - Os(1)	60.38(2)
Os(4) - Os(1) - Os(3)	57.50(2)	Os(3) - Os(5) - Os(1)	60.80(2)
Os(5) - Os(1) - Os(2)	57.70(2)	Os(3) - Os(5) - Os(2)	60.03(2)
Os(5) - Os(1) - Os(3)	57.39(2)	P(1) - Os(4) - Os(1)	165.3(1)
Os(4) - Os(2) - Os(1)	61.89(2)	C(11) - Os(1) - Os(2)	127.2(5)
Os(4) - Os(2) - Os(3)	59.68(2)	C(11) - Os(1) - Os(3)	123.4(5)
Os(5) - Os(2) - Os(1)	61.91(2)	C(11) - Os(1) - Os(5)	175.0(5)
Os(5) - Os(2) - Os(3)	59.87(2)	C(12) - Os(1) - Os(2)	118.7(5)
Os(2) - Os(3) - Os(1)	60.75(2)	C(12) - Os(1) - Os(3)	123.0(5)
Os(4) - Os(3) - Os(1)	62.15(2)	C(12) - Os(1) - Os(4)	176.8(5)
Os(4) - Os(3) - Os(2)	61.04(2)	C(13) - Os(1) - Os(2)	120.6(5)
Os(5) - Os(3) - Os(1)	61.80(2)	C(13) - Os(1) - Os(4)	91.7(5)
Os(5) - Os(3) - Os(2)	60.10(2)	C(13) - Os(1) - Os(5)	89.1(5)
Os(2) - Os(4) - Os(1)	59.59(2)	C(13) - Os(1) - C(11)	87.3(7)
Os(3) - Os(4) - Os(1)	60.34(2)	C(13) - Os(1) - C(12)	91.2(7)
Os(3) - Os(4) - Os(2)	59.28(2)	C(14) - Os(1) - Os(3)	120.4(4)

Table L.2 cont'd

C(14) - Os(1) - Os(4)	85.9(5)	C(42) - Os(4) - Os(1)	99.5(5)
C(14) - Os(1) - Os(5)	97.4(5)	C(42) - Os(4) - Os(2)	104.8(6)
C(14) - Os(1) - C(11)	86.3(7)	C(42) - Os(4) - Os(3)	158.3(6)
C(14) - Os(1) - C(12)	91.3(7)	C(42) - Os(4) - P(1)	90.8(6)
C(21) - Os(2) - Os(1)	108.0(5)	C(42) - Os(4) - C(41)	88.7(8)
C(21) - Os(2) - Os(3)	127.0(6)	C(51) - Os(5) - Os(1)	99.1(5)
C(21) - Os(2) - Os(4)	69.7(5)	C(51) - Os(5) - Os(2)	158.0(5)
C(21) - Os(2) - Os(5)	165.1(5)	C(51) - Os(5) - Os(3)	104.3(5)
C(22) - Os(2) - Os(1)	102.9(4)	C(52) - Os(5) - Os(1)	108.8(5)
C(22) - Os(2) - Os(3)	139.4(5)	C(52) - Os(5) - Os(2)	102.7(5)
C(22) - Os(2) - Os(4)	149.3(5)	C(52) - Os(5) - Os(3)	162.3(5)
C(22) - Os(2) - Os(5)	79.6(5)	C(52) - Os(5) - C(51)	91.1(7)
C(22) - Os(2) - C(21)	92.9(7)	C(53) - Os(5) - Os(1)	150.7(5)
C(23) - Os(2) - Os(1)	154.4(6)	C(53) - Os(5) - Os(2)	99.1(5)
C(23) - Os(2) - Os(3)	94.5(6)	C(53) - Os(5) - Os(3)	91.4(5)
C(23) - Os(2) - Os(4)	115.0(6)	C(53) - Os(5) - C(51)	96.6(7)
C(23) - Os(2) - Os(5)	99.8(6)	C(53) - Os(5) - C(52)	95.4(7)
C(23) - Os(2) - C(21)	93.0(8)	C(1) - P(1) - Os(4)	112.6(8)
C(23) - Os(2) - C(22)	90.2(7)	C(2) - P(1) - Os(4)	116.9(9)
C(31) - Os(3) - Os(1)	107.8(6)	C(2) - P(1) - C(1)	99.2(12)
C(31) - Os(3) - Os(2)	134.0(6)	C(3) - P(1) - Os(4)	117.8(10)
C(31) - Os(3) - Os(4)	74.1(6)	C(3) - P(1) - C(1)	100.7(13)
C(31) - Os(3) - Os(5)	158.4(6)	C(3) - P(1) - C(2)	106.9(13)
C(32) - Os(3) - Os(1)	107.1(6)	O(11) - C(11) - Os(1)	175.7(16)
C(32) - Os(3) - Os(2)	136.4(6)	O(12) - C(12) - Os(1)	175.2(16)
C(32) - Os(3) - Os(4)	154.8(6)	O(13) - C(13) - Os(1)	163.3(16)
C(32) - Os(3) - Os(5)	77.1(6)	O(14) - C(14) - Os(1)	163.1(14)
C(32) - Os(3) - C(31)	89.3(9)	O(21) - C(21) - Os(2)	168.8(17)
C(33) - Os(3) - Os(1)	149.8(7)	O(22) - C(22) - Os(2)	175.1(15)
C(33) - Os(3) - Os(2)	89.0(7)	O(23) - C(23) - Os(2)	178.3(19)
C(33) - Os(3) - Os(4)	105.1(8)	O(31) - C(31) - Os(3)	168.2(19)
C(33) - Os(3) - Os(5)	104.5(7)	O(32) - C(32) - Os(3)	173.9(18)
C(33) - Os(3) - C(31)	93.1(9)	O(33) - C(33) - Os(3)	175.7(24)
C(33) - Os(3) - C(32)	94.4(9)	O(41) - C(41) - Os(4)	177.6(17)
C(41) - Os(4) - Os(1)	100.0(5)	O(42) - C(42) - Os(4)	177.7(17)
C(41) - Os(4) - Os(2)	156.7(6)	O(51) - C(51) - Os(5)	178.2(16)
C(41) - Os(4) - Os(3)	102.0(6)	O(52) - C(52) - Os(5)	176.6(16)
C(41) - Os(4) - P(1)	90.7(5)	O(53) - C(53) - Os(5)	178.9(17)

Table M.1. Uij (Å^2 x 10^4) for $Os_5(CO)_{15}$(*eq*-PMe_3) **(21)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	245(3)	171(3)	244(3)	5(3)	13(2)	-12(2)
Os(2)	272(3)	169(3)	264(3)	29(3)	16(2)	-14(3)
Os(3)	253(3)	310(4)	253(3)	19(3)	-25(2)	1(3)
Os(4)	296(3)	241(4)	269(3)	-40(3)	52(3)	-8(3)
Os(5)	285(3)	276(4)	319(4)	0(3)	86(3)	13(3)
P(1)	285(22)	274(25)	441(27)	-6(21)	18(19)	-60(19)
O(11)	567(81)	586(94)	310(72)	-62(68)	92(59)	-21(68)
O(12)	919(106)	431(87)	398(80)	199(70)	-296(73)	-217(77)
O(13)	552(86)	468(93)	890(118)	118(84)	-285(79)	20(71)
O(21)	458(75)	294(76)	999(122)	167(78)	-33(74)	217(63)
O(22)	1188(133)	849(124)	206(74)	88(78)	62(77)	-42(104)
O(23)	535(84)	441(90)	1013(126)	-101(88)	-21(80)	-317(73)
O(31)	656(89)	891(122)	231(68)	21(74)	3(60)	84(81)
O(32)	915(130)	1364(189)	956(140)	21(134)	-121(105)	787(135)
O(33)	807(109)	862(128)	735(112)	225(98)	-277(87)	-530(100)
O(41)	773(98)	505(90)	440(82)	4(74)	228(72)	-181(77)
O(42)	284(67)	891(121)	657(98)	9(89)	29(63)	51(70)
O(43)	1297(138)	186(74)	616(98)	-294(71)	114(91)	-217(82)
O(51)	874(117)	525(104)	919(128)	-39(94)	131(95)	285(89)
O(52)	975(116)	747(118)	312(79)	-72(76)	-18(73)	-282(94)
O(53)	429(78)	1012(134)	627(97)	284(94)	-91(67)	-302(83)

Table O.2. Additional Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}(CNBu^t)$ (**24**)

Bond Lengths

Os(1) - C(11)	1.92 (1)	O(21) - C(21)	1.15 (1)
Os(1) - C(12)	1.93 (1)	O(22) - C(22)	1.17 (1)
Os(1) - C(13)	1.92 (1)	O(23) - C(23)	1.14 (1)
Os(2) - C(21)	1.91 (1)	O(31) - C(31)	1.15 (1)
Os(2) - C(22)	1.89 (1)	O(32) - C(32)	1.14 (1)
Os(2) - C(23)	1.88 (1)	O(33) - C(33)	1.11 (1)
Os(3) - C(31)	1.90 (1)	O(41) - C(41)	1.15 (1)
Os(3) - C(32)	1.92 (1)	O(42) - C(42)	1.13 (1)
Os(3) - C(33)	1.89 (1)	O(43) - C(43)	1.13 (1)
Os(4) - C(41)	1.88 (1)	O(51) - C(51)	1.13 (1)
Os(4) - C(42)	1.92 (1)	O(52) - C(52)	1.14 (1)
Os(4) - C(43)	1.90 (1)	O(53) - C(53)	1.15 (1)
Os(5) - C(51)	1.90 (1)	N(1) - C(1)	1.16 (1)
Os(5) - C(52)	1.90 (1)	N(1) - C(2)	1.44 (1)
Os(5) - C(53)	1.88 (1)	C(2) - C(3)	1.52 (1)
O(11) - C(11)	1.14 (1)	C(2) - C(4)	1.54 (2)
O(12) - C(12)	1.13 (1)	C(2) - C(5)	1.53 (2)
O(13) - C(13)	1.16 (1)		

Bond Angles

Os(2) - Os(3) - Os(1)	61.26 (2)	C(13) - Os(1) - Os(3)	122.3 (4)
Os(2) - Os(4) - Os(1)	60.81 (2)	C(13) - Os(1) - Os(4)	89.6 (3)
Os(3) - Os(4) - Os(1)	61.60 (2)	C(13) - Os(1) - Os(5)	96.6 (4)
Os(3) - Os(4) - Os(2)	59.69 (2)	C(13) - Os(1) - C(11)	87.6 (5)
Os(2) - Os(5) - Os(1)	60.85 (2)	C(13) - Os(1) - C(12)	90.1 (5)
Os(3) - Os(5) - Os(1)	61.36 (2)	C(1) - Os(1) - Os(2)	124.2 (3)
Os(3) - Os(5) - Os(2)	59.82 (2)	C(1) - Os(1) - Os(4)	93.3 (3)
C(11) - Os(1) - Os(2)	125.9 (4)	C(1) - Os(1) - Os(5)	92.4 (3)
C(11) - Os(1) - Os(3)	121.6 (4)	C(1) - Os(1) - C(11)	83.4 (5)
C(11) - Os(1) - Os(5)	175.8 (4)	C(1) - Os(1) - C(12)	87.3 (4)
C(12) - Os(1) - Os(2)	120.5 (3)	C(21) - Os(2) - Os(1)	109.5 (4)
C(12) - Os(1) - Os(3)	122.1 (3)	C(21) - Os(2) - Os(3)	132.7 (4)
C(12) - Os(1) - Os(4)	178.0 (3)	C(21) - Os(2) - Os(4)	75.4 (4)

Table M.2. Additional Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{15}$(*eq*-PMe_3) (**21**)

Bond Lengths

Os(1) - C(11)	1.90 (2)	P(1) - C(3)	1.80 (2)
Os(1) - C(12)	1.95 (2)	O(11) - C(11)	1.19 (2)
Os(1) - C(13)	1.93 (2)	O(12) - C(12)	1.15 (2)
Os(2) - C(21)	1.94 (2)	O(13) - C(13)	1.15 (2)
Os(2) - C(22)	1.93 (2)	O(21) - C(21)	1.13 (2)
Os(2) - C(23)	1.88 (2)	O(22) - C(22)	1.14 (2)
Os(3) - C(31)	1.93 (2)	O(23) - C(23)	1.13 (2)
Os(3) - C(32)	1.87 (2)	O(31) - C(31)	1.14 (2)
Os(3) - C(33)	1.86 (2)	O(32) - C(32)	1.14 (2)
Os(4) - C(41)	1.95 (2)	O(33) - C(33)	1.16 (2)
Os(4) - C(42)	1.91 (2)	O(41) - C(41)	1.10 (2)
Os(4) - C(43)	1.98 (2)	O(42) - C(42)	1.11 (2)
Os(5) - C(51)	1.86 (2)	O(43) - C(43)	1.08 (2)
Os(5) - C(52)	1.92 (2)	O(51) - C(51)	1.17 (2)
Os(5) - C(53)	1.85 (2)	O(52) - C(52)	1.11 (2)
P(1) - C(1)	1.78 (2)	O(53) - C(53)	1.20 (2)
P(1) - C(2)	1.85 (2)		

Bond Angles

Os(4) - Os(1) - Os(2)	58.54 (2)	P(1) - Os(1) - Os(3)	140.1 (1)
Os(4) - Os(1) - Os(3)	58.12 (2)	P(1) - Os(1) - Os(5)	154.4 (1)
Os(5) - Os(1) - Os(2)	57.38 (2)	C(11) - Os(1) - Os(2)	114.5 (5)
Os(5) - Os(1) - Os(3)	56.97 (2)	C(11) - Os(1) - Os(3)	115.6 (5)
Os(4) - Os(2) - Os(1)	60.61 (2)	C(11) - Os(1) - Os(4)	172.1 (5)
Os(4) - Os(2) - Os(3)	59.80 (2)	C(12) - Os(1) - Os(2)	120.7 (5)
Os(5) - Os(2) - Os(1)	62.19 (2)	C(12) - Os(1) - Os(4)	82.9 (5)
Os(5) - Os(2) - Os(3)	59.51 (2)	C(12) - Os(1) - Os(5)	98.8 (4)
Os(2) - Os(3) - Os(1)	60.82 (2)	C(12) - Os(1) - P(1)	81.8 (5)
Os(4) - Os(3) - Os(1)	60.69 (2)	C(12) - Os(1) - C(11)	98.7 (7)
Os(4) - Os(3) - Os(2)	60.32 (2)	C(13) - Os(1) - Os(3)	122.1 (5)
Os(5) - Os(3) - Os(1)	62.27 (2)	C(13) - Os(1) - Os(4)	85.5 (5)
Os(5) - Os(3) - Os(2)	60.04 (2)	C(13) - Os(1) - Os(5)	99.3 (5)
P(1) - Os(1) - Os(2)	143.2 (1)	C(13) - Os(1) - P(1)	85.0 (5)

Table M.2 cont'd

C(13) - Os(1) - C(11)	94.9 (7)	C(43) - Os(4) - Os(1)	157.8 (5)
C(21) - Os(2) - Os(1)	110.5 (5)	C(43) - Os(4) - Os(2)	99.3 (5)
C(21) - Os(2) - Os(3)	129.9 (5)	C(43) - Os(4) - Os(3)	101.4 (5)
C(21) - Os(2) - Os(4)	73.1 (5)	C(43) - Os(4) - C(41)	95.7 (8)
C(21) - Os(2) - Os(5)	165.5 (5)	C(43) - Os(4) - C(42)	98.2 (8)
C(22) - Os(2) - Os(1)	106.5 (6)	Os(2) - Os(5) - Os(1)	60.43 (2)
C(22) - Os(2) - Os(3)	138.8 (6)	Os(3) - Os(5) - Os(1)	60.76 (2)
C(22) - Os(2) - Os(4)	152.3 (6)	Os(3) - Os(5) - Os(2)	60.45 (2)
C(22) - Os(2) - Os(5)	79.7 (6)	C(51) - Os(5) - Os(1)	104.3 (6)
C(22) - Os(2) - C(21)	91.2 (8)	C(51) - Os(5) - Os(2)	161.2 (6)
C(23) - Os(2) - Os(1)	152.9 (5)	C(51) - Os(5) - Os(3)	103.4 (6)
C(23) - Os(2) - Os(3)	92.0 (5)	C(52) - Os(5) - Os(1)	104.3 (5)
C(23) - Os(2) - Os(4)	110.2 (5)	C(52) - Os(5) - Os(2)	103.1 (5)
C(23) - Os(2) - Os(5)	102.9 (5)	C(52) - Os(5) - Os(3)	161.3 (5)
C(23) - Os(2) - C(21)	88.5 (7)	C(52) - Os(5) - C(51)	90.9 (8)
C(23) - Os(2) - C(22)	91.6 (8)	C(53) - Os(5) - Os(1)	155.0 (6)
C(31) - Os(3) - Os(1)	109.8 (5)	C(53) - Os(5) - Os(2)	99.8 (6)
C(31) - Os(3) - Os(2)	131.6 (6)	C(53) - Os(5) - Os(3)	97.0 (6)
C(31) - Os(3) - Os(4)	73.7 (5)	C(53) - Os(5) - C(51)	91.3 (8)
C(31) - Os(3) - Os(5)	162.8 (6)	C(53) - Os(5) - C(52)	94.7 (7)
C(32) - Os(3) - Os(1)	105.9 (6)	C(1) - P(1) - Os(1)	117.8 (8)
C(32) - Os(3) - Os(2)	137.5 (6)	C(2) - P(1) - Os(1)	112.6 (6)
C(32) - Os(3) - Os(4)	152.4 (6)	C(2) - P(1) - C(1)	103.1 (10)
C(32) - Os(3) - Os(5)	77.9 (6)	C(3) - P(1) - Os(1)	114.3 (8)
C(32) - Os(3) - C(31)	90.7 (8)	C(3) - P(1) - C(1)	101.3 (10)
C(33) - Os(3) - Os(1)	150.5 (6)	C(3) - P(1) - C(2)	106.3 (10)
C(33) - Os(3) - Os(2)	90.1 (6)	O(11) - C(11) - Os(1)	168.5 (14)
C(33) - Os(3) - Os(4)	110.6 (6)	O(12) - C(12) - Os(1)	166.0 (14)
C(33) - Os(3) - Os(5)	100.7 (6)	O(13) - C(13) - Os(1)	166.6 (16)
C(33) - Os(3) - C(31)	92.5 (8)	O(21) - C(21) - Os(2)	172.7 (16)
C(33) - Os(3) - C(32)	92.4 (8)	O(22) - C(22) - Os(2)	172.4 (19)
Os(2) - Os(4) - Os(1)	60.86 (2)	O(23) - C(23) - Os(2)	175.9 (17)
Os(3) - Os(4) - Os(1)	61.19 (2)	O(31) - C(31) - Os(3)	172.0 (17)
Os(3) - Os(4) - Os(2)	59.88 (2)	O(32) - C(32) - Os(3)	169.6 (19)
C(41) - Os(4) - Os(1)	101.5 (6)	O(33) - C(33) - Os(3)	177.7 (19)
C(41) - Os(4) - Os(2)	159.3 (5)	O(41) - C(41) - Os(4)	176.3 (17)
C(41) - Os(4) - Os(3)	103.1 (5)	O(42) - C(42) - Os(4)	177.5 (17)
C(42) - Os(4) - Os(1)	95.9 (5)	O(43) - C(43) - Os(4)	175.4 (18)
C(42) - Os(4) - Os(2)	102.4 (5)	O(51) - C(51) - Os(5)	177.5 (18)
C(42) - Os(4) - Os(3)	155.4 (5)	O(52) - C(52) - Os(5)	177.9 (17)
C(42) - Os(4) - C(41)	89.5 (7)	O(53) - C(53) - Os(5)	176.2 (17)

Table N.1. Uij ($Å^2$ x 10^4) for $Os_5(CO)_{18}(CNBu^t)$ **(22)**

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	358 (2)	295 (2)	333 (2)	-71 (1)	-85 (2)	-43 (1)
Os(2)	420 (2)	402 (2)	409 (2)	-50 (2)	-76 (2)	-117 (2)
Os(3)	436 (2)	469 (2)	387 (2)	-164 (2)	-74 (2)	-64 (2)
Os(4)	324 (2)	313 (2)	507 (2)	-87 (2)	-114 (2)	-47 (2)
Os(5)	443 (2)	325 (2)	409 (2)	-116 (1)	-107 (2)	-24 (2)
O(11)	633 (47)	520 (38)	710 (44)	-176 (34)	-359 (39)	58 (34)
O(12)	656 (50)	582 (42)	686 (45)	-152 (35)	-291 (40)	-26 (37)
O(13)	948 (58)	427 (37)	578 (41)	-101 (31)	197 (42)	-199 (38)
O(21)	786 (59)	1046 (61)	783 (52)	-108 (46)	-314 (48)	-246 (48)
O(22)	783 (56)	920 (54)	529 (42)	109 (38)	-266 (41)	-266 (44)
O(23)	952 (66)	460 (44)	1576 (85)	-155 (48)	-32 (60)	-313 (44)
O(24)	543 (47)	903 (52)	606 (44)	-230 (39)	19 (38)	-76 (40)
O(31)	383 (43)	1050 (57)	679 (45)	-192 (41)	-152 (36)	-31 (39)
O(32)	628 (53)	972 (59)	902 (56)	-279 (45)	-378 (45)	9 (44)
O(33)	1456 (94)	1140 (74)	1386 (82)	-961 (69)	184 (72)	-205 (67)
O(34)	930 (65)	1085 (62)	517 (44)	76 (42)	-212 (44)	-363 (51)
O(41)	741 (54)	671 (46)	705 (49)	13 (38)	-60 (42)	-135 (40)
O(42)	443 (45)	665 (47)	1132 (63)	-87 (43)	-297 (44)	17 (37)
O(43)	991 (67)	700 (49)	1114 (64)	-495 (48)	-178 (53)	-195 (46)
O(51)	756 (52)	621 (42)	500 (39)	-166 (33)	-260 (38)	90 (37)
O(52)	1097 (69)	595 (45)	896 (55)	-202 (41)	-558 (52)	227 (45)
O(53)	602 (52)	579 (44)	1003 (57)	-146 (40)	79 (46)	-116 (38)
O(54)	1044 (66)	486 (41)	989 (58)	-297 (40)	-273 (50)	-252 (42)
N(1)	335 (48)	496 (46)	792 (58)	-131 (41)	-174 (43)	4 (39)
C(2)	397 (62)	506 (60)	942 (81)	-46 (55)	-204 (58)	27 (49)
C(3)	1901 (198)	1718 (165)	1437 (148)	-739 (132	-1136 (147)	808 (145)
C(4)	349 (76)	1090 (111)	2041 (174)	339 (110)	-52 (92)	-35 (71)
C(5)	935 (115)	511 (80)	3020 (238)	236 (105)	-978 (141)	-86 (75)

Table N.2. Additional Bond Lengths (Å) and Angles (°) for $Os_5(CO)_{18}(CNBu^t)$ **(22)**

Bond Lengths

Os(1) - C(11)	1.91 (1)	O(13) - C(13)	1.16 (1)
Os(1) - C(12)	1.93 (1)	O(21) - C(21)	1.14 (1)
Os(1) - C(13)	1.866 (9)	O(22) - C(22)	1.16 (1)
Os(2) - C(21)	1.94 (1)	O(23) - C(23)	1.16 (1)
Os(2) - C(22)	1.93 (1)	O(24) - C(24)	1.13 (1)
Os(2) - C(23)	1.89 (1)	O(31) - C(31)	1.13 (1)
Os(2) - C(24)	1.92 (1)	O(32) - C(32)	1.13 (1)
Os(3) - C(31)	1.96 (1)	O(33) - C(33)	1.15 (1)
Os(3) - C(32)	1.95 (1)	O(34) - C(34)	1.12 (1)
Os(3) - C(33)	1.89 (1)	O(41) - C(41)	1.14 (1)
Os(3) - C(34)	1.92 (1)	O(42) - C(42)	1.12 (1)
Os(4) - C(41)	1.91 (1)	O(43) - C(43)	1.14 (1)
Os(4) - C(42)	1.94 (1)	O(51) - C(51)	1.14 (1)
Os(4) - C(43)	1.89 (1)	O(52) - C(52)	1.13 (1)
Os(4) - C(1)	2.05 (1)	O(53) - C(53)	1.14 (1)
Os(5) - C(51)	1.94 (1)	O(54) - C(54)	1.14 (1)
Os(5) - C(52)	1.95 (1)	N(1) - C(1)	1.15 (1)
Os(5) - C(53)	1.91 (1)	N(1) - C(2)	1.45 (1)
Os(5) - C(54)	1.90 (1)	C(2) - C(3)	1.54 (2)
O(11) - C(11)	1.17 (1)	C(2) - C(4)	1.46 (1)
O(12) - C(12)	1.14 (1)	C(2) - C(5)	1.48 (1)

Bond Angles

Os(4) - Os(1) - Os(2)	151.64 (2)	C(12) - Os(1) - C(11)	174.4 (4)
Os(5) - Os(1) - Os(3)	150.44 (2)	C(13) - Os(1) - Os(2)	135.4 (3)
C(11) - Os(1) - Os(2)	79.6 (3)	C(13) - Os(1) - Os(3)	126.1 (3)
C(11) - Os(1) - Os(3)	96.2 (2)	C(13) - Os(1) - Os(4)	69.6 (3)
C(11) - Os(1) - Os(4)	87.5 (2)	C(13) - Os(1) - Os(5)	79.7 (3)
C(11) - Os(1) - Os(5)	96.9 (2)	C(13) - Os(1) - C(11)	91.9 (4)
C(12) - Os(1) - Os(2)	96.6 (3)	C(13) - Os(1) - C(12)	93.7 (4)
C(12) - Os(1) - Os(3)	80.3 (3)	C(21) - Os(2) - Os(1)	96.4 (3)
C(12) - Os(1) - Os(4)	94.2 (3)	C(21) - Os(2) - Os(5)	86.9 (3)
C(12) - Os(1) - Os(5)	84.3 (2)	C(22) - Os(2) - Os(1)	80.1 (3)

Table N.2 cont'd

C(22) - Os(2) - Os(5)	90.6 (3)	C(51) - Os(5) - Os(1)	80.8 (3)
C(22) - Os(2) - C(21)	176.3 (4)	C(51) - Os(5) - Os(2)	90.6 (3)
C(23) - Os(2) - Os(1)	155.7 (3)	C(52) - Os(5) - Os(1)	94.1 (3)
C(23) - Os(2) - Os(5)	97.3 (3)	C(52) - Os(5) - Os(2)	86.2 (3)
C(23) - Os(2) - C(21)	91.2 (4)	C(52) - Os(5) - C(51)	174.9 (4)
C(23) - Os(2) - C(22)	91.7 (4)	C(53) - Os(5) - Os(1)	102.8 (3)
C(24) - Os(2) - Os(1)	104.8 (3)	C(53) - Os(5) - Os(2)	163.3 (3)
C(24) - Os(2) - Os(5)	164.2 (3)	C(53) - Os(5) - C(51)	91.9 (4)
C(24) - Os(2) - C(21)	90.0 (4)	C(53) - Os(5) - C(52)	90.1 (4)
C(24) - Os(2) - C(22)	91.7 (4)	C(54) - Os(5) - Os(1)	157.3 (3)
C(24) - Os(2) - C(23)	98.2 (4)	C(54) - Os(5) - Os(2)	96.8 (3)
C(31) - Os(3) - Os(1)	81.4 (3)	C(54) - Os(5) - C(51)	94.1 (4)
C(31) - Os(3) - Os(4)	90.5 (3)	C(54) - Os(5) - C(52)	90.2 (4)
C(32) - Os(3) - Os(1)	98.2 (3)	C(54) - Os(5) - C(53)	99.5 (4)
C(32) - Os(3) - Os(4)	86.3 (3)	O(11) - C(11) - Os(1)	176.9 (8)
C(32) - Os(3) - C(31)	176.5 (4)	O(12) - C(12) - Os(1)	176.5 (8)
C(33) - Os(3) - Os(1)	157.5 (4)	O(13) - C(13) - Os(1)	172.6 (8)
C(33) - Os(3) - Os(4)	98.3 (3)	O(21) - C(21) - Os(2)	173.3 (10)
C(33) - Os(3) - C(31)	90.2 (5)	O(22) - C(22) - Os(2)	173.9 (8)
C(33) - Os(3) - C(32)	89.0 (5)	O(23) - C(23) - Os(2)	176.9 (9)
C(34) - Os(3) - Os(1)	102.5 (3)	O(24) - C(24) - Os(2)	177.0 (8)
C(34) - Os(3) - Os(4)	162.8 (3)	O(31) - C(31) - Os(3)	175.6 (8)
C(34) - Os(3) - C(31)	92.1 (4)	O(32) - C(32) - Os(3)	176.5 (9)
C(34) - Os(3) - C(32)	91.3 (4)	O(33) - C(33) - Os(3)	177.6 (12)
C(34) - Os(3) - C(33)	98.6 (4)	O(34) - C(34) - Os(3)	177.8 (9)
C(41) - Os(4) - Os(1)	110.0 (3)	O(41) - C(41) - Os(4)	176.1 (9)
C(41) - Os(4) - Os(3)	170.5 (3)	O(42) - C(42) - Os(4)	175.2 (9)
C(42) - Os(4) - Os(1)	84.1 (3)	O(43) - C(43) - Os(4)	177.3 (9)
C(42) - Os(4) - Os(3)	92.0 (3)	O(51) - C(51) - Os(5)	175.3 (8)
C(42) - Os(4) - C(41)	90.1 (4)	O(52) - C(52) - Os(5)	175.0 (9)
C(43) - Os(4) - Os(1)	152.4 (3)	O(53) - C(53) - Os(5)	176.9 (9)
C(43) - Os(4) - Os(3)	91.7 (3)	O(54) - C(54) - Os(5)	178.8 (9)
C(43) - Os(4) - C(41)	97.4 (4)	C(2) - N(1) - C(1)	176.4 (9)
C(43) - Os(4) - C(42)	92.5 (4)	C(3) - C(2) - N(1)	106.6 (9)
C(1) - Os(4) - Os(1)	93.8 (2)	C(4) - C(2) - N(1)	110.1 (9)
C(1) - Os(4) - Os(3)	90.2 (2)	C(4) - C(2) - C(3)	107.5 (12)
C(1) - Os(4) - C(41)	87.1 (4)	C(5) - C(2) - N(1)	109.2 (9)
C(1) - Os(4) - C(42)	175.7 (3)	C(5) - C(2) - C(3)	108.4 (12)
C(1) - Os(4) - C(43)	91.1 (4)	C(5) - C(2) - C(4)	114.7 (11)

Table O.1. Uij ($Å^2 \times 10^4$) for $Os_5(CO)_{15}(CNBu^t)$ (**24**)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Os(1)	344 (2)	394 (2)	341 (2)	-50 (2)	71 (2)	51 (2)
Os(2)	387 (2)	475 (3)	335 (2)	64 (2)	74 (2)	-59 (2)
Os(3)	305 (2)	341 (2)	342 (2)	-24 (2)	94 (2)	3 (2)
Os(4)	394 (2)	467 (3)	342 (2)	-59 (2)	-1 (2)	11 (2)
Os(5)	341 (2)	427 (2)	309 (2)	-41 (2)	46 (2)	-24 (2)
O(11)	856 (68)	695 (58)	1059 (76)	-435 (56)	30 (59)	85 (54)
O(12)	554 (51)	696 (56)	668 (54)	142 (44)	-21 (44)	143 (44)
O(13)	822 (65)	1255 (83)	784 (63)	-8 (59)	524 (57)	250 (62)
O(21)	1541 (109)	1840 (119)	416 (53)	221 (64)	235 (63)	-725 (96)
O(22)	581 (58)	1395 (90)	789 (63)	224 (61)	112 (49)	-385 (59)
O(23)	876 (73)	503 (54)	1747 (111)	346 (63)	319 (74)	85 (53)
O(31)	438 (45)	783 (57)	760 (58)	-152 (47)	106 (42)	-214 (44)
O(32)	731 (57)	926 (65)	398 (46)	6 (43)	216 (42)	-65 (50)
O(33)	817 (65)	461 (51)	1162 (74)	56 (48)	319 (58)	221 (47)
O(41)	854 (67)	606 (56)	1011 (71)	-105 (51)	169 (56)	-196 (52)
O(42)	1262 (87)	1415 (96)	667 (63)	-430 (63)	491 (63)	32 (76)
O(43)	764 (61)	695 (57)	791 (60)	123 (48)	9 (51)	294 (50)
O(51)	736 (59)	931 (66)	507 (50)	222 (47)	149 (44)	-40 (51)
O(52)	321 (42)	1037 (66)	556 (48)	-163 (47)	95 (37)	-31 (43)
O(53)	839 (63)	518 (51)	849 (61)	-152 (45)	406 (53)	-135 (46)
N(1)	463 (54)	485 (56)	560 (57)	-20 (46)	146 (47)	19 (46)
C(2)	671 (82)	405 (63)	579 (74)	90 (57)	36 (64)	-110 (60)
C(3)	446 (70)	518 (76)	1061 (108)	61 (70)	93 (72)	-110 (60)
C(4)	795 (97)	632 (84)	1015 (112)	408 (82)	-189 (85)	-10 (77)
C(5)	898 (106)	1066 (118)	721 (95)	-53 (86)	348 (86)	-207 (93)

Table O.2 cont'd

C(21) - Os(2) - Os(5)	161.9 (4)	C(43) - Os(4) - C(41)	95.7 (5)
C(22) - Os(2) - Os(1)	104.2 (4)	C(43) - Os(4) - C(42)	95.7 (5)
C(22) - Os(2) - Os(3)	135.6 (4)	C(51) - Os(5) - Os(1)	98.5 (3)
C(22) - Os(2) - Os(4)	154.4 (4)	C(51) - Os(5) - Os(2)	157.1 (3)
C(22) - Os(2) - Os(5)	76.3 (4)	C(51) - Os(5) - Os(3)	103.0 (3)
C(22) - Os(2) - C(21)	91.4 (5)	C(52) - Os(5) - Os(1)	105.1 (3)
C(23) - Os(2) - Os(1)	153.5 (4)	C(52) - Os(5) - Os(2)	104.6 (3)
C(23) - Os(2) - Os(3)	92.0 (4)	C(52) - Os(5) - Os(3)	162.5 (3)
C(23) - Os(2) - Os(4)	109.7 (4)	C(52) - Os(5) - C(51)	89.6 (5)
C(23) - Os(2) - Os(5)	103.0 (4)	C(53) - Os(5) - Os(1)	154.5 (3)
C(23) - Os(2) - C(21)	90.5 (5)	C(53) - Os(5) - Os(2)	98.7 (3)
C(23) - Os(2) - C(22)	92.0 (5)	C(53) - Os(5) - Os(3)	96.0 (3)
C(31) - Os(3) - Os(1)	106.2 (3)	C(53) - Os(5) - C(51)	98.0 (4)
C(31) - Os(3) - Os(2)	133.8 (3)	C(53) - Os(5) - C(52)	94.3 (4)
C(31) - Os(3) - Os(4)	73.9 (3)	C(2) N(1) - C(1)	175.5 (11)
C(31) - Os(3) - Os(5)	157.2 (3)	O(11) - C(11) - Os(1)	174.5 (11)
C(32) - Os(3) - Os(1)	107.0 (3)	O(12) - C(12) - Os(1)	175.7 (10)
C(32) - Os(3) - Os(2)	134.1 (3)	O(13) - C(13) - Os(1)	168.7 (11)
C(32) - Os(3) - Os(4)	157.0 (3)	O(21) - C(21) - Os(2)	169.8 (12)
C(32) - Os(3) - Os(5)	74.8 (3)	O(22) - C(22) - Os(2)	173.1 (11)
C(32) - Os(3) - C(31)	91.7 (4)	O(23) - C(23) - Os(2)	179.2 (12)
C(33) - Os(3) - Os(1)	154.4 (4)	O(31) - C(31) - Os(3)	172.9 (10)
C(33) - Os(3) - Os(2)	93.2 (4)	O(32) - C(32) - Os(3)	171.6 (9)
C(33) - Os(3) - Os(4)	108.3 (3)	O(33) - C(33) - Os(3)	179.3 (11)
C(33) - Os(3) - Os(5)	106.0 (3)	O(41) - C(41) - Os(4)	177.6 (11)
C(33) - Os(3) - C(31)	92.1 (5)	O(42) - C(42) - Os(4)	178.7 (12)
C(33) - Os(3) - C(32)	89.8 (5)	O(43) - C(43) - Os(4)	177.3 (10)
C(41) - Os(4) - Os(1)	98.9 (3)	O(51) - C(51) - Os(5)	179.0 (10)
C(41) - Os(4) - Os(2)	158.4 (3)	O(52) - C(52) - Os(5)	176.7 (10)
C(41) - Os(4) - Os(3)	105.4 (4)	O(53) - C(53) - Os(5)	179.5 (10)
C(42) - Os(4) - Os(1)	101.9 (4)	N(1) - C(1) - Os(1)	166.5 (9)
C(42) - Os(4) - Os(2)	101.9 (4)	C(3) - C(2) N(1)	108.1 (9)
C(42) - Os(4) - Os(3)	159.1 (4)	C(4) - C(2) N(1)	107.3 (10)
C(42) - Os(4) - C(41)	89.1 (5)	C(4) - C(2) - C(3)	111.0 (9)
C(43) - Os(4) - Os(1)	157.1 (3)	C(5) - C(2) N(1)	108.2 (9)
C(43) - Os(4) - Os(2)	101.5 (3)	C(5) - C(2) - C(3)	109.8 (11)
C(43) - Os(4) - Os(3)	97.6 (3)	C(5) - C(2) - C(4)	112.2 (11)