SOME OXIDATIVE ADDITION REACTIONS OF TRIOSMIUM CLUSTERS

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ABSTRACT

This thesis describes the chemistry of the triosmium carbonyl cluster $[Os_3(CO)_{10}(MeCN)_2]$ with phosphorus ylides and with nitrogen heterocycles. The aim of the work was to synthesize triosmium clusters displaying novel modes of attachment of ligands.

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with the the phosphorus ylide $Ph_3P{=}CHCHO$ resulted in five products, all characterised spectroscopically and by X-ray diffraction, from either thermal or photochemical routes. Initial oxidative addition of $Ph_3PCHCHO$ gave two light sensitive isomeric clusters $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCHCO)(CO)_{10}]$. The first isomer decarbonylates in daylight to give a μ_3–nonacarbonyl species where the ligand is coordinated through an alkylidene bridge and a formyl group. This nonacarbonyl species further decarbonylates thermally to give an octacarbonyl species $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ by *ortho*-metallation at one phenyl ring of the triphenylphosphonium group. The second decacarbonyl isomer also decarbonylates in daylight to give two isomers of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ which differ only in the stereochemistry about the carbon atom $Ph_3P\underline{C}HCO$. The X-ray structure of one isomer was determined.

Cyclopentadienylidenetriphenylphosphorane $(Ph_3PC_5H_4)$ reacts with $[Os_3(CO)_{10}(MeCN)_2]$ to give the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ which contains the C_5 ring bonded through a single carbon atom to two osmium atoms. In solution the compound exists as two slowly interconverting decarbonyl isomers differing only in the substitution position of the phosphonium group. Decarbonylation gave an isomeric mixture of a noncarbonyl complex which contains the C_5 ring coordinated to the three osmium atoms though two σ Os-C

bonds and an η^2- bond, which is a new type of cyclopentadienylidene coordination. The X-ray structures of both the deca- and nonacarbonyl species were determined.

The reactions of triosium clusters with nitrogen heterocycles were examined to establish whether the chemistry always initiates at the nitrogen lone pair of electons on the ligands, whether non-hydride species may be formed and to compare the occurrence of C-H versus N-H cleavage during reaction. The initial reaction of benzotriazole, indazole, 1,2,3- triazole, pyrazole, pyrimidine and nicotine all initially gave decacarbonyl hydrido -species of the type $[Os_3H(ligand)(CO)_{10}]$ but the compounds were resistant to thermal decarbonylation.

However, the cluster $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$ was synthesised from the corresponding decacarbonyl and shown to lose MeCN and dimerize thermally to give the new compound $[Os_6H_2(C_6H_4N_3)_2(CO)_{18}]$ which exhibits an unusual mode of bonding. The X-ray structure of the dimer was determined.

IN MEMORY OF MY MOTHER AND FATHER

AND FOR JAMES

CONTENTS

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CHAPTER 1 Introduction

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1.1 Introduction

The chemistry of metal clusters has been studied extensively for the past twenty years for a variety of reasons not the least of which is the direct relevence to heterogeneous catalysis. Particular interest lies in the ways in which reacting species can bond to the cluster as follows:

i) to a single metal atom only
ii) in an edge-bridging mode, usually to two metal atoms
iii) face-bridging, bonded to three or more metal atoms and
iv) interstitially

The types of bonding (i) to (iii) directly relate to the ways species might bond to metal atoms at a metal surface and are therefore directly related to **homogeneous catalysis. The only heterogeneous forms for which the types (iii)** and (iv) can be formed are clusters.

Dodecacarbonyltriosmium, $[Os_3(CO)_{12}]$, has been a key compound in the development of transition metal clusters and indeed may be considered to be the parent molecule for all triosmium clusters. Using the 18-electron rule, the structures of essentially all its trinuclear derivatives may be deduced since the majority of triosmium clusters closely fit this rule. The rule cannot always be applied metal atom by metal atom since, although the overall electron count is consistent with the rule, some metal atoms have a high count and others a low one. It is known that in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ the two μ-hydrides bridge a common Os-Os bond which is a double bond to maintain formally the

18-electron rule (Figure 1.1).[1] This is a 46-electron cluster and there are only a few of these since most Os_3 clusters have 48 electrons with three M - M bonds or 50 electrons with two M - M bonds.

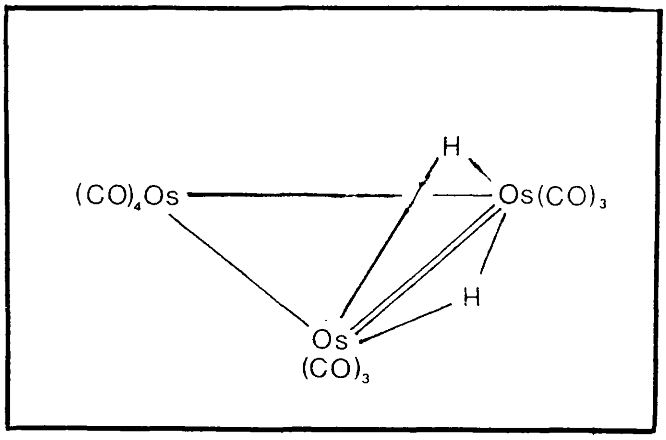


Figure 1.1 $[Os_3(\mu\text{-}H)_2(CO)_{10}]$

A further feature of these systems in the strength of the M - CO bond for third-row metals: 176 kJ mol^{-1} in $W(CO)_6$. The M-CO bond is formed by a combination of a σ bond developed by the overlap of a filled σ-orbital of the CO ligand with a vacant hybrid metal orbital and a π bond between a filled metal dπ or hybrid dpπ orbital and a vacant pπ* orbital of the carbon monoxide. This is a synergic effect as each component of the bonding tends to complement the other. Such bonding can be quite strong for third row metal compounds which are therefore usually robust.

Free CO has an electric dipole moment of 0.5 D which indicates that its polarity is fairly low. However, the group M-CO in metal carbonyls has a very intense infrared absorption spectra for the CO stretch around 2000 cm^{-1} which is probably the result of the large changes in dipole during the vibration. The frequencies of these stretches are very sensitive to differences in the electron density distribution. The absorptions for terminal carbonyl ligands occur in the region of 1940-2120 cm^{-1} for neutral triosmium clusters. With the introduction of a tertiary phosphine in a cluster, there is an increase in electron density with an asociated increase in M - C bond strength and a decrease in C=O bond strength. This change is reflected in a shift of some of the carbonyl absorptions to lower frequencies by about 10 - 20 cm^{-1}. A negative charge on the cluster, for example as in $[N(PPh_3)_2][HOs_3(CO)_{11}]$,[2] shows an even greater shift of about 50 cm^{-1}. Intermediate to these two cases is the zwitterionic cluster $[Os_3H(CHCH_2PMe_2Ph)(CO)_{10}]$.[3] The partial negative charge in this cluster is centred on the triosmium ring and causes a shift to lower frequency of about 20 - 30 cm^{-1}. Protonation has the opposite effect, whereby the addition of one proton to the triosmium ring causes the carbonyl infrared frequencies to shift to higher frequency by about 50 cm^{-1}. These characteristic changes in infrared absorptions make infrared monitoring of great value in following the reaction of metal carbonyl species. Not only do the frequencies indicate the electron density at the metal centres but also the rich spectra with up to nine or ten CO stretching bands allow individual clusters to have their own fingerprints.

Although $[Os_3(CO)_{12}]$ is able to undergo a wide range of reactions, in general its reactions with most common reagents such as PR_3, RNC and alkenes require temperatures in excess of 100°C. This reflects the strength of the M - CO bond and the rate of unimolecular carbon monoxide dissociation but working at these high temperatures does have a number of side effects; secondary processes such as further decarbonylation may occur preventing isolation of the initial product and thermal decomposition of some species may be found. In view of this, a more reactive starting material, itself a derivative of $[Os_3(CO)_{12}]$, is commonly used such as $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[5] $[Os_3(CO)_{11}L]$ [6-8] or $[Os_3(CO)_{10}L_2]$ [8-11] where L is a weakly bound, easily displaced ligand such as acetonitrile or cyclooctene thus enabling reactions to be carried out under less vigorous conditions. Reactions of these species commonly occur at room temperature.

The approach we and others employed in studying controlled synthesis of osmium and ruthenium clusters has been the utilization of stable intermediates that allow the displacement of ligand groups under mild conditions and, in particular, the ready preparation of $[Os_3(CO)_{10}(MeCN)_2]$ by trimethylamine N-oxide oxidation of two carbonyl groups of $[Os_3(CO)_{12}]$ in acetonitrile has led to an extensive chemistry of these clusters.[7,12] The trimethylamine N-oxide mediated reactions proceed via an anionic intermediate formed by nucleophilic attack of trimethylamine N-oxide at a metal carbonyl. The cluster resulting from replacement of two carbonyl ligands, $[Os_3(CO)_{10}(MeCN)_2]$, [13] has a much higher reactivity towards oxidative addition and substitution reactions than does $[Os_3(CO)_{12}]$ because of the acetonitrile ligands. However, one small disadvantage of the bis-acetonitrile cluster lies in its preparation which is best carried out under very high dilution conditions. Thus there is no guarantee that the only product is $[Os_3(CO)_{10}(MeCN)_2]$ and as it is more efficient in the expensive metal to use the derivative in its crude form a variety of products may result; some products may be formed from small quantities of $[Os_3(CO)_{11}(MeCN)]$ as an impurity. This problem is usually overcome by chromatography of all reaction products, the most abundant of these being formed from the bis-acetonitrile complex.

An important reaction of these compounds is the oxidative addition of organic molecules of the type HX which, with cleavage of C-H or other bonds, give species of the type $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$.[14] HX may be a wide range of organic species, for example, alkenes,[6,7] aldehydes,[9,15-17] heterocycles such as pyridine,[6,7,18] furan,[19] pyrrole [20-22] and others.[23-25] This has proved to be a very powerful route to many new, interesting and important ligands in clusters.

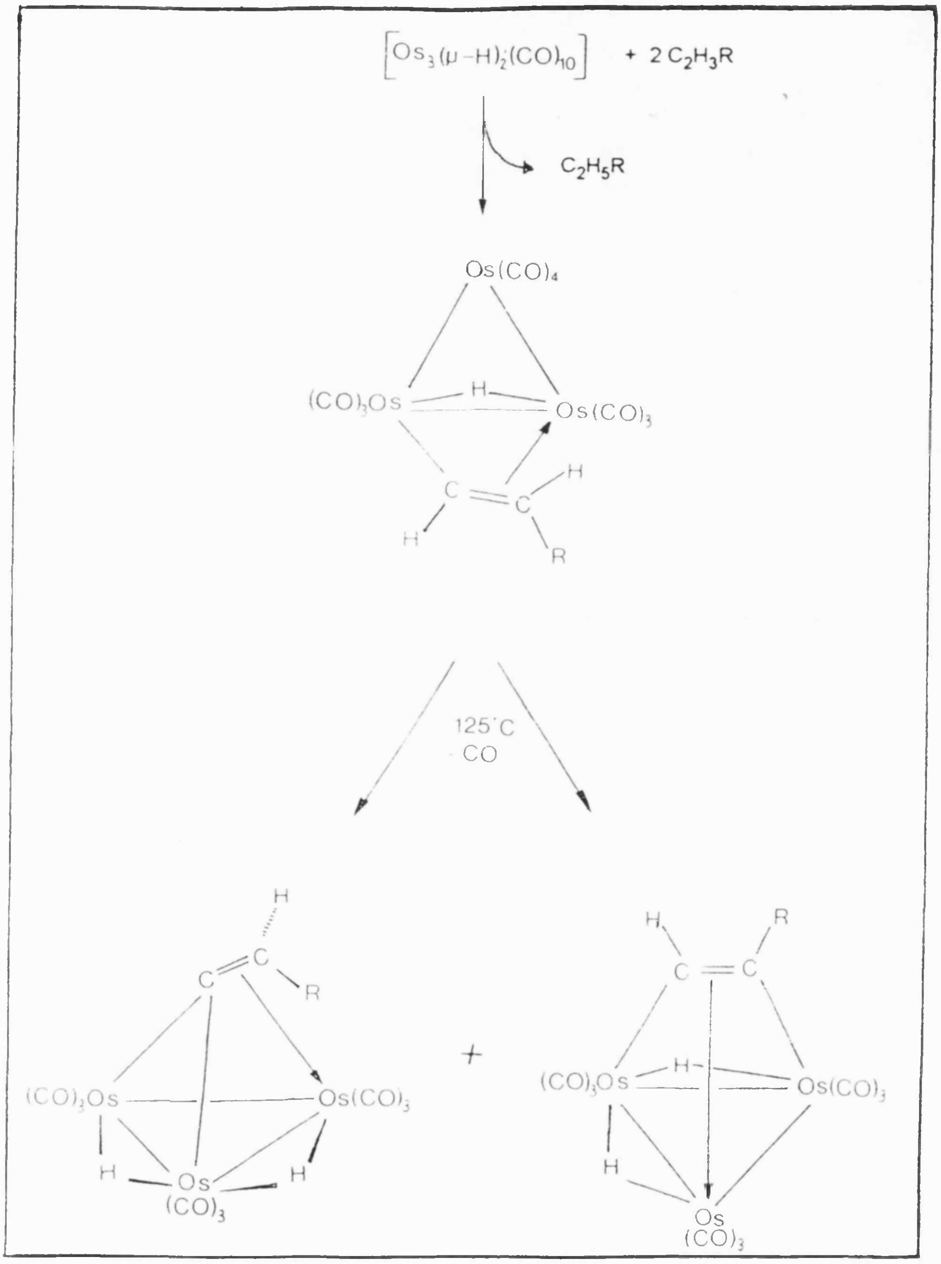
1.2 A Brief Survey of Oxidative Addition and C - H Bond Cleavage Reactions in Triosmium Cluster Chemistry

This is intended by no means to be an extensive or complete survey but merely a few examples of oxidative addition reactions where initial coordination of a ligand activates one or more C - H bonds in the ligand.

1.2.1 Group IV Ligands

The reactions of Group IV ligands with clusters in general have been the most extensively studied because of the relative ease with which C - H bonds are broken and M - C and M - H bonds formed and also because of the relevence of these reactions to catalysis and to dissociative chemisorption. Few thermodynamic measurements have been made, but it does seem that the strength of the M - C and M - H bonds is enough to compensate for the energy required to cleave the C - H bond.

Terminal alkenes and ethene (Scheme 1.1) react with $[Os_3(CO)_{12}]$ at temperatures in excess of 125°C to produce $[Os_3H_2(\mu_3,\eta^2\text{-}C{=}CHR)(CO)_9]$ by 1,1-diactivation of two C - H bonds. In addition products of 1,2-activation and containing the ligand CH=CR are formed. With internal alkenes only 1,2-diactivation occurs.[26] In refluxing octane the initially formed species is believed to be the vinyl cluster $[Os_3(\mu\text{-}H)(CH{=}CHR)(CO)_{10}]$ which undergoes further decarbonylation and C - H bond activation to produce $[Os_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}$



Scheme 1.1 Reaction of ethene (R = H) or terminal alkenes ($CH_2 = CHR$) with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$

C=CHR)$(CO)_9$] which contains a triply bridging vinylidene ligand in which the unsubstituted carbon atom is bonded to the third metal (Scheme 1.1).[27] The product of 1,2-activation contains the μ_3,η^2-alkyne ligand instead of vinylidene. In the reactions of $[Os_3(CO)_{12}]$ with disubstituted alkenes insertion reactions are important.

1.2.2 Group V Ligands

Phosphine will readily substitute for carbonyl groups; $[Os_3(CO)_{12}]$ reacts thermally at temperatures greater than 100°C with PR_3 (R=Me, Et, Ph)[28-30] to give the products $[Os_3(PR_3)_n(CO)_{12-n}]$ (n = 1, 2 or 3) in which the phosphine groups are in equatorial sites and each phosphine group is acting as a 2-electron donor. When PPh_3 was used in some early work which inspired much later research, six other products were identified [31,32] and these additional products are the result of C - H bond fission to give *ortho*-metallated phenyl rings and of C - P bond fission to give products containing C_6H_4 as a ligand, for example, in $[Os_3(C_6H_4)(PPh_2)_2(CO)_7]$. Similar C_6H_4 ligands are more directly made by the reaction of benzene with $[Os_3(CO)_{12}]$ to give the cluster $[Os_3H_2(C_6H_4)(CO)_9]$.[27] Similarly the susceptibility of the α-CH_2 in methyl and ethyl phosphines accounts for products from PMe_3 such as $[Os_3H_2(PMe_2CH)(CO)_9]$, although *ortho*-metallation of phenyl substituents occurs in preference to alkyl activation in mixed alkyl/aryl phosphine compounds. However, it should be noted that metallation of PEt_3 occurs at the more acidic α-CH_2 group rather than at the β-CH_3 which would correspond sterically to *ortho*-metallation of phenylphosphines.

Much attention has been directed to systems containing nitrogen; primary and secondary amines react with $[Os_3(CO)_{12}]$ to give initially $[Os_3H(NR^1R^2)(CO)_{10}]$ ($R^1 = R^2 = H$; $R^1 = H$, R^2 = Ph, CH_2Ph) in which the μ_2-

NR^1R^2 amido group acts as a three-electron donor. [33,34] Where R^1 = H, R^2 = Ph, thermal decarbonylation produces two isomers $[Os_3H_2(NPh)(CO)_9]$ and $[Os_3H_2(NHC_6H_4)(CO)_9]$ where the latter has an *ortho*-metallated phenyl ring and a μ_2-NH group (Figure 1.2).

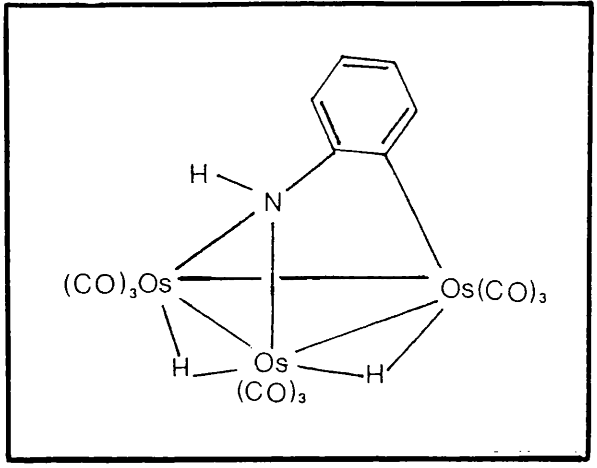


Figure 1.2 $[Os_3(\mu\text{-}H)_2(\mu\text{-}NHC_6H_4)(CO)_9)$

Thermal reaction of $[Os_3(CO)_{12}]$ and pyridine leads to the oxidative addition product [35] as does the room temperature reaction with $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3(C_8H_{14})_2(CO)_{10}]$ to give $[Os_3H(NC_5H_4)(CO)_{10}]$ by activation of an *ortho* C - H bond in the pyridine molecule (Figure 1.3). [36] The μ-2-pyridyl ligand in the product fits tidily between two metal atoms and it is a very stable ligand system.

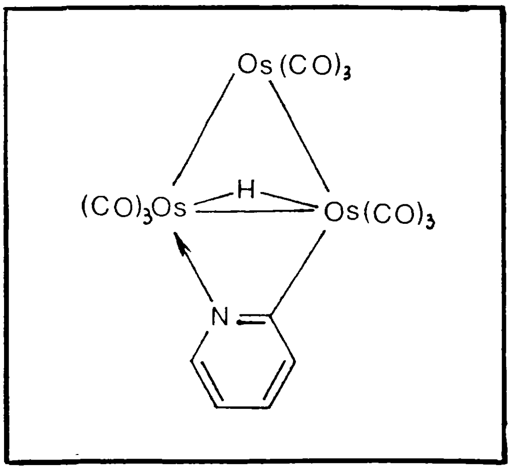


Figure 1.3 $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$

The bis-acetonitrile cluster, $[Os_3(CO)_{10}(MeCN)_2]$ reacts with triethylamine to give equimolar amount of the complexes $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}CHCH{=}NEt_2)(CO)_{10}]$ which is formed by C - H bond activation.[37] An important feature of the latter complex lies in the facile activation of three aliphatic C -H bonds. It is possible to take advantage of such facile C - H and N - H cleavages [38] as is shown in the $[Os_3(CO)_{12}]$-catalysed coupling of Me_2NPh:

$$PhNMe_2 \xrightarrow[134^\circ C]{[Os(CO)_{12}]} [(Me)_2NC_6H_4]_2CH_2$$

and in the exchange of substituents in MeNHPh:

$$PhNHMe \xrightarrow{[Os(CO)_{12}]} PhNH_2 + PhNMe_2$$

1.2.3 Group VI Ligands

Reaction of $[Os_3(CO)_{12}]$ with water, alcohols or thiols gives $[Os_3H(XR)(CO)_{10}]$ where X = O, S; R = H, Et, Ph. Alcohols with aromatic substituents react with dodecacarbonyltriosmium initially to produce the expected hydrido-aroxyl bridged species but, with further heating *ortho* activation of the aromatic C- H bond occurs. For example, thermolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}OCH_2Ph)(CO)_{10}]$ produces $[Os_3(\mu\text{-}H)_2(\mu\text{-}OCH_2C_6H_4)(CO)_9]$ which contains a five-membered metallocyclic ring [34,39] and $[Os_3(\mu\text{-}H)(\mu\text{-}OPh)(CO)_{10}]$ is converted into $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}OC_6H_4)(CO)_9]$ which contains three- and five-membered metallocyclic rings which include two osmium atoms (Figure 1.4).[40] Notably the phenolic ring has been trapped into a metallated cyclohexadienone ring, the Os - C bonds being strong enough to compensate for a loss of aromaticity.

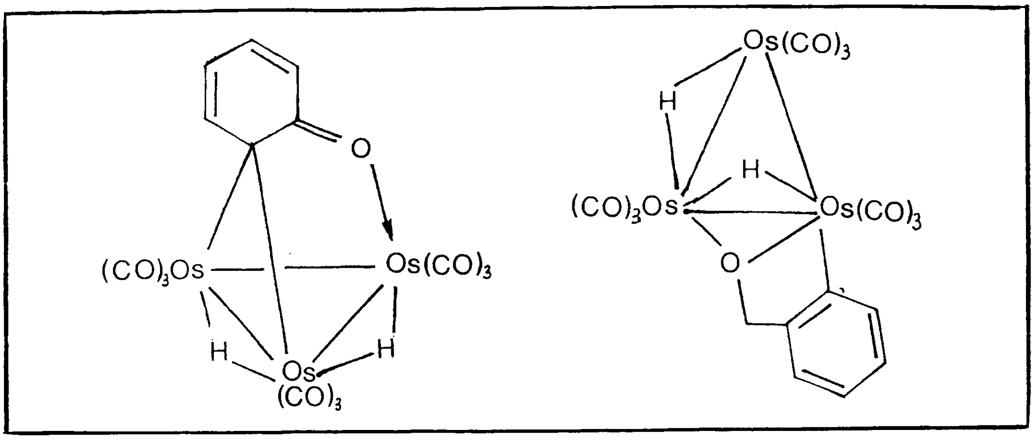


Figure 1.5 $[Os_3(\mu\text{-}H)_2(\mu\text{-}OCH_2C_6H_4)(CO)_9]$ and $[Os_3(\mu\text{-}H)_2\text{-}(\mu_3\text{-}OC_6H_4)(CO)_9]$

Ketones react by activation of the α-CH bonds and cyclohexanone gives a double oxidative addition product $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_8O)(CO)_9]$ in which two α-hydrogen atoms from the same carbon atom have been transferred to the metal atoms (Figure 1.5). Aldehydes react with $[Os_3(CO)_{12}]$ to give $[Os_3(\mu\text{-}H)(\mu_2\text{-}COR)(CO)_{10}]$ [41,42] (R = Ph, CH_2Ph, $CH(CH_3)_3$, C_5H_{11}, C_6H_{11} or C_6H_{13}) although the yields are poor to moderate.

Other molecules will add to $[Os_3(CO)_{10}(MeCN)_2]$ with cleavage of bonds other than C - H. Cleavage of N - H bonds has already been mentioned and another example is seleneophene which adds with Se - C bond cleavage.[43] In contrast thiophene and furan add with C - H cleavage.

A common feature of these adding molecules is that they are all capable of coordinating prior to the C - H bond cleavage step. Initial coordination before the oxidative addition step seems to be necessary since pyridine, alkenes and aldehydes react with decreasing rates in this order and alkanes do not react at all. Even with a good ligand such as pyridine the first observed product is the oxidative addition product, the 2-pyridyl complex $[Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$ [36] and the cluster $[Os_3(py)_2(CO)_{10}]$ is not observed. This result indicates that *ortho* metallation is extremely rapid when two

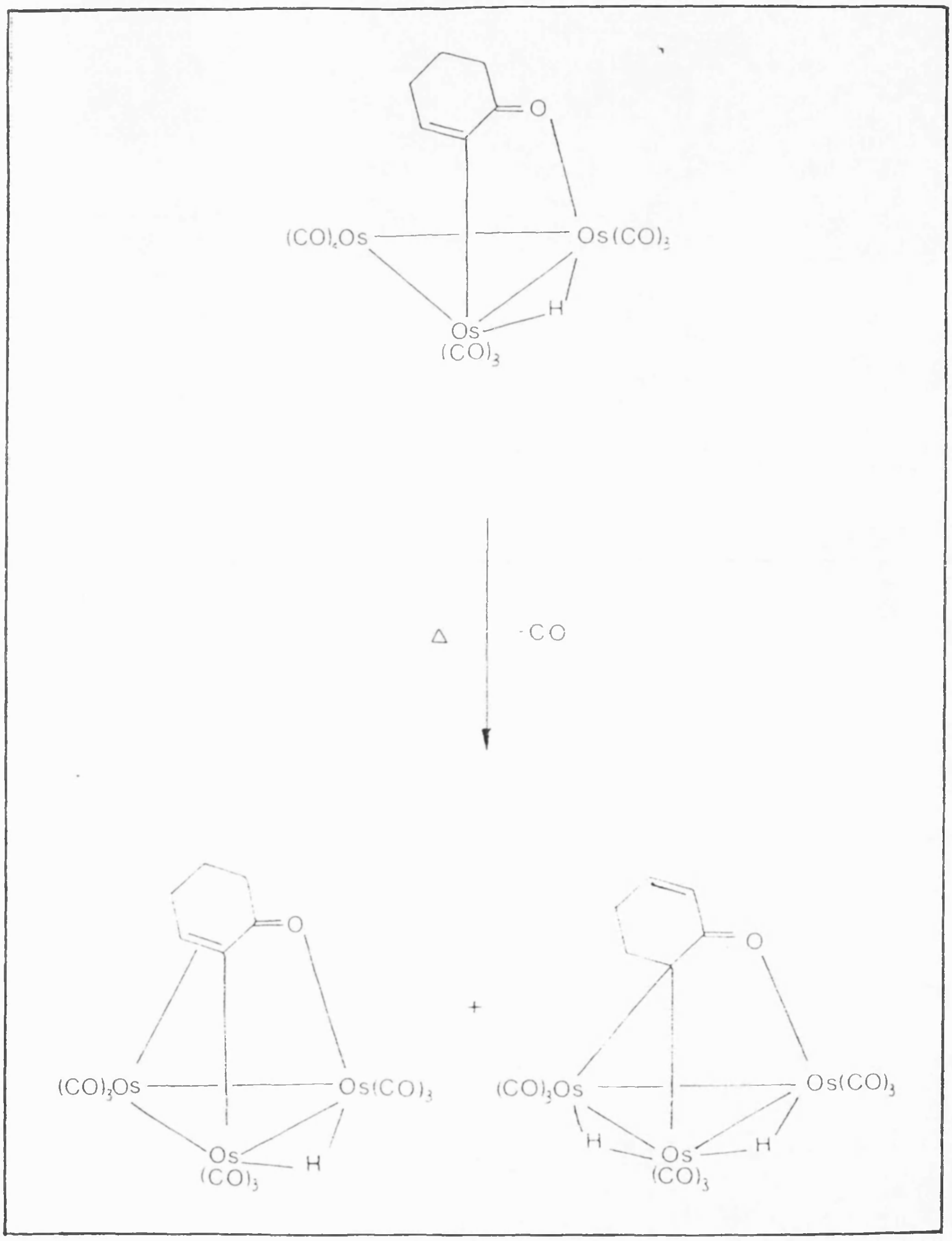


Figure 1.5 Products of thermal decarbonylation of $[Os_3(\mu\text{-}H)(\mu\text{-}OC_6H_7)(CO)_{10}]$

coordination sites are accessible. Simple pyridine complexes can only be obtained when there is one accessible site (i.e. one labile ligand is present) as in the reaction of $[Os_3(CO)_{11}(MeCN)]$ with pyridine to give $[Os_3(py)(CO)_{11}]$.[18]

The slow step in such reactions must be the one in which the acetonitrile (or the CO ligand) is displaced by the adding molecule; the following C - H bond cleavage is so rapid that it is not kinetically accesible. Even though the acetonitrile ligand is relatively labile compared with the carbonyl ligands at metal centres, its displacement remains the rate-determining step in oxidative addition reactions.

The work in this thesis resulted from our attempts to apply the high reactivity of $[Os_3(CO)_{10}(MeCN)_2]$ towards the synthesis of compounds containing Os - C bonds to new ligands. These few examples exemplify the main features of what is required for this chemistry: a donor site on the adding organic molecule (either lone-pairs or π-bonds) and suitable C - H bonds for cleavage adjacent to the donor site.

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CHAPTER 2

Oxidative addition of the phosphorus ylide $Ph_3PCHCHO$ to $[Os_3(CO)_{10}(MeCN)_2]$

CHAPTER 2

THE OXIDATIVE ADDITION OF THE PHOSPHORUS YLIDE $Ph_3PCHCHO$ TO A TRIOSMIUM CLUSTER

2.1 Introduction

Phosphoranes, or phosphorus ylides, are derived by deprotonation of a phosphonium compound which has at least one carbon atom attached to the phosphorus atom and three other substituents of any type covalently bound to the same phosphorus atom.[1] They are of the general type $R_3P=CR'R''$ and may be classified as phosphane-stabilized carbenes [2] which are very stable even in the absence of stabilizing substituents or salt components unlike the carbene complexes of the homologous nitrogen, arsenic, antimony or sulphur ylides which all decompose readily and act as carbene carriers.[3] This special stability has been attributed to the structural and electronic factors which contribute to stabilization of the ylidic carbanion as a result of delocalization of the non-bonded electrons of the carbanion. In a given ylide, stabilization of the dipolar form $X^+ - {}^-CR_2$ could be afforded both by the heteroatom portion X and by the two carbanion substituents R. The ability of the R groups to delocalize the carbanionic electrons does affect the stability of the ylide but it is not sufficient alone to account for the unique stability of phosphorus ylides - the phosphorus atom must itself play an important role in the stabilization of the carbanion. This special stabilization has been attributed to the use of vacant 3d-orbitals of the phosphorus atom, the carbanion taking advantage of the ability of the phosphorus atom to expand its outer shell to accommodate more than eight electrons. Therefore, in phosphorus ylides, it is possible to account for their properties on the basis that the ylide carbanion is stabilized to an appreciable extent by the overlap of the filled 2p-orbitals of carbon with the vacant 3d-orbitals of phosphorus.

Phosphorus ylides are polar molecules as indicated by the dipole moments reported. For example, 5.5 D for acetylmethylenetriphenylphosphorane,[4] so they may also be described as dipole carbene complexes with the formula (i) but also in the sense of a formal charge compensation, as neutral molecules (ii).[5,6]

$$R_3P: + :CH_2 \longrightarrow \{\underset{(i)}{R_3P^{+}\text{-}{}^{-}CH_2} \longleftrightarrow \underset{(ii)}{R_3P{=}CH_2}\}$$

The reactions of phosphoranes and most of their physical properties give a clear indication that their actual bonding pattern is much closer to the 1.2-zwitterionic structure (i): the phosphorus group remains uninvolved during the carbanion step of almost all reactions. In spite of the high dipole moments, phosphorus ylides exhibit solubility behaviour characteristic of covalent compounds and are very different in this respect from other zwitterionic substances, for example, amino acids. They are insoluble in water but are normally soluble in benzene, chloroform, ether and dichloromethane.

Polarization of the carbene function is obvious in ylides from their extraordinarily high Brϕnsted basicity which is of importance in the secondary processes known as transylidation in reactions with free ylides[7] and which has been the foundation of a rich coordination chemistry.

Phosphorus ylides exhibit an exceptional donor character with practically all metals which, in many cases, is sufficient to drive almost all other ligands out of the coordination sphere of the metal atom.[8,9] However, if an ylide attack is also possible at one of the ligands already present, the strong nucleophilicity of the ligand constitutes the most important characteristic of ylide reactivity in organic chemistry.[10] In organometallic chemistry the fact that the strongly nucleophilic phosphorus ylides attack metal complexes $M(CO)_6$ at the CO ligand [11,12] can be explained step-by-step as a transylidation reaction as in the formation of compound (iv) in Figure 2.1.[13]

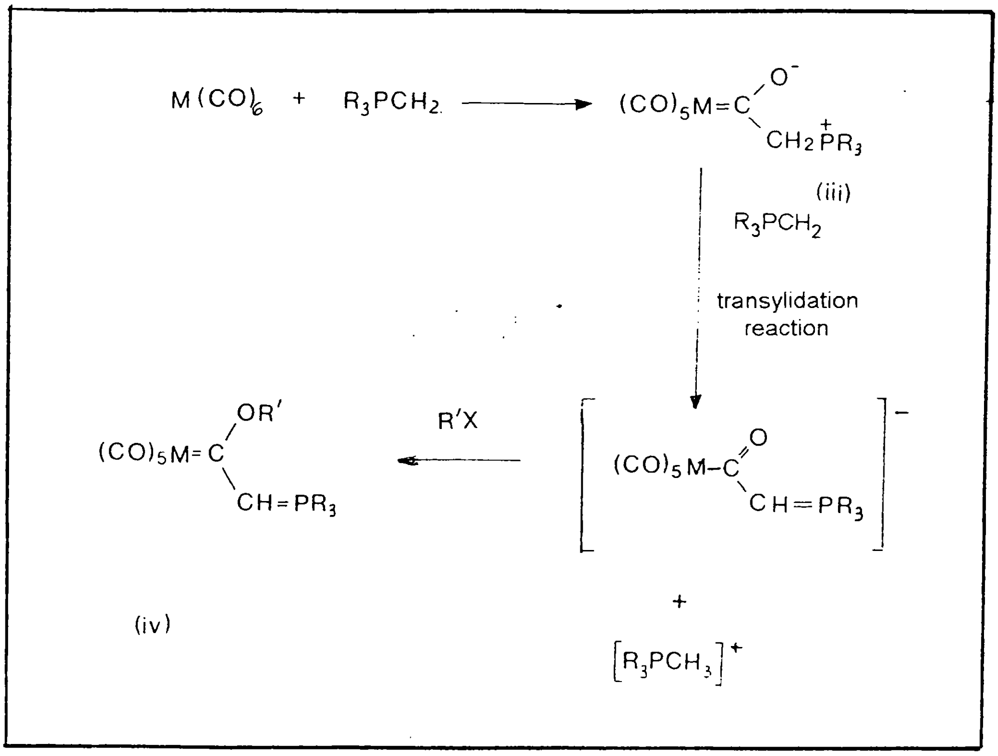


Figure 2.1 Transylidation reaction

Ultraviolet irradiation of $W(CO)_6$ and the double ylide $Ph_3P=C=PPh_3$ yields an acetylide which crystallizes as yellow needles.[14] This is basically a Wittig reaction and the by-product is $Ph_3P=O$.

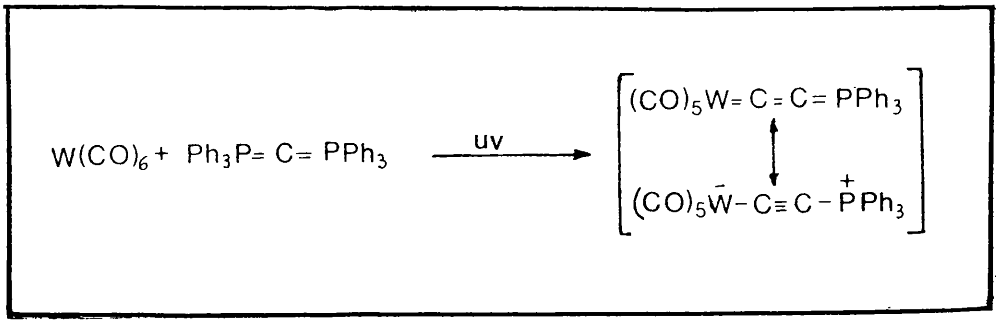


Figure 2.2 The photochemical reaction of $W(CO)_6$ and $Ph_3P = C = PPh_3$

One ruthenium complex has been found to incorporate the chelate-forming phosphorus ligand $(CH_3)_2PCH_2^-$ formed by deprotonation of a $P(CH_3)_3$ ligand.[15]

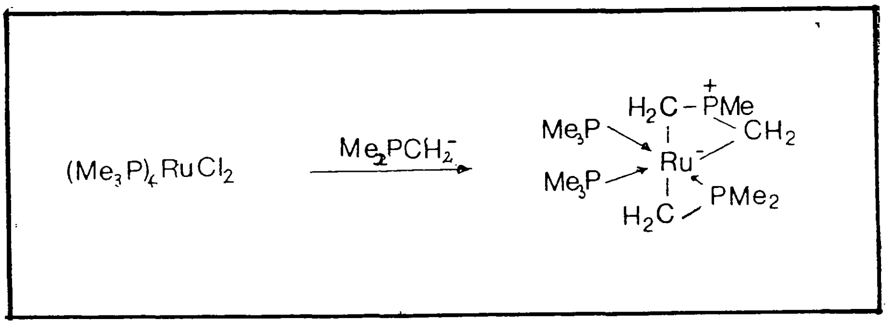


Figure 2.3 Reaction of a mononuclear ruthenium compound with $(CH_3)_3PCH_2$

Reaction of $Ph_3P{=}CH_2$ with the binuclear ruthenium complex (v) gives rise to a compound with a CH_2 bridge in which case the ylide is a carbene precursor.[16]

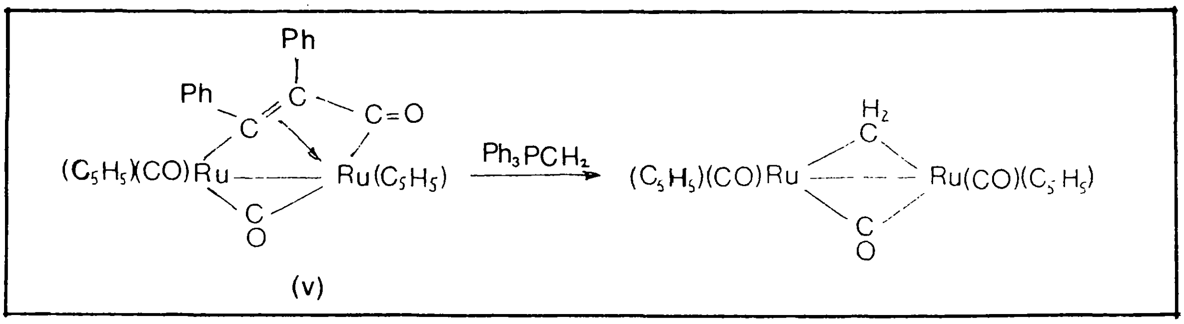


Figure 2.4 Reaction of a binuclear ruthenium complex with $Ph_3P = CH_2$

These examples indicate how the versatility of phosphorus ylide ligands has made them important reagents both in organic [2] and, to some extent, in inorganic chemistry.

2.2 Results and Discussion

2.2.1 The Synthesis and Characterization of [$Os_3H(Ph_3PCCHO)(CO)_{10}$] 1 and [$Os_3H(Ph_3PCHCO)(CO)_{10}$] 2

In this work the strong nucleophile used is (triphenylphosphoranylidene)ethanal, $Ph_3PCHCHO$, which exists in a form somewhere between the structures shown in Figure 2.5.

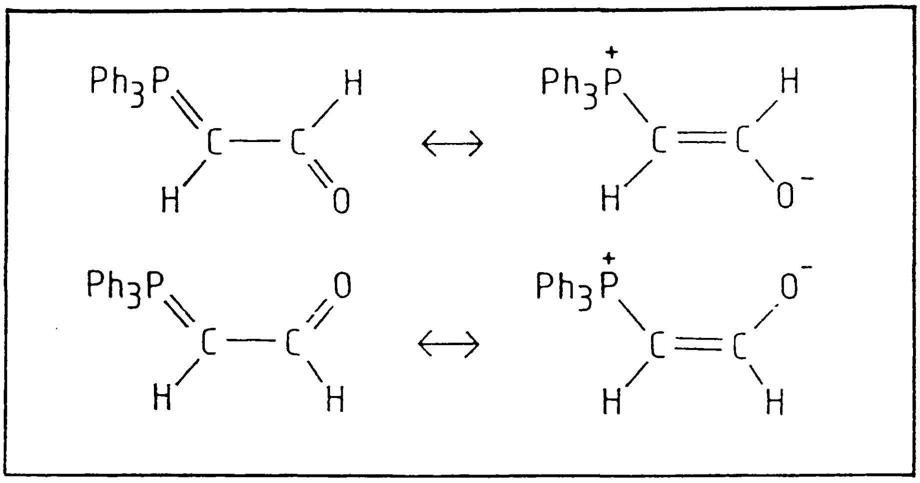
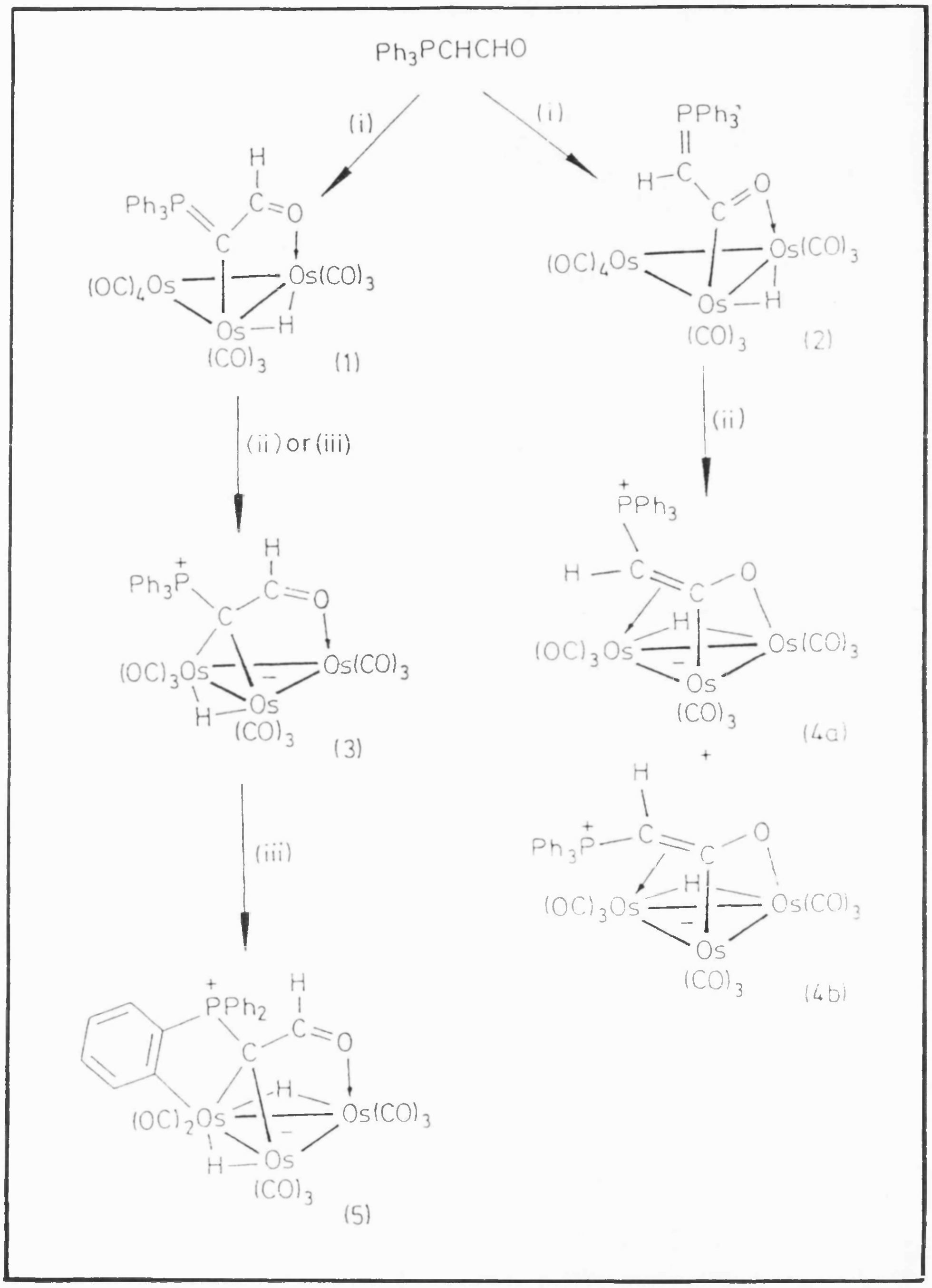


Figure 2.5 Representation of the dipolar contributions to the electronic structures of $Ph_3PCHCHO$ in its *cis* and *trans* forms which are in equilibrium

From its reactions it seems that there is a major contribution to the structure of the ligand from the zwitterionic form with a negative charge at the oxygen atom. This is a case in which the substituent at carbon has a strong stabilizing effect on the carbanionic carbon in addition to the phosphorus substituent. Scheme 2.1 summarizes the reactions and the compounds discussed in this chapter.

The work described in this chapter was initiated by Dr. Didier Nuel in this Department during 1987/88 but considerably extended by the author.



Scheme 2.1 (i) $[Os_3(CO)_{10}(MeCN)_2]$, CH_2Cl_2, 20 °C
(ii) daylight, CH_2Cl_2, 20 °C
(iii) toluene at 100 °C or heptane at 96 °C

The initial reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3PCHCHO$ was carried out in dichloromethane solution at room temperature. An infrared spectrum indicated that reaction was complete immediately after mixing although there was no apparent colour change from yellow. During the course of this work a study of the rates of reaction was not undertaken but qualitatively the reaction was found to be very rapid even at 0 °C. Two isomeric decacarbonyl complexes were the major products of the initial reaction, $[Os_3H(Ph_3PCCHO)(CO)_{10}]$ **1** and $[Os_3H(Ph_3PCHCO)(CO)_{10}]$ **2**, which could be separated by thin layer chromatography and each isolated as yellow crystals. The crystals of these isomeric products were found to be thermally and photochemically stable under normal laboratory conditions but when they were in dichloromethane solution each species underwent loss of CO in London daylight.

The infrared spectrum for each isomer is characteristic of a decacarbonyl complex (Table 2.1) and the ^1H NMR spectrum indicates the presence of a hydride ligand for each (Table 2.2). Also, there is one doublet in each ^1H NMR spectrum. Comparison with the spectrum of the free ligand indicates loss of H - H coupling and also loss of P - H coupling for one of the two hydrogen atoms (Table 2.3) which supports the assumption that C - H cleavage is the second step of the oxidative addition of $Ph_3PCHCHO$ to $[Os_3(CO)_{10}(MeCN)_2]$. Both the infrared and ^1H NMR data point to the clusters **1** and **2** being decacarbonyl hydride species but in order to establish unambiguously their respective structures it was necessary to carry out an X-ray crystal structure determination of each.

2.2.2 X-Ray Crystal Structures of Compounds $[Os_3H(Ph_3PCCHO)(CO)_{10}]$ **1** and $[Os_3H(Ph_3PCHCO)(CO)_{10}]$ **2**

A feature of structures of the type $[Os_3H(X)(CO)_{10}]$ and of many other carbonyl species is that the metal atoms closely maintain octahedral geometries so that the cluster geometry will depend upon the nature of X and primarily upon the number of atoms in the bridge.[16] The octahedral geometry in two- and three-atom bridges is maintained by a twist which moves the hydride ligand and the carbonyl ligand *trans* to it into the metal plane (Figure 2.6). In the three-atom bridge, the carbonyl ligands *trans* to bridging atoms A and C are strictly axial although this is not precisely true of the carbonyl ligands *trans* to A and B in the two-atom bridged structure.

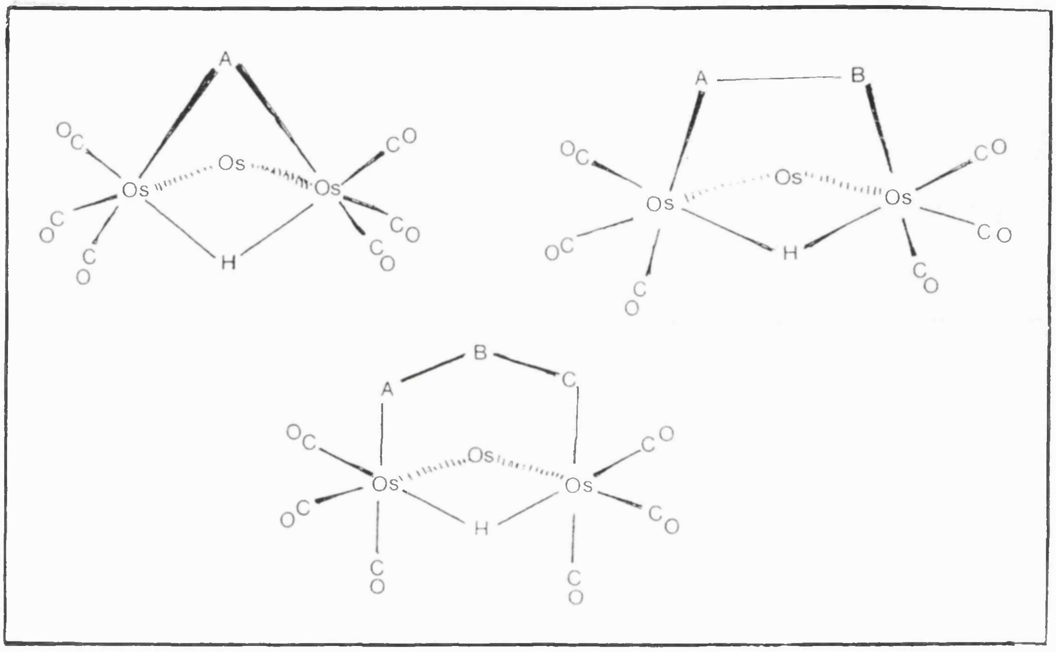


Figure 2.6 The geometry about osmium atoms in clusters containing one, two and three atom bridges

Structures **1** and **2** have a μ-bridging hydride ligand and it is well documented that a single hydrogen atom bridging a metal vector in a triosmium triangle causes an increase in the metal-metal distance compared with the length found in the parent compound [$M_3(CO)_{12}$]. This increase is generally greater than 0.1Å.[17]

The crystal structures of compounds **1** and **2** were determined by Dr. Didier Nuel in this Department. Following separation by thin-layer chromatography it was found that both the major products [$Os_3H(Ph_3PCCHO)(CO)_{10}$] **1** and [$Os_3H(Ph_3PCHCO)(CO)_{10}$] **2** were soluble in dichloromethane and it was possible to grow crystals from a dichloromethane/hexane mixture. Most of the crystals were too small but some were selected for each isomer which were suitable for analysis by X-ray diffraction.

The crystals of cluster **1** were yellow and monoclinic, a = 12.526(2), b = 14.926(5), c = 16.908(6) Å, β = 95.79(2), U = 3145(1) Å^3, Z = 4. The structure was solved in space group $P2_1/n$ and the molecular structure is shown in Figure 2.7. Selected bond lengths and angles are given in Table 2.4. The structure was refined to give R = 0.0627 and R' = 0.0665. Cluster **2** formed yellow triclinic crystals, a = 10.730(2), b = 12.989(5), c = 13.002(4) Å, α = 66.58(2), β = 86.96(2), γ = 83.26(2) °, U = 1651.5(8) Å^3, Z = 2 and the structure was solved in space group $P\bar{1}$. The molecular structure is shown in Figure 2.8 and selected bond lengths and angles are given in Table 2.5. The structure was refined to give R = 0.0491 and R' = 0.0484.

In the decacarbonyl structures **1** and **2**, the organic ligand bridges two metal atoms through C and O atoms. The structures are derived by initial formation of an Os - O bond followed by C - H cleavage at the C*H*CHO and CHC*H*O groups for **1** and **2** respectively. The representation of these structures in Scheme 2.1 showing P = C double bonds are extremes as the real situation will be one of delocalized bonding along the PCCO chain with significant positive charge centred on the phosphorus atom. Bonding descriptions A and C (Figure 2.9) correspond with those of known compounds without phosphorus centres, for example, $[Os_3H(RCH = CCHO)(CO)_{10}]$ and $[Os_3H(RCH = CHCO)(CO)_{10}]$ where R = methyl or phenyl.[18,19] However, the phosphorane nature of **1** and **2** allows contributions from the zwitterionic forms B and D (Figure 2.9).[1] The positive charge at phosphorus corresponds to the situation for the free ligand (Figure 2.5) and leads to accumulation of negative charge at the metal atoms.

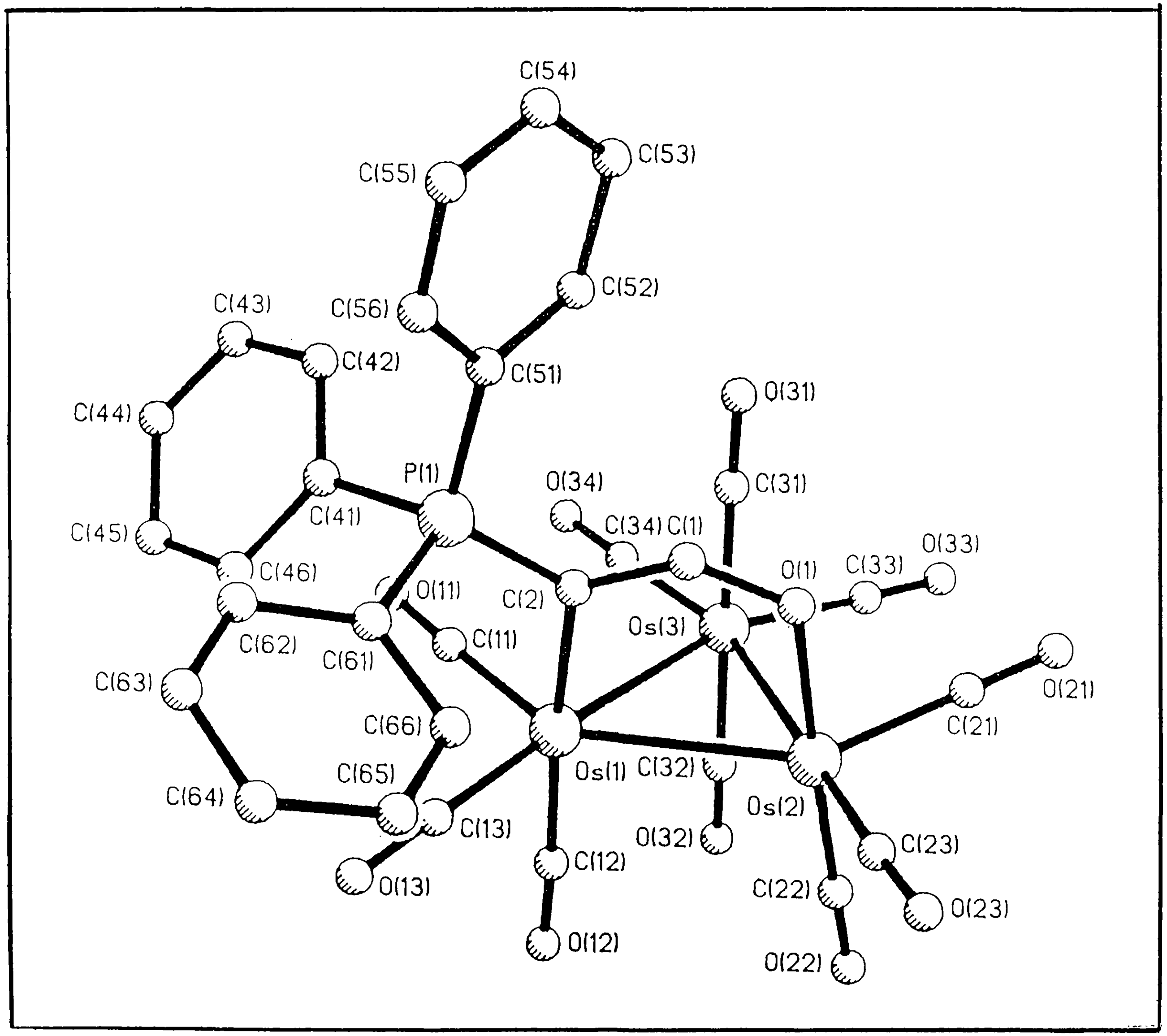


Figure 2.7 Molecular structure of the cluster [$Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_{10}$] 1

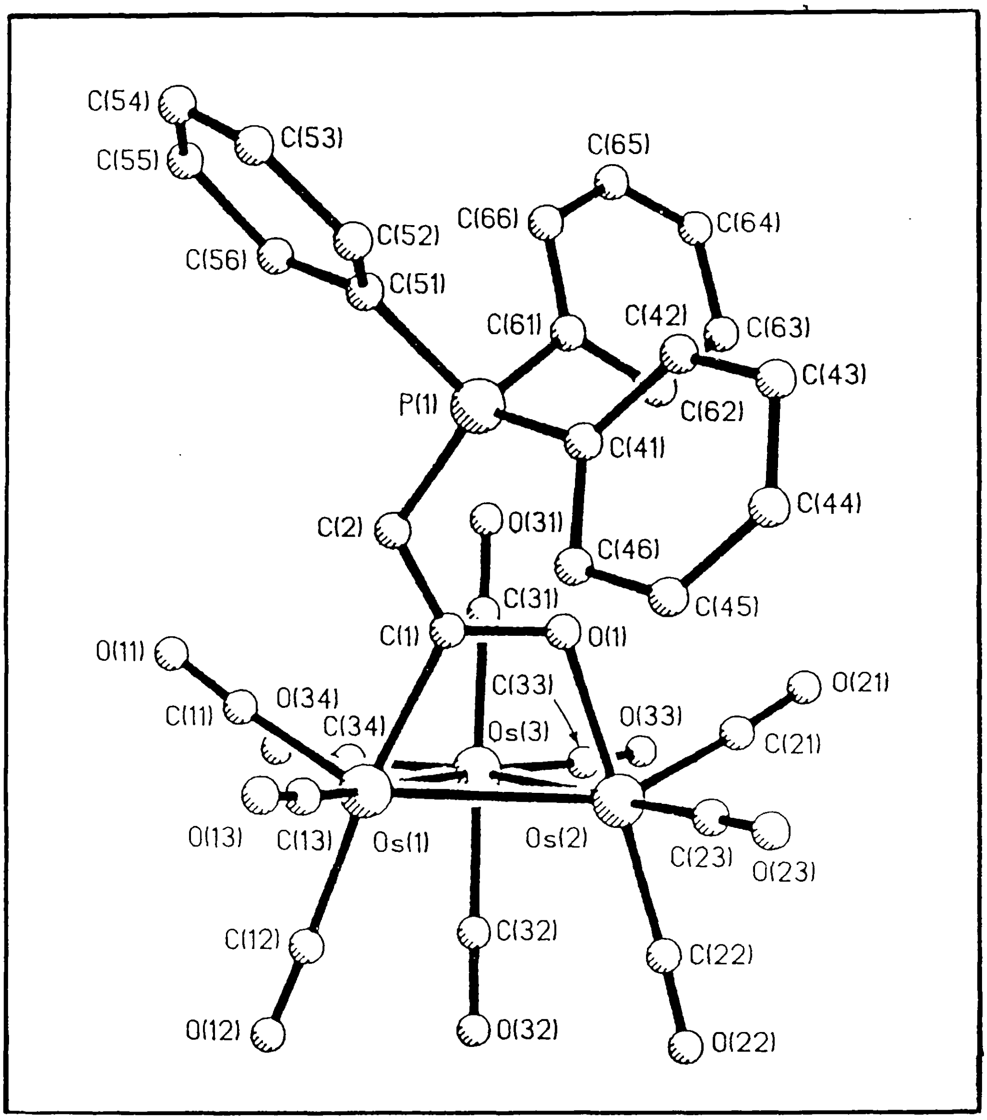


Figure 2.8 Molecular structure of the cluster $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_{10}]$ **2**

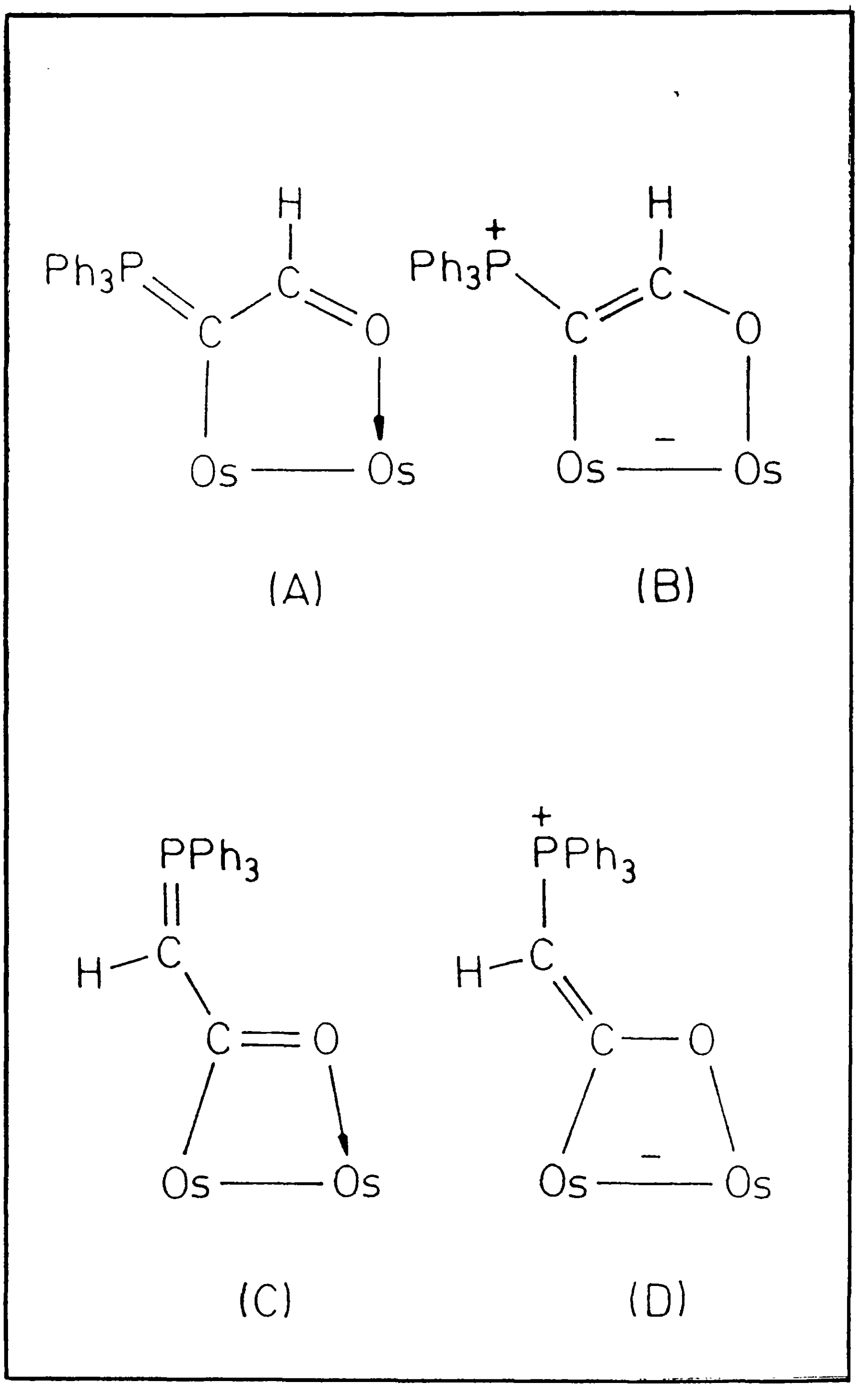


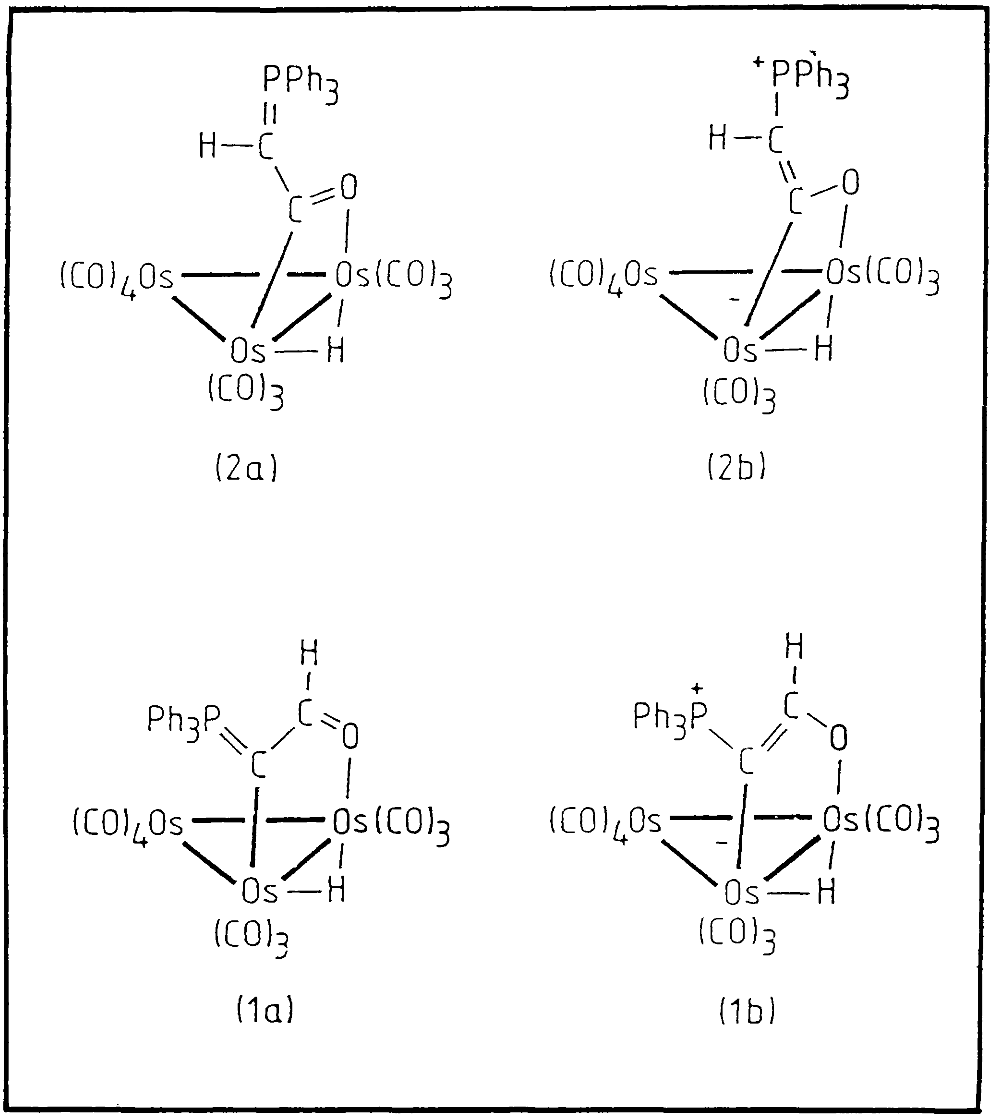
Figure 2.9

Bonding descriptions of zwitterionic and non-zwitterionic phosphorus-containing ligands at metal centres

The length of the P - C bonds indicated as double bonds in Scheme 2.1 are found to be 1.73(1) Å for **1** (Table 2.4) and 1.75(1) Å for **2** (Table 2.5) compared with P - C bonds to phenyl which are normally in the range 1.80 - 1.83 Å. In structures **3, 4a** and **5** in Scheme 2.1, to be described later in this chapter, the corresponding P - C distances were found to be 1.80(1), 1.80(1) and 1.77(1) Å respectively (Tables 2.6, 2.7, and 2.9), but in these cases the triphenylphosphine groups are regarded as fully developed phosphonium centres and the P - C bonds are believed to be single. Structures somewhere between 1a and 1b and between 2a and 2b (Figure 2.10) are therefore probably appropriate as there is some P - C multiple bonding together with a charge separation. The structure should also be apparent in C - O and C - C distances which are between those expected for single and double bonds but uncertainties in these preclude any firm deduction.

Free $Ph_3PCHCHO$ exists as a mixture of *cis* and *trans* isomers as a result of multiple bonding and restricted rotation about the central C - C bond [1] and it would not seem unreasonable to assume that each of clusters **1** and **2** is formed from its respective isomers since cluster **1** has the *trans* configuration and cluster **2** the *cis* configuration. Cluster **1** must have been formed from *trans*-$Ph_3PCHCHO$ since this configuration alone would allow oxygen coordination and metallation at the CH group. Cluster **2** could have been formed from either isomeric form. *cis-trans* Interconversion should be facile for cluster **2** and since only the *cis*-isomer is observed, this must indicate that it is the more stable arrangement. No evidence was obtained from spectroscopic studies for another isomer with the alternative configuration about the C - C bond in cluster **2**.

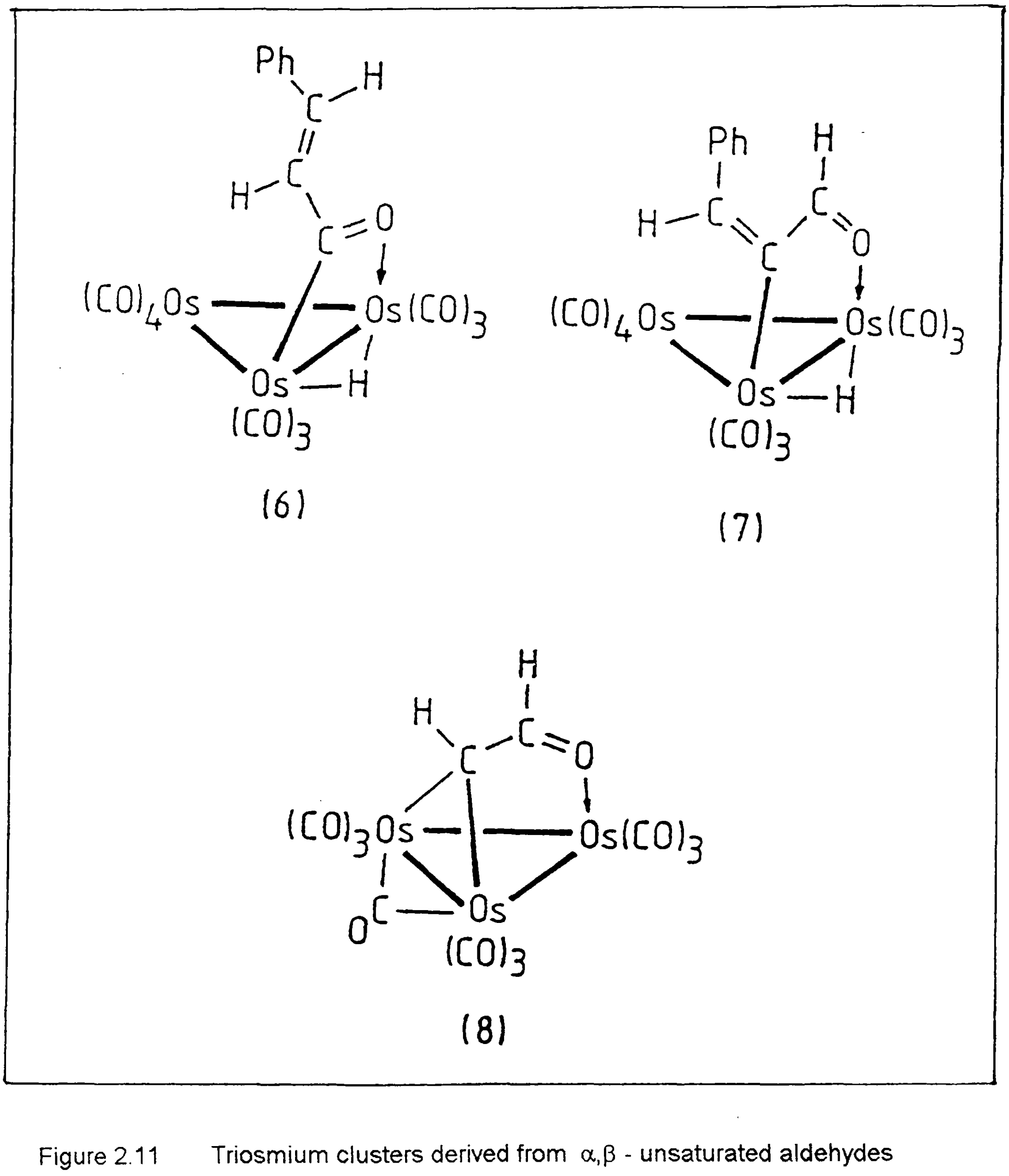
The infrared spectra for each of the clusters **1** and **2** is definitely that of a 4:3:3 decacarbonyl species which give characteristic patterns. However, there is a lowering of ν(CO) wavenumbers for the metal-carbonyl ligands relative to those for related compounds derived from α, β -unsaturated aldehydes. For example, the



(2a) (2b)

(1a) (1b)

Figure 2.10 Contributions 2a and 2b to the structure of cluster **2** and of 1a and 1b to the structure of cluster **1**



(6)

(7)

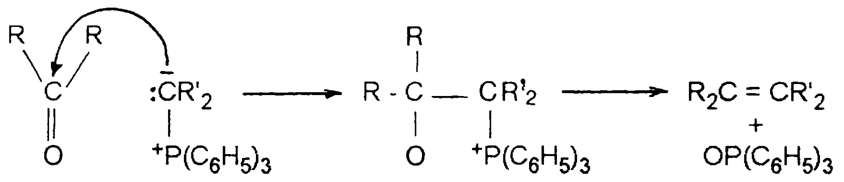
(8)

Figure 2.11 Triosmium clusters derived from α,β - unsaturated aldehydes cluster [$Os_3(\mu$-H)(μ-PhCH=CHCO)(CO)$_{10}$] **6** (Figure 2.11), has wavenumbers 7 - 17 cm^{-1} higher than for cluster **2** and in [Os_3- (μ-H)(μ-PhCH = CCHO)(CO)$_{10}$] **7** (Figure 2.11) they are 3 - 13 cm^{-1} higher than for cluster **1**.[18]

The lowering of the ν(CO) frequencies supports the view that there is a significant contribution from the zwitterionic form of the ligand: negative charge centred on the osmium atoms would cause just such an effect.

In view of the partial multiple P - C bonding, the reactions of both clusters with aldehydes were examined to see whether any residual Wittig-type reactivity was present.

The Wittig reaction provides a route for the synthesis of alkenes from carbonyl compounds using phosphorus ylides. The mechanism is thought to be that the carbonyl group undergoes nucleophilic attack by the negative carbon of the ylide to give a betaine which rearranges to give an alkene and a phosphorus oxide:



By analogy, the reaction of benzaldehyde and the zwitterionic triosmium clusters **1** and **2** might have reacted as shown in Figure 2.12:

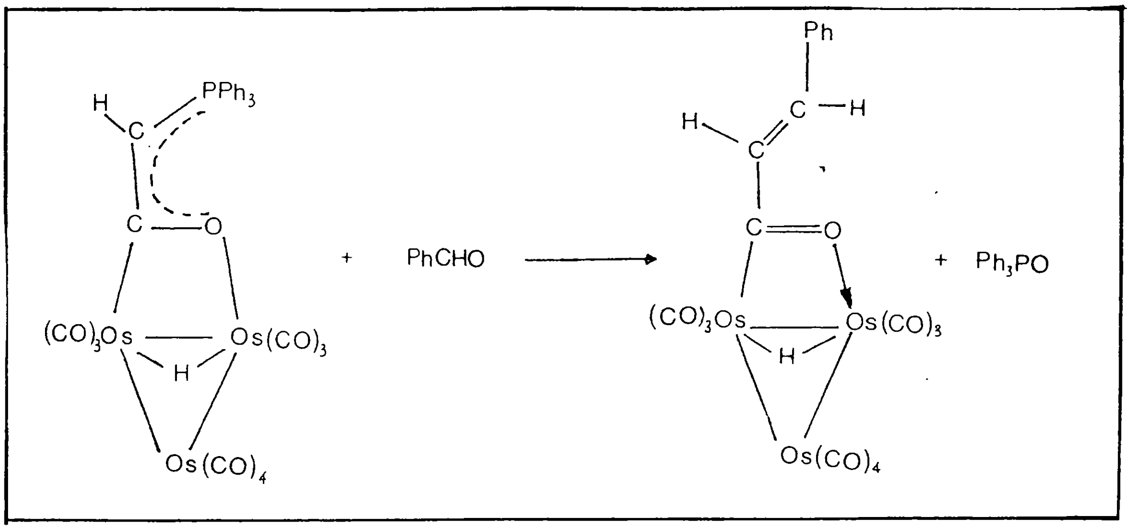


Figure 2.12 Possible products of a Wittig reaction between benzaldehyde and clusters **1** and **2**

The scope of the Wittig reaction is determined by the chemical characteristics of both the carbonyl and ylide components of the reaction. The reactivity of both components is important as too is their stability. If an ylide does not undergo the Wittig reaction it is usually because it is independently unstable or it is not sufficiently nucleophilic. Lowered nucleophilicity affects the initial step of the Wittig reaction, the attack of the ylidic carbanion on the carbonyl carbon to form a betaine intermediate. Such reductions in nucleophilicity are usually due to extensive delocalization of the electron density on the carbanion by its substituents. The nature of the phosphorus substituents also affects the nucleophilicity of an ylide. The replacement of a triphenylphosphonium group in an ylide by a trialkylphosphonium group increases the nucleophilicity of the ylide.[19] Electron withdrawing substituents on the three phenyl groups also decrease the rate of the first step of the Wittig reaction.

In view of these observations, it is perhaps unsurprising that we found no evidence of reactions of this type between benzaldehyde and compounds **1** or **2**. A slow reaction did take place but the products showed no hydride signals in their ^1H NMR spectra and were not present in sufficient quantities for a more detailed analysis. As the strength of the P - O bond normally provides a considerable driving force in many Wittig-type reactions it would appear that, in this instance, the carbanion of the triosmium cluster is not sufficiently nucleophilic for the initial step of forming the betaine. It is also possible that the reaction does not occur on steric grounds as Wittig-type reactions appear to be sensitive to steric effects and are supressed for sterically hindered molecules.[1]

2.2.3 Thermal and Photochemical Decarbonylation of the Decacarbonyl Clusters **1** and **2**

Unlike clusters **6** and **7** (Figure 2.11) which are difficult to decarbonylate, clusters **1** and **2** decarbonylate smoothly when in dichloromethane solution, exposed to fluorescent light whilst being stirred under a nitrogen atmosphere and at room temperature. The reactions lead to yields in excess of 70% of each of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3** from cluster **1** and of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4** from cluster **2**. We found that there was no reaction in solution in the dark. The structures of clusters **3** and **4** will be described later in this chapter.

The decarbonylation reactions of yellow dichloromethane solutions of clusters **1** and **2** took three days in London daylight. After two days, the yellow colour of the solution of cluster **1** had deepened to an orange/yellow colour; after a further 24 hours the colour was a bright clear orange. The solution of cluster **2** did not change from yellow throughout the exposure period. Thin layer chromatography of the photolysis product **3** gave one well-defined, major bright orange band and that of cluster **4** gave one broad major yellow band. Both these products were soluble in dichloromethane and were recrystallized from a dichloromethane/hexane mixture to give orange and yellow crystals of **3** and **4** respectively. These crystals were stable at room temperature.

The ν (CO) region of the infrared spectra of clusters **3** and **4** indicated that they were both nonacarbonyl species and the ^1H NMR spectra indicated that they were both hydride species. Cluster **3** shows only one hydride signal and also a signal at low field (δ 10.65) which is as expected for a -C*H*O resonance. There are no other signals except for the phenyl resonances. However, it was noted that two hydride signals appeared in the ^1H NMR spectrum of cluster **4** at δ -15.50 and δ -12.92. This indicated that this cluster was either a dihydride species or that the product was actually an isomeric mixture of two mono-hydride compounds. The spectrum also showed two signals at high field (δ 2.90 and δ 3.07) which could be assigned to two C*H*CO resonances. This, together with the two hydride signals, indicated that the solution of cluster **4** contained a pair of mono-hydride isomers. Separation of this mixture was attempted by both column and thin layer chromatography but without success. However, a mass of yellow crystals resulted from evaporation of a dichloromethane/heptane solution. Most of the crystals were very small or otherwise unsuitable for analysis but one crystal was selected for X-ray diffraction which established the structure **4a** from which the structure of **4b** was deduced for the other isomer as discussed later.

2.2.4 X-Ray Crystal Structures of the Clusters $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ 3 and $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ 4

A few of the crystals of cluster **3** were found to be suitable for X-ray diffraction determination which was carried out by Professor A. J. Deeming in this Department. The structure of the yellow triclinic crystal, a = 10.222(2), b = 11.014(2), c = 14.454(3) Å, α = 79.05(2), β = 86.67(2), γ = 74.86(2)°, U = 1542(1) Å^3 and Z = 2 was solved in space group $P\bar{1}$. An ORTEP picture is shown in Figure 2.13 and selected bond lengths and angles are given in Table 2.6. The structure was refined to give R = 0.0481 and R' = 0.0458. The structure clearly shows that one CO ligand has been lost from cluster **1** and that the organic ligand has remained intact but has been transformed from a μ_2 three-electron donor to a μ_3 five-electron donor. The μ_3-ligand is coordinated through an alkylidene bridging atom C(2) to Os(2) and Os(3) while a formyl group is coordinated through O(1) to Os(1). The C(1) - O(1) bond length of 1.27(1) Å is indicative of a C = O double bond and the structure is closely related to those of clusters $[Os_3(\mu_3\text{-CHCHO})(CO)_{10}]$ **8** and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_3RO)(CO)_9]$ where R = $PhCH_2$ formed from 2-benzylphenol.[20-22]

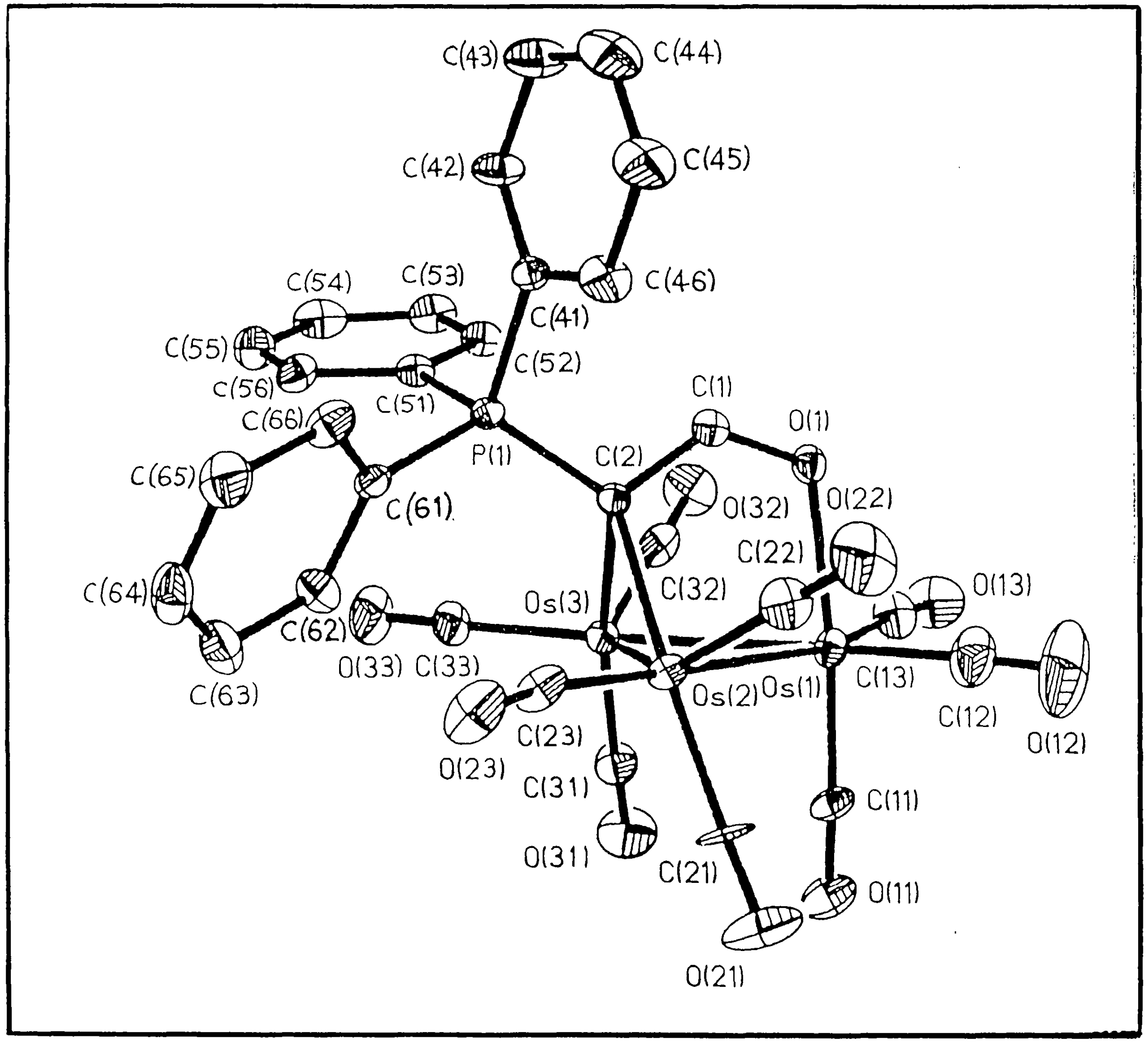


Figure 2.13 Molecular structure of the cluster [$Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9$] **3**

The P(1) - C(2) bond length is consistent with it being single (1.80(1) Å) and therefore the phosphorus atom is part of a phosphonium group which itself implies that the metal atoms carry a negative charge as the cluster is neutral overall. As expected, the ν(CO) wavenumbers for the metal carbonyl bonds are lower by approximately 20 - 30 cm^{-1} than those of cluster **8**, for example. The hydride ligand is apparent from the ^{1}H NMR spectrum (δ -12.71) but it was not located in the structure determination.

Apart from the asymetry of the PPh_3 group, the molecule has an approximate mirror plane. The Os(1) - Os(2) and Os(1) - Os(3) lengths are very similar at 2.785(1) and 2.783(1) Å respectively and it seems highly improbable that only one of these should carry a hydride bridge. The Os - Os - C(carbonyl) angles are also very similar for these two edges and are smaller than those for the other edge (Table 2.6). It seems probable therefore, that the hydride bridges Os(2) - Os(3) and lies at the intersection of the vectors C(22) - Os(2) and C(32) - Os(3).

The carbonyl ligands C(21)O(21) and C(31)O(31) are clearly *trans* to C(2) and C(32)O(32) and C(22)O(22) are also believed to be *trans* to hydride. Including the hydride in this position allows Os(2) and Os(3) to adopt closely octahedral geometries if the Os(2) - Os(3) bond is ignored. This Os(2) - Os(3) bond is not as long, at 2.811(1) Å, as is normally found for hydride-bridged osmium atoms but this is not uncommon when there is an alkylidene bridge along the same edge.[16] The effect of lengthening the Os - Os bond length by the hydride is presumed to be limited by the presence of the alkylidene bridge. In the compounds $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9]$ [23] and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}PhCH_2C_6H_3O)(CO)_9]$ [21,22] where an alkylidene ligand and a hydride ligand bridge the same two osmium atoms, these atoms are separated by 2.824(3) and 2.786(1) Å respectively. These bond lengths are very similar to the corresponding Os - Os bond of 2.811(1) Å in cluster **3**.

The structure of the selected crystal of cluster **4** was determined by X-ray diffraction by Professor A. J. Deeming in this Department. The yellow crystal was found to be triclinic, a = 9.809(3), b = 10.200(4), c = 16.513(7) Å, α = 85.80(3), β = 88.35(3) γ = 67.46(3)°, U = 1522(1) Å^3 and Z = 2 and the structure was solved in space group $P\bar{1}$. The structure was refined to R = 0.0664 and R' = 0.0568. The molecular structure is shown in an ORTEP picture (Figure 2.14) and selected bond lengths and angles are given in Table 2.7. As in the conversion of cluster **1** into cluster **3**, cluster **2** has been converted into cluster **4** by the loss of a CO ligand and the transformation of the μ_2 three-electron donating ligand into a μ_3 five-electron donating ligand. This μ_3-ligand is bonded through atoms C(1), C(2) and O(1) to the metal atoms and the hydrogen atoms of the phenyl rings and at C(2) were included in the model at idealized positions. It is clear from the geometry of C(2) that this atom carries a hydrogen atom so that no bonds have been broken in the ligand in the conversion of cluster **2** to cluster **4**.

Although it was not possible to produce a crystal structure of the other isomer of cluster **4**, arbitarily called **4b**, and thus unambiguously to state its structure, it may be inferred that it differs only in its stereochemistry about C(2). In cluster **4a** the hydride ligand bridges the Os(1) - Os(3) edge (3.031(2) Å) rather than the Os(1) - Os(2) or Os(2) - Os(3) edges which are shorter (2.798(2) and 2.775(2) Å respectively). The equatorial Os-Os-C(carbonyl) angles at the Os(1) - Os(3) edge are larger than those at the other two edges (116.7(6) and 117.7(7) ° against 90.2(7), 97(1), 96.0(7) and 88(1) ° for the edges Os(1) - Os(2) and Os(2) - Os(3)) as would be predicted were the hydride ligand positioned close to the Os_3 plane on the Os(1) - Os(3) edge near to the intersection of the Os(1) - C(11) and Os(3) - C(32) directions.

The cluster descriptions **a**, **b** and **c** shown in Figure 2.15 should all be considered as the actual structure probably lies somewhere between them. The

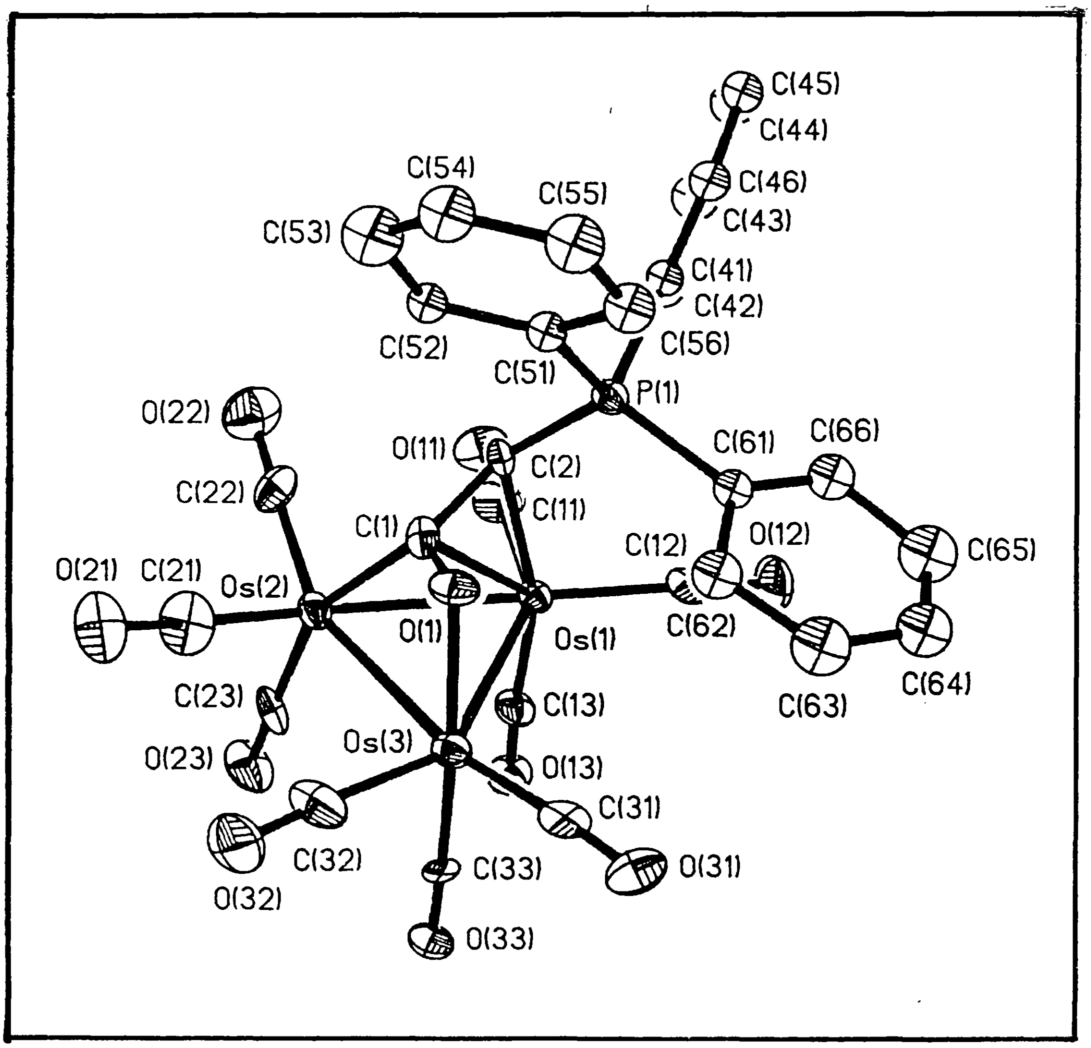


Figure 2.14a: Molecular structure of the cluster $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCHO)(CO)_9]$

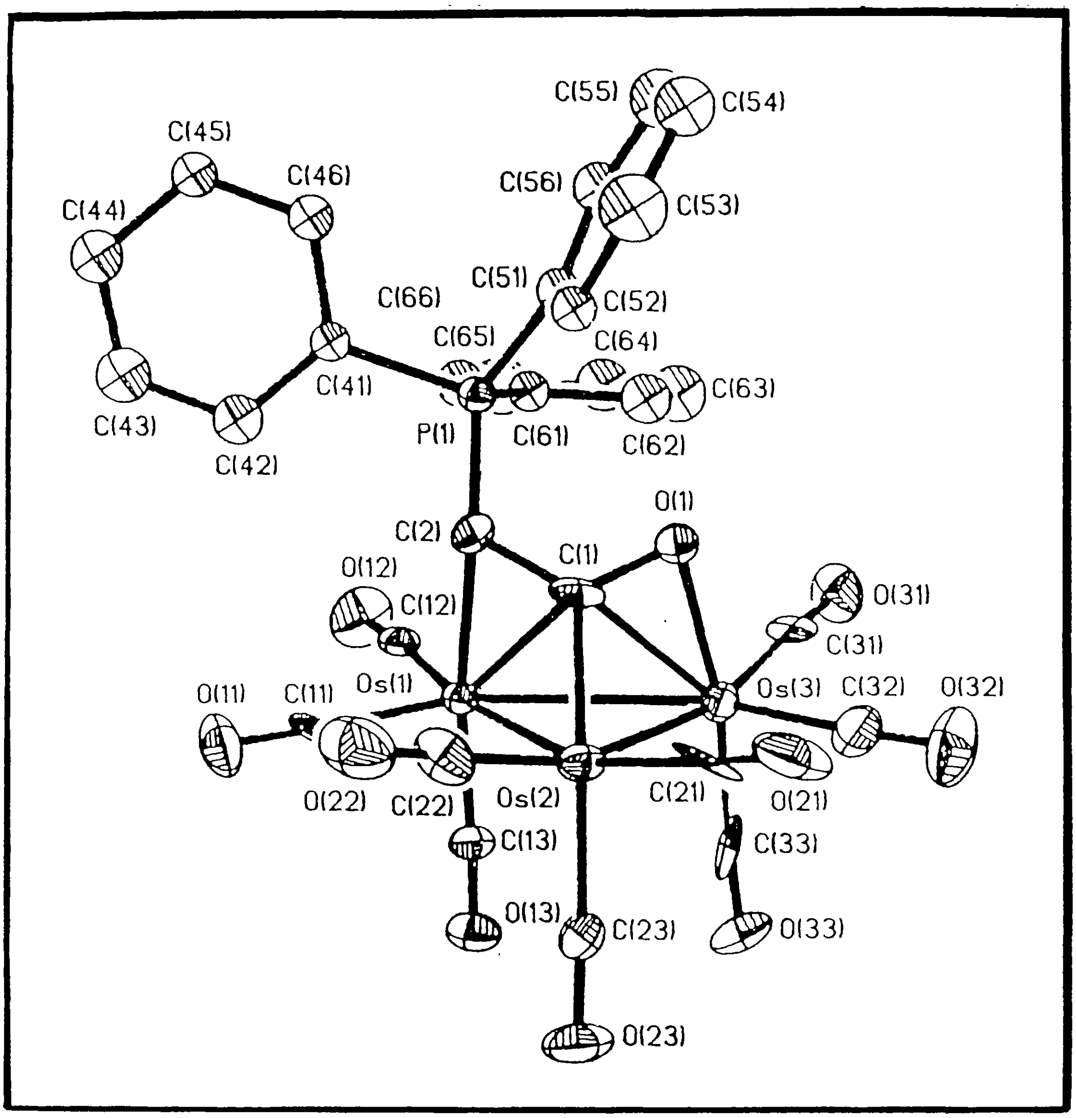


Figure 2.14b Molecular structure of the cluster $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4a**

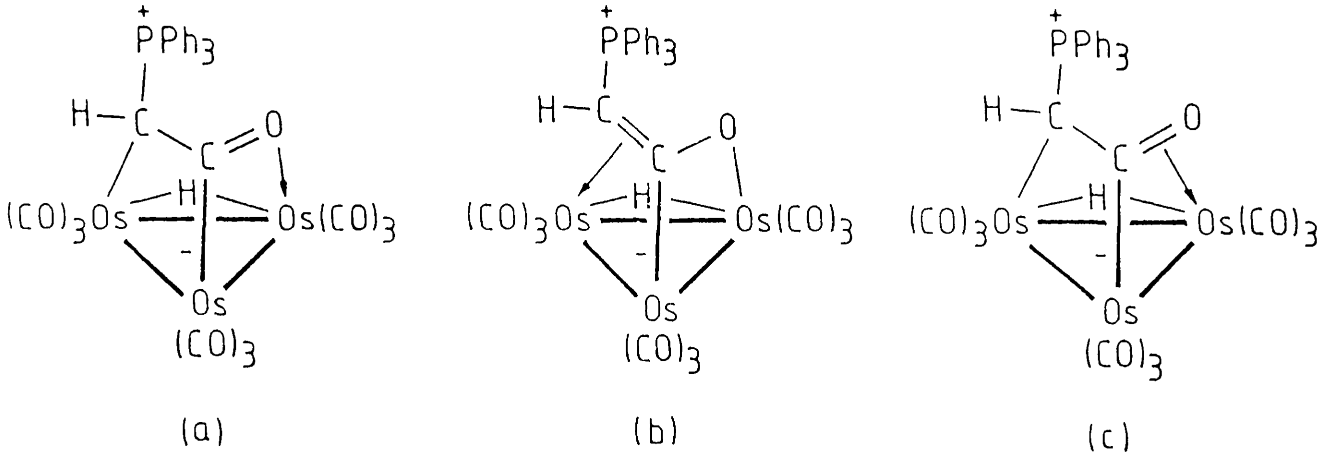
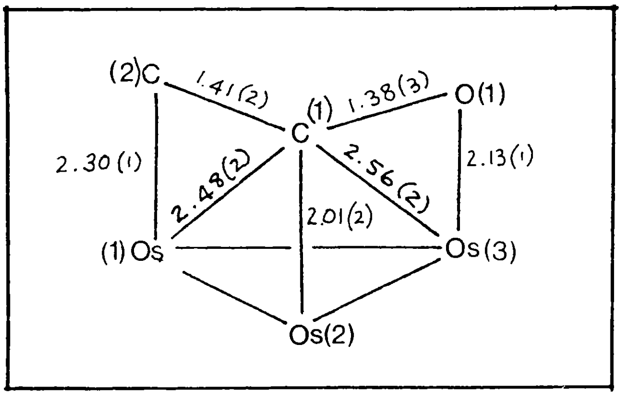


Figure 2.15 The extreme forms of bonding of the ligand in the formation of clusters 3 and 4

C(1) - O(1) bond length in **4a** is 1.38(3) Å and the corresponding bond in the ruthenium analogue, cluster **9**, (Scheme 2.3) is 1.31(3) Å. These lengths are only slightly longer than those expected for double bonds as given in the *Handbook of Chemistry and Physics*. However both C(1) and C(2) are bonded to Os(1). (Os(1)-C(1) is 2.48(2) Å and Os(1) - C(2) is 2.30(1) Å) so that the dihapto vinyl description (**b**) also has considerable validity. Even structure **c** (Figure 2.15) has some possible contribution since the C(1)O(1) group could be considered to be dihapto to Os(3) albeit coordinated in a slightly unsymmetrical manner; Os(3) - O(1) is 2.13(1) Å and Os(3) - C(1) is 2.56(2) Å. The distance Os(1) - C(2) of 2.30(1) Å is long for a σ bond and seems more consistent with a π interaction.



Probably the true picture of the structure lies somewhere between a and **b**, with a greater contribution from **a** and perhaps some small contribution from **c** (Figure 2.15). We have been unable to assign infrared absorptions to either C - C or C - O stretches and must presume that these are significantly below 1650 cm^{-1} consistent with bond orders between 1 and 2.

We also attempted thermal decarbonylation of the crude mixture containing both clusters **1** and **2**. This reaction was carried out in refluxing d_8-toluene with all light excluded as far as possible and the ^{1}H NMR spectrum was recorded at regular intervals over two and a half hours (Table 2.8). In d_8-toluene the hydride ligand of cluster **2** was found to have a characteristic resonance of δ -14.25 and this resonance did not change during the entire heating period. The inference then must be that cluster **2** is unaffected by thermolysis at 110 °C in the dark. However, cluster **1** decarbonylated under these conditions to give the same product, cluster **3**, as was obtained by photolysis and further decarbonylated to give another product, cluster **5**, which is discussed in the next section.

2.2.5 Thermal Decarbonylation of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3** and X-ray crystal structure of $[Os_3(\mu\text{-}H)_2(C_6H_4PPh_3CCHO)(CO)_8]$ **8**

Cluster **3** is photochemically stable at room temperature but decarbonylates further on heating in refluxing heptane. Over two hours of thermalizing, the bright orange solution of the starting material changed to yellow and chromatographic separation led to one major yellow band being isolated. This material was recrystallized to give a good yield of the dihydride product $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5** as yellow crystals. The ^1H NMR spectrum of this cluster shows two hydride signals at δ -12.69 and -11.64 and the low field signal for -CC*H*O is present at δ 10.73 (δ 10.65 in the parent cluster **3**). The two hydride signals indicate that a further C - H bond in cluster **3** has been cleaved in its transformation to cluster **5** and the wide spread of ^1H NMR signals in the phenyl region (δ 6.9 - 8.2, Table 2.2) indicates that a phenyl ring is involved in an *ortho*-metallation reaction.

Most of the crystals produced by recrystallization were too small to be useful for analysis and the larger crystals were twinned or had attached crystallites but two crystals were found to be suitable for analysis by X-ray diffraction. The structure determination was carried out by Professor A. J. Deeming in this Department and the structure of the yellow triclinic crystals, a = 10.290(3), b = 11.173(3), c = 13.290(4) Å, α = 83.29(2), β = 88.02(2), γ = 72.49(2) °C, U = 1447.2(7) Å^3, Z = 2 was solved in space group $P\bar{1}$. The structure was refined to give R = 0.0363 and R' = 0.0363. The molecular structure confirmed that one phenyl group of the triphenylphosphonium group had been *ortho* - metallated and an ORTEP picture is shown in Figure 2.16. Selected bond lengths and angles are given in Table 2.9.

The ligand $C_6H_4PPh_2CCHO$ is linked to the triosmium cluster through three fused metallocycles (two five-membered rings and one three-membered ring). Other than the small distortions caused by the sideways pull of the Os - C(42) bond, the central O(1)C(1)C(2) bonding to the triosmium triangle is the same as in its parent cluster, **3**.

As stated, two hydride signals were found in the ^{1}H NMR spectrum and although the hydride ligands were not detected during the structure determination, it seems probable that they are positioned along the Os(1) - Os(3) and Os(2) - Os(3) edges which are 2.993(1) and 2.823(1) Å respectively.The Os(1) - Os(2) and Os(2) - Os(3) bonds are fairly similar in clusters **3** and **5** but the Os(1) - Os(3) bond in cluster **5** shows an increase of 0.2 Å consistent with the introduction of a hydride ligand at that edge. The Os-Os-C(carbonyl) angles also show an increase at the Os(1) - Os(3) edge in **5** relative to those in **3** (Table 2.6).

A summary of the reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3PCHCHO$ is shown in Scheme 2.2:

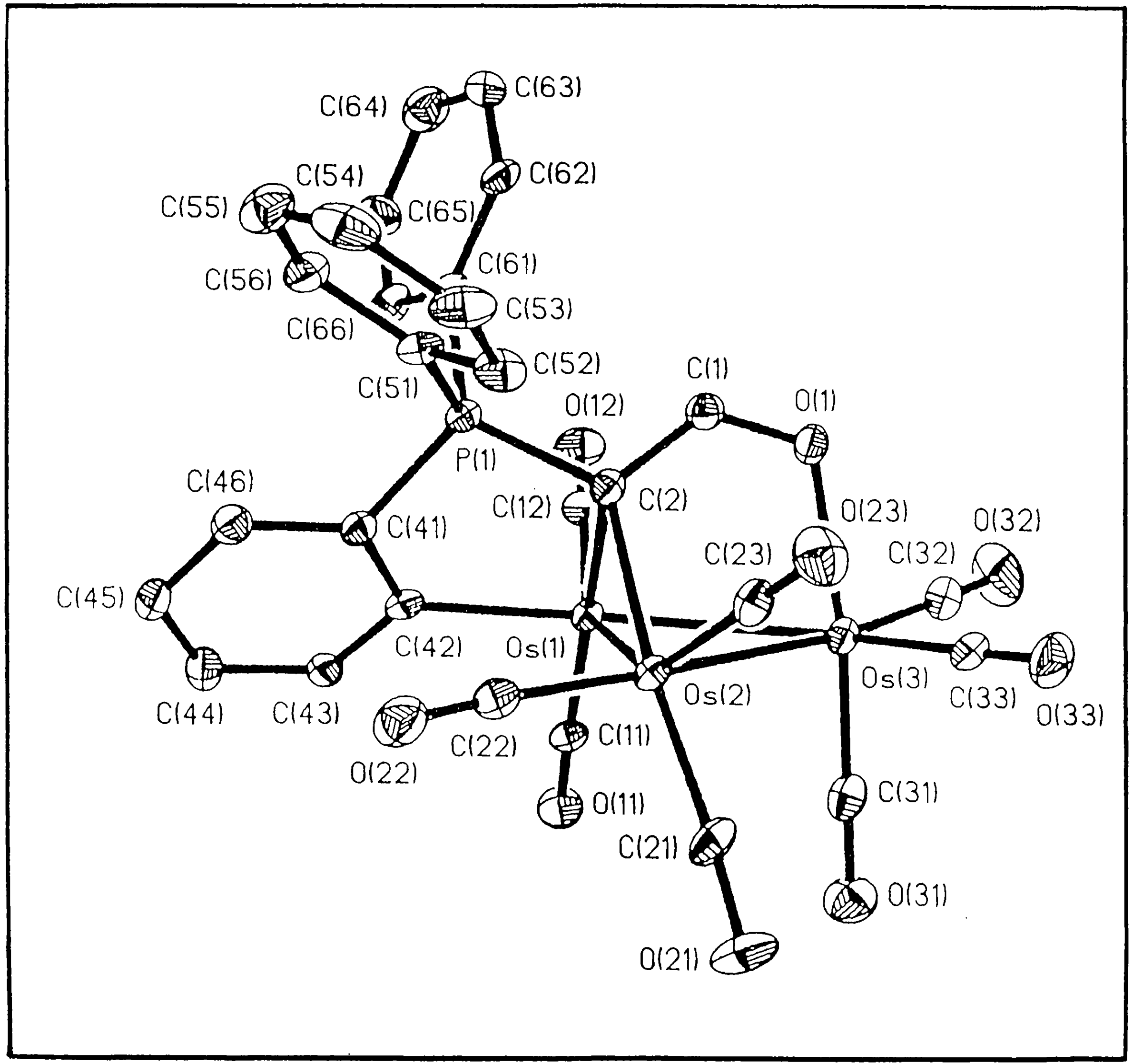


Figure 2.16 Molecular structure of the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}Ph_3PCCHO)(CO)_8]$ **5**

For thermal reactions:

$$\mathbf{1} \xrightarrow[\text{90 mins}]{\text{fast, }\Delta\text{ d-toluene}} \mathbf{3} \xrightarrow[\text{120 mins}]{\text{heptane }\Delta} \mathbf{5}$$

$$\mathbf{2} \nrightarrow \mathbf{4a, 4b}$$

For photochemical reactions:

$$\mathbf{1} \xrightarrow[\text{3 days}]{\text{slow, dichloromethane, R.T.}} \mathbf{3} \nrightarrow \mathbf{5}$$

$$\mathbf{2} \xrightarrow[\text{3 days}]{\text{slow, dichloromethane, R.T.}} \mathbf{4a, 4b}$$

Scheme 2.2: Summary of the reactions of [$Os_3(CO)_{10}(MeCN)_2$] with Ph_3PHCHO

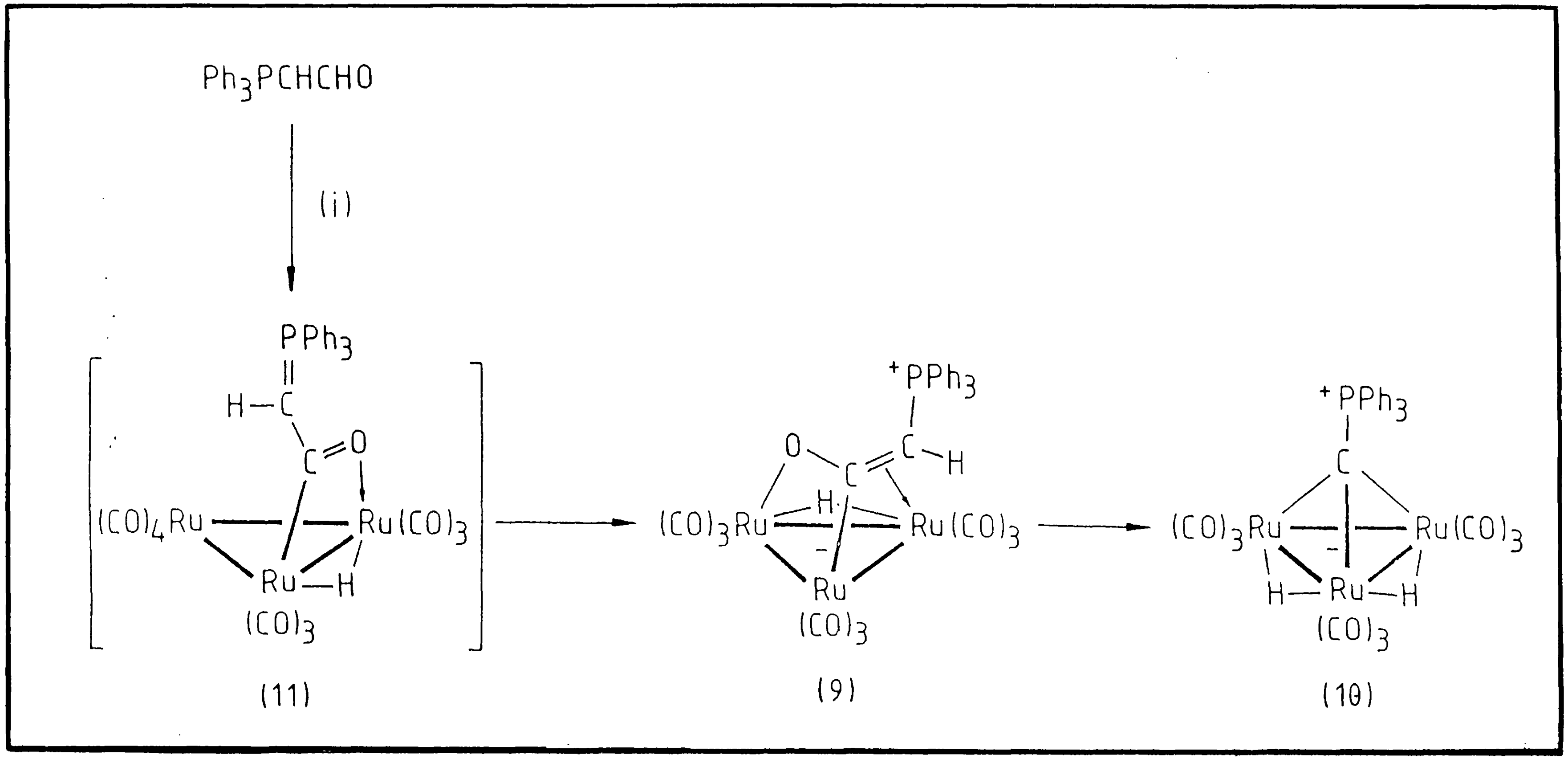
2.2.6 Reaction of [$Ru_3(CO)_{12}$] and $Ph_3PCHCHO$

Some work was carried out to investigate whether triruthenium clusters would also react with (triphenylphosphoranylidene)ethanal and it was clear that the reaction did not occur when the reagents were treated under the same conditions as were used with the triosmium cluster. However, before we could carry out any further investigation, Vahrenkamp *et al.* reported the analogous triruthenium reaction in full.[24] Vahrenkamp also examined the ylide $Ph_3P{=}CH_2$ in addition to the less reactive one, $Ph_3PCHCHO$, that we studied.

$[Ru_3(CO)_{12}]$ reacts with $Ph_3P{=}CH_2$ in tetrahydrofuran at -20 °C to give $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **9** amongst other products. The structure of this nonacarbonyl was determined by Vahrenkamp *et al.* and it was found to decarbonylate thermally to $[Ru_3(\mu\text{-}H)_2(CPPh_3)(CO)_9]$ **10**. Clusters **9** and **10** were also obtained by the reaction of $[Ru_3(CO)_{12}]$ with $Ph_3PCHCHO$ in refluxing cyclohexane (Scheme 2.3). This reaction is believed to go *via* the species **11** which is analogous to the triosmium cluster **2** which we characterized but which, in the ruthenium cluster, was not observed or isolated.

The reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with $Ph_3PCHCHO$ should give cluster **11** at low temperatures under conditions that might be expected to allow detection or isolation and this synthesis was attempted by us. However, although a crude mixture was obtained which was believed to contain the ruthenium cluster it proved impossible to separate by thin layer or column chromatography. As the temperature of the crude mixture rose during the separation procedure the nature of the material changed and it became completely intractable. We have described the triosmium cluster **4a** as having, as the best arrangement, the structure **a** (Figure 2.15) whereas the ruthenium analogue **9** was described as having structure **b**.[24] Now that both the structures are known, it may be seen that clusters **4a** and **9** are directly comparable. However, descriptions **a**, **b** and **c** (Figure 2.15) should all be considered as the actual structure probably lies somewhere between them.

A futher difference lies in the ready decarbonylation of the decacarbonyl ruthenium species to $[Ru_3(\mu\text{-}H)_2(CPPh_3)(CO)_9]$ which does not occur with the triosmium analogue. Also there appear to be no triruthenium analogues of the triosmium clusters **1**, **3** and **5**. It seems therefore that metallation with triosmium occurs competitively at the two carbon atoms but only at the one carbon atom with triruthenium.



Scheme 2.3 The reaction of $[Ru_3(CO)_{12}]$ with $Ph_3PCHCHO$

2.2.7 The Use of an Analogous Arsenic Ylide

One initial aim of this work was to use phosphorus ylides as a source of nucleophile with liberation of triphenylphosphine to leave a C_2O fragment at the cluster.

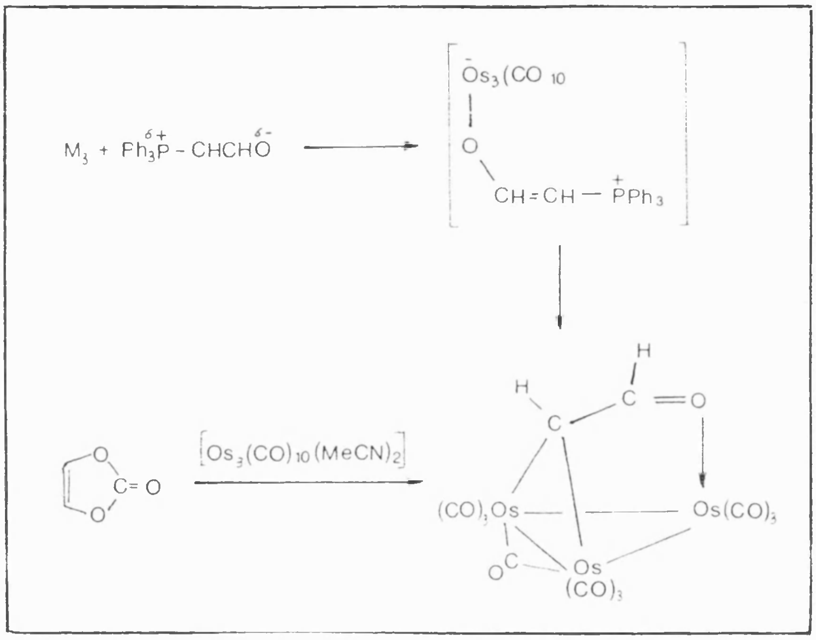


Figure 2.17 Projected reaction of $Ph_3PCHCHO$ as nucleophile with liberation of triphenylphosphine

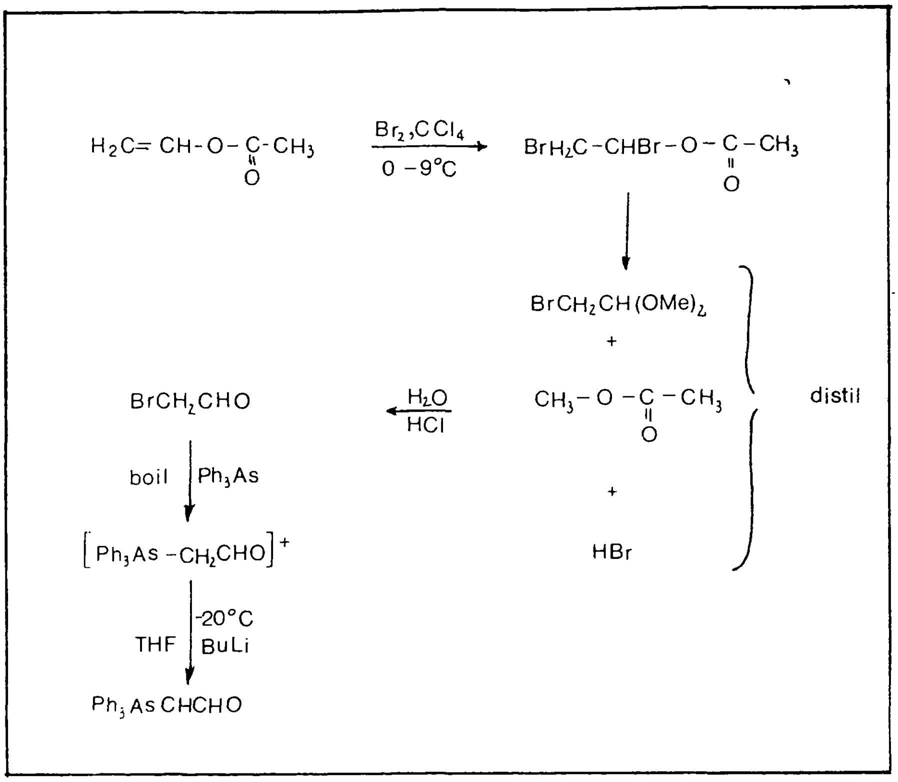
The cluster $[Os_3(CHCHO)(CO)_{10}]$ shown in Figure 2.17 had been previously prepared by Professor A.J. Deeming and Dr. A. J. Arce in this Department [25] but, when working with the phosphorus ylide $Ph_3PCHCHO$, it became increasingly apparent that the triphenylphosphine group would remain attached and indeed resisted all attempts to remove it. As a result some work was designed using the analogous arsenic ylide $Ph_3AsCHCHO$. Arsenic - carbon bonds are intrinsically weaker than phosphorus - carbon bonds and the overlap of the p-orbitals of carbon with the d-orbitals of arsenic is less effective than that of the d-orbitals of phosphorus.

$$\underset{\text{(i)}}{Ph_3As = CRR'} \longleftrightarrow \underset{\text{(ii)}}{Ph_3\overset{+}{As} - \overset{-}{C}RR'}$$

Therefore the 'covalent' canonical form (i) should make a smaller contribution to the overall structure of arsonium ylides than that of the corresponding phosphonium ylides.[26] This is supported by X-ray crystallographic data which showed that methylenetriphenylphosphorane has planar geometry whereas at carbon methylenetriphenylarsorane has pyramidal geometry.[27]

The removal of the triphenylarsine should be made easier by the relative weakness of the As - C bond compared with that of P - C and the arsenic ylides are better nucleophiles because of the greater contribution of the canonical form (ii) than is found with phosphorus ylides. Arsenic ylides often react with carbonyl compounds which are unresponsive to phosphorus ylides.[28] One additional reason for attempting to work with $Ph_3AsCHCHO$ was that it was felt that the ^1H NMR would be simpler as arsenic does not display coupling in the same way as phosphorus.

Unfortunately $Ph_3AsCHCHO$ is not commercially available. A synthesis exists for the formation of α-bromoheptaldehyde [31] which we felt could be adapted to lead to $Ph_3AsCHCHO$ as shown in Scheme 2.4



Scheme 2.4 Proposed synthesis route for $Ph_3AsCHCHO$

This plan was followed but there was no evidence of a C = O stretch in the carbonyl region of the infrared spectrum of the eventual product.

We then attempted to react $BrCH_2CH(OMe)_2$ with triphenylarsine varying the solvent, mole ratios of reactants and temperature of reaction but all efforts to synthesise $Ph_3AsCHCHO$ in the laboratory failed. Therefore it was not possible to make a direct comparison of the reactions of phosphorus and arsenic ylides with $[Os_3(CO)_{10}(MeCN)_2]$.

2.3 Tables

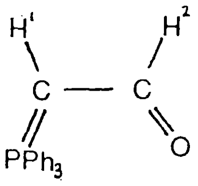
	ν(CO) cm^{-1}
$[Os_3H(Ph_3PCCHO)(CO)_{10}]$ * **1**	2097m 2058s 2042s 2009s 2003s 1980m 1956sh
$[Os_3H(Ph_3PCHCO)(CO)_{10}]$# **2**	2097m 2055s 2046s 2012s 2007s 1994m 1984sh 1979m 1974sh 1964
$[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$* **3**	2071m 2036vs 2015s 1985m 1955m
$[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$* **4a + 4b**	2078s 2047vs 2011s 1995m 1981m
$[Os_3(\mu\text{-}H)_2(C_6H_4PPh_2CCHO)(CO)_8]$ø **5**	2082s 2044s 2013vs 1992s 1973m 1944s

* in CH_2Cl_2 # in hexane ø in heptane

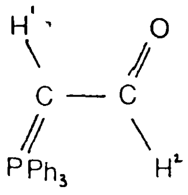
Table 2.1 Carbonyl region infrared spectroscopic data for the compounds **1**, **2**, **3**, **4a + 4b** and **5**

	^{1}H NMR (200MHz) δ ppm	Inference
$[Os_3H(Ph_3PCCHO)(CO)_{10}]$ **1**	-12.85s	Os*H*
	7.5 - 7.7 (m, Ph)	
	8.10 (d, J = 14.8 Hz)	CC*H*O
$[Os_3H(Ph_3PCHCO)(CO)_{10}]$ **2**	-14.45 (s)	Os*H*
	7.4 - 7.6 (m, Ph)	
	4.20 (d, J = 29.3 Hz)	C*H*CO
$[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3**	-12.71 (s)	Os*H*
	10.65 (d, J = 7.0 Hz)	CC*H*O
	7.1 - 7.8 (m, Ph)	
$[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PHCHCO)(CO)_9]$ **4a + 4b**	-15.50 (t, J = 1.1 Hz)	Os*H*
	-12.92 (s)	Os*H*
	7.3 - 7.7 (m, Ph)	
	3.07 (dd, J = 14.8, 1.1 Hz)	C*H*CO
$[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2PCCHO)(CO)_8]$ **5**	-12.69 (s)	Os*H*
	-11.64 (d, J = 5.3 Hz)	Os*H*
	10.73 (dd, J = 6.8, 1.3 Hz)	CC*H*O
	8.22 (m)	*o-H*, C_6H_4
	6.9 - 7.9 (m)	Ph + C_6H_4

Table 2.2 ^{1}H NMR: Key Spectroscopic data for pure compounds recorded in deuteriochloroform



A: *cis*-conformation



B: *trans*-conformation

δ ppm	δ ppm
3.65 dd H^1 (A)	4.08 dd H^1 (B)
$J_{PH^1} = 24.5$ Hz	$J_{PH^1} = 13.0$ Hz
$J_{HH} = 3.5$ Hz	$J_{HH} = 4.3$ Hz
8.95 dd H^2 (A)	8.20 dd H^2 (B)
$J_{PH^2} = 38.2$ Hz	$J_{PH^2} = 10.8$ Hz
$J_{HH} = 3.5$ Hz	$J_{HH} = 4.3$ Hz

7.4 - 7.7 (m, Ph)

Table 2.3 ^{1}H NMR of the free ligand $Ph_3PCHCHO$ in deuteriochloroform

	Å		Å
Os(1) - Os(2)	2.933(1)	C(1) - O(1)	1.32(2)
Os(1) - Os(3)	2.928(1)	C(1) - C(2)	1.38(2)
Os(2) - Os(3)	2.871(1)	P - C(2)	1.73(1)
Os(2) - C(22)	1.99(2)	P - C(41)	1.81(1)
Os(2) - O(1)	2.11(1)	P - C(51)	1.82(1)
Os(1) - C(2)	2.21(2)	P - C(61)	1.78(1)

	degrees
Os(1) - C(2) - C(1)	122(1)
Os(2) - O(1) - C(1)	124(1)
Os(1) - C(2) - P(1)	123.6(8)
P(1) - C(2) - C(1)	113(1)
C(2) - C(1) - O(1)	126(1)

Table 2.4 Selected bond lengths and angles for compound 1

	Å		Å
Os(1) - Os(2)	2.890(1)	C(1) - O(1)	1.32(2)
Os(1) - Os(3)	2.858(1)	C(1) - C(2)	1.40(2)
Os(2) - Os(3)	2.856(1)	P - C(2)	1.75(1)
Os(2) - C(22)	1.89(2)	P - C(41)	1.79(1)
Os(2) - O(1)	2.104(8)	P - C(51)	1.82(1)
Os(1) - C(1)	2.10(1)	P - C(61)	1.79(1)

	degrees
Os(1) - C(1) - O(1)	114.1(7)
Os(1) - C(1) - C(2)	127.0(8)
Os(2) - O(1) - C(1)	109.8(6)
Os(1) - C(1) - C(2)	119(1)
C(1) - C(2) - P	121.7(9)

Table 2.5 Selected bond lengths and angles for compound **2**

	Å		Å
Os(1) - Os(2)	2.785(1)	C(1) - O(1)	1.27(2)
Os(1) - Os(3)	2.783(1)	C(1) - C(2)	1.42(2)
Os(2) - Os(3)	2.811(1)	P - C(2)	1.80(1)
Os(3) - C(2)	2.25(1)	P - C(41)	1.80(1)
Os(1) - O(1)	2.24(1)	P - C(51)	1.83(1)
Os(1) - C(2)	2.14(1)	P - C(61)	1.83(1)

	degrees		degrees
Os(2) - Os(1) - Os(3)	60.6(1)	C(1) - C(2) - P	110.0(9)
Os(1) - Os(2) - Os(3)	59.7(1)	Os(1) - Os(2) - C(22)	86.0(5)
Os(1) - Os(3) - Os(2)	59.7(1)	Os(1) - Os(2) - C(21)	90.14(4)
Os(2) - Os(3) - C(2)	51.5(3)	Os(1) - Os(3) - C(32)	83.1(4)
Os(3) - Os(2) - C(2)	51.4(4)	Os(1) - Os(3) - C(31)	92.4(4)
Os(1) - Os(3) - C(2)	76.9(3)	Os(2) - Os(1) - C(12)	97.7(6)
Os(1) - Os(2) - C(2)	76.7(3)	Os(2) - Os(1) - C(11)	91.3(4)
Os(3) - Os(1) - O(1)	83.7(2)	Os(3) - Os(1) - C(13)	103.0(4)
Os(2) - Os(1) - O(1)	83.6(2)	Os(3) - Os(1) - C(11)	89.8(4)
Os(2) - C(2) - Os(3)	77.5(4)	Os(2) - Os(3) - C(33)	120.3(5)
Os(1) - O(1) - C(1)	117.6(8)	Os(2) - Os(3) - C(31)	114.9(5)
Os(1) - C(1) - C(2)	124(1)	Os(3) - Os(2) - C(23)	119.1(4)
Os(2) - C(2) - C(1)	111.0(7)	Os(3) - Os(2) - C(21)	113.1(5)
Os(3) - C(2) - C(1)	111.9(9)		

Table 2.6 Selected bond lengths and angles for compound **3**

	Å		Å
Os(1) - Os(2)	2.798(2)	Os(3) - C(1)	2.56(2)
Os(1) - Os(3)	3.031(2)	C(1) - O(1)	1.38(3)
Os(2) - Os(3)	2.775(2)	C(1) - C(2)	1.41(2)
Os(2) - C(1)	2.01(2)	P - C(2)	1.79(1)
Os(1) - C(2)	2.30(1)	P - C(41)	1.80(2)
Os(3) - O(1)	2.13(1)	P - C(51)	1.79(2)
Os(1) - C(1)	2.48(2)	P - C(61)	1.80(2)

	degrees		degrees
Os(2) - Os(1) - Os(3)	57.7(1)	Os(2) - C(1) - O(1)	121(1)
Os(1) - Os(2) - Os(3)	65.9(1)	Os(2) - C(1) - C(2)	124(2)
Os(1) - Os(3) - Os(2)	57.4(1)	Os(1) - Os(2) - C(22)	96.0(7)
Os(2) - Os(3) - O(1)	73.3(3)	Os(1) - Os(2) - C(23)	99.9(6)
Os(1) - Os(3) - O(1)	76.7(3)	Os(2) - Os(1) - C(11)	90.2(7)
Os(3) - Os(2) - C(1)	62.2(7)	Os(2) - Os(1) - C13)	89.5(6)
Os(1) - Os(2) - C(1)	59.4(6)	Os(2) - Os(3) - C(32)	88(1)
Os(2) - Os(1) - C(2)	72.3(2)	Os(2) - Os(3) - C(33)	95.9(8)
Os(3) Os(1) - C(2)	83.7(3)	Os(3) - Os(2) - C(21)	97(1)
Os(3) - O(1) - C(1)	91(1)	Os(3) - Os(2) - C(23)	99.7(8)
O(1) - C(1) - C(2)	111(1)	Os(1) - Os(3) - C(31)	116.7(6)
C(1) - C(2) - P	123(1)	Os(1) - Os(3) - C(33)	93.3(7)
Os(1) - C(2) - P	122.9(7)	Os(3) - Os(1) - C(12)	117.7(7)
Os(1) - C(2) - C(1)	80(1)	Os(3) - Os(1) - C(13)	86.9(7)

Table 2.7 Selected bond lengths and angles for compound **4a**

Heating time/min	^{1}H NMR (200 MHz)/δ ppm	Inference	Species
0	-14.25 (s)	Os*H*	**2**
	-12.62 (s)	Os*H*	**1**
	8.30 (d, J =14.8 Hz)	CC*H*O	**1**
	4.30 (d, J = 29.3 Hz)	C*H*CO	**2**
33	-14.25 (s)	Os*H*	**2**
	-12.55 (s)	Os*H*	**3**
	-12.63 (s)	Os*H*	**1**
	10.44 (d, J = 7.8 Hz)	CC*H*O	**3**
	8.30 (d, J = 14.8 Hz	CC*H*O	**1**
	4.30 (d, J = 29.3 Hz)	C*H*CO	**2**
90	-14.25 (s)	Os*H*	**2**
	-12.50 (s)	Os*H*	**3**
	-12.40 (s)	Os*H*	**5**
	-11.25 (d, J = 5.6 Hz)	Os*H*	**5**
	10.55 (dd, J = 6.8, 1.3 Hz)	CC*H*O	**5**
	10.44 (d, J = 7.8 Hz)	CC*H*O	**3**
	8.25 (m)	*o*-H, C_6H_4	**5**
	4.50 (d, J = 29.3 Hz)	C*H*CO	**2**
150	-14.25 (s)	Os*H*	**2**
	-12.40 (s)	Os*H*	**5**
	-11.25 (d, J = 5.3 Hz)	Os*H*	**5**
	10.55 (dd, J = 6.8, 1.3 Hz)	CC*H*O	**5**
	8.25 (m)	*o*-H, C_6H_4	**5**
	4.40 (d, J = 29.3 Hz)	C*H*CO	**2**

Table 2.8 ^{1}H NMR of thermolysis of the crude mixture of Compounds **1** and **2** in d_8-toluene

	Å		Å
Os(1) - Os(2)	2.805(1)	C(1) - O(1)	1.24(1)
Os(1) - Os(3)	2.993(1)	C(1) - C(2)	1.41(1)
Os(2) - Os(3)	2.823(1)	P - C(2)	1.76(1)
Os(2) - C(2)	2.22(1)	P - C(41)	1.773(8)
Os(3) - C(2)	2.240(9)	P - C(51)	1.82(1)
Os(1) - O(1)	2.144(8)	P - C(61)	1.80(1)
Os(3) - C(42)	2.11(1)		

	degrees		degrees
Os(2) - Os(1) - Os(3)	58.2(1)	C(2) - P - C(51)	117.3(5)
Os(1) - Os(2) - Os(3)	64.3(1)	C(2) - P - C(61)	119.9(5)
Os(1) - Os(3) - Os(2)	57.6(1)	C(41) - P - C(51)	112.7(4)
Os(2) - Os(1) - O(1)	84.9(2)	C(41) - P - C(61)	107.5(2)
Os(3) - Os(1) - O(1)	80.4(2)	C(51) - P - C(61)	102.7(5)
Os(1) - Os(2) - C(2)	77.0(3)	P - C(41) - C(42)	115.2(7)
Os(1) - Os(3) - C(2)	72.8(3)	C(41) - C(42) - Os(1)	118.6(6)
Os(2) - Os(3) - C(2)	50.5(3)	Os(1) - Os(2) - C(22)	90.0(3)
Os(3) - Os(2) - C(2)	51.0(2)	Os(1) - Os(2) - C(21)	90.1(3)
Os(2) - Os(3) - C(42)	94.5(3)	Os(2) - Os(1) - C(11)	90.4(3)
Os(1) - O(1) - C(1)	116.2(6)	Os(2) - Os(1) - C(12)	90.4(3)
Os(3) - C(2) - P	106.7(4)	Os(2) - Os(3) - C(31)	118.4(3)
Os(2) - C(2) - P	120.4(5)	Os(3) - Os(2) - C(23)	106.2(3)
Os(3) - C(2) - C(1)	106.9(7)	Os(3) - Os(2) - C(21)	117.4(3)
Os(2) - C(2) - C(1)	117.0(8)	Os(1) - Os(3) -C(32)	107.5(3)
O(1) - C1) - C(2)	127(1)	Os(1) - Os(3) - C(31)	105.5(3)
C(1) - C(2) - P	117.5(8)	Os(3) - Os(1) - C(13)	113.5(3)
C(2) - Os(3) - C(42)	85.5(3)	Os(3) - Os(1) - C(11)	92.4(3)
C(2) - P - C(41)	104.5(5)		

Table 2.9 Selected bond lengths and angles for compound **5**

2.4 Experimental

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3PCHCHO$

An off-yellow solution of the compound $[Os_3(CO)_{10}(MeCN)_2]$ (0.150 g, 1.608×10^{-4} mol) in dichloromethane (25 cm^3) was placed in a flask wrapped in aluminium foil to exclude all light. A colourless solution of $Ph_3PCHCHO$ (0.054 g, 1.774×10^{-4} mol) in dichloromethane (2 cm^3) was added to the flask and the solutions shaken to mix thoroughly. The flask was left to stand at room temperature for 10 minutes and the solvent was removed under reduced pressure. The residue was redissolved in dichloromethane (5 cm^3) and chromatographed (eluent, dichloromethane: petroleum ether (distilled, b.p. < 40 °C), 15:85 v/v) to give two yellow bands. Both bands were extracted from the silica into dichloromethane. The faster moving band gave the cluster $[Os_3H(Ph_3PCHCO)(CO)_{10}]$ **1** as yellow crystals from a dichloromethane/hexane mixture (0.0721 g, 34%). (Found: C, 31.65; H 1.5. $C_{30}H_{17}O_{11}Os_3P$ requires: C, 31.2; H, 1.5%) The slower moving band gave $[Os_3H(Ph_3PCCHO)(CO)_{10}]$ **2** as yellow crystals from a dichloromethane/hexane mixture (0.0827 g, 39%). (Found: C, 32.7; H, 1.85. $C_{30}H_{17}O_{11}Os_3P$ requires C, 31.2; H, 1.5%).

Both the products are photochemically sensitive in solution so the reaction, work-up, chromatography and crystallization were all carried out in the dark. As crystalline substances they are stable at room temperature.

Attempted Wittig Reaction of $[Os_3(Ph_3PCHO)(CO)_{10}]$ 1 with Benzaldehyde in Refluxing Toluene

Benzaldehyde (10 cm^3) was diluted with diethyl ether (10 cm^3) and the resulting solution was washed with sodium hydroxide solution (0.1 M, 3 x 10 cm^3 aliquots) to remove any traces of PhCOOH which may have been present. The solution was dried over magnesium sulphate and the solution filtered under gravity. The solvent was removed under reduced pressure to give faintly yellow, viscous benzaldehyde. The compound $[Os_3H(Ph_3PCHCO)(CO)_{10}]$ **1** (0.0832 g, 7.2×10^{-5} mol) was dissolved in toluene (15 cm^3) to give a clear bright yellow solution. The dried benzaldehyde (7.5 cm^3) was added and the solution immediately turned bright orange. An infrared sprectrum was recorded and the solution was heated to reflux under a nitrogen atmosphere for one hour with all light excluded from the reaction vessel. An infrared spectrum of the golden yellow solution was recorded. Reflux of the solution was continued for a further hour. Another infrared spectrum was recorded and the solvent was then removed under reduced pressure. The residue was redissolved in toluene (5 cm^3) and the clear, light brown liquid chromatographed in the dark (eluent, dichloromethane: petroleum ether (distilled, b.p. < 40 °C) 10:90 v/v) to give two very minor yellow bands.

$\nu(CO)$ cm^{-1}/toluene

$[Os_3H(Ph_3PCHCO)(CO)_{10}]$: 2098m 2054s 2045s 2011vs 2006s 1994m 1979m 1965m

On mixing, orange solution: 2138m 2108m 2096m 2069s 2055vs 2043vs 2026vs 2007vs 1975v.broad, vs

Reflux 1 hour, gold solution: 2138m 2082m 2059s 2052sh 2025vs

Reflux 2 hours, brown solution: 2116w,br 2139m 2120m 2083s 2060s 2051s 2025vs

Band A, yellow: 2139w 2093m 2059vs 2035s 2027s 2010s
(trace only) 1999s,br

Band B, yellow:	2138m 2108w 2096m 2069s 2055vs 2043vs
(trace only)	2026vs 2007vs 1975vs,v.br

Attempted Wittig Reaction of [$Os_3H(Ph_3PCHCO)(CO)_{10}$] with Benzaldehyde at Room Temperature

Yellow crystals of the compound [$Os_3(Ph_3PCHCO)(CO)_{10}$] (0.0414 g, 3.51 x 10^{-5} mol) were dissolved in toluene (10 cm^3) to give a clear bright yellow solution. Prepared benzaldehyde (2 cm^3) was added and the resulting orange solution was allowed to stand in the dark for 48 hours. The reaction was monitored by infrared spectroscopy but there was no apparent change from the spectrum of the starting material.

Photolysis of [$Os_3(Ph_3CCHO)(CO)_{10}$] 1

The cluster $Os_3(Ph_3PCCHO)(CO)_{10}$] (0.0954 g, 8.26 x 10^{-5} mol) was dissolved in dichloromethane (25 cm^3) to give a clear yellow solution. The solution was stirred in natural daylight under a nitrogen atmosphere for three days by which time the colour had changed from yellow to clear bright orange. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C), 10:90 v/v) to give one major orange band. This was extracted into dichloromethane to give the compound [$Os_3H(Ph_3PCCHO)(CO)_9$] **3** as orange crystals (0.0745 g, 80%) from a dichloromethane/hexane mixture. The crystalline product was found to be stable in daylight at room temperature. (Found: C, 31.9; H, 1.7. $C_{29}H_{17}O_{10}Os_3P$ requires C, 30.9; H, 1.5%).

Photolysis of [$Os_3Ph_3PCHCO)(CO)_{10}$] **2**

Yellow crystals of the cluster [$Os_3H(Ph_3PCHCO)(CO)_{10}$] **2** (0.0900 g, 7.79 x 10^{-5} mol) were dissolved in dichloromethane (30 cm^3) to give a clear yellow solution. This was stirred in daylight under a nitrogen atmosphere for three days. The solution remained clear and yellow throughout this period. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent, dichloromethane:petroleum ether (distilled, b.p. < 40 °C) 15:85 v/v) to give two yellow bands. The faster moving band was extracted into dichloromethane and proved to be starting material. The slower moving band was also extracted into dichloromethane and gave yellow microcrystals of a mixture of isomers of the compound [$Os_3H(Ph_3PCHCO)(CO)_9$] **4** (0.0658 g, 75%). (Found: C,31.5; H,1.6. $C_{29}H_{17}O_{10}Os_3P$ requires C, 30.9; H, 1.5%).

Thermolysis of [$Os_3H(Ph_3PCCHO)(CO)_9$] **3**

Orange crystals of the compound [$Os_3H(Ph_3PCCHO)(CO)_9$] **3** (0.0444 g, 4.07 x 10^{-5} mol) were dissolved in warm n-heptane (11 cm^3) to give an orange solution which was heated to reflux and stirred under a nitrogen atmosphere for two hours. The progress of the reaction was monitored by infrared spectroscopy. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent; dichloromethane:petroleum ether(distilled, b.p. < 40 °C), 15:85 v/v) to give one major yellow band. This was extracted into dichloromethane to give the product [$Os_3H_2(C_6H_4Ph_2PCCHO)(CO)_8$] **5** as yellow crystals from a dichloromethane/heptane mixture (0.0366 g, 85%). (Found: C, 32.9; H, 1.9. $C_{28}H_{17}O_9Os_3P$ requires C, 30.6; H, 1.6%).

Thermolysis of $[Os_3H_2(C_6H_4Ph_2PCCHO)(CO)_8]$ **5**

Yellow crystals of the compound $[Os_3H_2(C_6H_4Ph_2PCCHO)(CO)_8]$ (0.044 g, 4.00×10^{-5} mol) were dissolved in dichloromethane (2 cm^3) and added to n-heptane (25 cm^3). The dichloromethane was boiled off and the yellow solution heated to reflux and stirred under a nitrogen atmosphere for two hours. The progress of the reaction was monitored by infrared spectroscopy and, after two hours, the major component present was identified as the starting material, compound **5**. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (2 cm^3) and nonane (25 cm^3) was added. The dichloromethane was boiled off and the yellow solution heated to reflux under a nitrogen atmosphere for 15 hours. The progress of the reaction was again monitored by infrared spectra. After 15 hours the solution was clear and brownish. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (2.cm^3) and chromatographed (eluent: dichloromethane:petroleum ether, (distilled, b.p. < 40 °C) in all mixtures from 0:100 to 100:0 v/v) but the material remained adsorbed on the baseline.

Photolysis of $[Os_3H(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ and $[Os_3H(\mu\text{-}Ph_3PCHCO)(CO)_{10}]$ in d_8-toluene

The cluster $[Os_3(CO)_{10}(MeCN)_2]$ (0.100 g, 1.072×10^{-4} mol) was dissolved in dichloromethane (10 cm^3) in a flask wrapped in aluminium foil to exclude light. A colourless solution of $Ph_3PCHCHO$ (0.0340 g, 1.072×10^{-4} mol) in dichloromethane (2 cm^3) was added and the solutions were shaken well and left to stand at room temperature for 15 minutes. The solvent was removed under reduced pressure and the khaki residue was redissolved in d_8-toluene (3 cm^3). An infrared spectrum and an ^1H NMR spectrum were run immediately keeping the samples in the dark as far as was possible. The sample was then placed in a narrow diameter tube (5 mm) and exposed to daylight over a period of six days. The progress of the reaction was monitored by infrared spectra and ^{1}H NMR.

After three and a half days, the ^{1}H NMR spectrum indicated that two products were present and, from the characteristic resonances found in the ^{1}H NMR spectra of the pure samples, these were **3** and **4** (as a mixture of isomers **4a** and **4b**). After six days the solution was no longer homogeneous. A beige/khaki precipitate formed in the bottom of the tube and did not respond to chromatography but became irreversibly adsorbed on to the silica surface.

Thermolysis of compounds 1 and 2 in d_8-toluene

A crude mixture of compounds **1** and **2** was produced by thermal reaction of $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3PCHCHO$ in d_8-toluene (25 cm^3) in the dark over a period of two and a half hours. The reaction was monitored by ^{1}H NMR at regular intervals and the spectra recorded were compared with those of the pure compounds **3**, **4** (**a** + **b**) and **5**. Throughout the heating period the resonances characteristic of cluster **2** did not change at all. However, the characteristic resonances of compound **3** gradually appeared followed by those of compound **5**. At the beginning of the heating period only compound **1** was present (in addition to cluster **2** which remained throughout); during the middle period compounds **1**, **3** and **5** were all present and at the end only compound **5** remained. (Table 2.8)

Reaction of [$Ru_3(CO)_{12}$] and $Ph_3PCHCHO$ at room temperature in the dark

Orange crystals of the compound [$Ru_3(CO)_{12}$] (0.126 g, 1.9849 x 10^{-4} mol) were dissolved in hot dichloromethane (80 cm^3) and $Ph_3PCHCHO$ (0.0604 g, 1.9849 x 10^{-4} mol) was added. The flask was wrapped in foil and allowed to stand at room temperature and the progress of the reaction was monitored by infrared spectroscopy for 14 days. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C) 15:85 v/v). One fast moving major yellow band was extracted into dichloromethane and identified as the starting material [$Ru_3(CO)_{12}$]. A very minor yellow band was irreversibly adsorbed onto the silica surface just above the baseline.

Reaction of [$Ru_3(CO)_{10}(MeCN)_2$] with $Ph_3PCHCHO$

Orange crystals of the compound [$Ru_3(CO)_{12}$] (0.1980 g, 3.097 x 10^{-4} mol) were dissolved in hot dichloromethane (250 cm^3) and acetonitrile (20 cm^3) added. The solution was cooled and then placed in a dry ice/acetone bath so that its temperature could be maintained at -78 °C. A solution of trimethylamine N-oxide (0.0626 g, 5.634 x 10^{-4} mol) in acetonitrile (10 cm^3) and dichloromethane (25 cm^3) was added dropwise over a period of 30 minutes whilst the solution was stirred under a nitrogen atmosphere. The stirring was continued for 45 minutes and the solution was then allowed to warm slowly to room temperature when silica gel (60 - 120 mesh) was added to equal half the volume of the solution. The flask was repeatedly swirled to remove excess trimethylamine N-oxide by adsorption onto the silica and the yellowish orange solution was filtered under gravity into a solution of $Ph_3PCHCHO$ (0.0960 g, 3.100 x 10^{-4} mol) dissolved in dichloromethane (7 cm^3). The solutions were shaken together and allowed to stand at room temperature for two hours when the solvent was removed under reduced pressure and the residue redissolved in dichloromethane (8 cm^3) and the solution chromatographed (eluent: dichloromethane:petroleum ether (distilled, b.p. < 40 °C), 20:80 v/v) to give one major bright yellow band which was extracted into dichloromethane. An infrared spectrum of this material showed it to be starting material $[Ru_3(CO)_{12}]$. A very minor yellow band was irreversibly adsorbed onto the silica surface just above the baseline.

Reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with $Ph_3PCHCHO$ at low temperature

The previous reaction was repeated but the $Ph_3PCHCHO$ (0.083 g, 2.6802 x 10^{-4} mol) in dichloromethane (8 cm^3) was added to the reaction flask at -78 °C and before addition of the silica gel. The solution was stirred for one hour and then silica gel added, swirled and filtered under gravity. The temperature of the reaction mixture was then -48 °C and the solvent was removed under reduced pressure and the residue redissolved in cold dichloromethane (8 cm^3) and chromatographed (eluent: dichloromethane:petroleum ether (distilled, b.p. < 40 °C), 1:4 v/v) to give one major yellow band. This was extracted into dichloromethane and an infrared spectrum showed it to be starting material, $[Ru_3(CO)_{12}]$.

Synthesis of CH_2BrCHO and the preparation of $Ph_3AsCHCHO$

Route 1

A solution of vinyl acetate (20 cm^3, 0.215 mol) in carbon tetrachloride (25 cm^3) in a two-necked flask was placed in an ice-bath. A mixture of bromine (11.1 cm^3, 0.226 mol) in carbon tetrachloride (12 cm^3) was added dropwise to the vinyl acetate solution over two hours whilst stirring contstantly. The temperature of the reaction mixture was kept at -10 °C. The dark brown bromine solution decoloured as it mixed into the vinyl acetate solution and the final mixture had a yellow cast. It was allowed to come to room temperature slowly when methanol (180 cm^3) was added. The resulting solution was allowed to stand at room temperature for 48 hours and then distilled water (50 cm^3) was added. An oil separated in the reaction flask which was separated and then washed with distilled water (5 x 10 cm^3 aliquots) and sodium carbonate (5% solution, 5 x 10 cm^3 aliquots). The washed oil was then distilled and the $BrCH_2CH(OMe)_2$ fraction was collected to which was added concentrated hydrochloric acid (30 cm^3) and Ph_3As (10 g, 3.26 x 10^{-2} mol) and the mixture was boiled gently. The resulting solution was then reacted with butyl lithium in tetrahydrofuran (50 cm^3) at -20 °C. However, the infrared spectrum of the finished product showed no stretches in the carbonyl region so it was discarded.

Route 2

Slightly pinkish crystals of triphenylarsine (0.5 g, 1.6327 x 10^{-3}, 97% pure) were placed in a flask with methanol (7 cm^3) in which it is insoluble. Liquid $BrCH_2CH(OMe)_2$ (0.5 g, 2.9581 x 10^{-3} mol) was poured into the triphenylarsine solution. The mixture was warmed to 62 °C and stirred until all the solid dissolved. Stirring was continued for two hours whilst the temperature was maintained. When the solution was allowed to cool, white crystals dropped out but ^1H NMR analysis proved that these were of pure Ph_3As.

Route 3

White crystals of triphenylarsine (1.47 g, 4.8 x 10^{-3} mol) were suspended in methanol (20 cm^3) and $BrCH_2CH(OMe)_2$ (1.47 g, 8.697 x 10^{-3} mol) was added. The mixture was heated to reflux and heating was continued for four hours under a nitrogen atmosphere.

The homogeneous solution was allowed to cool to room temperature and the flask was sealed and allowed to stand overnight. Chunky white crystals formed in the solution and these were removed by gravity filtration, washed in methanol and air dried. The ^1H NMR spectrum showed that these crystals were pure triphenylarsine.

Route 4

White microcrystals of triphenylarsine (0.5 g, 1.6327 x 10^{-3} mol) were dissolved in trimethylamine (5 cm^3) and $BrCH_2CH(OMe)_2$ (0.5 g, 2.9581 x 10^{-3} mol) was mixed in triethylamine (5 cm^3). The two solutions were mixed and then heated to reflux for four hours. A pale yellowish solution resulted with a brown oily residue at the bottom of the flask. Neither of these was the required product.

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31. *Org. Synth. Coll.*, 1953, **3**, 127.

CHAPTER 3

The Oxidative Addition of Cyclic Ylides to Triosmium Clusters

CHAPTER 3

The Oxidative Addition of Cyclic Ylides to a Triosmium Cluster

3.1 Introduction

The cyclopentadienyl ligand, (C_5H_5), has been central to the development of organometallic chemistry because of its widespread use and it different coordination modes with transition metals. Apart from its normal η^5 coordination mode, it can coordinate as a σ or η^3 ligand and, depending upon the requirements of the metal atom, it may also bridge metal atoms in various ways. The derived ligand, cyclopentadienylidene, (C_5H_4), also appears in a number of coordination types. For example, the cyclopentadiene derivative [$Os_3H_2(C_5H_4)(CO)_9$] is obtained in very low yield from the reaction of [$Os_3(CO)_{12}$] and cyclopentadiene.[1] The normal mode of (C_5H_4) binding is as shown in (a) (Figure 3.1) but in [$Os_3H_2(C_5H_4)(CO)_9$] (Figure 3.2) it binds in the alternative form (b) shown in Figure 3.1.

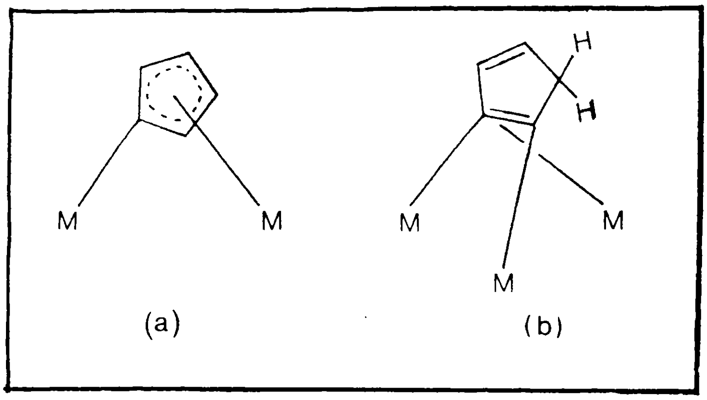


Figure 3.1 Two forms of attachment of the cyclopentadienyl ligand

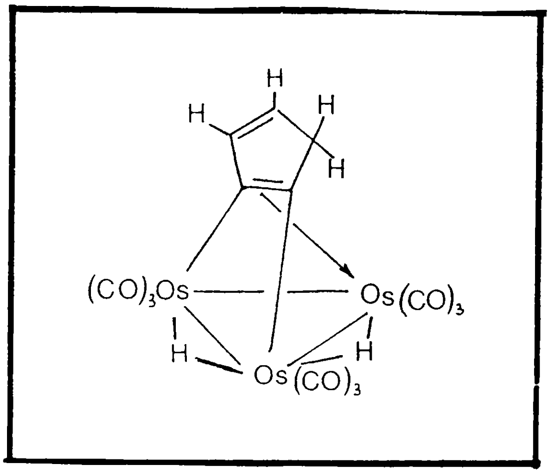


Figure 3.2 $[Os_3H_2(C_5H_4)(CO)_9]$

The related complex $[Os_3H_2(\mu_3\text{-indyne})(CO)_9]$ is formed by reacting $[Os_3(CO)_{12}]$ with indene in refluxing nonane. Both the vinylic hydrogen atoms of the five-membered ring are transferred to the metal and the complex displays indyne rotation with respect to the metal triangle which is accompanied by flipping so the η^2-coordination of the hydrocarbon alternates between opposite ligand faces. This process is slightly slower than independent hydride exchange [2] (Figure 3 3)

The synthesis of ring-containing ylides has been known for many years. The phosphorus ylide, cyclopentadienylidenetriphenylphosphorane was reported in 1956 [3-5] and pyridinium cyclopentadienylide was reported in 1955, [6,7] but the equivalent arsonium ylides were not prepared until much later.[8] Previously the only arsonium cyclopentadienylides had either phenyl [9] or acyl [10] substituents attached to the five-membered ring or had benzene rings annealated to it. [11]

The difficulties experienced in the synthesis of triphenylarsonium cyclopentadienylide may reflect the differences in stability between the phosphorus and arsenic analogues. Phosphorus ylides posses an especially high degree of

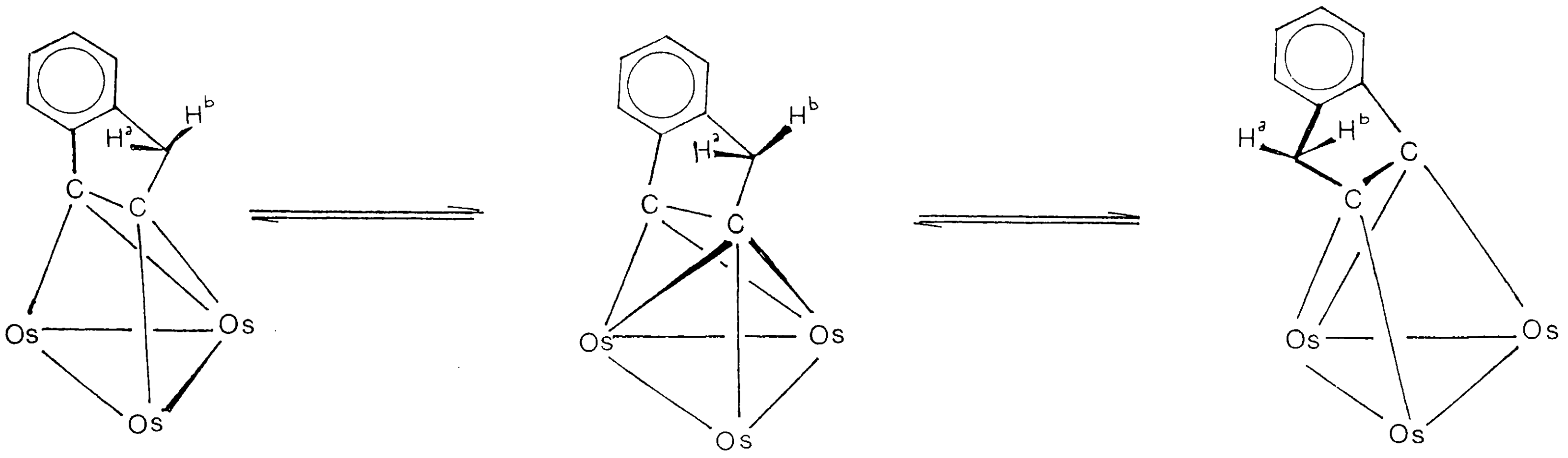


Figure 3.3 Indyne rotation with respect to the metal triangle

stability as outlined in the previous chapter but arsenic ylides were reported to break up rapidly and therefore have been used in synthesis as carbene carriers.

It has been suggested that the colour, stability and ability to react with carbonyl compounds reflects the distribution of negative charge and especially of that at the carbon atom bonded to phosphorus.[3] Triphenylphosphonium cyclopentadienylide, which is a stable and high-melting solid, does not react with aldehydes or ketones and is resistant to alkaline hydrolyis. The added resonance stabilization afforded by delocalization of the electrons in the carbon 2p-orbital throughout the cyclopentadienyl ring together with overlap of a 3d-orbital of phosphorus is thought to account for this unusual stability and lack of reactivity.[12]

The chemistry of fluorene is similar to that of cyclopentadiene but the former is considerably less reactive. In many cases this is due to a increased tendency for electron delocalization in the fluorenyl anion compared to that in the cyclopentadienyl anion. Triphenylphosphoniumfluorenylide has been found to be intermediate in reactivity between the alkyl derivative $Ph_3P = CH_2$ and the cyclopentadienyl derivative $Ph_3P^+ - (C_5H_4)^-$.[2] It may be concluded that the orbitals of the fluorenyl portion of the molecule compete favourably with the 3d-orbitals of phosphorus for the available electron pair in the carbon 2p-orbital and that this interaction affords added stability to the molecule

It is also evident that the attack of a negative carbon at a positive carbonyl carbon is the controlling step in the reaction of phosphine methylenes with organic carbonyls. Substitution of benzaldehyde by a group such as a nitro group which increases the polarization of the carbonyl facilitates reaction.

3.2 Results and Discussion

3.2.1 Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with Cyclopentadienyltriphenylphosphorane

Cyclopentadienyltriphenylphosphorane [3,13] is expected to contain a nucleophilic C_5 ring as a result of a major contribution from the canonical form (ii) in addition to a minor contribution from form (i). (Figure 3.4)

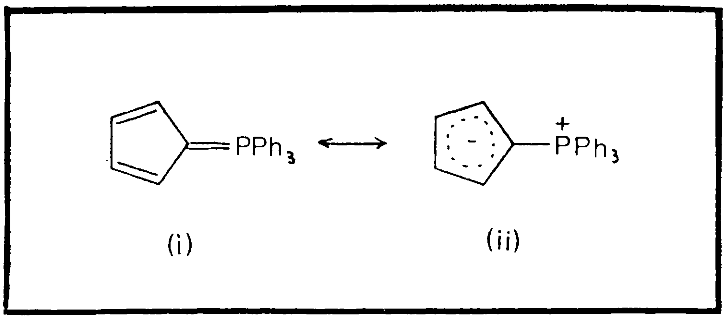


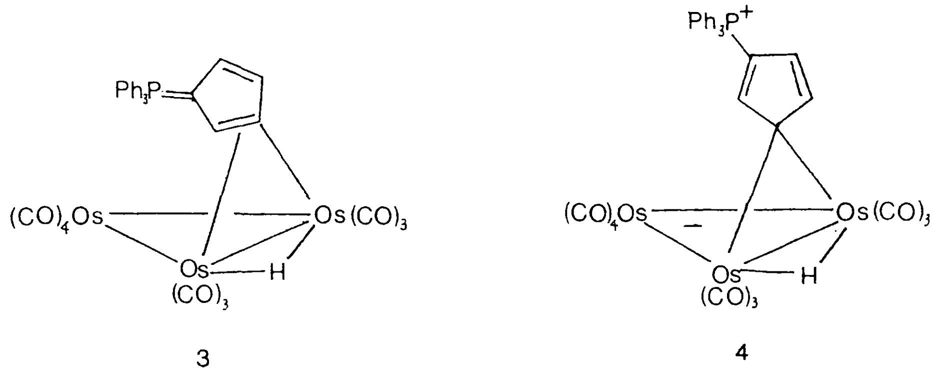
Figure 3.4 Canonical forms of the $Ph_3PC_5H_4$ ligand

The zwitterionic representation (ii) could be regarded as a cyclopentadienyl anion substituted with the phosphonium group and the five-membered ring would therefore be expected to have enhanced nucleophilicity over neutral alkenes even though it is apparently too weakly nucleophilic to undergo normal Wittig chemistry.

It might be expected that the formation of η^5-$C_5H_4PPh_3$ would dominate the chemistry with mononuclear systems and indeed there are many examples of this. [12,15,16] However, clusters frequently have very different chemistry from that of mononuclear compounds. In particular, $[Os_3(CO)_{10}(MeCN)_2]$ usually reacts with unsaturated hydrocarbons by a process of oxidative addition whereby a C-H bond is cleaved in the ligand rather than by the formation of π-complexes. For example, indene, (C_9H_8), commonly gives η^5-indenyl compounds by deprotonation at the acidic CH_2 group. However, with triosmium clusters. indene undergoes oxidative addition with C-H bond cleavage at the vinylic sites to give the μ_3-indyne cluster $[Os_3H_2(\mu_3,\eta^2\text{-}C_9H_6)(CO)_9]$ rather than an η^5-complex. [2,17]

The reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3PC_5H_4$ in dichloromethane and at room temperature is essentially complete within a few seconds to give the ruby-red oxidation product $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** which could be separated by chromatography on silica. Reaction with this phosphorane is very much more rapid than is the reaction with alkenes and this finding is consistent with the considerable negative charge associated with the five-membered ring. Although a kinetic study of the system was not undertaken, qualitatively it seems that carbon-hydrogen bond activations of this kind are controlled by the rate of initial coordination of the ligand rather than by the rate of the secondary bond cleavage step. This is also apparent from the fact that better donors appear to undergo more facile C-H bond cleavage than do poorer donors.

The infrared spectrum of the product $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** is characteristic of a decacarbonyl compound with a 4:3:3 distribution of CO ligands at the metal centres. The alternative structures for such a decacarbonyl species are shown in Figure 3.5.



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4

Figure 3.5 The alternative structures for $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$

Further alternative structures with metallation at the α- rather than at the β-site might also be envisaged. However, we have shown by ^1H NMR and X-ray crystallograhy that the formation of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** results from cleavage of a C-H bond in the C_5 ring remote from the phosphorus atom with formation of a hydride ligand on one edge of the triosmium cluster. The three remaining hydrogen atoms on the ring give multiplets in the ^1H NMR spectrum at δ 8.17, 6.95 and 6.26 with coupling between them and with the ^{31}P nucleus consistent with this position for oxidative addition (Table 3.1). On the basis of this evidence it seemed probable that the decacarbonyl species **1** had either structure **3** or **4** (Figure 3.4) corresponding to the two representations of the ylide (i) and (ii) (Figure 3.1) or of some resonance hybrid of **3** or **4**. Although the infrared spectrum around 2000 cm^{-1} is characteristic of a species of the general type $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$, the ν (CO) values are lower by between 28 and 19 cm^{-1} than those found for $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ [18,19] which is itself a good model for structure **3** (Figure 3.5). The lowering of the carbonyl stretching region values for **1** may indicate the presence of a partial negative charge accumulation across the three osmium atoms which points to structure **4** having a role to play in the actual structure. Further comparisons of infrared data may be made with $[Os_3(\mu\text{-}H)(PhCO)(CO)_{10}]$ and again the same degree of lowering of the values found in the carbonyl region of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** is apparent.

A similar situation has been encountered in the chemistry of furan and of N-methylpyrrole with triosmium clusters. Whereas the fur-2-yl complex $[Os_3(\mu\text{-}H)(\eta^2\text{-}C_4H_6O)(CO)_{10}]$ adopts μ,η^2-vinyl type coordination corresponding to the structure of **3** (Figure 3.4), [17] the N-methylpyrrol-2-yl analogue $[Os_3(\mu\text{-}H)(\mu,\sigma\text{-}C_4H_3NMe)(CO)_{10}]$ is found to have the C_4N ring close to perpendicular to the triosmium plane and the cluster adopts a zwitterionic form closely corresponding to the form of 4 (Figure 3.4). [24] It is generally found that the infrared carbonyl stretching frequencies are lower for this type of zwitterionic structure.

These conclusions were validated by a single-crystal X-ray structure determination of [Os_3(μ -H)(μ -$Ph_3PC_5H_3$)$(CO)_{10}$] **1**.

3.2.2 X-ray crystal structure of [Os_3(μ -H)(μ -$Ph_3PC_5H_3$)$(CO)_{10}$] **1**

After separation from the crude mixture by thin layer chromatography, a few ruby-red crystals of [Os_3(μ -H)(μ -$Ph_3PC_5H_3$)$(CO)_{10}$] **1** which were suitable for analysis by X-ray diffraction were selected from a mass of crystals obtained from evaporation of a dichloromethane/heptane solution. The crystallographic analysis was carried out by Professor A. J. Deeming and Dr. N. I. Powell in this Department. The decacarbonyl species, **1**, was found to be orthorhombic, *a* = 9.358(3), *b* = 15.420(5), *c* = 23.033(4) Å, *U* = 3324(1) Å^3, Z = 4 and the structure was solved in space group *P2/cn*. The molecular structure is shown in an ORTEP picture in Figures 3.6 and a space-filling model is shown in Figure 3.7. Selected bonds lengths and angles are given in Table 3.3. The structure was refined to give R = 0.0420 and R' = 0.0403.

The crystal structure determination for [Os_3(μ -H)(μ -$Ph_3PC_5H_3$)$(CO)_{10}$] **1** established that it adopts the vertical zwitterionic form **4** (Figure 3.4). The $Ph_3PC_5H_5$ ligand is coordinated through atom C(1) alone; C(2) and C(5) are not considered to be bonding to Os(1) or to Os(3) since the distances between them are too long. Os(1) - - - C(2) is 3.19 Å and Os(3) - - - C(5) is 3.19Å. The C(1)C(2)C(3)C(4)C(5) plane is at 88.9 ° to the triosmium plane and is essentially perpendicular. The best description may be that C(1) is involved as a normal μ-alkylidene bridge as in structure **4** (Figure 3.4). The molecule is symmetrically bridged (Os(1) - C(1) is 2.20(2) Å and Os(3) - C(1) is 2.25(2) Å) which would not be expected for a bridging vinyl. The C - C bonds shown as single in the structure **4** (Figure 3.4) are the longer

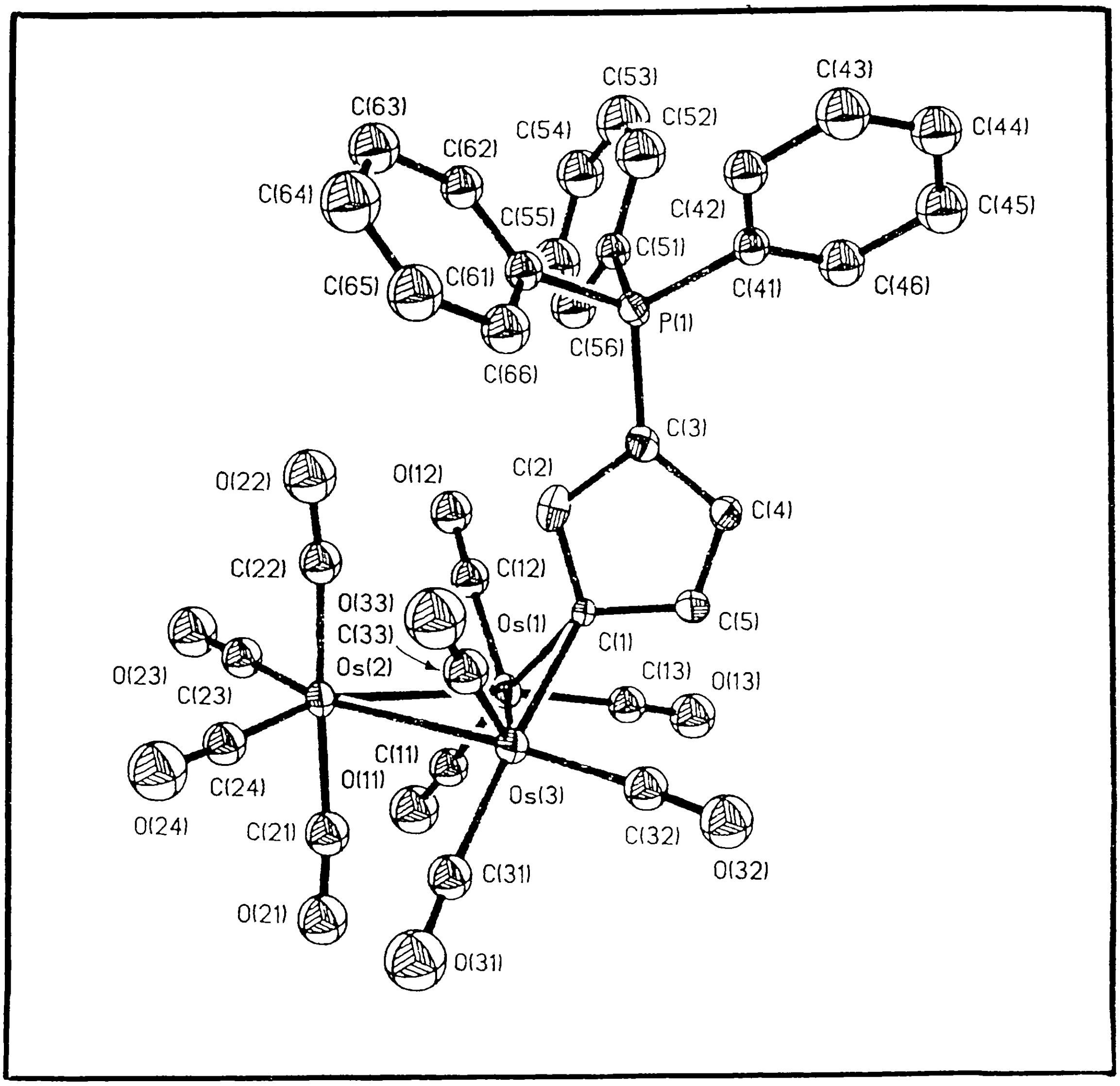

Figure 3.6 Molecular structure of $[Os_3H(Ph_3PC_5H_3)(CO)_{10}]$

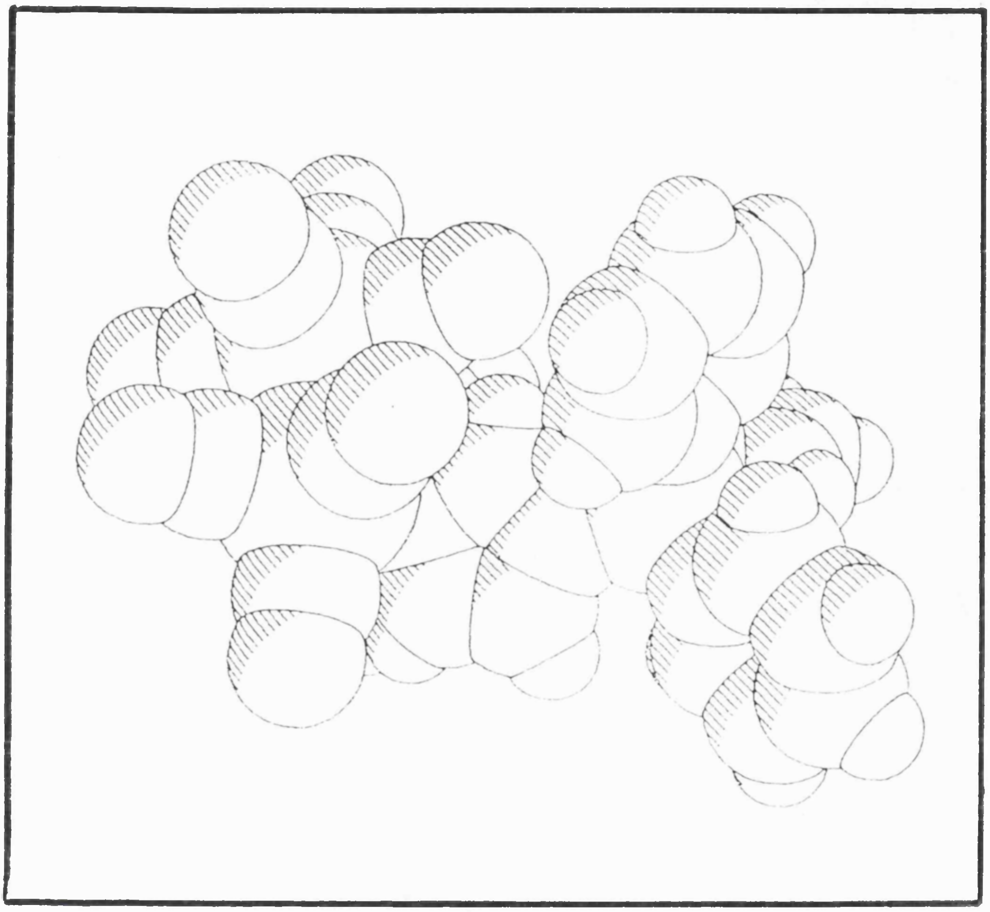

Figure 3.7 Space filling model of [$Os_3H(Ph_3PC_5H_3)(CO)_{10}$]

ones in the C_5 ring but when assessed in the light of the estimated standard deviations these cannot be considered to be significantly longer than those that are formally described as double bonds in the same description. As is common for heavy metal clusters, C - C bond lengths in ligands cannot be determined accurately enough for comparison purposes so assumptions have been made in the representation of structure **4**.

The distance P(1) - C(3), 1.74(2) Å, is rather shorter, but only just significantly so, than the other P - C bonds, 1.80(2), 1.80(2) and 1.81(2) Å. It is possible that there is some minor contribution from structure **3** (Figure 3.4) to shorten the P(1) - C(3) bond, but clearly the structure of **4** is overwhelmingly supported by the structural data The site of triphenylphosphine substitution is consistent with the ^{1}H NMR data but the data could have been analysed satisfactorily for the isomer with the triphenylphosphine substituent at C(4); the coupling patterns would be expected to be essentially the same for that isomer.

3.2.3 The reaction of $[Ru_3(CO)_{12}]$ and $Ph_3PC_5H_4$

The $Ph_3PC_5H_4$ ligand has also been used successfully with both mononuclear and trinuclear ruthenium species. With mononuclear ruthenium complexes η^5-coordination complexes are formed.[19] However, in work carried out by Vahrenkamp *et al.*, subsequently to our studies on osmium, $[Ru_3(CO)_{12}]$ gave $[Ru_3(Ph_3PC_5H_4)(CO)_9]$ **5** [21] (Figure 3.8).

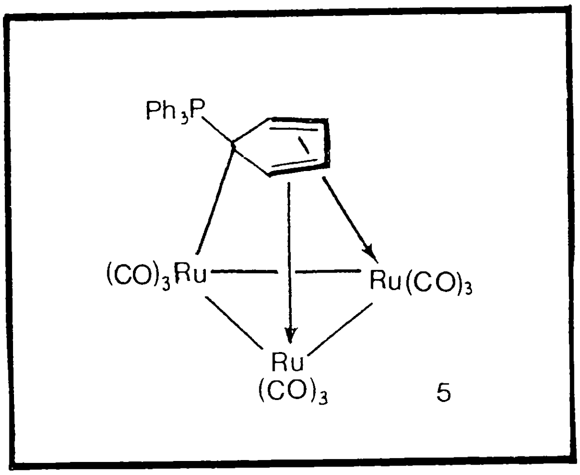

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Figure 3.8 $[Ru_3(Ph_3PC_5H_4)(CO)_9]$

By-products of the reaction were $[Ru_3(Ph_3P)(CO)_{11}]$ and $[Ru_3(Ph_3P)_2(CO)_{10}]$. The ^1H and ^{13}C NMR spectra of $[Ru_3(Ph_3PC_5H_4)(CO)_9]$ **5** indicate that the ring is bound by one σ and two π bonds to the metal skeleton as η^5-coordination of the cyclopentadienyl ring as found in $[Ph_3P(C_5H_4)RhL_2]$ [14] can be ruled out by the spectroscopic data.

The binding of the triphenylphosphoniumcyclopentadienylide ligand by one σ bond and two π bonds requires that there be a charge separation within the molecule and the positive charge be centred on the phosphorus atom and the negative charge distributed across the metal cluster as is found in the trisomium clusters. We surmise that $[Ru_3(CO)_{12}]$ loses CO more readily than osmium clusters and the μ_3 bonding type is accessible. In our use of $[Os_3(CO)_{10}(MeCN)_2]$ only two ligands are readily lost so that C - H cleavage occurs in preference to μ_3 complexation.

The μ^3-benzene cluster has been prepared [22] and the coordination in $[Ru_3(Ph_3PC_5H_4)(CO)_9]$ **5** is essentially equivalent to that of form (iv) of the benzene-bridged cluster (Figure 3.9) on the grounds of spectroscopic data: form (iii) would require the aromatic π-system in the C_5 ring to be retained. The infrared data support this as the ν(CO) frequencies are lower for $[Ru_3(Ph_3PC_5H_4)(CO)_9]$ **5** than they are for isomer (iv) of the benzene-bridged molecule due to the negatively charged metal skeleton in **5**.

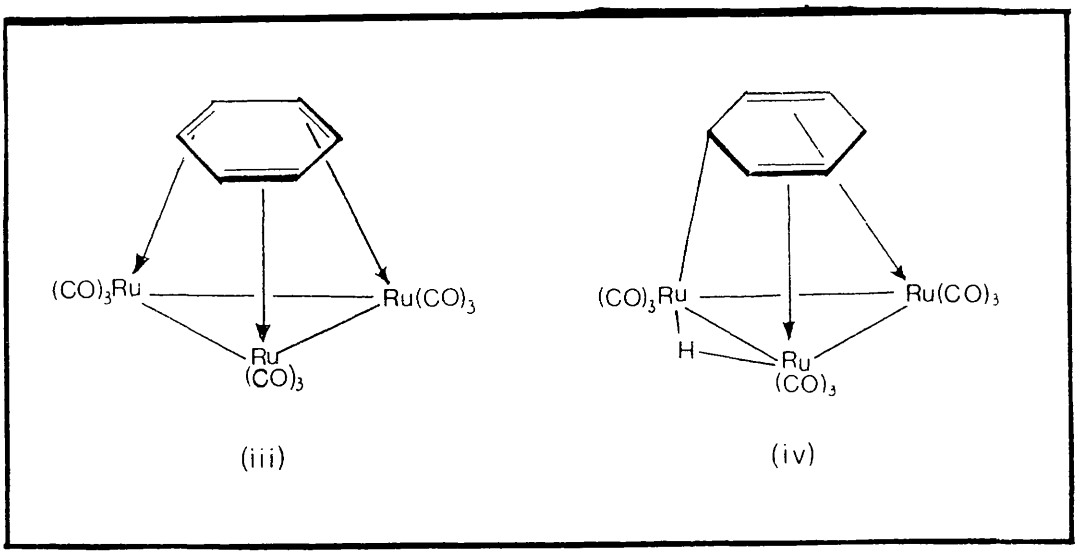
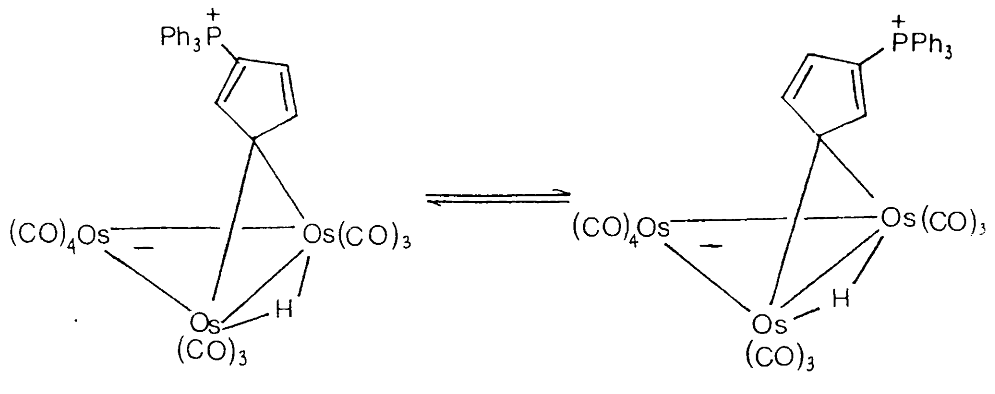


Figure 3.9 Benzene-bridged triosmium clusters

These findings correspond well with those on the infrared data found for the triosmium clusters but no product analogous to $[Ru_3(Ph_3PC_5H_4)(CO)_9]$ **5** was found in the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3PC_5H_4$ and equally the oxidative addition product was not found for ruthenium, so direct comparisions are not possible.

3.2.4 Isomerization of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1**

The crystal of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** used for the structure determination was obtained from a sample of the cluster as it was first formed from oxidative addition of the ligand to $[Os_3(CO)_{10}(MeCN)_2]$ and immediately crystallized. However, when a solution of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1** in deuteriated chloroform was allowed to stand at room temperature for several hours, it was found that new signals of another species appeared in the ^1H NMR spectrum. After several days, the new signals corresponded to approximately 40% of the total material present. No further change was observed in this ratio so it appeared that equilibrium had been reached. Whenever a solution of **[Os_3(μ-H)(μ-$Ph_3PC_5H_3$)$(CO)_{10}$] 1 was left** to stand at room temperature the growth of the second species became apparent after about four hours. This second species never exceeded 40% of the total material present. Thin layer chromatography gave two species, one pink and one a darker orange/red, which had indistinguishable infrared spectra around 2000 cm^{-1}. In the ^1H NMR spectra of these species similar signals with similar couplings were obtained for both species but with different chemical shifts (Table 3.1) indicating the presence of two isomeric species, each with the same arrangement of substituents Proposed Structures for these isomers are shown in Scheme 3.1. Solutions of each purified isomer were converted over several days to the same equilibrium mixture of isomers.



1a

1b

Scheme 3.1 Proposed structures for [$Os_3H(Ph_3PC_5H_3)(CO)_{10}$]

The mechanism of this interconversion was not investigated and it seems that the intramolecular rotation of a μ-alkylidene ligand has not previously been demonstrated except by a mechanism involving σ-alkylidene intermediates.[25-27] Reversible transformation of **4** into **3** (Figure 3.5) does not suggest an obvious route for the isomerization even bearing in mind that μ,η^2-vinyl ligands can rapidly exchange σ-bonds between the bridged metal atoms. *Exo-endo* conversion is required in this case and this has not been established except in the case of the

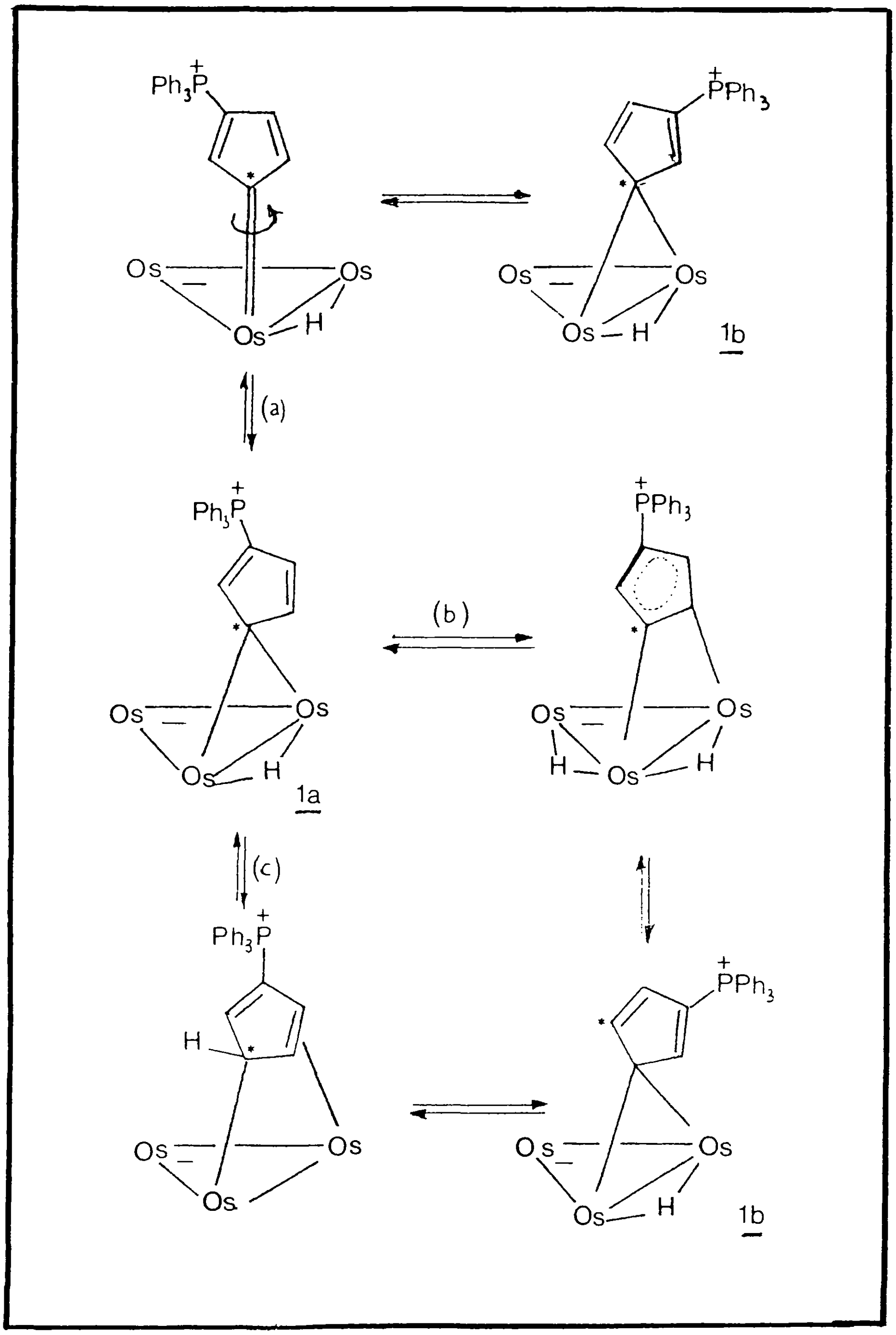
η^2-thien-2-yl ligand in $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}C_4H_3S)H_3(CO)_9]$.[28] Here, *exo-endo* conversion probably occurs *via* an S-bonded species which is a special case and not appropriate to the isomerization of **$[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ 1. It is possible that the** mechanism is not a σ-alkylidene rotation but rather an H-atom transfer process with the intermediate $[Os_3(Ph_3PC_5H_4)(CO)_{10}]$ or $[Os_3H_2(Ph_3PC_5H_2)(CO)_{10}]$, in which case atom C(1) does not remain bonded to the metal atoms throughout but after the transformation C(5) becomes bonded to osmium. The two possible paths to isomerization are illustrated in Scheme 3.2 showing the route *via* H-atom migrations (routes **b** and **c**) as well as σ-alkylidene intramolecular rotation (route a).

In order to demonstrate whether or not the isomerization led to H-atom transfer from osmium or carbon atoms, the deuteriated analogue, $[Os_3(\mu\text{-}D)(Ph_3PC_5H_3)(CO)_{10}]$, was proposed as a model. Unfortunately, protonation with deuteriated acid followed by deprotonation did not lead to the required product so we were unable to test the H-atom migration hypothesis.

3.2.5 Decarbonylation of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1**

Thermolysis of isomer **1a**, or a mixture of **1a** and **1b**, (Scheme 3.1) in refluxing toluene led to a yellow decarbonylation product $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ 8 which was surprising as known decarbonylation reactions of other decacarbonyl triosmium alkene derivatives give dihydride products.[29] The product we had expected was $[Os_3(\mu\text{-}H)_2(Ph_3PC_5H_2)(CO)_9]$ but the ^{1}H NMR spectrum clearly showed that only one hydride ligand per molecule was present in the product.

When left in solution, the nonacarbonyl species resolved into two isomeric forms in the same way as did the parent compound but in this case it was not



Scheme 3.2 Possible paths of isomerization for $[Os_3H(Ph_3PC_5H_3)(CO)_{10}]$

possible to separate the isomers chromatographically in spite of several attempts. The infrared spectrum of the nonacarbonyl mixture is simple indicating that the spectra of the isomers are essentially the same. Again the carbonyl region stretching frequencies are low which suggest a zwitterionic form with an exocyclic phosphonium group within an overall neutral cluster. The ^{1}H NMR spectrum was not easy to interpret as phenyl resonances partially obscure the C_5 ring resonances.

3.2.6 X-ray Structure Determination of $[Os_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}Ph_3PC_5H_3)(CO)_9]$ **8**

One crystal was selected from a mass of yellow crystals of $[Os_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}Ph_3PC_5H_3)(CO)_9]$ **8** obtained from evaporation of a dichloromethane/hexane solution. The structure determination was carried out by Professor A. J. Deeming in this Department and the structure of the monoclinic crystal, a = 13.016(3), b = 12.279(2), c = 20.250(3) Å, β = 91.65(2) °, U = 3235(2) Å^3 and Z = 4 was solved in space group $P2_1/n$. The structure was refined to give R = 0.0497 and R' = 0.0514. The molecular structure of what is probably the major isomer in solution is shown in Figures 3.10 and 3.11 and selected bonds lengths and angles are given in Table 3.4.

The carbon atoms C(1), C(2) and C(5) are all involved in the bonding of the ligand to the metal atoms with the ligand in a μ_3 mode. The hydrogen atoms were not located but are believed to be correctly positioned at C(2), C(4) and C(5) as in the decacarbonyl parent compound. The hydride ligand bridges Os(1) and Os(3) on the basis of Os - Os bond lengths: Os(1) - Os(3) is 2.957(1) Å compared with Os(1) - Os(2) 2.838(1) Å and Os(2) - Os(3) 2.782(1) Å and this is supported by the CO ligand positions. The $Ph_3PC_5H_3$ ligand could be thought to donate four electrons through two Os - C σ bonds (Os(1) -C(5) 2.27(1) Å and Os(3) - C(1) 2.11(1) Å) and by an

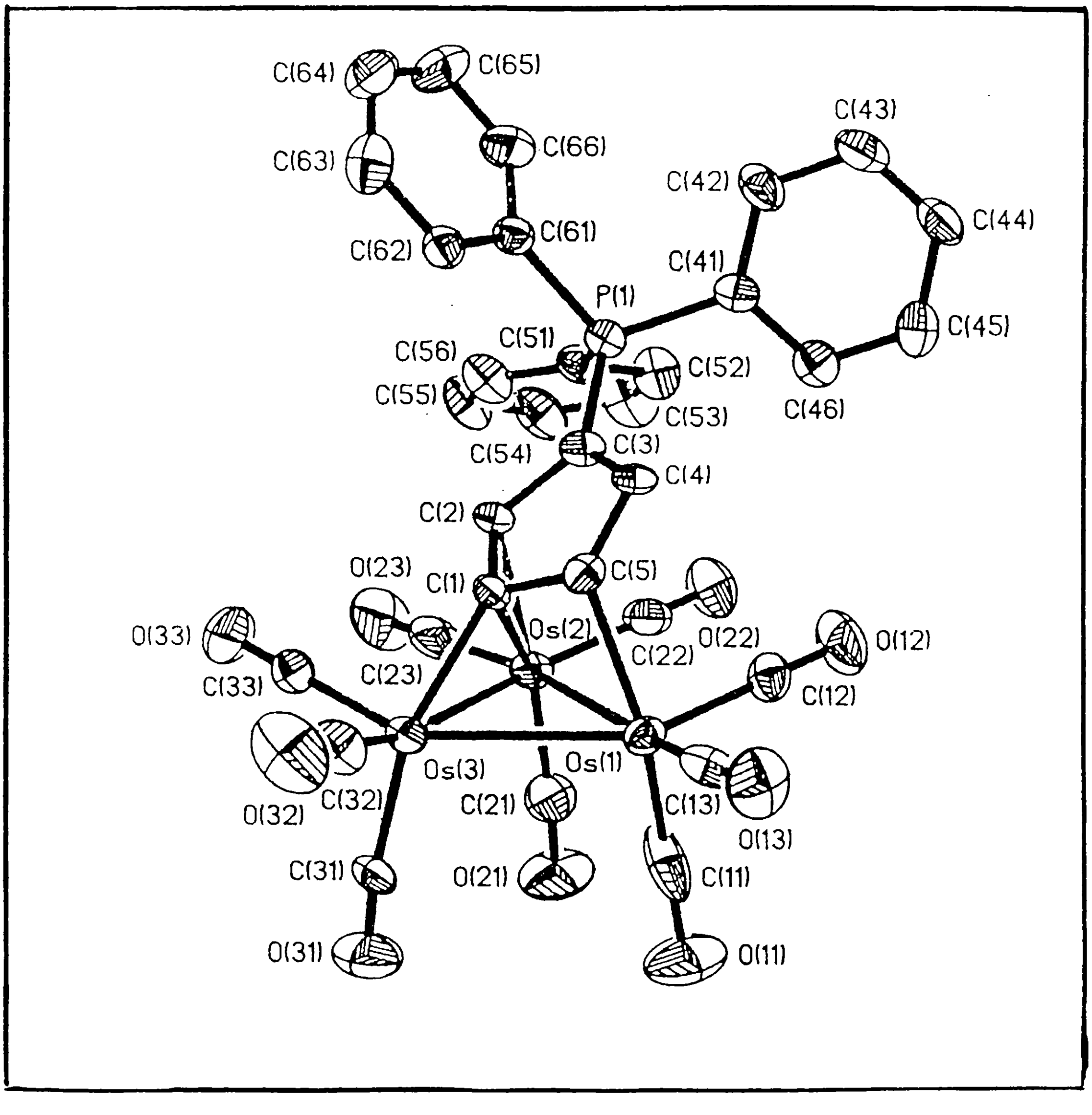


Figure 3.10 Molecular structure of $[Os_3H(Ph_3PC_5H_3)(CO)_9]$

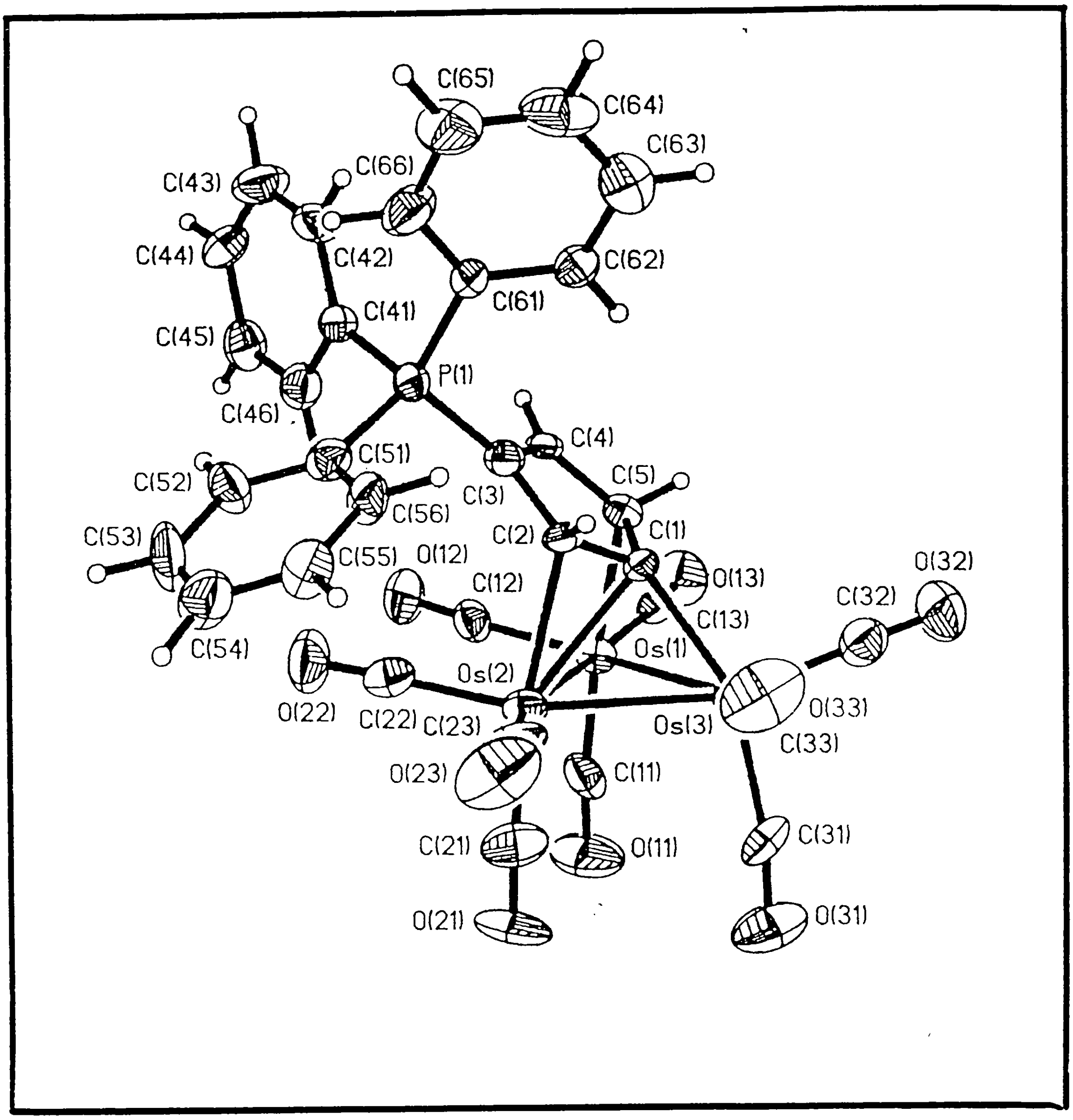
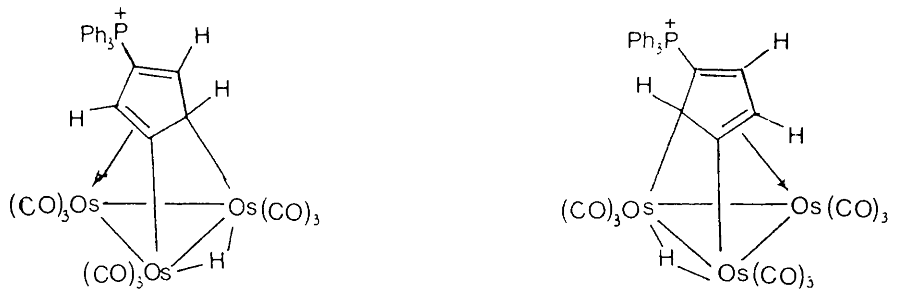


Figure 3.11 Molecular structure of $[Os_3H(Ph_3PC_5H_3)(CO)_9]$

η^2 interaction through C(1) and C(2) to Os(2) (Os(2) - C(1) 2.45(1) Å and Os(2) - C(2) 2.36(1) Å).

As with the cluster $[Os_3(\mu\text{-}H)(Ph_3PC_5H_3)(CO)_{10}]$ **1**, a negative charge is formally located at the metal atoms and the cluster is electron precise. However, the C_5 ring is not too far from symmetrical with respect to atoms Os(1) and Os(2). For instance, the bond length Os(2) - C(1) of 2.45(1) Å might be compared with the corresponding (non-bonding) distance Os(1) - - - C(1) of 2.63 Å. For the isomeric form, breaking bond Os(2) - C(1) and making Os(1) - C(1) would shift the η^2 interaction to the other side, that is to Os(1). The hydride ligand would need to shift from the Os(3) - Os(1) to the Os(2) - Os(3) edge. The net effect of these movements would be to generate an isomer with the triphenylphosphonium group at the other carbon atom not bonded to osmium (Scheme 3.3). Because the isomeric mixture resisted all attempts at separation we have not been able firmly to establish the structure of the other isomer but we postulate that the two isomers detected in the ^1H NMR spectrum are those shown in Scheme 3.3.



Scheme 3.3 Isomeric forms of $[Os_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}Ph_3PC_5H_3)(CO)_9]$

The manner in which the organic ligands are bonded to the metal atoms in $[Os_3(\mu\text{-}H)(Ph_3PC_5H_3)(CO)_{10}]$ **1** and $[Os_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}Ph_3PC_5H_3)(CO)_9]$ **8** does not seem to depend upon the presence of the triphenylphosphonium substituent at the C_5 ring and there should be directly related systems without this moiety. For example, the complex $[Os_3(\mu\text{-}H)_2(\mu\text{-}C_5H_4)(CO)_{10}]$ which is related both to $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_4)(CO)_{10}]$ and to $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ [30] should be accessible as should $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_5H_4)(CO)_9]$ which would be analogous to $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3C_5H_3)(CO)_9]$. An extra hydride ligand is needed in each case for the compound to be neutral overall.

3.2.7 Photolysis of a mixture of the isomers of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_{10}]$

Photolysis in fluorescent light of a mixture of **1a** and **1b** resulted in dark yellow/brown crystals suspended within a very pale yellow supernatant solution. ^1H NMR spectra showed that there were no hydride signals present in the region scanned (δ 0 to -25). The pattern of multiplets, doublets and triplets downfield was the same as in the parent molecule and very close to the shifts for the free ligand. No further investigation was undertaken of these crystals.

3.2.8 The Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3AsC_5H_4$

Triphenylarsoniumcyclopentadienylide was prepared by a combination of literature methods [7,31-33] to give colourless crystals which slowly reddened on exposure to light and air or on attempted recrystallization. This colouration is superficial and has been noted in the literature.[8]

Initially the use of the arsenic analogue was designed in order to incorporate the C_5 ring into the cluster and then to induce cleavage of the $AsPh_3$ group. It was felt that this might be more easily achieved than removal of the PPh_3 substituent because of the difference in strength of the P - C and As - C bonds, the latter being weaker. This could provide a route to clusters containing only the ring moiety. Also in view of the failure to deuteriate the phosphorus ylide it was decided to attempt the deuteriation of the arsonic ylide cluster. It is known that a solution of triphenylarsoniumcyclopentadienylide in deuteriated chloroform shows no change when the solution is shaken with deuterium oxide but that addition of deuterium oxide and a few drops of trifluoroacetic acid causes the complete disappearance of the signals due to the hydrogen atoms atached to the five-membered ring, thus showing that each position in the ring is easily deuteriated (or protonated) in strong acid.[35]

The reddish-brown crystalline triphenylarsoniumcyclopentadienylide was reacted with $[Os_3(CO)_{10}(MeCN)_2]$ under the same conditions employed in the triphenylphosphoniumcyclopentadienylide reaction and there was a rapid reaction which was monitored by infrared spectrometry. However, expectations were only partly justified and the consequences of the reaction were different from those expected. The reaction led to $[Os_3(AsPh_3)_2(CO)_{10}]$ as the major product at room temperature. When the preparation was attempted at temperatures of up to 10 degrees below room temperature the same product dominated The ^1H NMR spectrum of the material resulting from the reaction showed no hydride ligands and none of the coupled hydrogen signals for the cyclopentadiene moiety although these are very clear in the spectrum of the free ligand and in the product of the phosphorus reaction. It proved impossible to isolate any compounds containing the C_5 ring or to establish the fate of this group during the reaction despite repeated attempts.

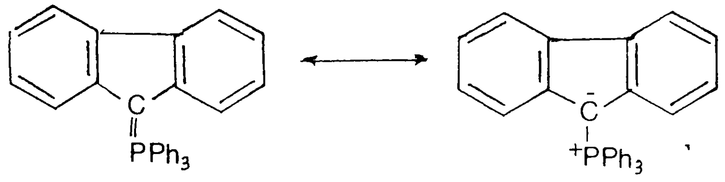
3.3 Attempted Reactions of [$Os_3(CO)_{10}(MeCN)_2$] with other cyclic ylide ligands

3.3.1 Reaction of $Os_3(CO)_{10}(MeCN)_2$] with triphenylphosphoniumfluorenylide and triphenylarsoniumfluorenylide

The reaction of triphenylphosphoniumfluorenylide with symmetrical ketones has been examined as a method of introducing a disubstituted carbon atom into the C(9) position of fluorene. It was found that it would not react with dimethyl acetone dicarboxylate or acetone but it does react with benzaldehyde in high yield.[4,37]

The chemistry of fluorene is similar to that of cyclopentadiene but the former is much less reactive possibly due to the increased tendency for electron delocalization in the fluorenyl anion. Triphenylphosphoniumfluorenylide is intermediate in reactivity between the alkyl $(C_6H_5)_3P^+ - {}^-CH_2$ and cyclopentadienyl derivatives so it may be concluded that the π-orbitals of the fluorenyl portion of the molecule compete favourably with the 3d-orbitals of phosphorus for the available electron pair in the carbon 2p-orbital and that this interaction affords additional stability to the molecule.

The dipole moment of triphenylphosphoniumfluorenylide is 7.09 D and indicates nearly equal contributions of structure (v) and the structures summarized as (vi) in the resonance hybrid (Figure 3.12). Hence the bond must contain nearly 50% double bond character and it is interesting that the same applies to triphenylphosphoniumcyclopentadienylide in view of their very different reactivites. The reactions of these were therefore expected to reflect this difference.



(v) (vi)

Figure 3.12 Canonical forms of triphenylphosphoniumfluorenylide

Triphenylphosphoniumfluorenylide was prepared by an adapted literature method[4] and was recrystallized to give yellow crystals in high yield. The crystals were reacted with $[Os_3(CO)_{10}(MeCN)_2]$ in dichloromethane at room temperature but after several days there was no change in the infrared spectrum. There was also no discernable reaction after reflux in dichloromethane and it may be that there is some steric hindrance preventing the reaction from occurring. Likewise there is no reaction between $[Ru_3(CO)_{12}]$ and triphenylphosphoniumfluorenylide at room temperature to give the ligand-bridged hydride product which may present further evidence of steric hindrance. However, to date there has not been any study of such steric effects and the subject is not covered in the major reviews of ylide activity. The chemistry of these reagents was not developed in view of their lack of reactivity.

3.3.2 Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with triphenylarsoniumfluorenylide

Comparative studies involving fluorenylides[36] and cyclopentadienylides[38-41] show that the arsonium yides are markedly more reactive than their phosphonium analogues. In many cases reactions proceed only in the case of arsonium ylides; this is particularly true the more electron withdrawing are the substituents on the ylidic carbon atom. There is a general tendency for the more basic ylides to be the more reactive [41] although other factors , such as steric factors, must affect the reactivity.[40,42,43] It was hoped that the arsonium ylide would react under conditions where the phosphonium analogue would not as the former is more basic; that is, there is more driving force towards the arsonium carbanion than the phosphonium carbanion. Also there is less stabilization afforded to an adjacent carbanion by valence shell expansion of an arsonium group than there is by a phosphonium group. Therefore the canonical form (vii) (Figure 3.13) contributes less to the actual structure of triphenylarsoniumfluorenylide than it does in the triphenylphosphonium analogue.

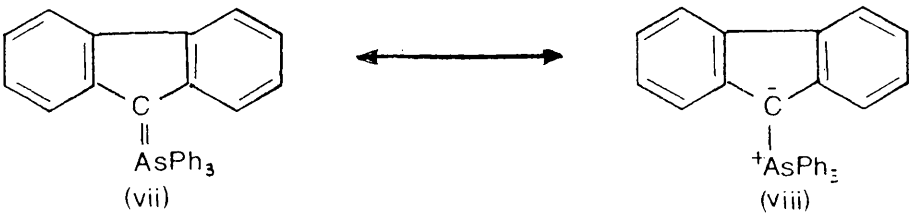


Figure 3.13 The canonical forms of triphenylarsoniumfluorenylide

Triphenylarsoniumfluorenylide was synthesized using a literature method [31] and the resulting reddish-brown crystals were reacted with $[Os_3(CO)_{10}(MeCN)_2]$ and there was an almost immediate reaction to give $[Os_3(AsPh_3)_2(CO)_{10}]$ exactly as occurred in the reaction with triphenylarsoniumcyclopentadienylide. The reaction was repeated at 10 °C with exactly the same result. The ligand also reacts with $[Ru_3(CO)_{12}]$ at room temperature and in the dark to give the analogous ruthenium product, $[Ru_3(AsPh_3)(CO)_{10}]$, and it would therefore appear that this reaction is facile.

3.4 Conclusion

The rapid reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with cyclopentadienylidene triphenyphosphorane and the following much slower intramolecular conversion of

40% of the first formed product to an isomeric form indicates that there is one facile pathway available for binding of this ligand as the first product formed is of a single isomer only. From the lack of reactivity of the bulkier ligand, triphenylphosphoniumfluorenylide, it appears that steric hindrance has prevented binding by this pathway. This supposition is supported by the product found in reaction of triphenylphosphoniumfluorenylide with $[Ru_3(CO)_{12}]$. Here, again, there is a very rapid reaction but, in this instance, reaction leads to the disubstituted product $[Ru_3(AsPh_3)_2(CO)_{10}]$ indicating either that the disubstitution reaction is more rapid even than binding of the ligand or that the facile pathway available for reaction found with cyclopentadienylidene triphenyphosphorane is blocked, probably for steric reasons.

3.5 Tables

	δ	Hz	
$[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1a**	8.17 (dt, H^A)	$J(PH^A)$	6.3
	7.75 - 7.55 (m, Ph)	$J(PH^B)$	4.2
	6.95 (dt, H^B)	$J(PH^C)$	1.6
	6.26 (dt, H^C)	$J(H^AH^B)$	1.6
	-15.34 (s, Os*H*)	$J(H^AH^C)$	4.2
		$J(H^AH^C)$	1.6
$[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)(CO)_{10}]$ **1b**	7.95 (dt, H^B)	$J(PH^A)$	6.3
	7.75 - 7.55 (m, Ph)	$J(PH^B)$	4.2
	7.02 (dt, H^A)	$J(PH^C)$	1.6
	6.39 (dt, H^C)	$J(H^AH^B)$	1.6
	-15.59 (s, Os*H*)	$J(H^BH^C)$	4.2
		$J(H^AH^C)$	1.6
$[Os_3(\mu\text{-}H)(\eta^3,\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ **2**	-16.35 (s, Os*H*)	Isomer **2a**	
	-16.37 (s, Os*H*)	Isomer **2b**	
	7.0 - 7.9 (m, unassigned, Ph overlapping C_5H_3 resonances)		

Table 3.1 Key ^1H NMR data for the compounds **1a**, **1b** and **2** recorded in $CDCl_3$

	$\nu(CO)$ cm^{-1}
$[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_4)(CO)_{10}]$ **1a**	2083m 2067w 2039vs 2031s 1994vs 1965s
$[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_4)(CO)_{10}]$ **1b**	2083m 2067w 2039vs 2031s 1994vs 1965s
$[Os_3(\mu\text{-}H)(\eta^2,\mu_3\text{-}Ph_3PC_5H_4)(CO)_9]$ **2**	2067s 2036vs 2004vs 1978s 1958s 1926m

Table 3.2 Key infrared spectroscopic data recorded in dichloromethane

	Å		Å
Os(1) - Os(2)	2.882(2)	C(3) - C(4)	1.45(3)
Os(1) - Os(3)	2.782(1)	C(4) - C(5)	1.30(3)
Os(2) - Os(3)	2.863(1)	C(5) - C(1)	1.45(3)
Os(1) - C(1)	2.20(2)	P - C(3)	1.74(2)
Os(3) - C(1)	2.25(2)	P - C(41)	1.81(2)
C(1) - C(2)	1.44(2)	P - C(51)	1.80(2)
C(2) - C(3)	1.43(3)	P - C(61)	1.80(2)

	degrees		degrees
Os(2) - Os(1) - Os(3)	60.7(1)	Os(3) - Os(1) - C(1)	52.1(5)
Os(1) - Os(2) - Os(3)	57.9(1)	Os(3) - C(1) - C(2)	118(1)
Os(1) - Os(3) - Os(2)	61.4(1)	Os(3) - C(1) - C(5)	118(1)
Os(2) - Os(3) - C(1)	91.3(4)	Os(1) - C(1) - Os(3)	77.3(5)
Os(2) - Os(1) - C(1)	91.7(5)	Os(1) - C(1) - C(2)	121(1)
Os(1) - Os(3) - C(1)	50.6(4)	Os(1) - C(1) - C(5)	120(1)

Table 3.3 Selected bond lengths and angles for $[Os_3H(Ph_3PC_5H_3)(CO)_{10}]$

	Å		Å
Os(1) - Os(2)	2.838(1)	Os(1) - Os(3)	2.957(1)
Os(2) - Os(3)	2.782(1)	Os(1) - C(5)	2.27(1)
Os(1) - - - C(1)	2.63(1)	Os(2) - C(1)	2.45(1)
Os(2) - C(2)	2.36(1)	Os(3) - C(1)	2.11(1)
C(1) - C(2)	1.42(2)	C(2) - C(3)	1.48(2)
C(3) - C(4)	1.37(2)	C(4) - C(5)	1.42(2)
C(1) - C(5)	1.44(2)	P - C(3)	1.75(1)
P - C(41)	1.79(1)	P - C(51)	1.79(1)
P - C(61)	1.82(1)		

	degrees		degrees
Os(2) - Os(1) - Os(3)	57.3(1)	Os(3) - Os(2) - C(1)	47.0(2)
Os(1) - Os(2) - Os(3)	63.5(1)	Os(3) - Os(2) - C(2)	75.7(3)
Os(1) - Os(3) - Os(2)	59.2(1)	Os(2) - C(1) - Os(3)	74.9(3)
Os(1) - Os(2) - C(1)	59.9(3)	Os(2) - C(1) - C(2)	69.2(6)
Os(1) - Os(2) - C(2)	86.5(3)	Os(2) - C(1) - C(5)	115.2(7)
Os(1) - Os(3) - C(1)	59.6(3)	Os(3) - C(1) - C(2)	126.7(9)
Os(2) - Os(1) - C(1)	80.4(3)	Os(3) - C(1) - C(5)	122.4(8)
Os(2) - Os(3) - C(1)	58.1(3)	Os(1) - C(5) - C(1)	86.9(7)
Os(3) - Os(1) - C(5)	72.1(3)	Os(1) - C(5) - C(4)	121.5(7)

Table 3.4 Selected bond lengths and angles for $[Os_3H(Ph_3PC_5H_3)(CO)_9]$

3.6 Experimental

Reaction of $Ph_3PC_5H_4$ with $[Os_3(CO)_{10}(MeCN)_2]$

To a brown solution of $Ph_3PC_5H_4$ (0.0350 g, 1.077×10^{-4} mol) in dichloromethane (2 cm^3) was added a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.100 g, 1.072×10^{-4} mol) in dichloromethane (15 cm^3) at room temperature. There was an immediate colour change to dark ruby red. After 5 minutes the solvent was removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and chromatographed on silica, (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C):diethylether 12:83:5 v/v/v). The major orange-red band was extracted into dichloromethane and the solvent was then removed under reduced presure and the residue redissolved in dichloromethane (2 cm^3) and heptane (4 cm^3) was floated on the surface. Evaporation at room temperature and at atmospheric pressure gave ruby-red crystals of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ **1a** (0.0805 g, 61%). (Found C, 33.65; H, 1.65% $C_{33}H_{19}O_{10}Os_3P$ requires 33.30; H, 1.45%)

Isomerization of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ **1a**

A red solution of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ **1a** (0.100 g, 8.5×10^{-5} mol) in dichloromethane (10 cm^3) and heptane (10 cm^3) was allowed to stand at room temperature for 24 hours. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (2 cm^3) and chromatographed, (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C) 3:17 v/v) to give one orange-red band and one minor pink band. The two bands were extracted into dichloromethane. The orange-red band was characterized as the starting material, isomer **1a**, and the pink band as isomer **1b**. The ν(CO) spectra in the infrared carbonyl region of **1a** and **1b** were indistinguishable so the characterization was made on the basis of ^1H NMR spectra. After 24 hours the ratio of the isomers in solution was **1a**:**1b**, 60:40

Isomerization of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ **1b**

An isomerically pure sample of isomer **1b** dissolved in dichloromethane was allowed to stand at room temperature for 4 hours. ^1H NMR signals associated with isomer **1a** formed rapidly until again the ratio **1a**:**1b** was 60:40 after 4 hours and this ratio was unchanged after a further 24 hours.

Thermolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ **1a** + **1b**

A red solution of a mixture of the isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3C_5H_3)(CO)_{10}]$ (0.1380 g, 1.172×10^{-4} mol) in toluene (75 cm^3) was heated to reflux under a nitrogen atmosphere. After 4 hours the solution was a clear yellow colour and the solvent was removed under reduced pressure. The residue was redissolved in dichloromethane (2 cm^3) and chromatographed (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C) 7:3 v/v) to give one major yellow band which was extracted into dichloromethane. The solvent was removed under reduced pressure and redissolved in dichloromethane (2 cm^3) and heptane (4 cm^3) added to float on the surface of the solution. Evaporation at room temperature and atmospheric pressure gave yellow crystals of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3C_5H_3)(CO)_9]$ **2** (0.096 g, 70%). (Found: C, 33.0, H, 1.60; P, 2.85% $C_{32}H_{19}O_9Os_3P$ requires C, 33.45; H, 1.65; P, 2.7%).

Photolysis of [Os_3(μ-H)(μ-$Ph_3C_5H_3$)$(CO)_{10}$] **1a** + **1b**

Red crystals of mixture of the isomers of of [Os_3(μ-H)(μ-$Ph_3C_5H_3$)$(CO)_{10}$] **1a** + **1b** (0.002 g, 1.7 x 10^{-6} mol) were dissolved in d_8-toluene (2 cm^3) to give a clear orange-red solution which was placed in a narrow diameter tube (5 mm) and exposed to fluorescent light for 24 hours. A pale yellow supernatant liguid with dark crystals suspended within it resulted. The crystals were not soluble in d_6-benzene but were dissolved in $CDCl_3$ (0.5 cm^3) and the ^1H NMR spectrum showed no signal in the hydride region scanned (δ 0 to -25) and the downfield signals were very similar to those of the free ligand both in pattern and chemical shift. Too little material was available for proper characterization and no further work was carried out on this system.

^1H NMR experiment to deuteriate [Os_3(μ-H)(μ-$Ph_3C_5H_3$)$(CO)_{10}$] 1

A red solution of [Os_3(μ-H)(μ-$Ph_3C_5H_3$)$(CO)_{10}$] **1** (0.100 g, 8.5 x 10^{-5} mol) in $CDCl_3$ (0.75 cm^3) was analysed by examination of the ^1H NMR (400 MHz) spectrum and was found to be a mixture of the isomers **1a** and **1b** after it had been standing for 4 hours at room temperature. Deuteriomethanol (0.0765 cm^3) was added to the solution and a further ^1H NMR spectrum was taken immediately which showed a broadening of all signals. However, the two characteristic hydride signals were clearly visible (δ -15.34 and - 15.59). The solution was allowed to stand at room temperature for 30 minutes and the ^1H NMR was then repeated. Two sets of triplets were present between δ 10.0 and 12.2 with no change in the hydride region. After 24 hours at room temperature there was no discernable change in the spectrum.

Trifluoroacetic acid (4 drops from a Pasteur pipette) was then added to the solution and mixed well. The solution was allowed to stand for a further 18 hours at room temperature. An 1H NMR spectrum indicated the broadening of the triplet signals and both hydride signals had disappeared. Loss of the hydride signal would be consistent with deuteriation at the hydride site but very little material was available so no further work was undertaken.

Preparation of triphenyarsoniumcyclopentadienylide[31]

Cyclopentadiene (10 g) was dissolved in chloroform (33 cm^3) to give a colourless solution which was cooled in an ice/salt bath. Bromine (23.5 g, 7.5 cm^3) in chloroform (30 cm^3) was added dropwise to the stirred cyclopentadiene solution over 1 hour and the temperature of the mixture was maintained at between -25 and -30 °C. After the addition of the bromine the solution of the disubstituted cyclopentadiene was a clear yellow/orange colour and it was stored in a deep freeze overnight. Triphenylarsine (8.46 g) was dissolved in chloroform (10 cm^3) and nitromethane (50 cm^3) was added to give a faintly pink solution. The previously prepared orange/yellow dibrominated cyclopentadiene solution (25 cm^3) was added to the triphenylarsine solution and the mixture was stirred at room temperature under a nitrogen atmosphere for 10 days. The solution was colourless immediately on mixing but after 30 minutes it turned green and after 12 hours the solution was black. The solvent was removed under reduced pressure and the resulting oil was extracted into warm water (distilled, 3 x 25 cm^3 aliquots). The combined extracts were cooled in an ice bath and then made alkaline by the addition of sodium hydroxide (5M, 100 cm^3). A pale yellow precipitate formed which changed colour to rust when it was being filtered under gravity. The precipitate was washed with distilled water and dried in a vacuum desiccator. It was then suspended in petroleum ether (distilled, b.p. < 40 °C) and filtered again which resulted in a terracotta powder when air dried.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with triphenylarsoniumcyclopentadienylide

To a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.0999 g, 1.071 x 10^{-4} mol) in dichloromethane (5 cm^3) was added a claret solution of $Ph_3AsC_5H_4$ (0.0396 g, 1.069 x 10^{-4} mol) in dichloromethane (5 cm^3). The solutions were swirled to mix and allowed to stand at room temperature for 30 minutes when the solution was a clear reddish-tan colour. An infrared speactrum was taken after 30 minutes and again an hour after initial mixing to check that any reaction was complete. The solvent was removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and a layer of n-heptane was floated on top of the solution. After three days standing at room temperature two clusters of reddish-claret crystals in a claret coloured oil were visible. The crystals were removed and dissolved in dichloromethane (2 cm^3) and chromatographed (eluent, dichloromethane:petroleum ether (b.p. < 40 °C) 20:80 v/v). One major yellow band was extracted from the silica into dichloromethane. Three very minor yellow bands, one minor peach band and one minor pink band were also extracted into dichloromethane but contained only minute quantities of material and thus were not analysed. The major yellow band was dried under vacuum and recrystallization attempted from a dichloromethane/heptane mixture. (Found C, 38.25, H, 1.94% $C_{33}H_{19}O_{10}As$ requires C, 38.6, H, 2.1) Unfortunately the material showed no hydride signal in the ^1H NMR spectrum and no coupled hydrogen signals which would be expected for the cyclopentadiene moiety although these were very clear in the free ligand and in the phosphorus analogue. The product was finally identified as $[Os_3(Ph_3As)_2(CO)_{10}]$ by comparison with those reported.[46]

Preparation of Triphenylphosphoniumfluorenylide

A white solution of triphenylphosphine (3.211 g, 1.2242 x 10^{-2} mol) in nitromethane (60 cm^3) was added in aliquots (4 cm^3) over a period of an hour to a yellow solution of 9-bromofluorene (3.00 g, 1.2239 x 10^{-2} mol) in nitromethane (40 cm^3). The reaction mixture was cooled in a water bath as necessary and the resulting yellow solution was alowed to stand at room temperature for 2 hours. A white, powdery precipitate formed which was filtered under gravity, washed with nitromethane (3 x 5 cm^3 aliquots) and air dried. Some of the white bromide (1.5410 g) was dissolved in boiling alcohol (75 cm^3) and undissolved bromide filtered off. The resulting saturated solution was made alkaline by the addition of ammonium hydroxide (4 cm^3). Upon addition of the base, the solution turned bright yellow immediately and on cooling in an ice-bath a heavy yellow precipitate formed. This was filtered off under vacuum, dried and recrystallized from boiling alcohol to give bright yellow, sparking microcrystals. (Found C, 83.6; H, 5.0% $C_{31}H_{23}P$ requires C, 87.3; H, 5.4%)

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with triphenylphosphoniumfluorenylide

A gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.0984 g, 1.055 x 10^{-4} mol) in dichloromethane (25 cm^3) and bright yellow triphenylphosphoniumfluorenylide (0.045 g, 1.055 x 10^{-4} mol) was allowed to stand in the dark at room temperature for 48 hours. The supernatant liquid was cloudy and buff coloured with a dirty-looking precipitate at the bottom of the flask. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent; dichloromethane:petrolem ether (distilled, b.p. < 40 °C) 3:7

v/v) to give one slow-moving yellow band and three fast-moving yellow bands which together represented most of the material present. These were extracted into dichloromethane and the three fast-moving bands were characterized as $[Os_3(CO)_{10}(MeCN)_2]$ and free ligand from ^1H NMR and infrared spectra. The slow-moving band had no hydride signal in the ^1H NMR spectrum and was not unambiguously identified as very little material was available.

Preparation of triphenylarsoniumfluorenylide

A solution of triphenylarsine (6.250 g, 2.0264 x 10^{-2} mol) and 9-bromofluorene (5.0024 g, 2.0408 x 10^{-2} mol) in nitromethane (100 cm^3) was warmed on a steam bath for one hour. The solvent was removed under reduced pressure and analar acetone (100 cm^3) was added to give a colourless precipitate of triphenylfluorenylarsonium bromide (2.8731 g, 5.2204 x 10^{-3} mol). The precipitate was filtered off under gravity, washed in acetone and air dried. (Found C, 65.8, H, 4.5; Br, 14.3% $C_{31}H_{24}AsBr$ requires C, 67.5; H, 4.4; Br, 14.5%)

To a stirred solution of colourless crystals of triphenylfluorenylarsonium bromide (2.8731 g, 5.2204 x 10^{-3} mol) in absolute ethanol (25 cm^3) was added sodium hydroxide (2M, 8 x 0.5 cm^3 aliquots). A copious yellow precipitate formed which was filted under vacuum, washed with absolute alcohol and air dried. The triphenylarsoniumfluorenylide was recrystallized from hot heptane as bright yellow microcrystals. (Found C, 77.4; H, 5.2% $C_{31}H_{23}As$ requires C, 79.1, H, 5.0%)

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with triphenylarsoniumfluorenylide

A gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.036 g, 3.86 x 10^{-5} mol) in dichloromethane (10 cm^{-1}) was added to a bright yellow solution of triphenylarsoniumfluorenylide (0.023 g, 4.18 x 10^{-5} mol) in dichloromethane (10 cm^3). The solutions were mixed and there was an immediate colour change to tawny brown-gold. The solution was then allowed to stand at room temperature for 48 hours when the solution was found to have changed colour to very dark brown. The solvent was removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and chromatographed (eluent; dichloromethane:petroleum ether (b.p. < 40 °C) 15:85 v/v) to give two yellow bands with the bulk of the dark brown material irreverisbly adsorbed onto the base line. The two yellow bands were identified as the starting materials. More polar eluents did not remove the material from the baseline but resulted in smearing up the plate and no further work was carried out on the system.

Reaction of $[Ru_3(CO)_{12}]$ with triphenylarsoniumfluorenylide

Bright orange crystals of $[Ru_3(CO)_{12}]$ (0.114 g, 1.81×10^{-4} mol) were dissolved in hot dichloromethane (15 cm^3) and a solution of triphenylarsoniumfluorenylide (0.0866 g, 1.84×10^{-4} mol) in dichloromethane (10 cm^3) was added to give a clear orange/yellow solution. The flask was wrapped in foil and the solution was left to stand at room temperature for 36 hours when the solution was a red/orange colour. After 4 days the solution was a claret colour. The solvent was removed under reduced pressure and the residue redissolved in $CDCl_3$ and the ^1H NMR spectrum was taken which showed that there were no hydride signals present. The infrared spectrum of the material was also taken:

	$\nu(CO)/cm^{-1}$
$[Ru_3(CO)_{12}]$	2058vs 2029s 2009s
[Product]	2096w 2057vs 2045sh 2026vs 2011s

The product was identified as $[Ru_3(Ph_3As)_2(CO)_{10}]$. [46]

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CHAPTER 4

The reactions of 5-membered ring nitrogen heterocycles with triosmium and triruthenium clusters

CHAPTER 4

THE REACTIONS OF $[Os_3(CO)_{10}(MeCN)_2]$ WITH NITROGEN HETEROCYCLES

4.1 Introduction

There are several modes of coordination of nitrogen heterocycles to triosmium clusters. Compounds of the formula $[Os_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}]$ represent a common type of cluster derivative [1] and may be prepared from a variety of species (X-H) in reactions with $[Os_3(CO)_{10}(MeCN)_2]$ which is commonly used as a source of the fragment $Os_3(CO)_{10}$.[2,3] Substituted heterocycles can give coordination to the ring substituent and/or to the heterocyclic functionality depending on the ligand. Whereas with mononuclear complexes simple coordination of nitrogen heterocycles dominates their chemistry, clusters have been shown to have much more varied reactivity, in particular C-H bond cleavage may occur at the heterocyclic ring or at a ring substituent.

In general, amines are expected to behave as Lewis bases and therefore the site of initial attack would be through the nitrogen lone pair of electrons at suitable sites in the cluster as would be expected for reaction with mononuclear compounds.

4.1.1 Initial attack at metal carbonyl clusters

(i) Attack through nitrogen at metal atoms

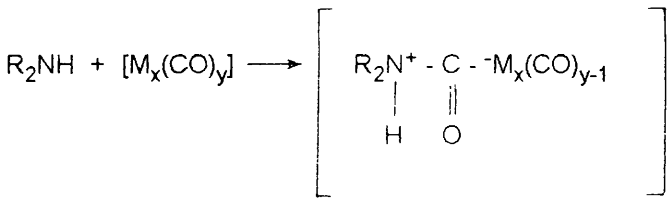
Commonly simple metal carbonyls react with donor ligands by dissociative mechanisms where the metal centre loses a carbonyl ligand leaving a vacant coordination site for the donor ligand to occupy:

$$[M_x(CO)_y] \xrightarrow{-CO} [M_x(CO)_{y-1}] \xrightarrow{+L} [M_x(CO)_{y-1}L]$$

The labile acetonitrile ligands in $[Os_3(CO)_{10}(MeCN)_2]$ are lost first, thus allowing coordination to the metal by any good donor ligand. Without such ligands that are easily lost, associative processes may become important; recently $[Ru_6C(CO)_{17}]$ has been shown to undergo totally associative processes.[4]

(ii) Attack of amine at carbonyl ligands

Dodecacarbonyltriosmium does not have any easily displaced ligands and primary or secondary amines react at carbon as outlined below:



$$R_2NH + [M_x(CO)_y] \longrightarrow \left[\underset{\displaystyle H}{\underset{|}{R_2N^+}} - \underset{\displaystyle O}{\underset{\|}{C}} - {}^-M_x(CO)_{y-1} \right]$$

The final products are of the type $[Os_3H(\mu\text{-}R_2NCO)(CO)_{10}]$ Heterocycles with both basic N-atoms and N-H bonds would be expected to behave in this way. However, it has been found that when the heterocycle contains a basic nitrogen atom, this is usually coordinated to an osmium atom in the cluster on reaction with $[Os_3(CO)_{10}(MeCN)_2]$. A non-basic nitrogen atom frequently does not coordinate and certainly not in the primary coordination step. It is assumed that the aromaticity of the heterocyclic rings would be retained in the derivative, that is, that the coordination of the *imino* nitrogen **(2)** would be preferred over coordination of the *amino* nitrogen **(1)**.[5] (Figure 4.1)

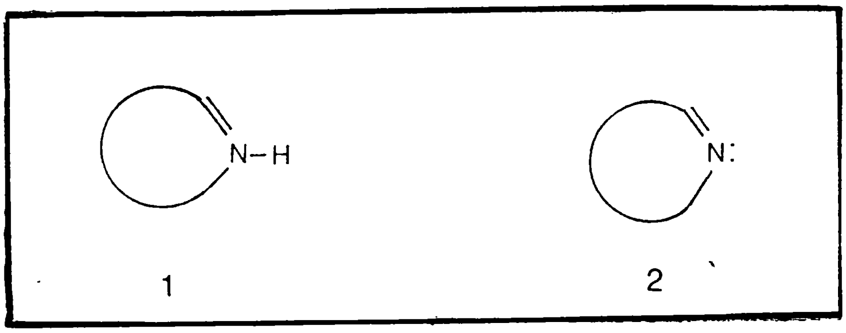


Figure 4.1 General representation of an *amino*, **1**, and an *imino*, **2**, nitrogen atom

4.1.1 (iii) Attack through carbon at metal atoms

For example, pyridine (C_5H_5N) coordinates initially through the donor N-atom whereas pyrrole (C_4H_4NH) apparently does not. In both cases there is a subsequent C-H cleavage to give the 2-pyridyl complex [$Os_3H(C_5H_4N)(CO)_{10}$] and the pyrrolyl complex [$Os_3H(C_4H_3NH)(CO)_{10}$] respectively. In the latter case the N-H group is essentially a bystander and the ligand is purely C-bonded to osmium. These modes of reactivity relate, as one would expect, to the basicity of the nitrogen atoms, pyridine being much more basic than pyrrole.

4.1.2 Carbon-Hydrogen Bond Cleavage: Pyridine and related ligands

Reactions where a C-H bond is cleaved are of particular interest. A good example of this is the example just given, that of the formation of the 2-pyridyl compound [$Os_3H(\mu\text{-}NC_5H_4)(CO)_{10}$] from pyridine and the triosmium cluster.[2,3,6] This reaction and its products serve as a useful model for the reactions of many other similar heterocyclic compounds.[7,8] The reaction of [$Os_3(CO)_{10}(MeCN)_2$] with imidazole [9] and several other heterocycles and their derviatives [9,10] (L-H) proceed analogously to provide compounds of the general type [$Os_3H(\mu\text{-}L)(CO)_{10}$]. Interaction of the heterocycles provides compounds that are readily formulated as metallated derivatives and isomeric compounds are found in cases where non-equivalent C-H bonds may be cleaved. An interesting range of bridging ligands has been formed in this way and the chemistry of these ligands in clusters is generally very different from that found in mononuclear compounds. Indeed, this is a dominant feature of the chemistry and the main reason for examining the heterocyclic ligands.

Sometimes the heterocyclic ligand may be incorporated via a ring substituent. For example, when 2-formylpyrrole is reacted with $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$, oxidative addition of the aldehyde function occurs to give the acyl cluster $[\mathrm{Os_3H}(\overline{\mathrm{NHCH{=}CHCH{=}C}}\mathrm{CO})(\mathrm{CO})_{10}]$ which may be decarbonylated subsequently to give $[\mathrm{Os_3H_2}(\overline{\mathrm{HNCH{=}CHC{=}C}})(\mathrm{CO})_9]$ [11] in which the pyrrole ligand is bonded to osmium through two adjacent carbon atoms. [12,13] Further reaction gives a C-N bonded ligand as shown in Scheme 4.1. Up to this last step the NH group is not involved directly with the metal atoms.

In this current work, nitrogen heterocycles react with the triosmium cluster by a process of oxidative addition, either by C-H cleavage or by C-H activation. Many examples are known and a few are outlined in the next section.

4.1.3 C-H bond activation: pyrrole and related ligands

Generally C-H bond interaction results in a vertical addition of the ligand:

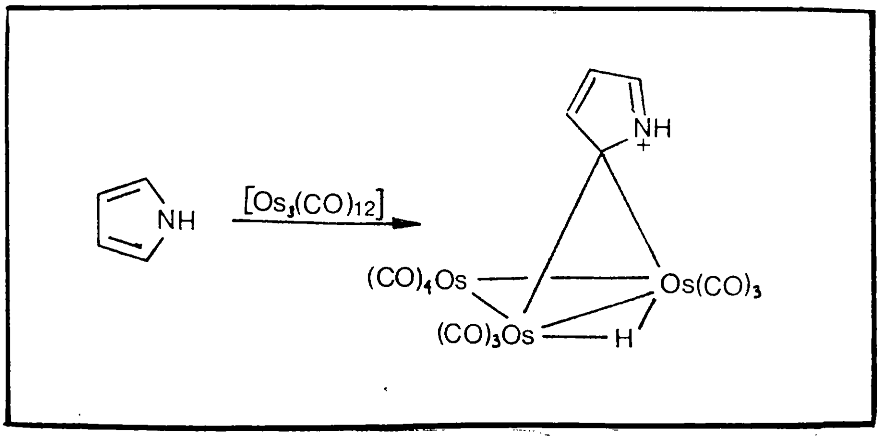
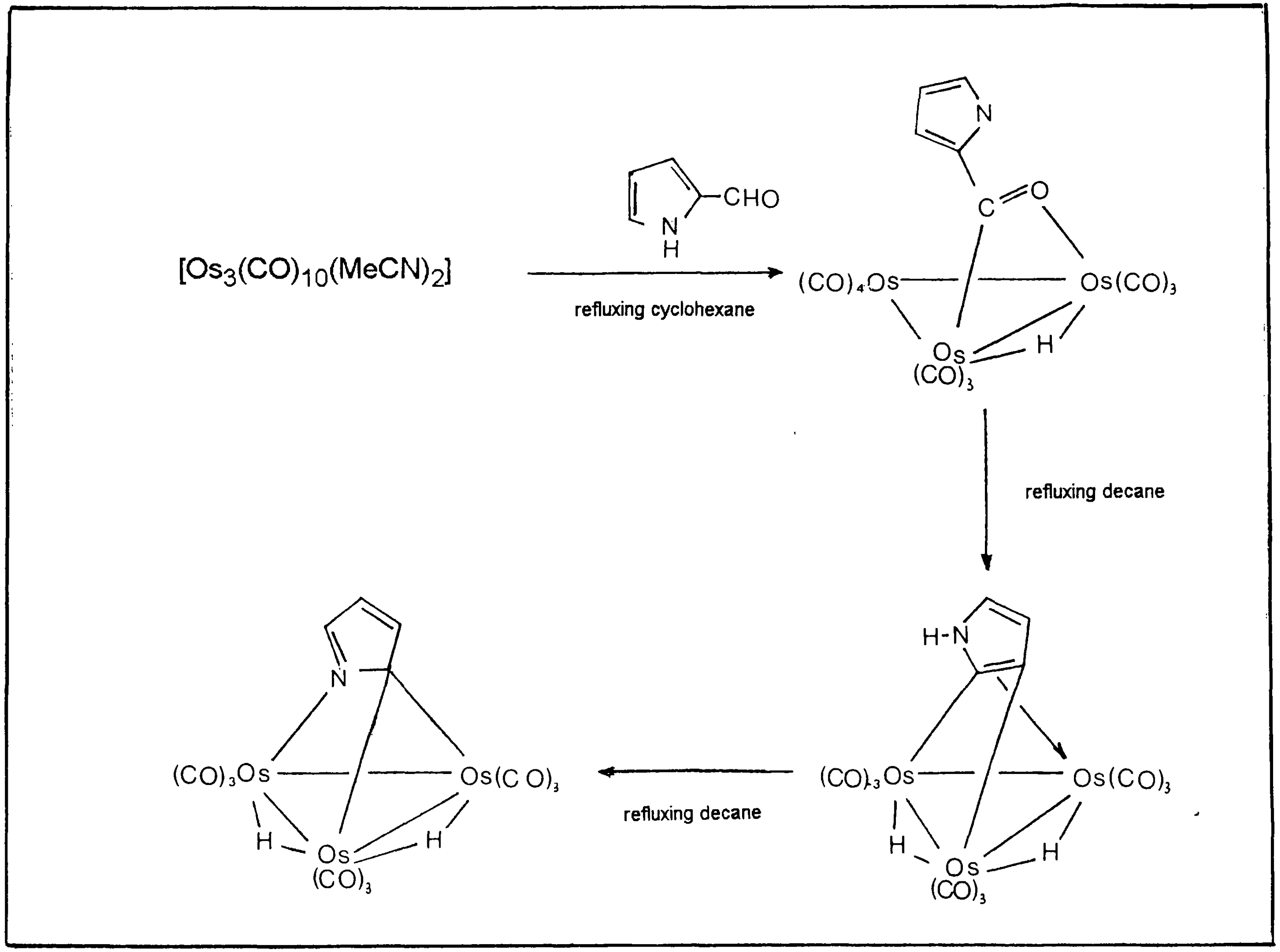


Figure 4.2 The vertical addition of the pyrrole ligand to $[\mathrm{Os_3(CO)_{12}}]$



Scheme 4.1 Reaction scheme of 2-formylpyrrole with $[Os_3(CO)_{10}(MeCN)_2]$

This is found when pyrrole is reacted with $[Os_3(CO)_{12}]$ at high temperature to give a complex in which the nitrogen atom is not coordinated. [9] In this case the lone pair on the nitrogen atom is part of the 6π electron aromatic (4n + 2) set so nitrogen coordination would be unlikely. The reaction is related to similar oxidative additions of furan [14] and thiophene [15] in which all the chemistry occurs at carbon to give μ,η^2-vinyl type ligands:

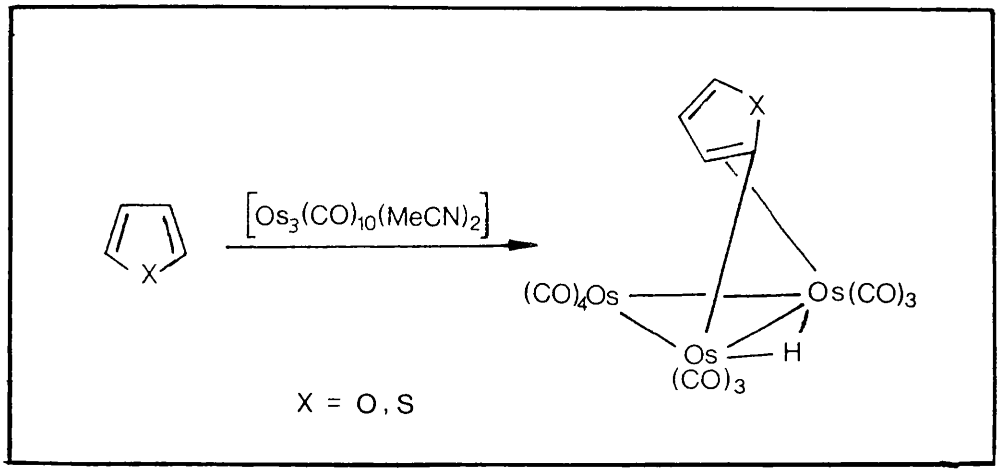


Figure 4.3 The addition of furan and thiophene to $[Os_3(CO)_{12}]$

A proposed mechanism for the initial oxidative addition reaction is shown in Figure 4.4. It is almost certain that there is an initial η^2 coordination through a C=C bond since simple cyclic alkenes behave similarly.

As stated, this reaction is as found for simple cyclic alkenes and the heteroatom is purely incidental. In the case where X = NH the ligand adopts the vertical mode of bonding as shown above with the ligand coordinated through only one carbon atom.

Decarbonylation leads to further C - H bond activation and the formation of the μ_3-ligand system shown in Figure 4.5.

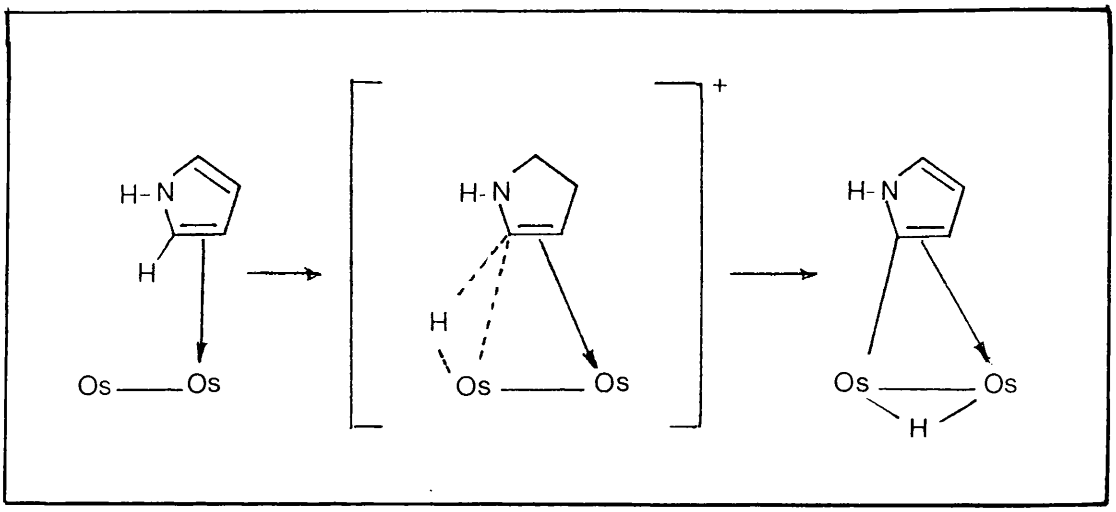


Figure 4.4 Proposed mechanism for the coordination of pyrrole

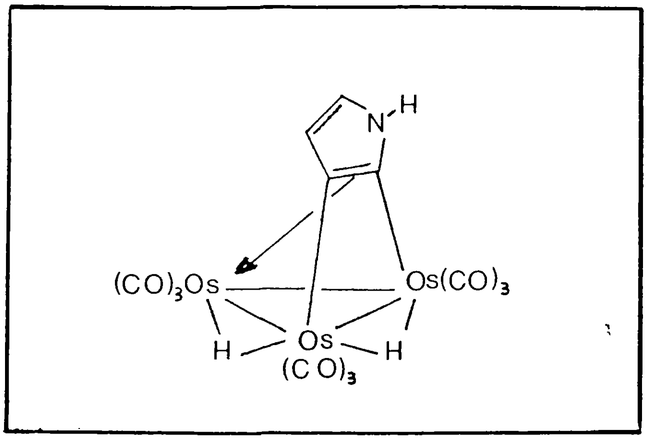


Figure 4.5

However, methylpyrrole [2] gives different products depending on the reaction conditions as shown in Figure 4.6

In the second case the heterocycle is a 4-electron donor [16] and relates to alkyne [17-19] and aryne [17,20,21] ligands. It is interesting that the nitrogen-bound complex is not found:

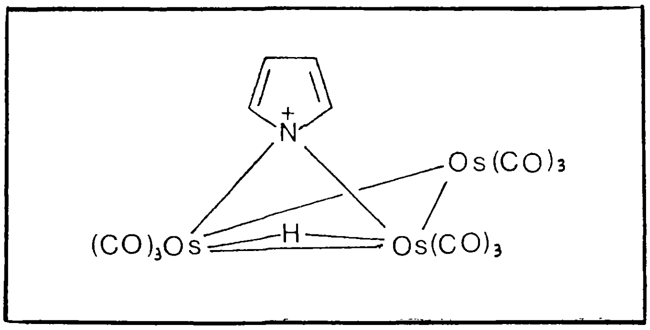


Figure 4.7

In this case the nitrogen atom would have to be tetrahedral which would require some loss of π-electron delocalization and this finding lends weight to the assumption that the aromaticity is preserved in these complexes.

An interesting aspect of cluster chemistry is the stabilization of unstable tautomers.

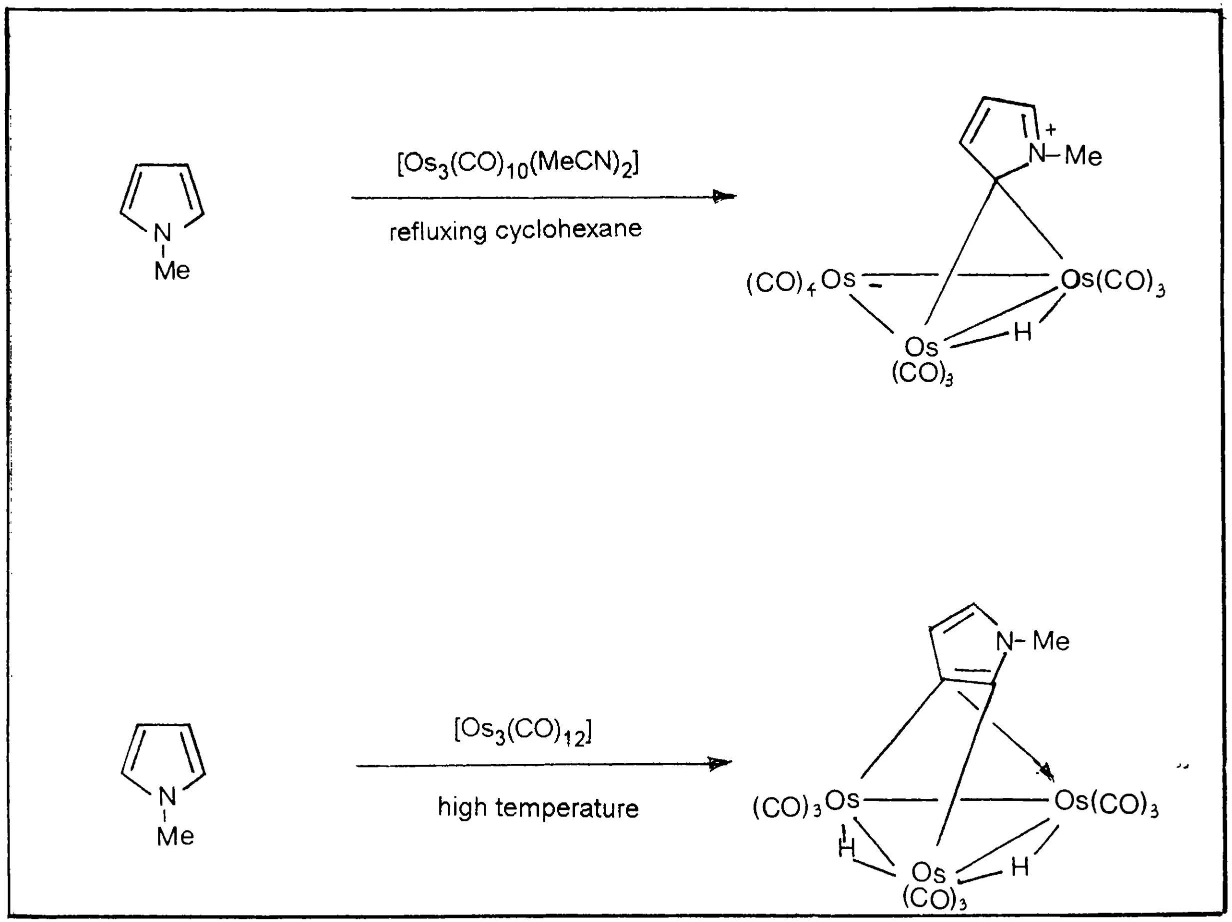


Figure 4.6 The products of reaction of methyl pyrrole at different temperatures

For example, indole has two less favourble isomeric forms both containing donor N-atoms:

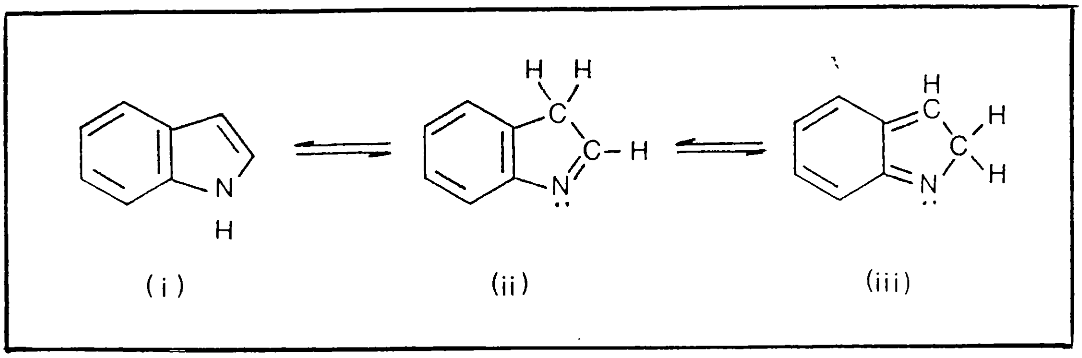


Figure 4.8 The tautomers of indole

The tautomers are derived by transferring a hydrogen atom from nitrogen to carbon. Tautomer (iii) is very unfavourable and apparently plays no role in the chemistry of indole. However, in the reaction of indole with $[Os_3(CO)_{12}]$ two products are formed (Figure 4.9). The major product could be derived by reaction of the stable tautomer (i) followed by N-H cleavage and subsequent rearrangement or it could be formed by reaction of the unstable tautomeric form (ii) and the cluster is indeed believed to proceed from *ortho* metallation of (ii) [22] as pyridine is known to react in the same fashion.[6]

The reactions are of the general type shown in Figure 4.10 and occur when the nitrogen atom in the heterocycle is basic and therefore a good donor.

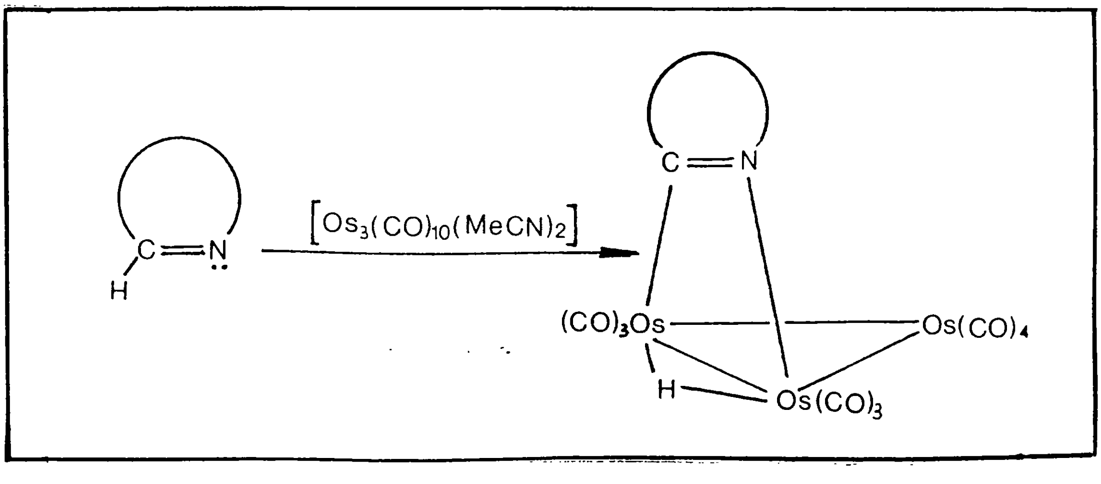


Figure 4.10 General reaction of a basic nitrogen atom with $[Os_3(CO)_{12}]$

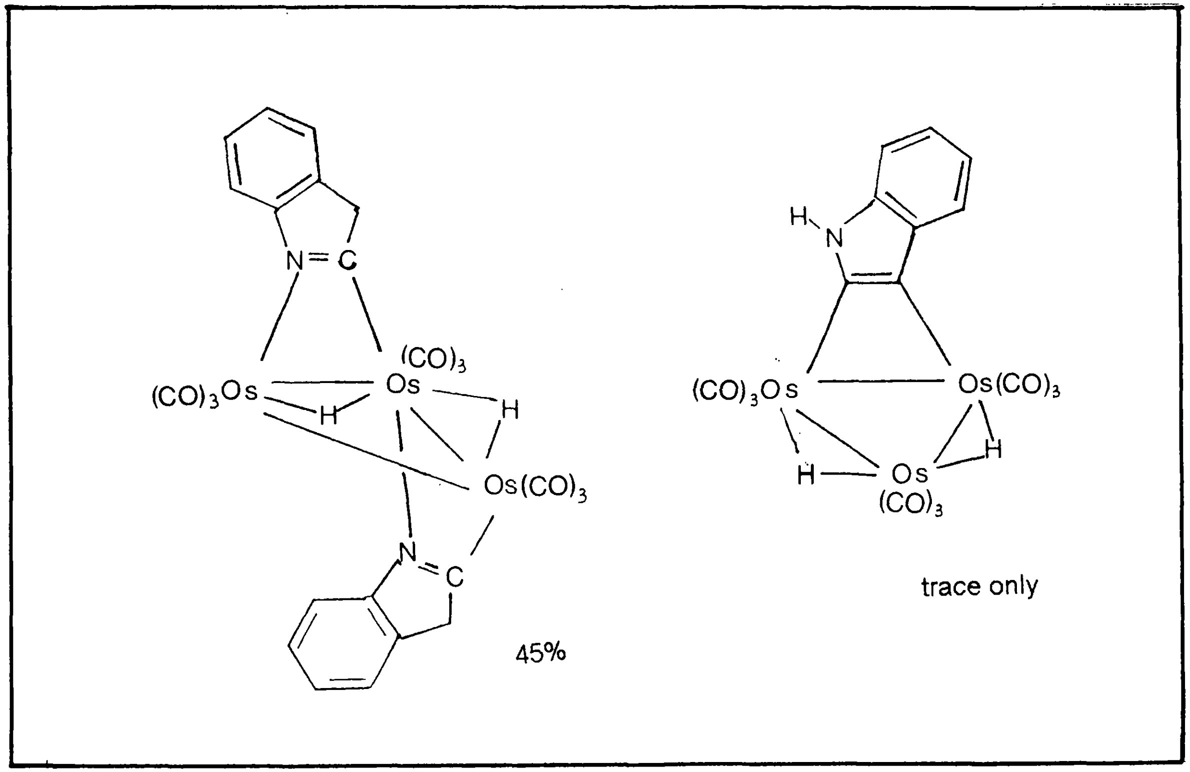


Figure 4.9 The isomeric products of the reaction of indole with $[Os_3(CO)_{12}]$

In diaza- and triazo-heterocycles both non-basic and basic nitrogen atoms may be found in the same heterocycle. Some of these exist as a mixture of tautomers so there is always a possibility of the reaction of minor tautomers.

4.1.4 Diaza-compounds

Examples of monocyclic and bicyclic diaza heterocycles are shown in Figures 4.11 and 4.12

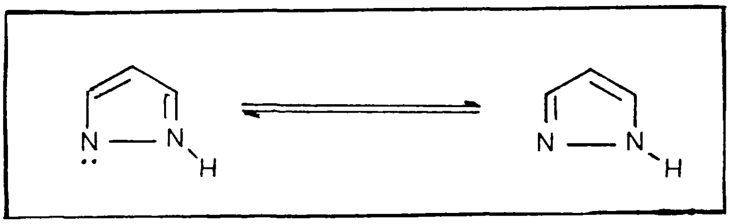


Figure 4.11 A monocyclic diaza heterocycle

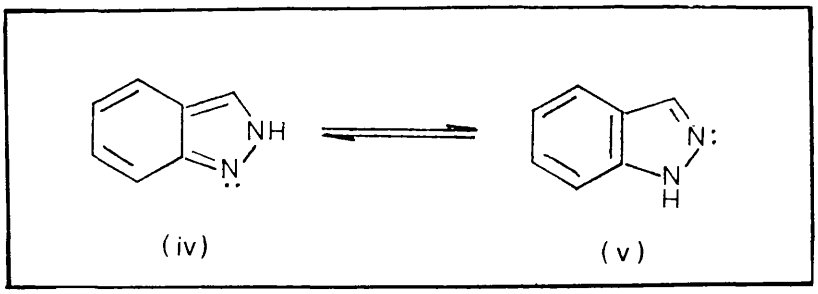


Figure 4.12 A bicyclic diaza heterocycle

In the case of monocyclic diaza-heterocycles there is clearly a donor nitrogen atom for initial coordination but there are two possible sites for subsequent *ortho* metallation as shown in Figure 4.13.

The mole ratio of dominant product to minor product gives a direct measure of the kinetics of C-H versus N-H cleavage. The diaza-monocyclic amine imidazole has one

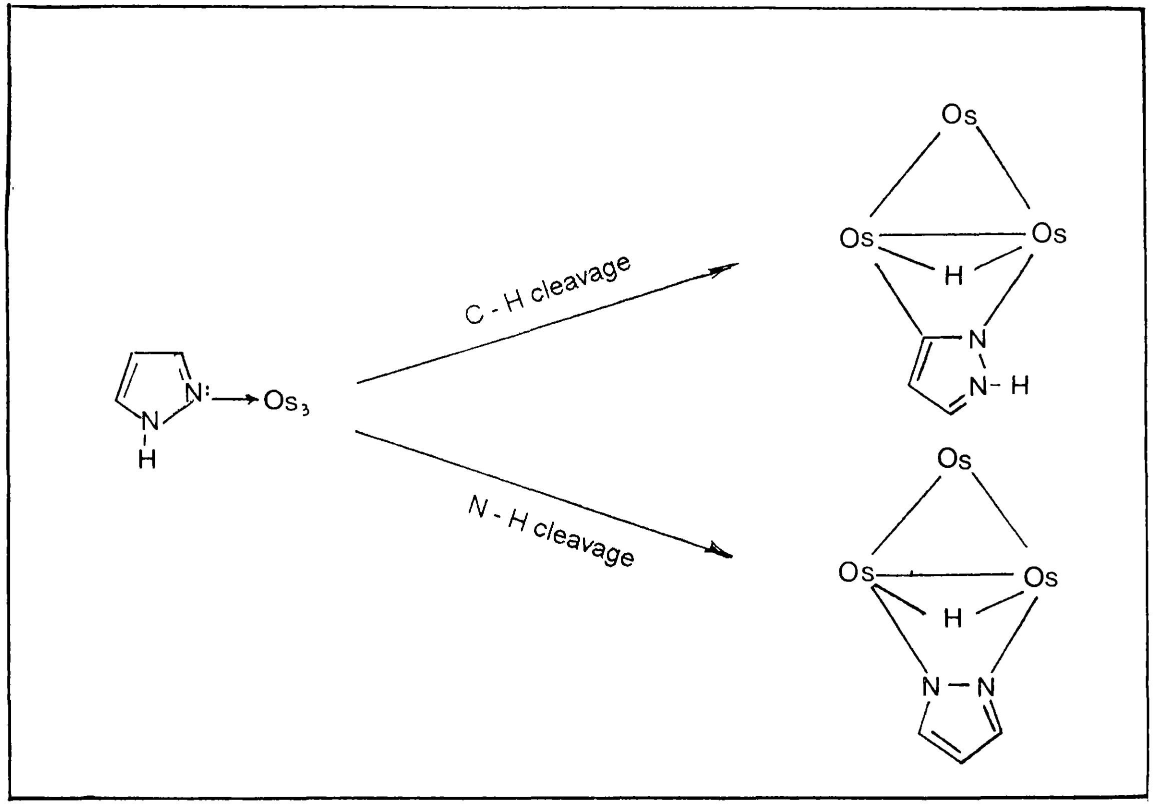


Figure 4.13 Possible sites for *ortho* metallation in monocyclic diaza heterocycles

one basic and one non-basic nitrogen atom and the latter has a lone pair which is not part of the aromatic set. Reaction with $[Os_3(CO)_{10}(MeCN)_2]$ leads to two isomeric clusters [23] which correspond to metallation on either side of the basic nitrogen in the heterocycle as shown in Figure 4.14 .

Bicyclic systems may offer an additional site for metallation as is demonstrated by imidazole later in this chapter. In this case metallation on the other side of the basic nitrogen is precluded by the attached benzene ring so an osmium atom inserts into the next available C-H bond giving the *ortho* metallated product. The possible products are shown in Scheme 4.2.

4.1.5 Triaza-compounds

Although most of the discussion pertaining to mono-and diaza-systems applies also to triaza-systems, the additional nitrogen atom in the triazo-systems does increase the number of isomeric forms which may be produced. In monocyclic triazo-systems three isomeric products are possible as shown in Figure 4.15.

These products arise from N-H cleavage, C-H cleavage or N,N coordination. In bicyclic triazo-systems again several products are predicted and these too arise from the same routes as found in triazo-monocyclic systems. However, as the C-H bond available is attached to the adjoining ring system, an *ortho* metallated product is also found in place of the straightforward C-H cleavage of the monocyclic systems.

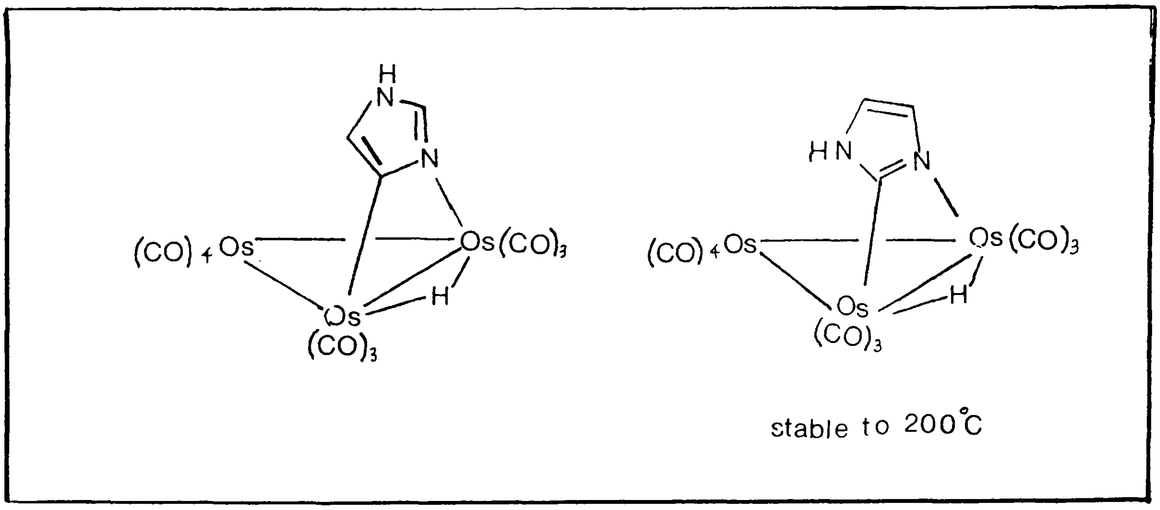
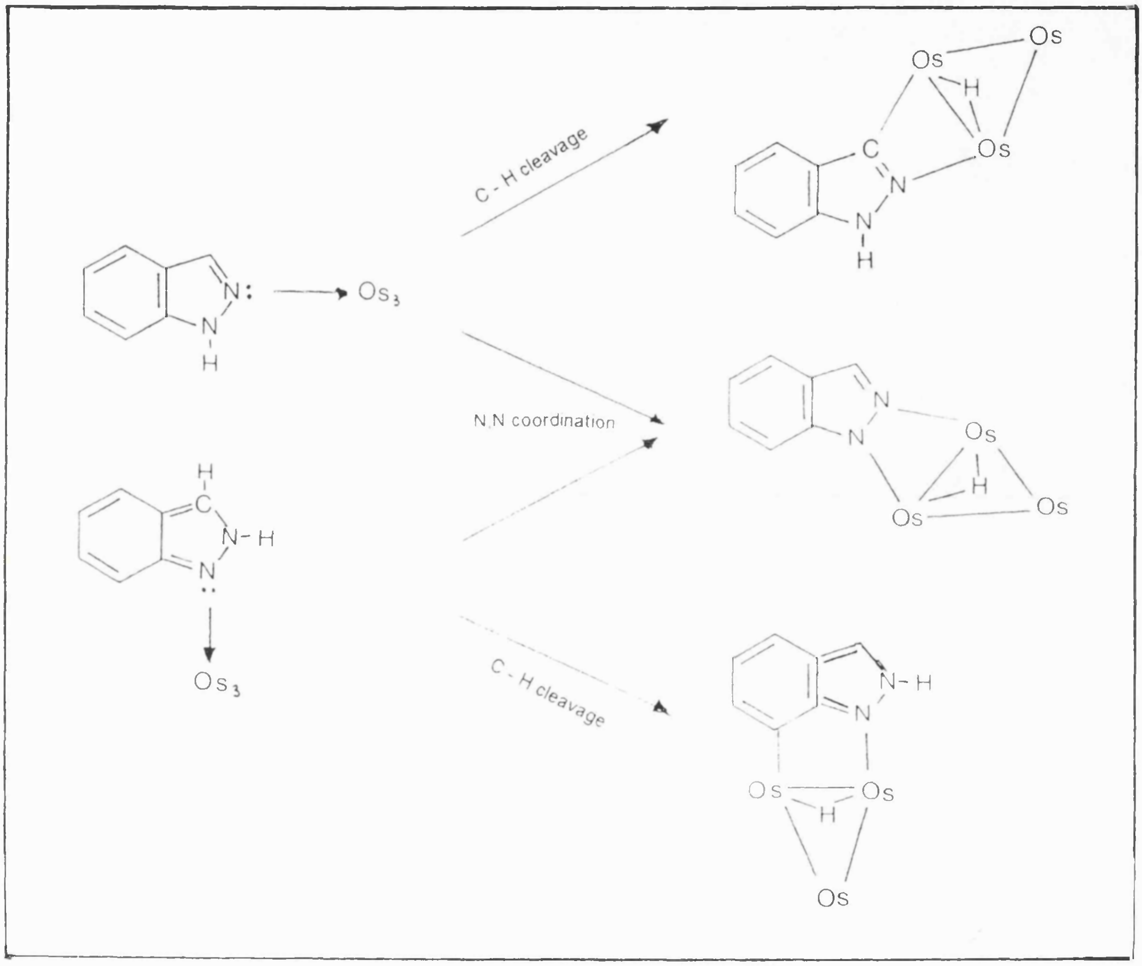


Figure 4.14 The isomeric forms of $[Os_3H(C_3H_3N_2)(CO)_{10}]$ resulting from metallation on either side of the basic nitrogen atom



Scheme 4.2 Reaction paths leading to the possible isomeric forms of $[Os_3H(C_7H_6N_2)(CO)_{10}]$

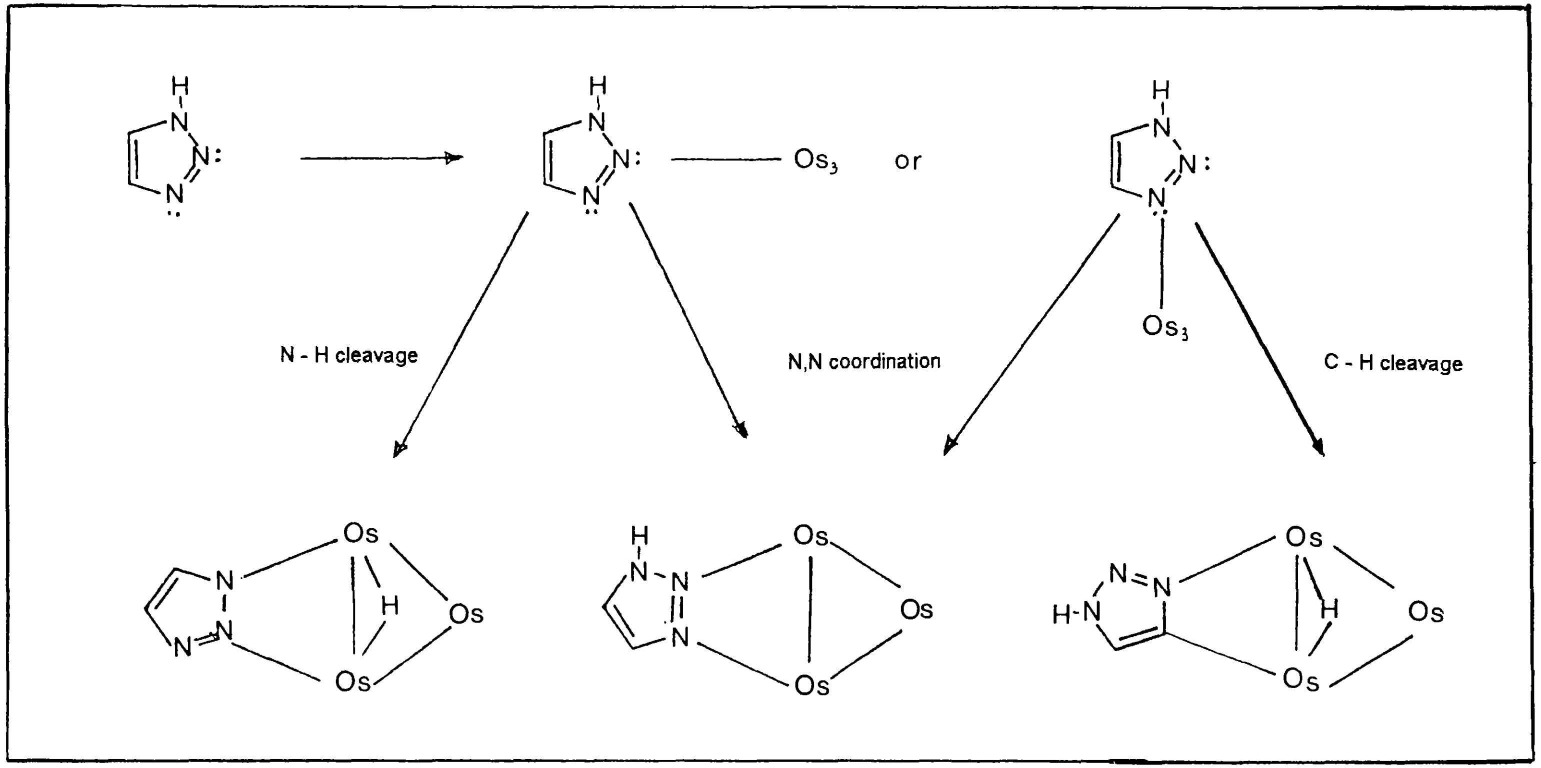


Figure 4.15 Possible sites for the coordination of monocyclic triazo heterocycles

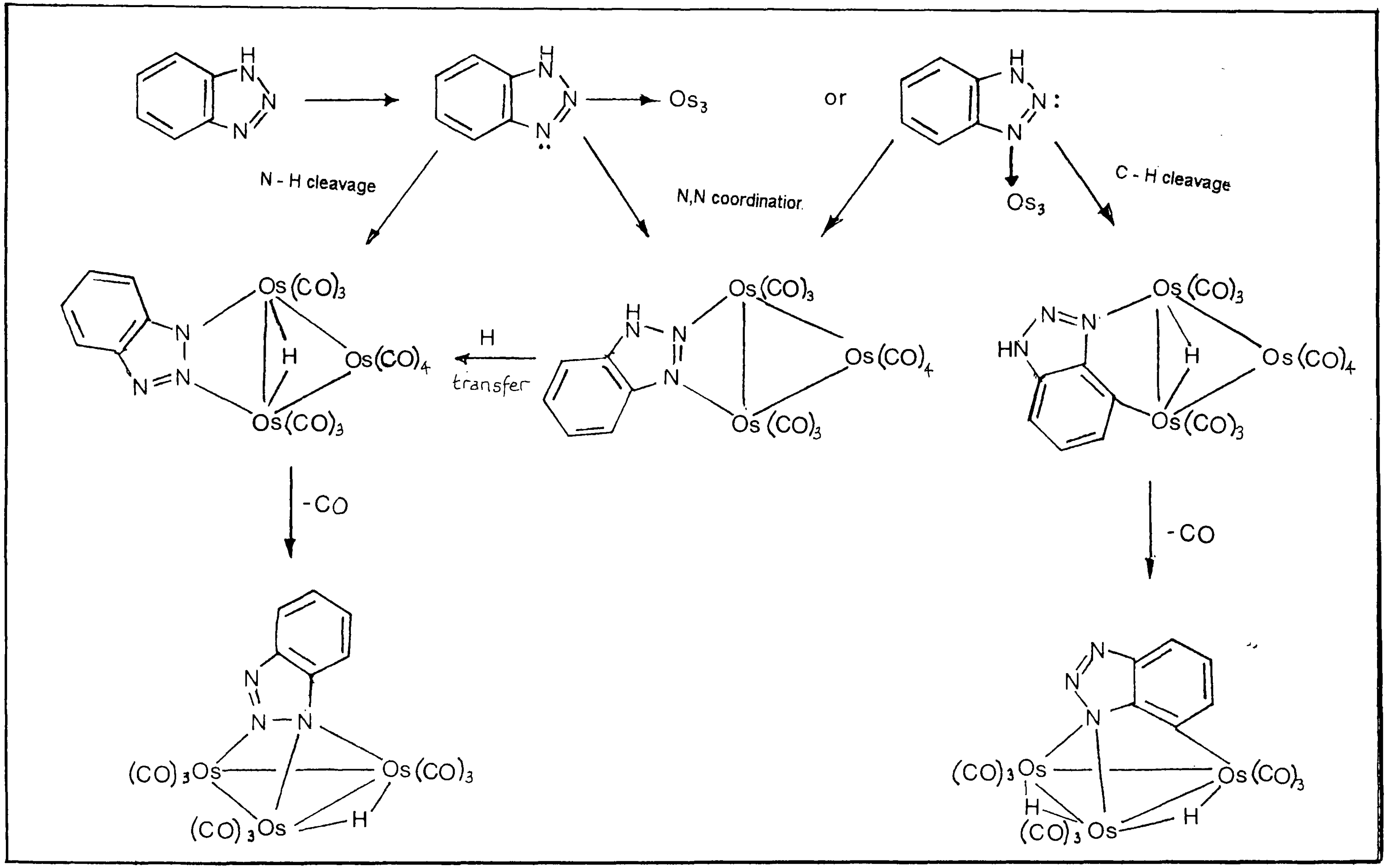


Figure 4.16 Possible products of the coordination of bicyclic triazo heterocycles to a triosmium centre

4.2 RESULTS AND DISCUSSION

4.2.1 Objectives of our work

Although a great deal of work has been carried out using nitrogen donor ligands, including nitrogen heterocycles, with trisomium clusters much of it has been carried out at the high temperatures required for the reactions of [$Os_3(CO)_{12}$]. We felt that it would be interesting to see whether room temperature reactions would lead to the same products in the same yields as we felt that the less vigorous conditions might provide a suitable environment where perhaps less stable intermediates could become important and that this would be reflected in the products obtained. Such products would give a qualitative understanding of the energetics of N-H versus C-H bond cleavage reactions from the mole ratios of the yields obtained.

We also felt that it would be of interest to use a representative sample of a variety of nitrogen heterocycles to establish a pattern of reaction, for example to see whether initial attack of the nitrogen lone pair is invariably the first step.

4.2.2 The reaction of pyrazole and [$Os_3(CO)_{10}(MeCN)_2$]

Shapley and co-workers [9] reacted [$Os_3(CO)_{10}(MeCN)_2$] with pyrazole in refluxing benzene to obtain two major products and when the work was repeated at room temperature in dichloromethane similar results were obtained by ourselves. One major product and one minor product were separated by thin layer chromatography and these were identified from assignments based on the chemical shifts in conjunction with those of the free ligand (Table 4.1).

The pyrazole ligand contains one basic (*imino*) nitrogen atom and one non-basic (*amino*) nitrogen atom so a proposed mechanism for initial attack at the triosmium centre would be as shown in Scheme 4.3. This would lead to the two isomeric products shown in Figure 4.17. At room temperature these two isomers do not interconvert but at 180°C, isomer **2** will convert to isomer **1**.[9]

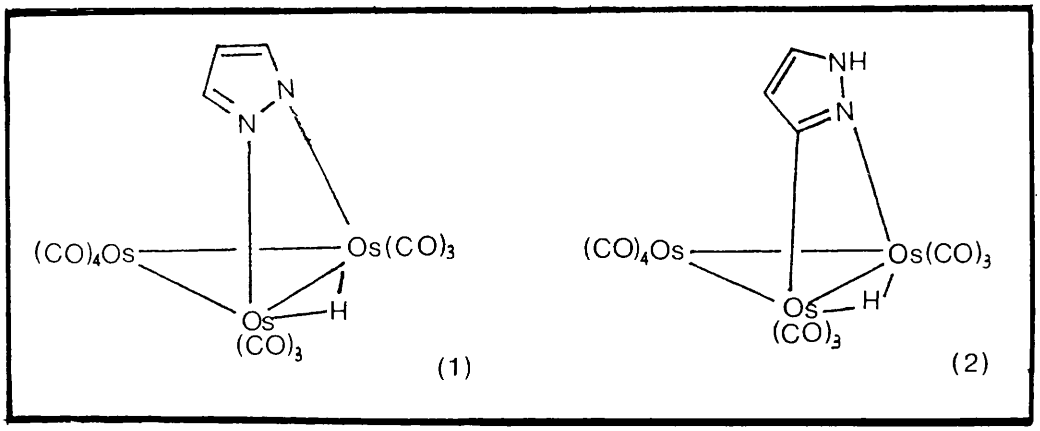
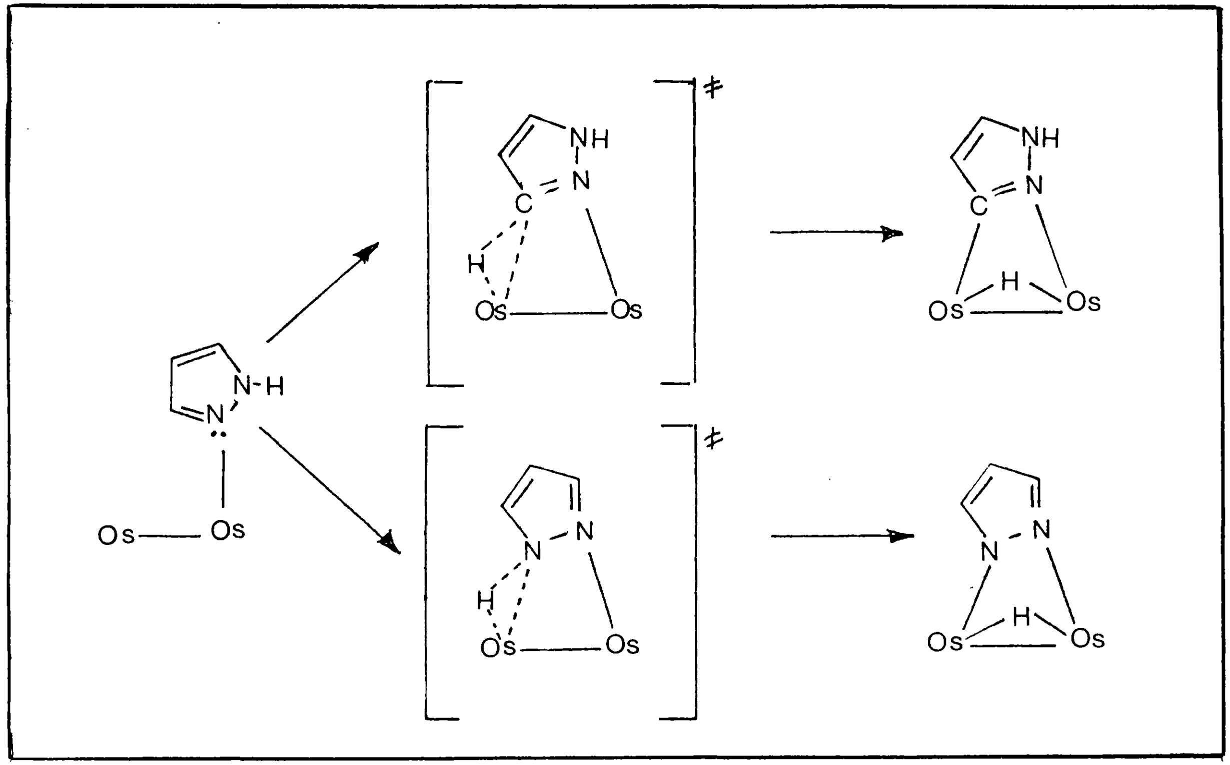


Figure 4.17 The isomeric products of pyrazole and $[Os_3(CO)_{10}(MeCN)_2]$

Isomer **1** was the major product with a mole ratio **1**:**2** = 2:1. Each isomer gave four ^1H NMR signals, one of which corresponded to a hydride ligand. It is possible to assign the other three signals either to three adjacent CH groups or to two CH groups and one NH group. These assignments are based partly on chemical shifts and partly on the greater broadness of the NH signal. The ^1H NMR spectrum for isomer **1** does not indicate the presence of an N-H bond and the compound chromatographed more easily in petroleum ether which is also consistent with the lack of an NH function. However, the ^1H NMR spectrum of isomer **2** indicates that an N-H bond is retained in the product and the material required a much more polar eluent for chromatography. This last is a feature observed in all complexes which retain an N-H bond and it seems possible that the weakly acidic N-H group interacts with the silica surface by H-bonding which thus impedes its progress. A similar phenomenon is observed when comparing analogous N-H and N-CH_3 imidazole derivatives.[9]



Scheme 4.3 Proposed mechanism for initial attack by nitrogen lone pair at a triosmium centre

Shapley found that N-H resonances, when they were observable, were broad and had concentration dependent chemical shifts.[9] This he ascribed to self-associated equilibria; interaction promoting proton exchange between the two nitrogen atoms which equilibrates C(3) and C(5) in pyrazole so that they become indistinguishable (Figure 4.18). This applies only to the free ligand and is not true of the complexed ligand.

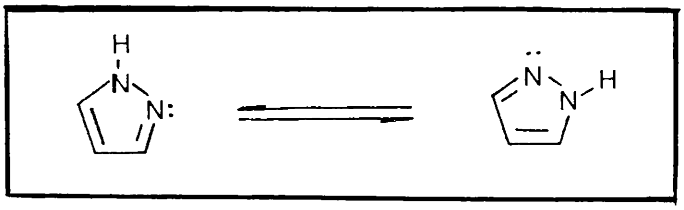


Figure 4.18 The tautomeric forms of pyrazole

The formation of the two isomers of clusters derived from pyrazole does indicate that the *amino* nitrogen atom can play a part in this chemistry and in this particular instance the cleavage of a C-H bond is twice as favourable as cleavage of an N-H bond.

4.2.3 The reaction of indazole with [$Os_3(CO)_{10}(MeCN)_2$]

Pyrazole and indazole bear the same relationship to each other as do imidazole and benzotriazole:

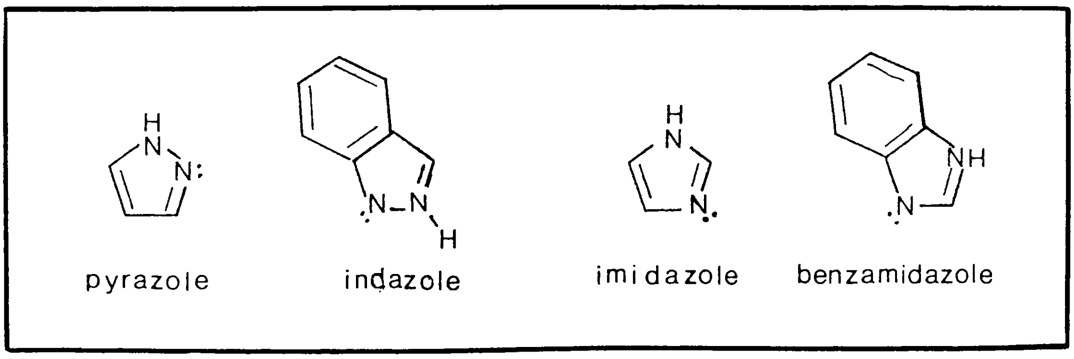


Figure 4.19

Assuming that the initial attack at the triosmium centre is invariably from the nitrogen lone pair it is possible to predict that two isomeric products are possible (isomers **3** and **4**, Figure 4.20). However if this is a false assumption then there is another possibility in which the N-H group is retained and there is metallation of the aromatic ring (isomer **5**, Figure 4.20). If **5** were found, it would be formed from the less stable tautomer (iv) shown below and in Scheme 4.2

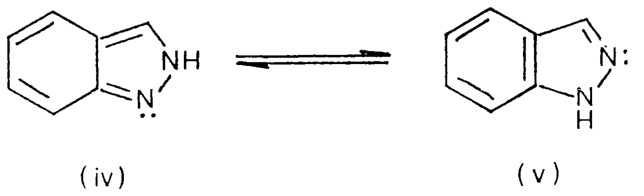


Figure 4.21 The tautomers of indazole

The tautomeric form (iv) is likely to be much less stable than (v) because it can only be considered to be in a "quinoidal" form and is therefore much less likely to lead to *ortho* metallation of the benzene ring which is in direct contrast to the chemistry of benzotriazole. Additionally, the ^{1}H NMR spectrum of the free ligand shows only two singlets for the 5-membered ring, one broad and one sharp consistent with the one tautomeric form (v). Had the structure been that of (iv), these signals would have been doublets through coupling of the hydrogen atoms. Thus it seems most improbable that isomer **5** should be formed as a product of this reaction except by some H-atom transfer rearrangement of the cluster-coordinated ligand.

If the tautomeric form of indazole which is reacting is indeed (v), then initial attack at the triosmium centre by the nitrogen lone pair followed by metallation at one or other of the *ortho* sites would give only the two isomeric products **3** and **4** (Figure 4.20) and the ratio of the mass of each product will give a direct measure of the rates of C-H *versus* N-H cleavage. We indeed found that these were the only

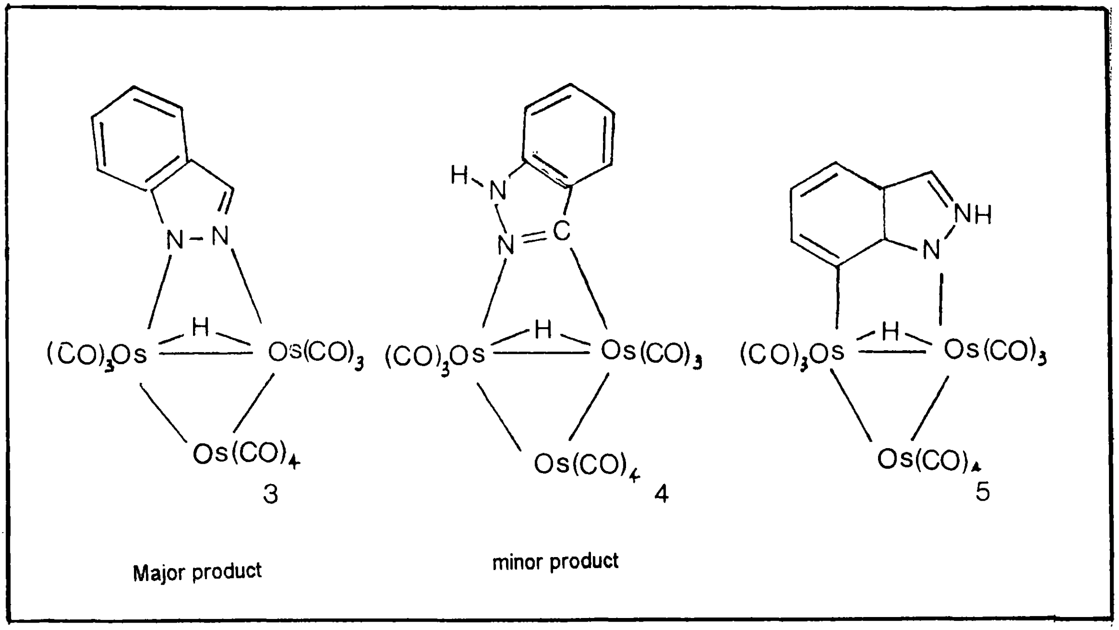


Figure 4.20 The possible products of the reaction of indazole with [$Os_3(CO)_{10}(MeCN)_2$]

products and the actual mole ratio observed is **3**:**4** = 5.1 so N-H cleavage is obviously the preferred route.

Identification of the products was made initially from ^{1}H NMR spectra and by comparison of these with the spectrum of the free ligand. The major isomer **3** showed a C-H signal in the spectrum which is also found in the free ligand and the minor isomer **4** showed a signal at the correct chemical shift for an N-H group. However, the N-H signal in the free ligand is broad and in the coordinated ligand it is sharp, so assignment was made primarily on the basis of chemical shift alone. Some comparison of infrared data of the carbonyl region frequencies of other N,N and C,N bonded species was possible and confirmed the ^{1}H NMR assignments made. There are small but significant differences between ν(CO) data for the two bonding modes which can be used effectively in structure assignment. Further supporting evidence is provided by the results of a chromatographic separation since the minor isomer required dichloromethane as eluent but the major isomer eluted readily in low-boiling petroleum ether, that is the compound with the N-H group elutes more slowly.

Yellow crystals of both isomeric forms were grown from a dichloromethane/heptane mixture and some of these were found to be suitable for analysis by X-ray diffraction so, to confirm our assignment of structure, X-ray diffraction analysis was carried out. Broadly both structures appear to be very similar and confirm that these are isomers **3** and **4** and that structure **5** is not observed. To identify which of the crystals contained isomer **3** and which isomer **4**, it would be necessary to unambiguously distinguish between carbon and nitrogen atoms in the 5-membered rings. Unfortunately, this is rarely possible in the presence of the heavy metal atoms and in the cases described here, the refinement of data was inadequate for this purpose. Accordingly we assigned carbon and nitrogen atom positions on the basis of spectroscopic and additional information described above.

The structure of the yellow crystals of the major product, isomer **3**, was determined by Professor A. J. Deeming in this Department. The crystals are triclinic, a = 8.905(2), b = 15.852(5), c = 16.481(4) Å, α = 86.78(2), β = 79.19(2), γ =76.99(2) °, U =2226(1) $Å^3$ and Z = 4. The structure was solved in space group $P\bar{1}$ and an ORTEP picture is shown in Figure 4.22. Selected bond lengths and angles are given in Table 4.2. The structure was refined to give R = 0.0576 and R' = 0.0589. The crystals of the C,N bonded isomer **4** are also yellow and triclinic, a = 8.841(4), b = 15.740(9), c = 16.630(7) Å, α = 86.02(4), β = 79.79(4), γ = 77.57(4) °, U = 2223(2) $Å^3$, Z = 4. The structure was solved in space group $P\bar{1}$ by Professor A. J. Deeming in this Department and an ORTEP picture is shown in Figure 4.23. Selected bonds and angles are given in Table 4.3. The structure was refined to give R = 0.0596 and R' = 0.0615.

The average bond length of Os-Os in $[Os_3(CO)_{12}]$ has been determined as 2.877(3) A [24] which may be used for comparison of the two isomers of $[Os_3H(C_7H_5N_2)(CO)_{10}]$ and it is also helpful in determining the position of the hydride ligand. In structures **3** and **4** the longest Os-Os bonds are the Os(1) - Os(2) bonds which are 2.959(2) and 2.989(2) Å respectively. The hydride ligand has been positioned along this edge in each case as it is well documented that a single hydrogen atom bridging a metal vector in a triosmium cluster causes an increase in the M-M distance compared to the length of the parent compound $[M_3(CO)_{12}]$ and that this increase is generally greater than 0.1Å.[25] Also, where there are two-atom bridges across Os-Os edges, the M-M bond is likely to be the longest in the cluster (Table 4.4).[26]

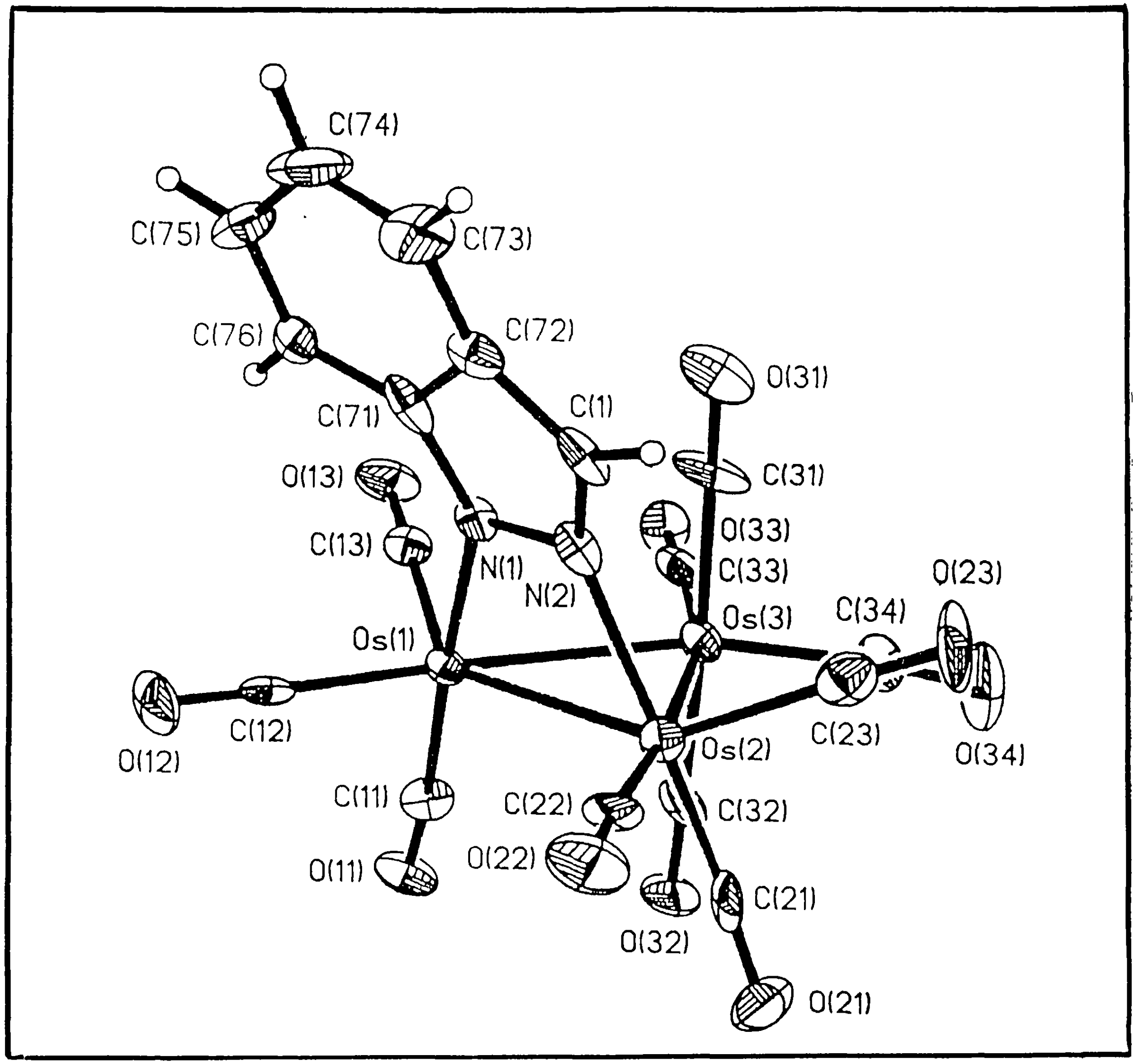


Figure 4.22 ORTEP picture of N,N-bonded $[Os_3H(C_7H_5N_2)(CO)_{10}]$ **3**

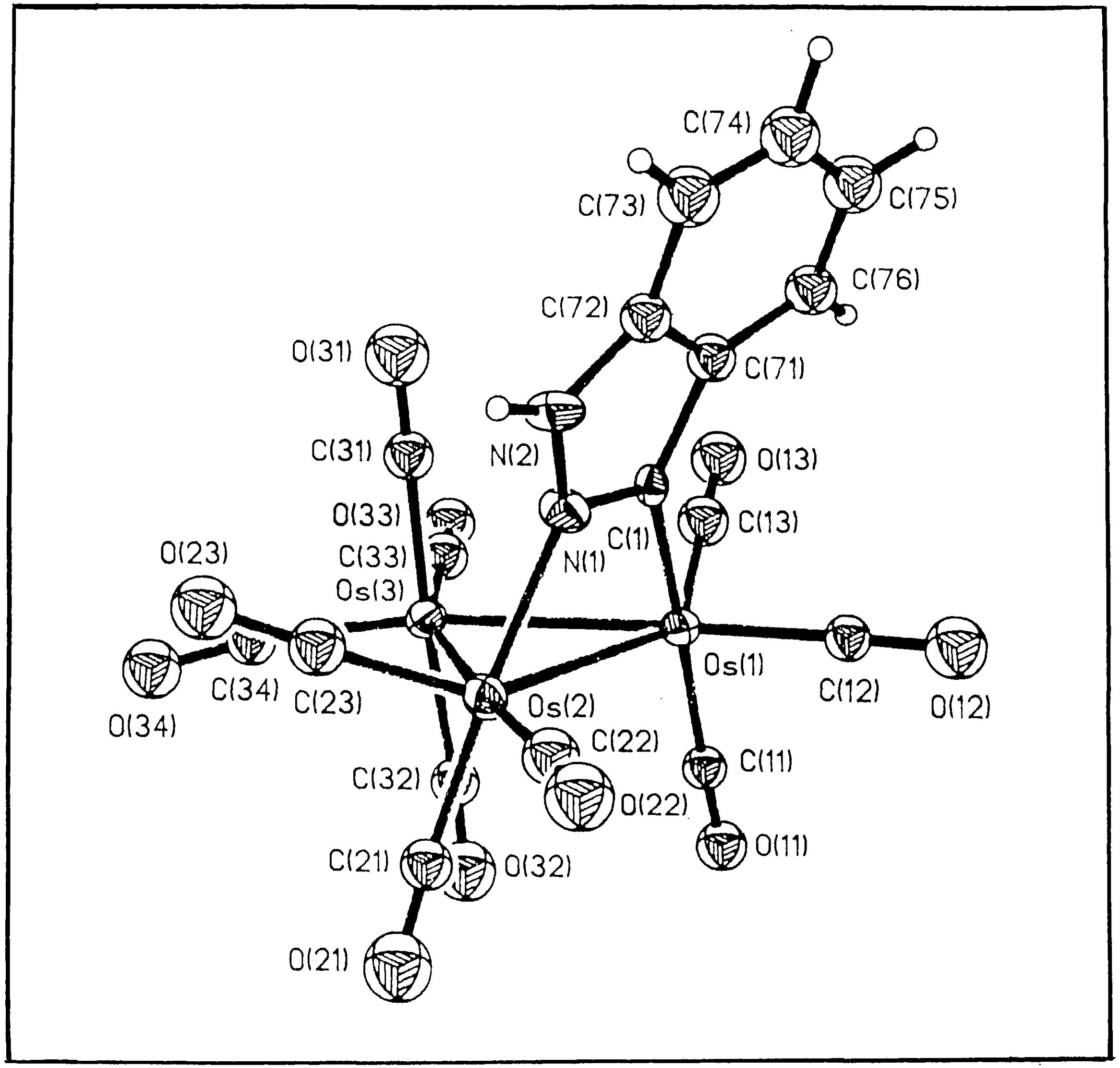


Figure 4.23 ORTEP picture of C,N-bonded $[Os_3H(C_7H_5N_2)(CO)_{10}]$ **4**

4.2.4 Attempted Decarbonylation of [$Os_3H(C_7H_5N_2)(CO)_{10}$]

Thermal decarbonylation of N,N-bonded [$Os_3H(C_6H_4N_2)(CO)_{10}$] **3** was attempted but the material decomposed in each of the solvents used. Treatment with trimethylamine N-oxide in acetonitrile gave a green product which, when heated to reflux in cyclohexane and separated by thin layer chromatography, gave three products each in minute yield. The major product of these three was bright yellow but contained insufficient material to undertake a full analysis. Infrared ν(CO) data were collected for each product as shown in Table 4.5 and recrystallization was attempted but no crystals suitable for analysis by X-ray diffraction were obtained.

The infrared spectrum indicated that the major product was probably unreacted starting material and none of the species could be formulated as a nona- or octa-carbonyl cluster so it appears that no decarbonylation was achieved.

When the same thermal decarbonylation and catalysed decarbonylation reactions were attempted using the C,N-bonded isomer **4** the compound decomposed immediately. The resulting dark brown tar-like residue did not respond to extraction into solvent or to separation by column or thin layer chromatography.

Photolysis was also attempted but with no result.

4.2.5 Reaction of [$Ru_3(CO)_{12}$] with Indazole

We attempted to synthesise analogues of the isomeric products obtained in the reaction with [$Os_3(CO)_{10}(MeCN)_2$] but reaction of [$Ru_3(CO)_{12}$] and indazole at room temperature or in refluxing dichloromethane or high-boiling petrol produced only a black precipitate which was extremely insoluble. This type of precipitate was found to a greater or lesser extent from all the triruthenium reactions and may be explained by fragmentation or polymerization of the triruthenium cluster. However, the monosubstituted cluster [$Ru_3H(C_6H_4N_2)(CO)_{10}$] does not seem to be accessible by these routes. The cyclometallated complex [$Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}$] has been obtained from the reaction between pyridine and [$Ru_3(CO)_{12}$] [27] but in the presence of excess ligand the di-substituted product [$Ru_3(\mu\text{-}H)_2(\mu\text{-}C_5H_4N)_2(CO)_8$] is obtained.[28,29] It is possible that the additional sites available for reaction on the indazole ligand does lead to a polymeric product. This result from the indazole reactions is in direct contrast to the results obtained using triosmium [9] as shown in this chapter.

However, the monosubstituted product [$Ru_3H(C_7H_5N_2)(CO)_{10}$] (Figure 4.24) has been reported and was obtained from the reaction of [$Ru_3(CO)_{12}$] with benzamidazole [30,31]

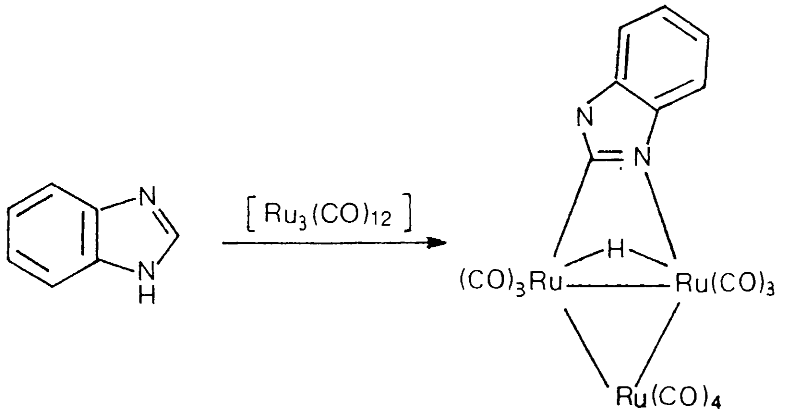


Figure 4.24

4.2.6 Reaction of 1,2,3-Triazole with [$Os_3(CO)_{10}(MeCN)_2$]

1,2,3-Triazole exists in two tautomeric forms:

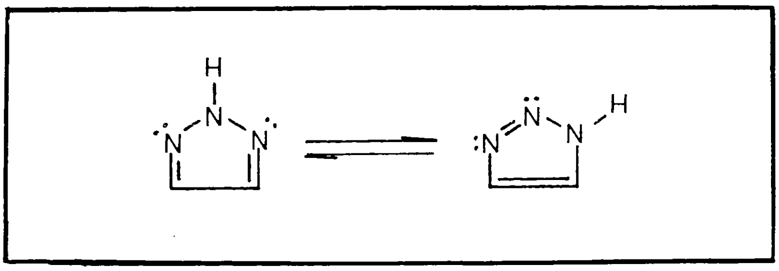
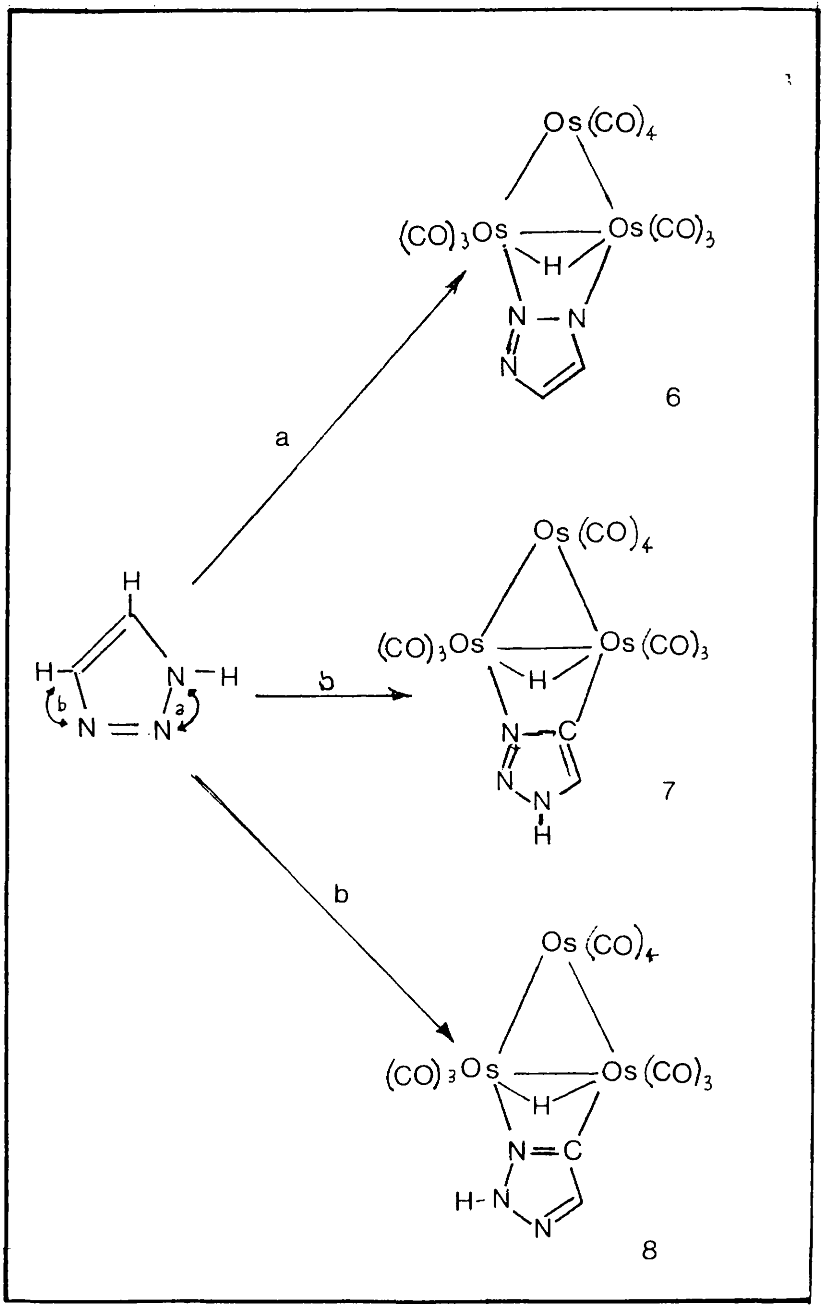


Figure 4.25 The tautomers of 1,2,3-triazole

Each tautomer contains two nitrogen atoms with lone pairs and the compound is therefore basic. It reacts at room temperature in dichloromethane solution with the triosmium cluster to give one major product. This is one of the three possible products shown in Scheme 4.4.

From the ^1H NMR data, it seems probable that the major product has structure **6**. If this were the case then initial attack at the triosmium centre would be through the lone pair on one of the nitrogen atoms followed by N-H cleavage (that is *via* route a in Scheme 4.4). There is no evidence of an N-H signal in the ^1H NMR spectrum of this product but it was observed that, in the spectrum of the crude reaction mixture before separation, there was an N-H signal. On rechromatographing the residue with a more polar solvent a very minor product was isolated in very small quantity. The ^1H NMR spectrum of the minor product indicated the presence of an N-H signal (a singlet at δ 8.04). On this basis the minor isomer was assigned the structure of either **7** or **8** as shown in Scheme 4.4. There was no interconversion between the isomers at room temperature.



Scheme 4A

Possible products of the reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and 1,2,3-triazole. Compounds **7** and 8 are tautomers and are not likely to be isolated separately.

4.2.7 Protonation of the Isomers of $[Os_3H(C_2H_2N_3)(CO)_{10}]$

Protonation of the N,N-bonded isomer of $[Os_3H(C_2H_2N_3)(CO)_{10}]$ was attempted using trifluoroacetic acid but only on a scale suitable for infrared analysis in order to see whether protonation at a nitrogen atom would lead to any significant increase in ν (CO) values. The frequencies in the ν (CO) region of the IR spectrum increased by between 2 cm^{-1} and 6 cm^{-1} above those of the parent compound, lower than expected for protonation and possibly the result of a change in solvent alone so the result must be regarded as inconclusive.

	ν (CO) cm^{-1}
Parent compound:	2110m 2073vs 2061vs 2024vs 2012s 2002sh 1978m
'Protonated' complex:	2112m 2077vs 2064vs 2029vs 2016s 2000sh 1984m

Table 4.6

4.2.8 Reaction of Benzotriazole with $[Os_3(CO)_{10}(MeCN)_2]$

The bicyclic equivalent of 1,2,3-triazole is benzotriazole. Again a tautomeric equilibrium exists between the two limiting forms of the free ligand (Figure 4.26):

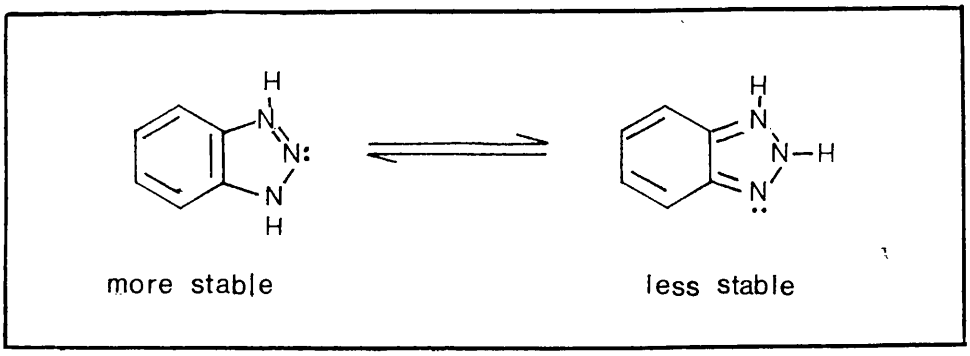


Figure 4.27 The tautomers of benzotriazole

We did not observe an N-H signal in the ^{1}H NMR spectrum of the free ligand: the chemical shift of this resonance is known to be solvent, temperature and concentration dependent and is generally very broad when it is observed.[9]

Benzotriazole has been widely used as a corrosion inhibitor [32] and it has been suggested that the inhibiting action is due to the formation of insoluble organometallic complexes on the metallic surface. [33] Generally the chemicals employed as corrosion inhibitors are species which act as good ligands for transition metals through their N, O or S donor atoms. A knowledge of the structural, chemical and electrochemical properties of the molecular species obtained by reacting such ligands with metal clusters could provide an insight into their action in protecting metal surfaces. It is also believed that the reactions of metallic clusters may be a good model for the reactions of a metal derivative in solution [34] and this could be of practical relevence for other processes that occur at metallic surfaces. In the light of this, some investigation has been made of the reaction of benzotriazole with triosmium clusters. Aime and his coworkers investigated the spectroscopic and cyclovoltrametric properties of the two products of the reaction of triosmium with benzotriazole.[35] We have repeated their syntheses to confirm their results and to extend the chemistry of these compounds.

Benzotriazole has one more nitrogen atom than indazole and has two *imino*-nitrogen atoms. There is no C-H bond immediately adjacent to either of these so coordination through one nitrogen atom would lead to the N,N-bonded isomer *via* N-H cleavage and coordination through the other would give an isomeric product where the benzene ring is *ortho*-metallated. There are three possible products all of which may be explained by predicting initial coordination through an *imino*-nitrogen atom and these are shown in Scheme 4.5.

Aime *et al.* unambiguously identified the major product as having structure **9a** on the basis of ^{15}N NMR resonances for the product and for the free ligand. They also asigned ^{13}C NMR resonances which can be useful for a rigid structure of this type. ^{1}H NMR chemical shifts established that there was no N-H group present so all the data indicate that **9a** is indeed the structure of the major isomer.

The minor product does, however, have a signal corresponding to the presence of an N-H group and this isomer corresponds to a product of oxidative addition with cleavage of a C-H bond by *ortho*-metallation of the aromatic ring. There is a good correlation and marked similarity between the spectra of this isomer and that of the analogous derivative of $[Os_3(CO)_{10}(MeCN)_2]$ and benzamidazole.[9]

The major isomeric N,N-bonded product was produced with respect to the minor *ortho*-metallated isomer in the mole ratio of 6:1. The third possible product, if present at all, was in such low yield that it was not possible to identify it unambiguously.

Our results were totally consistent with those reported by Aime *et al.*

4.2.9 Protonation of [$Os_3H(C_6H_4N_3)(CO)_{10}$]

An IR scale test was carried out with a solution of each isomer of [$Os_3H(C_6H_4N_3)(CO)_{10}$] in dichloromethane to which a few drops of trifluoroacetic acid were added. The solutions were allowed to stand at room temperature for five minutes and then infrared spectra were recorded for each (Table 4.7).

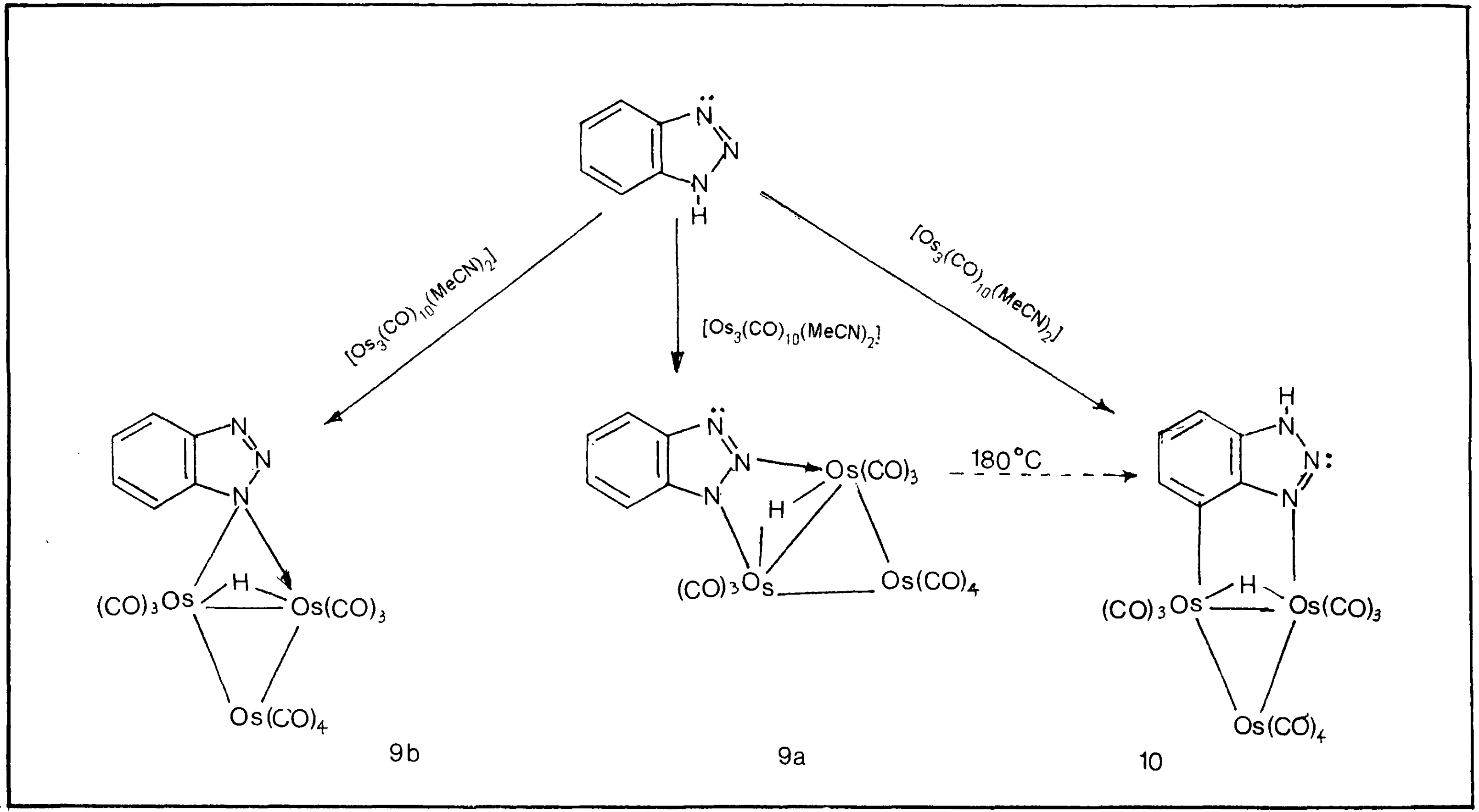
In the N,N-bonded isomer there is only one *imino* nitrogen site available for protonation (Figure 4.27).

However, in the *ortho*-metallated isomer, one nitrogen atom already has an attached proton which is able to exchange between the two nitrogen lone pairs available. If the *imino*-nitrogen were to be protonated, it would be expected that there would be a reduction in back-donation which would be reflected in the ν (CO) values (Figure 4.28).

Even though both isomers contain $\geqslant$ N: and so could be protonated and the IR data for the *ortho*-metallated isomer indicate that there was a small amount of protonation it seems most likely that only partial protonation has occurred and that there is no fundamental difference between the isomers at all.

4.2.10 Decarbonylation and Dimerization of [$Os_3H(C_6H_4N_3)(CO)_{10}$]

Dimerization of all the complexes so far described was attempted without success as decomposition was the invariable result. Thermal loss of a carbonyl ligand from the N,N-bonded benzotriazole derivative was attempted in refluxing cyclohexane but this did not lead to any loss of CO but only, again, to decomposition



Scheme 4.5 Possible products of the reaction of [Os$_3$(CO)$_{10}$(MeCN)$_2$] with benzotriazole

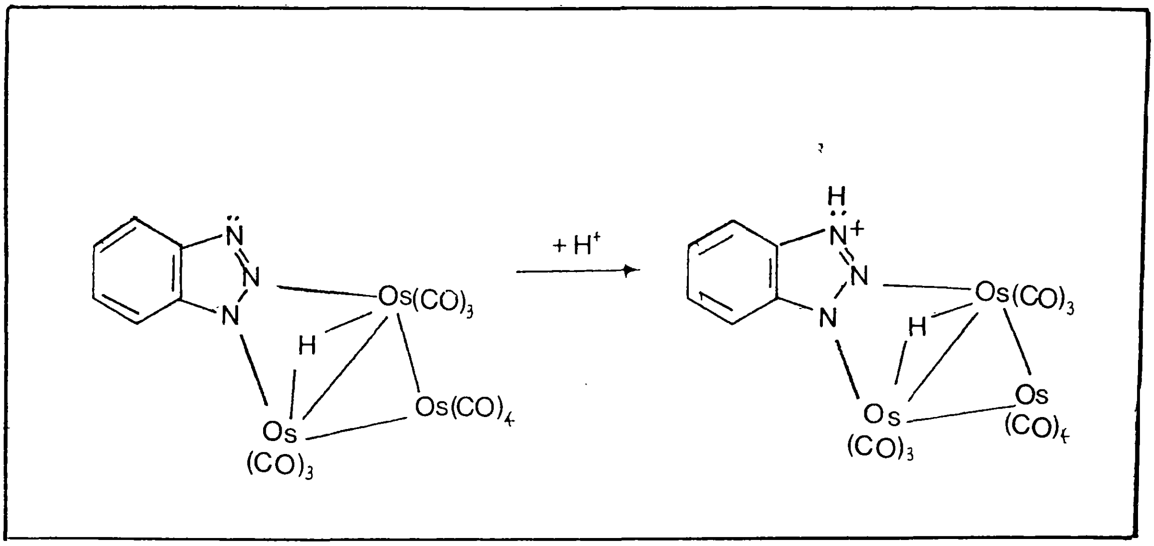


Figure 4.27 Protonation of N,N-coordinated $[Os_3H(C_6H_4N_3)(CO)_{10}]$

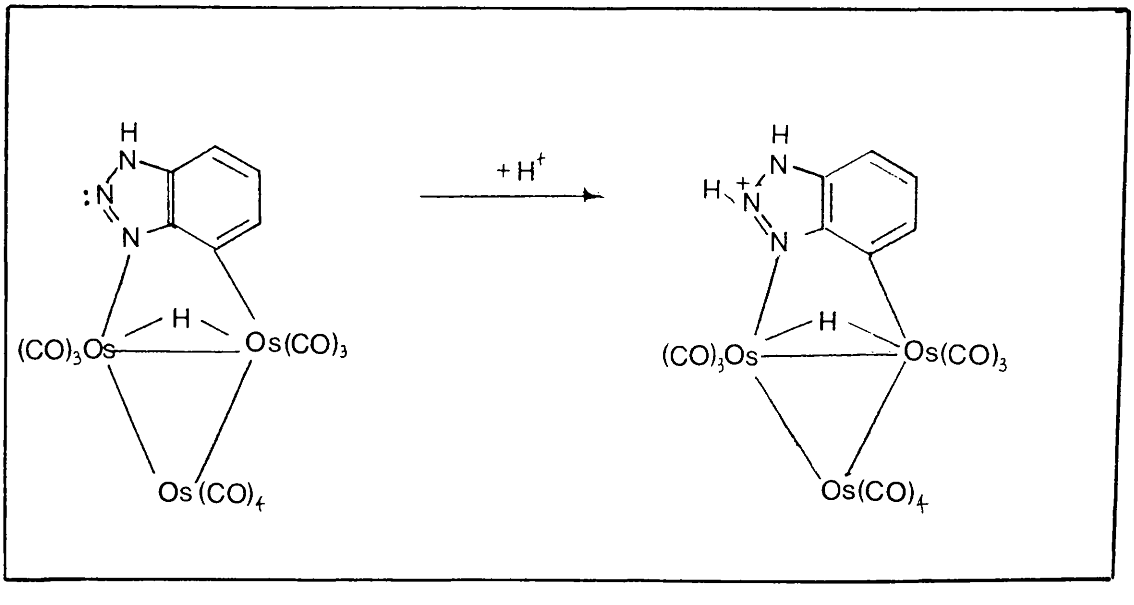


Figure 4.28 Proposed protonation of the *ortho* metallated isomer of $[Os_3H(C_6H_4N_3)(CO)_{10}]$

of the complex. However, treatment of this isomer with trimethylamine N-oxide in the presence of acetonitrile lead to the the nonacarbonyl acetonitrile substituted compound [$Os_3H(MeCN)(C_6H_4N_3)(CO)_9$].[36] This compound was identified in the crude reaction mixture from IR data which clearly showed the presence of a nonacarbonyl species (Table 4.9). The material was not isolated at this stage but used in the form of the solvent-free residue of the crude mixture. When this (MeCN)-subsitituted compound was treated thermally in refluxing cyclohexane one major and two minor products resulted which were separated chromatographically. The major yellow product was believed to be the hexa-osmium complex [$Os_6(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4N_3)_2(CO)_{18}$] formed by the ready loss of the acetonitrile ligand in [$Os_3H(MeCN)(C_6H_4N_3)(CO)_9$] followed by dimerization of the residual clusters (Figure 4.29). The IR spectrum was that of a nonacarbonyl species which supported this belief.

The major product is only sparingly soluble in petroleum ether but on warming with distilled petroleum ether (b.p. < 40°C) some dissolved and yellow crystals formed. Most of these were very small but a few were selected from the mass which were suitable for analysis by X-ray diffraction. The structure was determined by Professor A. J. Deeming in this Department and the yellow crystals were found to be monoclinic, a = 32.907(9), b = 14.811(5), c = 23.868(5) Å, β = 128.20(2) , U = 9141 $Å^3$, Z = 8. The structure was solved in space group $C2/c$ and pictures of the structure are shown in Figures 4.30 and 4.31. Selected bonds lengths and angles are given in Tables 4.9 and 4.10.

The structure shows that all six nitrogen atoms are coordinated and it contains the 6-membered ring $\overline{\text{Os - N - N - Os - N - N}}$ linking the clusters. This ring assumes the boat conformation. However, the [$Os_3H(C_6H_4N_3)(CO)_9$] unit formed by removal of one carbonyl ligand from the decacarbonyl parent compound remains intact; the CO ligand is lost from an osmium atom bonded to nitrogen and the coordination site is then occupied by a nitrogen atom which is itself part of another

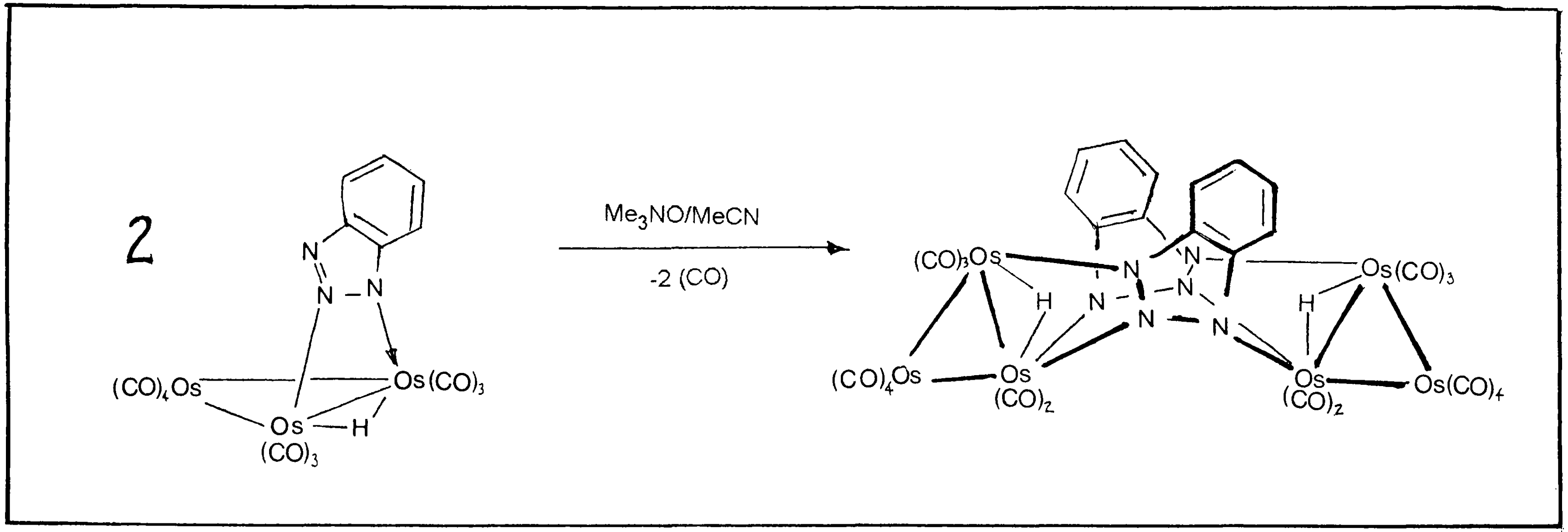


Figure 4.29 Dimer of N,N-cordinated [$Os_3H(C_6H_4N_3)(CO)_9$]

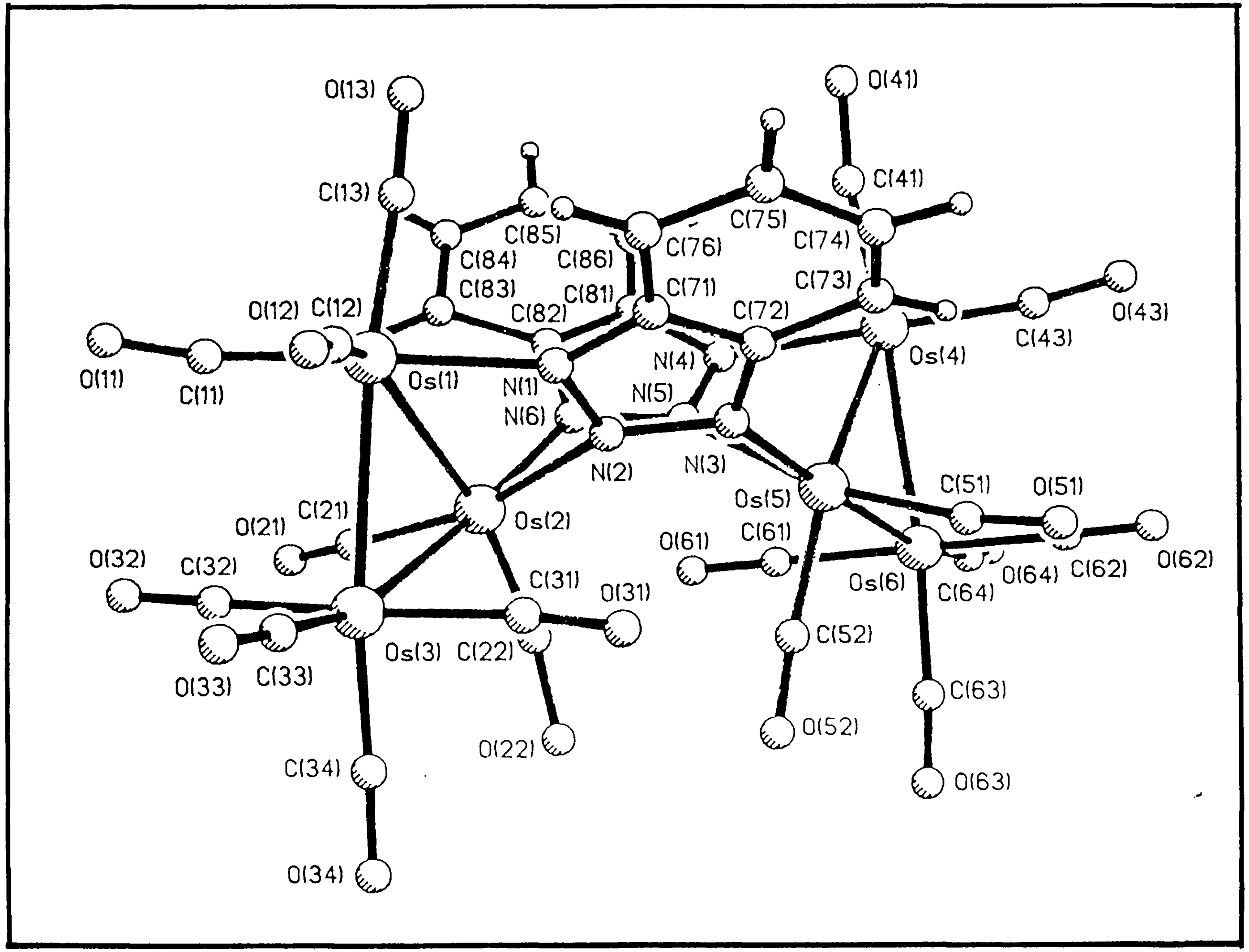


Figure 4.30 picture of $[Os_6(\mu\text{-}H)_2(C_6H_4N_3)_2(CO)_{18}]$ (1)

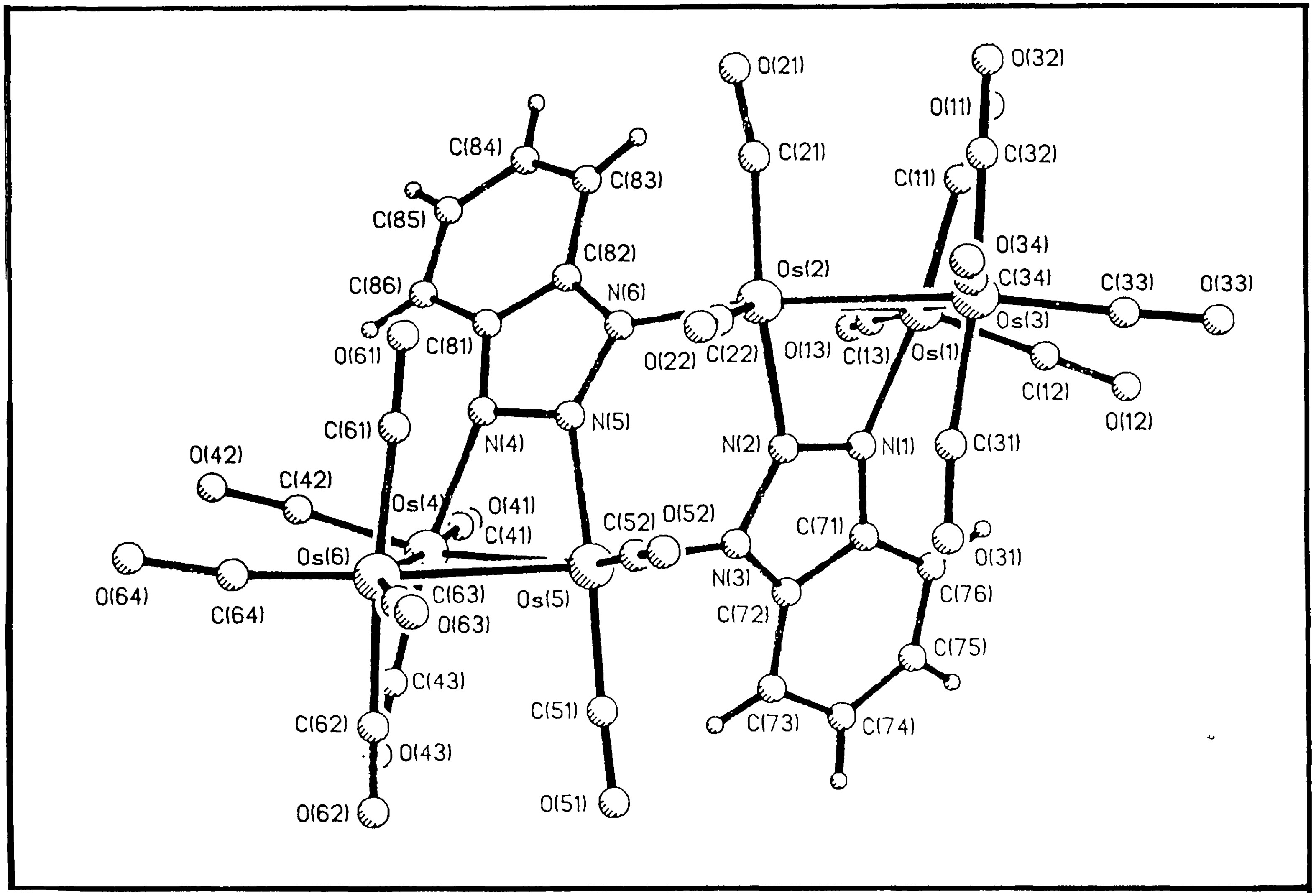


Figure 4.31 picture of [$Os_6(\mu\text{-}H)_2(C_6H_4N_3)_2(CO)_{18}$] (2)

cluster. Thus the ligand links the clusters such that the clusters appear to interact only minimally with each other and with only a minor **perturbation of one cluster by** the other. The space filling model (Figure 4.32) shows just how closely the two clusters are impacted without the need for any gross distortion. The two clusters are related by a two-fold rotation axis within the dimer molecule.

4.2.11 Reaction of [$Ru_3(CO)_{12}$] with Benzotriazole

It is known that the thermal reaction between [$Ru_3(CO)_{12}$] and benzotrizole leads to a disubstituted product.[30]

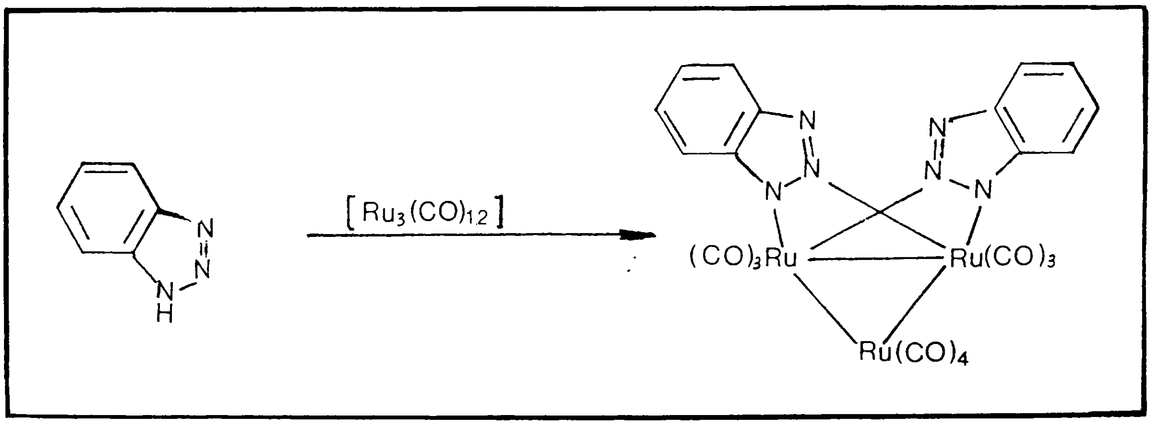


Figure 4.33

The monosubstituted osmium analogue has not, however, been reported. We attempted to synthesise [$Ru_3H(C_6H_4N_3)(CO)_{10}$] using a variety of routes. Initially dodecacarbonyltriruthenium was reacted thermally with a solution of benzotriazole in refluxing cyclohexane which resulted in a black precipitate which was insoluble in all solvents tried. The supernatant liquid contained only unreacted [$Ru_3(CO)_{12}$]. When the black precipitate was crushed it appeared actually to be a dark purple colour and a solid state IR spectrum was recorded. The spectrum was very difficult to interpret

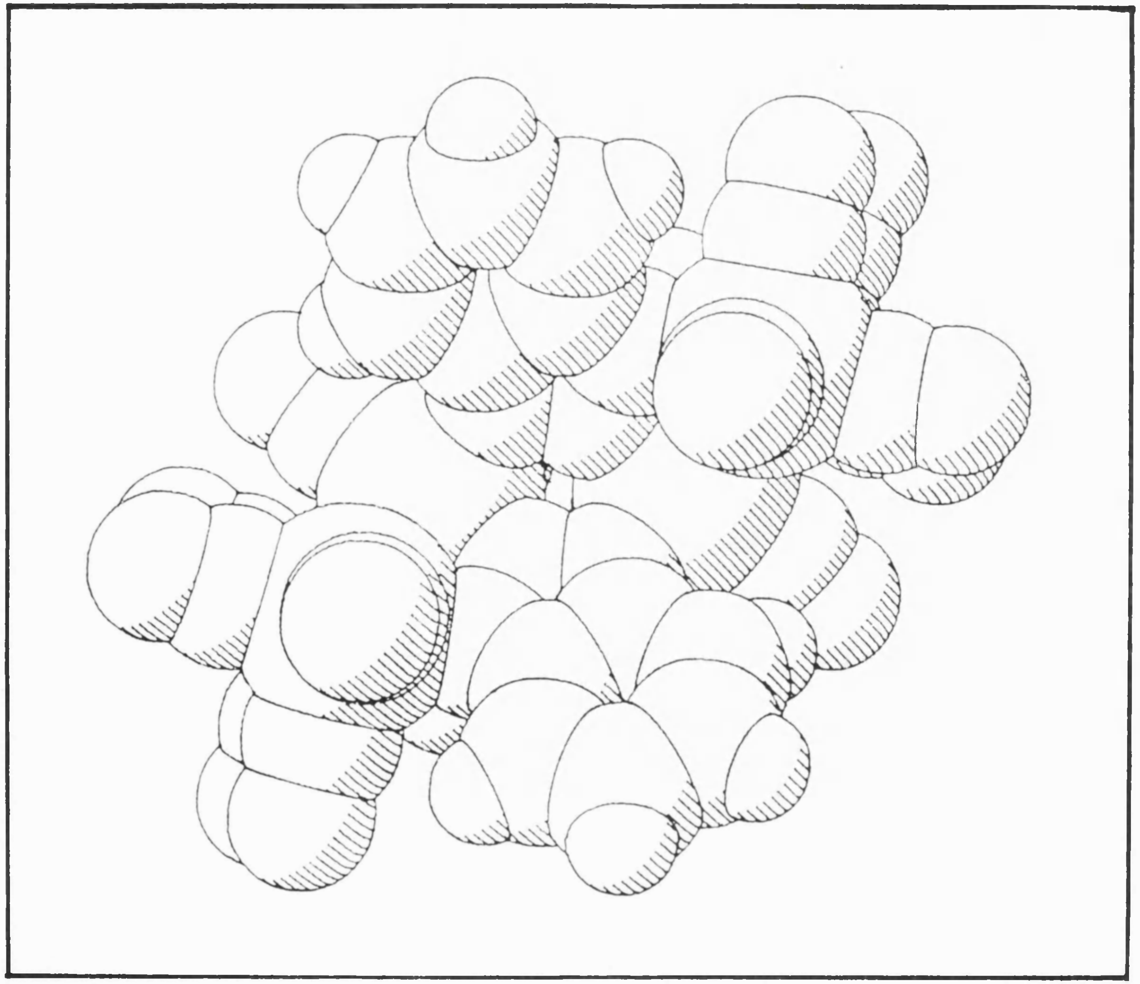


Figure 4.32 Space filling model of $[Os_6(\mu\text{-H})_2(C_6H_4N_3)_2(CO)_{18}]$

as the absorbances were very broad but the compound did not appear to be a decacarbonyl species from the shape of of the spectrum. The reaction was repeated using tetrahydrofuran as the solvent and it was noted that the bright orange colour of solutions of [$Ru_3(CO)_{12}$] changed within an hour to produce a clear grey solution. Unfortunately it proved impossible to remove the products from the silica surface following thin layer chromatography using dichloromethane or methanol. Analar acetone did remove the majority of the material from the silica but it appeared to change the nature of the compound which dramatically changed colour from yellow to bright emerald green. We were unable to characterize these materials.

The reaction of [$Ru_3(CO)_{12}$] and an excess of benzatriazole in dichloromethane at room temperature was attempted but there was no reaction after several days. We felt that the reaction might prove to be cleaner if it were to be carried out using the ruthenium analogue of [$Os_3(CO)_{10}(MeCN)_2$]. This reaction was carried out by a one-pot method at -68° C after which the reaction mixture was allowed to come to room temperature slowly: the only identifiable product of the reaction was dodecacarbonyltriruthenium. Reflux of [$Ru_3(CO)_{12}$] and benzotriazole in n-heptane in an atmosphere of carbon monoxide appeared to form a product after one hour. Analysis of the major bulk of the material again showed that it was largely unreacted starting material and the product was present in such small yield (< 0.1 mg) that it could not be identified by routine analysis.

A heavy black, insoluble precipitate was found in most of the [$Ru_3(CO)_{12}$] reactions which were run in paralled with those of [$Os_3(CO)_{10}(MeCN)_2$]. One explanation of its presence might be that triruthenium clusters show a much greater tendency to fragment than do triosmium clusters and this has been ascribed to the greater M - M bond strength of the Os - Os *versus* Ru - Ru bond (i.e. 94 kJ mol^{-1} *vs.* 78 kJ mol^{-1} respectively).[31]

Conclusion

We were able to predict which products might result from the majority of the reactions of nitrogen heterocycles with [$Os_3(CO)_{10}(MeCN)_2$] working from the assumption that initial coordination at the metal cluster would be through the lone pair of electrons on any *imino*-nitrogen atom in the heterocycle followed by cleavage of either an adjacent N-H or C-H bond. From the yields of product obtained it was concluded that cleavage of an N-H bond, where possible, was the favoured route by as much as 6:1 in one case.

Most of the isomeric products of the reactions are stable at room temperature and display no interconversion between the isomeric forms when they are crystalline. However, one isomer of the imidazole product and one isomer of the benzotriazole product may be converted into another isomer at elevated temperatures (200° C and 180° C respectively). [9,23] This confirms the order of thermodynamic stability shown below and is applicable to both these systems.

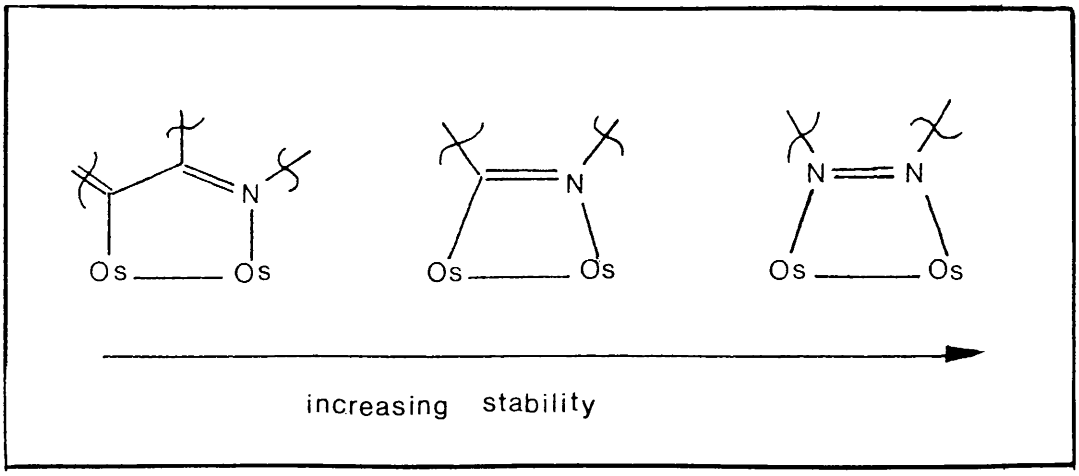


Figure 4.34

4.3 Tables

TABLE 4.1a

^{1}H NMR SPECTRA OF FREE LIGANDS*

	Chemical Shift,δ	Assignment
Pyrazole	10.09 (s, 1H)	N - H
	7.69 (d, 2H)	C(3) H; C(5) - H
	6.31 (t, 1H; J, 1.9 Hz)	C(4) - H
Indazole	8.08 (s, 1H)	N - H
	7.76 (d, 1H; J, 8.11 Hz)	C(3) - H
	7.49 (d, 1H; J, 8.42 Hz)	C(8) - H; C(5) - H
	7.38 (dt, 1H; J, 1.1, 7.2 Hz)	C(7) - H
	7.16 (dt, 1H; J, 0.90, 8.4 Hz)	C(6) - H
1,2,3-triazole	7.90 (s, 1H)	N - H
	7.85 (d, 1H)	C(5) - H
	7.84 (d, 1H)	C(4) - H
Benzotriazole	7.98 (m, 2H)	C(5) - H; C(8) - H
	7.46 (m, 2H)	C(6) - H; C(7) - H

* recorded in deuteriochloroform

TABLE 4.1b

^{1}H NMR DATA FOR HETEROCYCLIC DERIVATIVES*

	Chemical Shift,δ	Assignment
$[Os_3H(C_3H_3N_2)(CO)_{10}]$	2.27 (d, 2H; J, Hz)	C(3) - H, C(5) - H
(N,N-bonded)	6.00 (d, 1H; J, 3.3 Hz)	C(4) - H
	-13.37 (s, 1H)	Os - H
$[Os_3H(C_3H_3N_2)(CO)_{10}]$	10.09 (s, 1H)	N - H
(C,N-bonded)	7.15 (d, 1H; J_{CHNH} 2.4 Hz)	C(2) - H
	6.26 (d, 1H; J_{NHCH} 1.7 Hz)	C(3) - H
	-14.99 (s, 1H)	Os - H
$[Os_3H(C_7H_5N_2)(CO)_{10}]$	7.90 (s, 1H)	C(3) - H
(N,N-bonded)	7.54 (d, 1H; J, 8.6 Hz)	C(8) - H
	7.33 (t, 1H; J, 7.7, 15.3 Hz)	C(7) - H
	7.10 (d, 1H; J, 8.8 Hz)	C(5) - H
	6.98 (t, 1H; J, 7.7, 15.3 Hz)	C(6) - H
	-13.22 (s, 1H)	Os - H
$[Os_3H(C_7H_5N_2)(CO)_{10}]$	9.72 (s, 1H)	N - H
(C,N-bonded)	7.60 (d, 1H; J, 9.7 Hz)	C(8) - H
	7.37 (t, 1H; J, 7.6, 15.0 Hz)	C(7) - H
	7.31 (d, 1H; J, 8.2 Hz)	C(5) - H
	7.17 (t, 1H; J, 7.4, 14.8 Hz)	C(6) - H
	-14.92 (s, 1H)	Os - H
$[Os_3H(C_2H_2N_3)(CO)_{10}]$	7.51 (s, 1H)	C(4) - H
(N,N-bonded)	7.35 (s, 1H)	C(5) - H
	-13.37 (s, 1H)	Os - H
$[Os_3H(C_2H_2N_3)(CO)_{10}]$	8.04 (s, 1H)	N - H
(C,C-bonded)	7.75 (s, 1H)	C(4/5) - H
	-13.37 (s, 1H)	Os - H
$[Os_3H(C_6H_4N_3)(CO)_{10}]$	7.82 (d, 1H; J, 8.7 Hz)	C(5) - H
(N,N-bonded)	7.42 (dd, 1H; J, 7.3,11.2 Hz)	C(7) - H
	7.25 (d, 1H; J, 6.9 Hz)	C(6) - H
	7.27 (dd, 1H; J, 4.3, 8.4 Hz)	C(8) - H
	-13.28 (s, 1H)	Os - H

$[Os_3H(C_6H_4N_3)(CO)_{10}]$	12.20	(br,s, 1H)	N - H
(C,N-bonded)	7.81	(d, 1H; J, 7.3 Hz)	C(5) - H
	7.24	(t, 1H; J, 1.5, 8.4 Hz)	C(6) - H
	7.04	(d, 1H; J, 8.1 Hz)	C(7) - H
	-13.82	(s, 1H)	Os - H
$[Os_6(\mu\text{-}H)_2(C_6H_4N_3)_2(CO)_{18}]$	7.89	(dd, 1H; J, 1.1, 7.5 Hz)	
	7.44	(dt, 1H; J, 1.9, 5.3 Hz)	
	7.34	(d, 1H; J, 6.8 Hz)	
	7.26	(d, 1H; J, 7.3 Hz)	
	-11.35	(s, 1H)	

* recorded in deuteriochloroform

	Å
Os(1) - Os(2)	2.959(2)
Os(1) - Os(3)	2.873(2)
Os(2) - Os(3)	2.867(2)
N(1) - Os(1)	2.12 (2)
N(2) - Os(2)	2.11 (2)
N(1) - C(7)	1.40 (3)
N(2) - C(1)	1.31 (3)

	degrees °
Os(2) - Os(1) - Os(3)	58.9(1)
Os(3) - Os(1) - N(1)	88.4(5)
Os(2) - Os(1) - N(1)	106.2(7)
Os(1) - Os(2) - N(2)	68.8(5)
Os(1) - Os(3) - Os(2)	62.1(1)
Os(2) - N(2) - N(1)	110 (1)
N(1) - N(2) - C(1)	110 (2)
Os(1) - Os(2) - Os(3)	59.1(1)
Os(3) - Os(2) - N(2)	89.7(6)

TABLE 4.2

Selected bond lengths and angles for $[Os_3H(\mu\text{-}C_7H_4N_2)(CO)_{10}]$ **3**

	Å
Os(1) - Os(2)	2.989(2)
Os(1) - Os(3)	2.902(2)
Os(2) - Os(3)	2.878(2)
C(1) - Os(1)	2.10(2)
N(1) - Os(2)	2.10(2)
N(1) - N(2)	1.41(3)
N(1) - C(1)	1.29(3)
N(2) - C(72)	1.38(4)

	degrees °
Os(2) - Os(1) - Os(3)	58.5(1)
Os(2) - Os(1) - C(1)	66.3(6)
Os(3) - Os(2) - N(1)	88.0(6)
Os(1) - Os(2) - N(1)	66.1(6)
Os(3) - Os(1) - C(1)	88.1(7)
Os(1) - C(1) - N(1)	114 (2)
Os(1) - Os(3) - Os(2)	62.3(1)
Os(3) - Os(2) - Os(1)	59.3(1)
Os(2) - N(1) - C(1)	114 (2)
C(1) - N(1) - N(2)	112 (2)
Os(2) - N(1) - N(2)	133 (2)

TABLE 4.3: Selected bond lengths and angles for $[Os_3H(\mu\text{-}C_7H_4N_2)(CO)_{10}]$ 4

Type	Bridged Os - Os (Å)	Non-bridged Os - Os (Å)
Two-atom bridges		
All examples	2.90 (5)	2.88 (2)
μ,η^2-vinyl	2.83 (1)	2.88 (3)*
All except vinyl	2.93 (3)	2.88 (2)
Three-atom bridges	2.93 (3)	2.89 (2)

*on side of η^1-bond 2.86(1) Å; on side of η^2-bond 2.90(2) Å

Table 4.4: Mean Os - Os distances in clusters of the type [$Os_3H(\mu\text{-}X)(CO)_{10}$]

	ν (CO) cm^{-1*}
Starting material:	2107s 2069vs 2058vs 2018vs 1999s 1976m
Major product: (yellow)	2088m 2074w 2064w 2052s 2047sh 2036s 2021w 2008vs 1998s 1982m 1970w 1963vw
Trace product: (peach)	2106m 2059vw 2085sh 2066vs 2058vs 2045sh 2022vs 2017vs 2007s 2000s 1986m 1978m 1961m 1949vw
Trace product: (green)	2093w 2076m 2072m 2065sh 2048w 2041vw 2026s 2019vs 2013vs 1998m

*recorded in cyclohexane

TABLE 4.5: ν (CO) for the products of the decarbonylation and dimerization reaction of $[Os_3(\mu\text{-}H)(C_7H_4N_2)(CO)_{10}]$

	ν (CO) cm^{-1} *
N,N-bonded isomer	
Parent compound:	2109m 2074vs 2061s 2025vs 2016s 1980m
Parent compound plus acid:	2131w 2113m 2078vs 2065vs 2031vs 2018vs 2000sh 1989m
C,N-bonded isomer	
Parent compound:	2101m 2061vs 2048vs 2017s 2003s 1989m 1967w
Parent compound plus acid:	2140w 2132w 2115w 2102m 2062vs 2050vs 2018s 2004s 1991m

* recorded in dichloromethane

TABLE 4.7. ν (CO) for the attempted protonation of N,N bonded and C,N-bonded $[Os_3H(C_6H_4N_3)(CO)_{10}]$

INFRARED CARBONYL REGION FREQUENCIES FOR $[Os_3H(C_6H_4N_3)(CO)_{10}]$ AND FOR THE DIMERIZED PRODUCT $[Os_3(\mu\text{-}H)_2(C_6H_4N_3)(CO)_{18}]$*

	v (CO) cm^{-1}
$[Os_3H(MeCN)(C_6H_4N_3)(CO)_9]$ (crude mix)	2110s 2073vs 2063vs 2026vs 2014vs 1999sh
$[Os_3H(\mu\text{-}H)_2(C_6H_4N_3)_2(CO)_{18}]$ (crude mix)	2110w 2095m 2073s 2060s 2025vs 2019vs 2005s 2001sh 1995sh 1990m 1980vw
Chromatographic Separation	
Yellow band; major product	2101vw 2094m 2060s 2021vs 1999br,s 1937vw
Gold band: trace only	2092m 2061s 2021vs
Pale yellow; trace only (starting material)	2110m 2074vs 2062s 2026vs 2016s 2006sh 1979m, br

* recorded in dichloromethane

TABLE 4.8

	Å		Å
Os(1) - Os(2)	2.951(3)	Os(2) - N(6)	2.12(3)
Os(2) - Os(3)	2.852(2)	N(5) - N(6)	1.36(4)
Os(1) - Os(3)	2.866(4)	N(5) - Os(5)	2.16(3)
Os(4) - Os(5)	2.944(3)	N(5) - N(6)	1.36(4)
Os(5) - Os(6)	2.854(3)	N(2) - Os(2)	2.15(3)
Os(4) - Os(6)	2.880(4)	N(3) - N(2)	1.45(4)
N(6) - C(82)	1.32(6)	N(4) - C(81)	1.40(5)
N(1) - C(71)	1.35(6)	N(3) - C(72)	1.25(8)

TABLE 4.9 . Selected bond lengths for $[Os_6(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4N_3)_2(CO)_{18}]$

	degrees °		degrees °
Os(2) - Os(1) - Os(3)	58.7(1)	Os(1) - Os(2) - Os(1)	59.2(1)
Os(2) - Os(3) - Os(1)	62.1(1)	Os(2) - N(6) - N(5)	121 (2)
N(6) - Os(2) - N(2)	80 (1)	N(6) - N(5) - Os(5)	139 (2)
N(5) - Os(5) - N(3)	82 (1)	Os(5) - N(3) - N(2)	116 (3)
N(3) - N(2) - Os(2)	141 (3)	Os(5) - Os(4) -Os(6)	58.7(1)
Os(4) - Os(5) - Os(6)	59.5(1)	Os(5) - Os(6) - Os(4)	61.8(1)
C(71) - N(1) - N(2)	108 (3)	Os(1) - N(1) - N(2)	112 (3)
Os(1) - Os(2) - N(2)	66.8(9)	Os(1) - N(1) - C(71)	139 (4)
Os(2) - N(2) - N(1)	112 (2)	N(1) - N(2) - N(3)	107 (3)
N(2) - N(3) - C(72)	108 (3)	C(82) - N(6) - N(5)	107 (3)
N(6) - N(5) - N(4)	111 (3)	Os(4) - N(4) - C(81)	139 (3)
Os(5) - Os(4) - N(4)	69.3(8)	N(3) - Os(5) - Os(4)	115 (1)
Os(2) - Os(1) - N(1)	69 (1)		

TABLE 4.10 Selected bond angles for $[Os_6(\mu\text{-}H)_2(\mu\text{-}C_6H_4N_3)_2(CO)_{18}]$

TABLE 4.11

CARBONYL REGION INFRARED FREQUENCIES FOR HETEROCYCLIC DERIVATIVES*

	ν (CO) cm^{-1}
$[Os_3H(C_3H_3N_2)(CO)_{10}]$ (N,N-bonded)	2107m 2068vs 2057m 2038w 2022vs 2016s 2010m 1998s 1986m 1967w
$[Os_3H(C_3H_3N_2)(CO)_{10}]^{\#}$ (C,N-bonded)	2101m 2059vs 2049vs 2013vs 1991m 1967s 1947m
$[Os_3H(C_7H_5N_2)(CO)_{10}]$ (N,N-bonded)	2106s 2069vs 2058vs 2018vs 1977s
$[Os_3H(C_7H_5N_2)(CO)_{10}]$ (C,N-bonded)	2102m 2061vs 2050vs 2015vs 1996sh 1989m 1968sh
$[Os_3H(C_2H_2N_3)(CO)_{10}]$ (N,N-bonded)	2110m 2073vs 2061vs 2024vs 2006sh 2001sh 1979m
$[Os_3H(C_2H_2N_3)(CO)_{10}]$ (C,N-bonded)	2118sh 2110w 2102w 2037vs 2060s 2051sh 2024vs 2014vs
$[Os_3H(C_6H_4N_3)(CO)_{10}]$ (N,N-bonded)	2109m 2074vs 2061s 2025vs 2016vs 2011s 1991m 1980m
$[Os_3H(C_6H_4N_3)(CO)_{10}]$ (C,N-bonded)	2101m 2061vs 2048vs 2017vs 2003s 1989m 1980w 1967w
$[Os_6(\mu\text{-}H)_2(C_6H_4N_3)_2(CO)_{18}]$	2101w 2094m 2060vs 2021vs 1999m 1937w

* in cyclohexane # in dichloromethane

4.4 EXPERIMENTAL

Preparation of $[Os_3H(C_3H_3N_2)(CO)_{10}]$

A colourlesss solution of pyrazole (0.015 g, 2.203×10^{-4} mol) in dichloromethane (15 cm^3) was added to a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.0092 g, 9.900×10^{-5} mol) in dichloromethane (15 cm^3). The two solutions were thoroughly mixed and stirred for five hours at room temperature to give a brown/gold solution. The solvent was removed under reduced pressure and the residue chromatographed (eluent dichloromethane:petroleum ether (b.p. < 40° C) 2:3 v/v). One major yellow band and three very minor bands (2 yellow and 1 blue) were extracted into dichloromethane from the silica and recrystallization attempted from a dichloromethane/heptane mixture. The major band gave the title compounds.
(Found C, 20.98; H, 1.24; N, 2.69% : $C_{13}H_4N_2O_{10}Os_3$ requires C, 16.99; H, 0.44; N, 3.05%). The sample appears to be contaminated with hydrocarbon.

Preparation of $[Os_3H(C_7H_5N_2)(CO)_{10}]$

A clear, colourless solution of indazole (0.027 g, 2.362×10^{-4} mol) in dichloromethane (10 cm^3) was added to a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.220 g, 2.358×10^{-4} mol) in dichloromethane (20 cm^{-3}). The solutions were shaken together and stirred at room temperature for 4 hours whilst the progress of the reaction was monitored by IR spectroscopy. After this time the solvent was removed under reduced pressure and the residue redissolved in dichloromethane (*ca.* 4 cm^3) and chromatographed (eluent dichloromethane: petroleum ether (b.p < 40° C) 1:4 v/v) to give two major yellow bands. One band was the N,N-bonded isomer of $[Os_3H(C_7H_5N_2)(CO)_{10}]$ (79%) and the other was the C,N-bonded isomer (16%). The bands were extracted from the silica into dichloromethane and recrystallized from a dichloromethane/hexane mixture. A structure determination of each isomer was carried out by X-ray diffraction.

(Found (N,N-bonded isomer) C, 20.58; H, 0.81; N, 2.80: (C,N-bonded isomer) C, 22.95; H, 0.90; N, 2.49%: $C_{17}H_6N_2O_{10}Os_3$ requires C, 21.07; H, 0.62; N, 2.89%).

Attempted decarbonylation of C,N-bonded isomer of $[Os_3H(C_7H_5N_2)(CO)_{10}]$

A bright yellow solution of C,N-bonded compound $[Os_3H(C_7H_5N_2)(CO)_{10}]$ (0.040 g, 4.12×10^{-5} mol) dissolved in acetonitrile (25 cm^3) was stirred under a nitrogen atmosphere at room temperature and a colourless solution of trimethylamine N-oxide (0.0164 g, 1.476×10^{-4} mol) in warmed acetonitrile (15 cm^3) was added dropwise. The progress of the reaction was monitored by IR. The solution changed colour from gold to dark brown within five minutes of the addition of the trimethylamine N-oxide and was immediately passed down a column (1" dimeter, silica gel mesh 60-120, eluent acetonitrile) to remove excess trimethylamine N-oxide. The solvent was removed under reduced pressure and the fraction of the residue which was soluble in dichloromethane was chromatographed (eluent dichloromethane: petroleum ether (b.p. < 40 C) 3:7 v/v). Two very diffuse bands were found which were extracted into dichloromethane to give one yellow and one pink solution, each of which contained < 0.001 g of material.

Attempted decarbonylation of N,N-bonded isomer of $[Os_3H(C_7H_5N_2)(CO)_{10}]$

A yellow solution of N,N-bonded $[Os_3H(C_7H_5N_2)(CO)_{10}]$ (0.030 g, 3.22×10^{-5} mol) in acetonitrile (60 cm^3) was stirred under a nitrogen atmosphere at room temperature. To this was added dropwise over ten minutes a colourless solution of trimethylamine N-oxide (0.017 g, 1.53×10^{-4} mol) in warmed acetonitrile (10 cm^3). The solution was monitored by IR after each addition of trimethylamine N-oxide and during the reaction period thereafter. The solutions were stirred together for 60 minutes at room temperature after which time the mixture was passed down a column (1" diameter, silica gel mesh size 60-120, eluent acetonitrile) to remove excess trimethylamine N-oxide. The solvent was then removed under reduced pressure to leave a green residue which was used for further reaction in its crude state as the IR spectrum indicated the presence of a nonacarbonyl species.

v (CO)/cm $^{-1}$: 2096vw 2090w 2034w 2018vs 2000s 1996m 1986s

Attempted Dimerization of [$Os_3H(C_7H_5N_2)(MeCN)(CO)_9$]

The green crude residue which was thought to be largely [$Os_3H(C_7H_4N_2)(MeCN)(CO)_9$] formed in the previous reaction was dissolved in cylcohexane (40 cm^3) by stirring at room temperature and under a nitrogen atmosphere for 45 minutes. The solution was then heated to reflux and the progress of the reaction was monitored by IR. Heating was continued for eight hours when the solvent was removed under reduced pressure, the residue redissolved in dichloromethane (5 cm^3) and chromatographed (eluent dichloromethane:petroleum ether (b.p. < 40 C) 1:2 v/v) to give two major bands (one green and one yellow) and one very minor peach coloured band These were extracted from the silica into dichloromethane.

v (CO)/cm^{-1} (cyclohexane)

Parent compound: 2107s 2069vs 2058vs 2018vs 1999s 1976m

Major yellow product: 2088m 2074w 2064w 2052s 2047sh 2036s 2021w 2008vs 1999m 1970w 1963vw

Major green product: 2093w 2076m 2072m 2065sh 2048w 2041vw 2026s 2019vs 2013vs 1998m

Minor peach product: 2106m 2095vw 2085sh 2066vs 2058vs 2045sh 2022vs
(trace only) 2017vs 2007s 2000s 1986m 1978m 1961w 1949vw

The major yellow isomer was present in sufficient quantity for analysis. (Found: C, 25.22; H, 1.70; N, 3.63% $C_{30}H_{10}N_6O_{18}Os_3$ requires C, 19.13 H, 0.53; N, 4.46%).

Reaction of $[Ru_3(CO)_{12}]$ with indazole

Bright orange crystals of $[Ru_3(CO)_{12}]$ (0.3352g, 5.243 x 10^{-4} mol) were dissolved in hot refluxing heptane to give a bright orange solution. A clear colourless solution of indazole (0.1477g, 1.25 x 10^{-3} mol) in dichloromethane (8 cm^3) was added and the mixture heated to reflux which was continued for two hours, stirred under a carbon monoxide atmosphere. The progress of the reaction was monitored by IR spectroscopy. At the end of the heating period a heavy black precipitate had formed which was removed by gravity filtration. The supernatant liquid contained only unreacted $[Ru_3(CO)_{12}]$.

The reaction was repeated using different solvents: dichloromethane and high boiling petroleum ether gave the same reaction result.

The black precipitate was washed in petroleum ether and air dried. A sample was sent for analysis by mass spectrometry but the result was inconclusive. IR spectra in nujol mull were attempted but resulted in spectra with very broad indecipherable peaks in the $\nu(CO)$ region.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 1,2,3-triazole

To a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.1080g, 1.158 x 10^{-4} mol) in dichloromethane (25 cm^3) was added 1-H, 1,2,3-triazole (0.0494g, 7.159 x 10^{-4} mol) dissolved in dichloromethane (10 cm^3). The yellow solution was stirred and allowed to stand at room temperature for five hours and the progress of the reaction was monitored by IR spectroscopy. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (*ca.* 4 cm^3) and chromatographed (eluent dichloromethane:petroleum ether (b.p.< 40° C) 1:4 v/v). One major yellow band was extracted from the silica into dichloromethane and the product was recrystallized from a dichloromethane/heptane mixture. The product was identified as $[Os_3H(C_2H_2N_3)(CO)_{10}]$ from IR and ^1H NMR data and by comparison with the free ligand. The yield was 0.074 mg, 70%. (Found: C, 16.47; H, 0.36; N, 4.57% $C_{12}H_3N_3O_{10}Os_3$ requires C, 15.67; H, 0.33; N, 4.57%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with benzotriazole

To a gold solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.2590 g, 2.777 x 10^{-4} mol) in dichloromethane (25 cm^3) was added a solution of benzotriazole (0.0350 g, 2.78 x 10^{-4} mol) in dichloromethane (10 cm^3). The solution was diluted by the addition of more dichloromethane (65 cm^3) to give a golden yellow solution which was stirred at room temperature under a nitrogen atmosphere for two hours. The progress of the reaction was monitored by IR spectroscopy. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (*ca.* 6 cm^3) and chromatographed (eluent dichloromethane:petroleum ether (b.p. < 40° C) 1:1 v/v) to give three yellow bands. One band was identified as unreacted $[Os_3(CO)_{10}(MeCN)_2]$ and the other two bands corresponded to the isomers of $[Os_3H(C_6H_4N_3)(CO)_{10}]$, one

N,N-bonded (0.2041 g, 76%) and one *ortho*-metallated C,H-bonded isomer (0.0420 g, 15%). Each band was extracted from the silica into dichloromethane and recrystallized from a dichloromethane/heptane mixture. (For the N,N-bonded isomer, found: C, 21.03; H, 0.87; N, 4.13% $C_{16}H_5N_3O_{10}Os_3$ requires C, 19.82; H, 0.52; N, 4.33%).

Thermolysis of N,N-bonded $[Os_3(C_6H_4N_3)(CO)_{10}]$

Bright yellow crystals of $[Os_3H(C_6H_4N_3)(CO)_{10}]$ (0.0560 g, 5.77 x 10^{-5} mol) were dissolved in warm octane (16 cm^3) and the solution was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. The progress of the reaction was monitored by IR spectroscopy. The solvent was removed under reduced pressure and the brown residue redissolved in dichloromethane (4 cm^3) and chromatographed (eluent dichloromethane:petroleum ether (b.p. < 40 C) 3:7 v/v) to give two yellow bands, a blue band (trace only) and a purple band (trace only) which were too close together to separate effectively. The major yellow band was extracted into dichloromethane. The IR spectrum indicated that this major band did contain a nonacarbonyl species but it was very impure. Repeated chromatography did not result in any further separation. Recrystallization was attempted from a deuteriochloroform/heptane mixture but no crystals were found.

Photolysis of N,N-bonded $[Os_3H(C_6H_4N_3)(CO)_{10}]$

A bright yellow solution of N,N-bonded $[Os_3(C_6H_4N_3)(CO)_{10}]$ (0.018 g, 1.86 x10^{-5} mol) dissolved in n-heptane (5 cm^3) was placed in a 5 mm diameter tube, loosely sealed and then taped to a fluorescent light strip for 18 hours. A pale yellow-buff coloured precipitate formed with a pale yellow supernatant liquid. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane to give a suspension of the precipitate in pale yellow liquid. A homogeneous solution was not obtained in any solvent available and chromatography of the suspension failed in all the solvent/solvent mixtures tried as there was no movement off the baseline.

Thermolysis of *ortho*-metallated $[Os_3H(C_6H_4N_3)(CO)_{10}]$

A yellow solution of $[Os_3H(C_6H_4N_3)(CO)_{10}]$ (0.0440 g, 4.54×10^{-5} mol) in dichloromethane (8 cm^3) was diluted with octane (25 cm^3). The solution was heated to drive off the dichloromethane and then heated to reflux and stirred under a nitrogen atmosphere for 24 hours to give a yellow suspension. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane and an ^1H NMR and an IR spectrum was run of the fine particulate suspension.

$\nu(CO)/cm^{-1}$ (dichloromethane): 2110w 2102m 2074w 2063s 2050s 2027sh
2021s 2003s 1991m 1981w 1972

The ^1H NMR sample was not homogeneous and the only clear signal was that of a hydride at δ -13.991 so the results proved inconclusive.

Decarbonylation of N,N-bonded $[Os_3H(C_6H_4N_3)(CO)_{10}]$

A yellow solution of $[Os_3H(C_6H_4N_3)(CO)_{10}]$ (0.1386 g, 1.429×10^{-4} mol) in acetonitrile (20 cm^3) was prepared by stirring at room temperature under a nitrogen atmosphere for 15 minutes. A colourless solution of trimethylmine N-oxide (0.016 g, 1.449×10^{-4} mol) in acetonitrile (12 cm^3) was prepared by warming the solvent and stirring for 10 minutes. It was then added dropwise over 10 minutes to the stirred triosmium solution. Stirring was continued at room temperature for a further 35 minutes and the progress of the reaction was monitored by IR. The solution was passed down a column (1" diameter, silica gel mesh size 60 - 120, eluent MeCN) to remove excess trimethylamine N-oxide. The solvent was removed under reduced pressure to leave a yelow residue which was redissolved in MeCN (5 cm^3) and chromatographed (eluent acetonitrile:dichloromethane:petroleum ether (b.p. < 40 C) 80:5:15 v/v/v) to give one major yellow band which was extracted into acetonitrile and the solvent removed under reduced pressure. Yield of $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$ = 0.084 g, 60%.

ν (CO) /cm^{-1} (acetonitrile): 2110s 2073vs 2063vs 2026br,vs 2014br,vs 1999sh 1980br,s.

Dimerization of $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$

To the yellow residue of $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$ (0.084 g, 8.92x 10^{-5} mol) was added cyclohexane (80 cm^3). The mixture was heated gently and stirred to dissolve the yellow solid residue. Stirring was continued for 30 minutes at room temperature under a nitrogen atmosphere and the resulting khaki solution was heated to reflux for a further 30 minutes. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane and chromatographed (eluent dichloromethane:petroleum ether (b.p. < 40° C) 2:3 v/v). One major yellow band was extracted from the silica into dichloromethane. The solvent was removed under reduced pressure. The residue was sparingly soluble in warm low-boiling petrol and small yellow crystals formed. Yield 0.067 g, 80% Some of the crystals were suitable for X-ray analysis and a structure determination was carried out.

(Found: C, 25.22; H, 1.70: N,3.63% $C_{30}H_{10}N_6O_{18}Os_6$ requires C, 19.13; H, 0.53; N, 4.46%).

Reaction of $[Ru_3(CO)_{12}]$ and benzotriazole

Bright orange crystals of $[Ru_3(CO)_{12}]$ (0.1464 g, 2.290×10^{-4} mol) were dissolved in cyclohexane (40 cm^3) by gently warming under a nitrogen atmosphere and stirring. A colourless solution of benzotriazole (0.0508 g, 4.264×10^{-4} mol) in cyclohexane (40 cm^3) was added and the solutions were heated to reflux, stirred under a nitrogen atmosphere for three hours. The progress of the reaction was monitored by IR spectroscopy. After three hours the solvent was removed under reduced pressure. The residue was the colour of milk chocolate and was partially redissolved in dichloromethane (35 cm^3) and the suspension was filtered under vacuum to give a clear orange solution and a black particulate solid. The solid was washed in dichloromethane (10 cm^3) and was allowed to air dry. It was then crushed to give a purple-black powder and an IR spectrum was recorded in nujol mull. Unfortunately the spectrum showed very broad peaks in the carbonyl frequency region.

ν (CO)/cm^{-1} (nujol): 2075m 2061s 2049sh 2023m

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CHAPTER 5

The Reactions of Nitrogen 6-membered Ring Heterocycles with Triosmium Clusters

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5.1 Introduction

The incorporation of nitrogen 6-membered ring heterocycles into triosmium clusters generally gives analogous complexes to those found in the reactions with 5-membered ring heterocycles.

It is known that 2-substituted pyridines, when reacted with lightly stabilized clusters such as $[Os_3(CO)_{10}(MeCN)_2]$, can give metallated 2-pyridyl systems in which the substituent is not coordinated. [1-3]

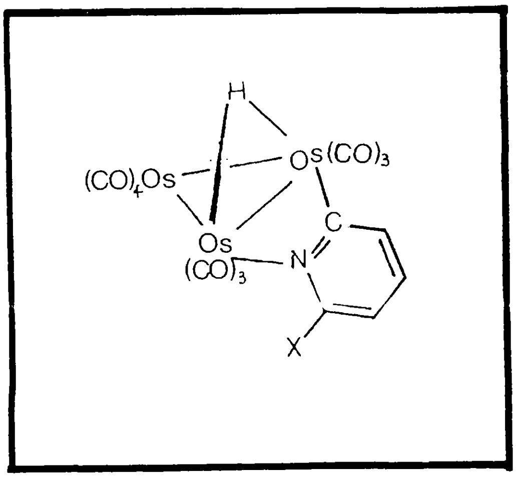


Figure 5.1 Metallation of a 2-substituted pyridine ligand where X = H, Cl, CN, CH_3 or CH_2Ph

In other cases in which X = vinyl or alkynyl the chemistry does occur at the substituent.

In the reaction of 1,2-pyridazine and $[Os_3(CO)_{12}]$ a metallocyclic cluster is formed which is exceptional in that it has no hydride bridging ligand.[4] The two nitrogen atoms are coordinated so that *ortho* metallation cannot occur easily.

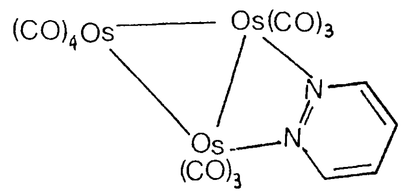


Figure 5.2 The coordination of 1,2-pyridazine to $[Os_3(CO)_{12}]$

1,2-diazine (pyridazine) reacts with $[Os_3(CO)_{12}]$ at 125 °C or with $[Os_3H(C_4H_3N_2)(CO)_{10}]$ at room temperature to form $[Os_3(C_4H_4N_2)(CO)_{10}]$. Whilst this complex has no hydride ligand, at 150 °C, it slowly isomerizes to give $[Os_3H(C_4H_3N_2)(CO)_{10}]$ in low yield. In the latter compound the pyridazine has been *ortho* metallated. Even in the high temperature reaction there was no evidence for the formation of $[Os_3(C_4H_4N_2)(CO)_9]$ by decarbonylation of the decacarbonyl species. The small bite of the pyridazine ligand and the inflexibility and strength of the N - Os bond might all prevent movement of the ligand into the correct position above the triosmium plane for μ_3-coordination.

1,4-Diazine (pyrazine) forms an *ortho* metallated product with triosmium but relatively slowly when compared with pyridine under similar conditions.

2-Azidopyridine exists mainly as its tetrazole tautomer. (Figure 5.3).

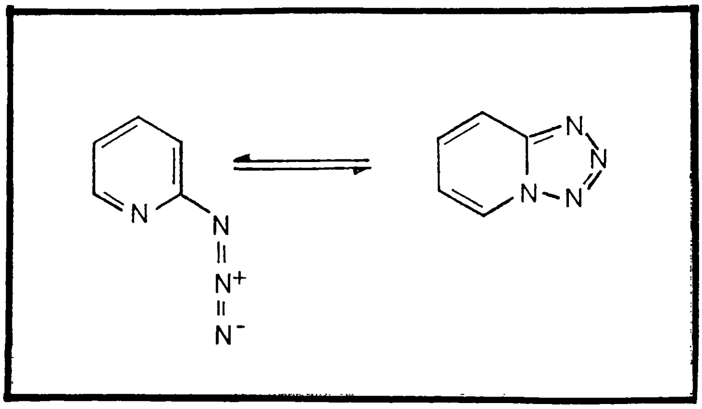


Figure 5.3 The tautomers of 2-azidopyridine

It reacts in the tetrazole form with $[Os_3H_2(CO)_{10}]$ to form the metallated product.[5]

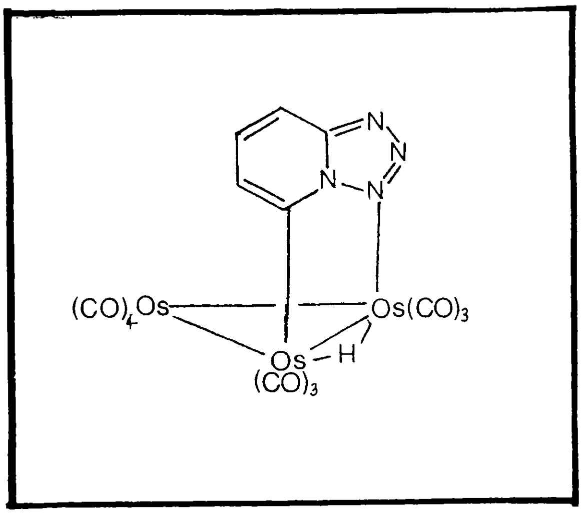


Figure 5.4 The product of 2-azidopyridine with $[Os_3H_2(CO)_{10}]$

5.2 Results and Discussion

5.2.1 Reaction of 1,3-diazine (pyrimidine) with $[Os_3(CO)_{10}(MeCN)_2]$

Pyrimidine as the free ligand has two nitrogen atoms, each of which has a lone pair of electrons. The hydrogen atom at the 2-position is activated by electron withdrawal by both nitrogen atoms simultaneously and the ^1H NMR chemical shift of this hydrogen atom is 9.1 ppm which does indicate a high degree of deshielding. Pyrimidine is a weaker base than pyridine as the presence of the second ring nitrogen leads to a loss of basicity. The effect is not simply related to the electronegativity of the second nitrogen atom since the basicity of the diazines varies inversely with the separation between the nitrogen atoms. Hence pyrimidine and 3-nitropyridine are similar in basicity. However, electron donating substituents attached to the diazine ring increase the basicity of the compounds.[6]

Some previous work has been published on both the 1,3-diazine [7] and 1,4-diazine [4] systems but in the published work the yields obtained were very poor. One of the difficulties encountered in this published work was that both the diazines were only sparingly soluble in the cyclooctane solvent which was then used. For the 1,3-diazine products the published yields were 9.1% for the 2-metallated product and 38% for the 6-metallated product. We repeated the synthesis of these compounds but used different reagents and conditions. When pyrimidine was reacted by us with $[Os_3(CO)_{10}(MeCN)_2]$ in dichloromethane at room temperature we found that both products were obtained but still only in moderate yield (10% and 39% respectively) as shown in Figure 5.5. The products were identified by ^1H NMR analysis; one product clearly showed the low-field signal associated with the 2-position hydrogen atom but this signal was not present in the spectrum of the other product. Hence it was possible to assign structure on the basis of the spectra.

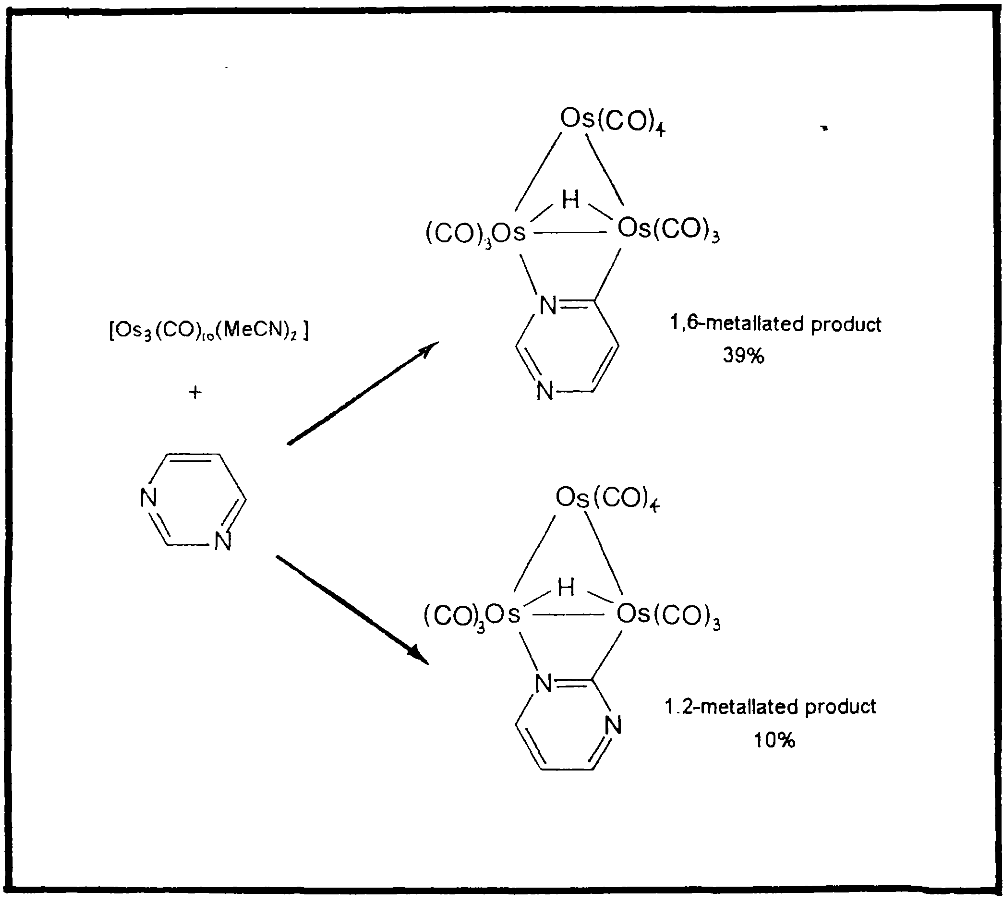


Figure 5.5 Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ and pyrimidine

It seems then that the only difference between the two isomeric products is in the position of metallation. Statistically, 1,6-metallation is twice as favourable as 1,2-metallation and yet the products were obtained in a 4:1 ratio in favour of the 1,2-metallated product. Therefore it seems that there is an activation of the 2-position rather then the 6-position.

5.2.2 Attempted decarbonylation of 1,2 - and 1,6 - metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$

We attempted decarbonylation by thermolysis of both the isomers of $[Os_3H(C_4H_3N_2)(CO)_{10}]$ in order to see whether the non-coordinated nitrogen atom could be induced to become coordinated. After eight hours of heating in n-heptane there was no discernable chemical change. However, when each isomer was treated with a solution of trimethylamine N-oxide in the presence of acetonitrile [8] the infrared spectrum in the carbonyl stretching region indicated the formation of the nonacarbonyl species of the respective isomer in each case. The spectra were characteristic of species in which CO has been substituted by acetonitrile as shown in Figure 5.6.

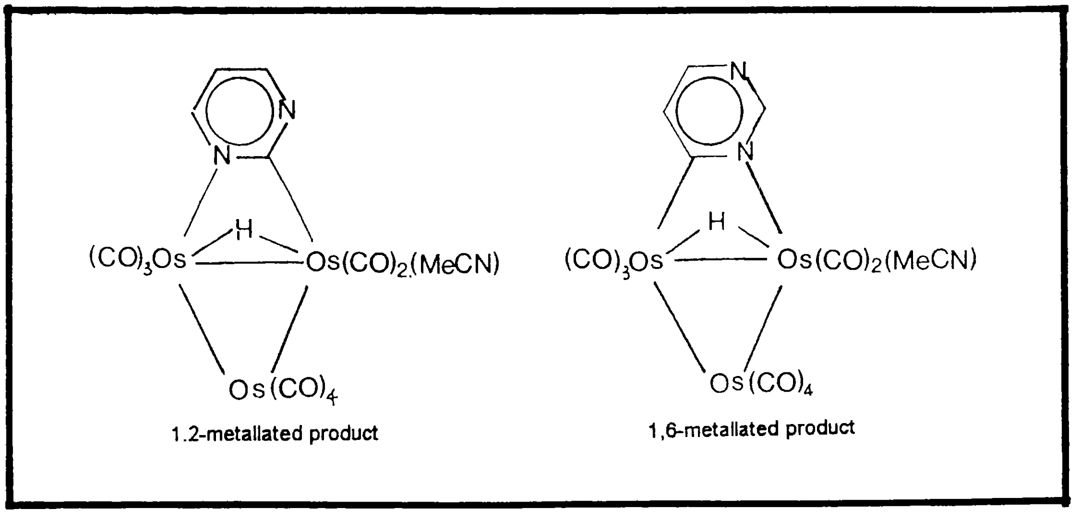
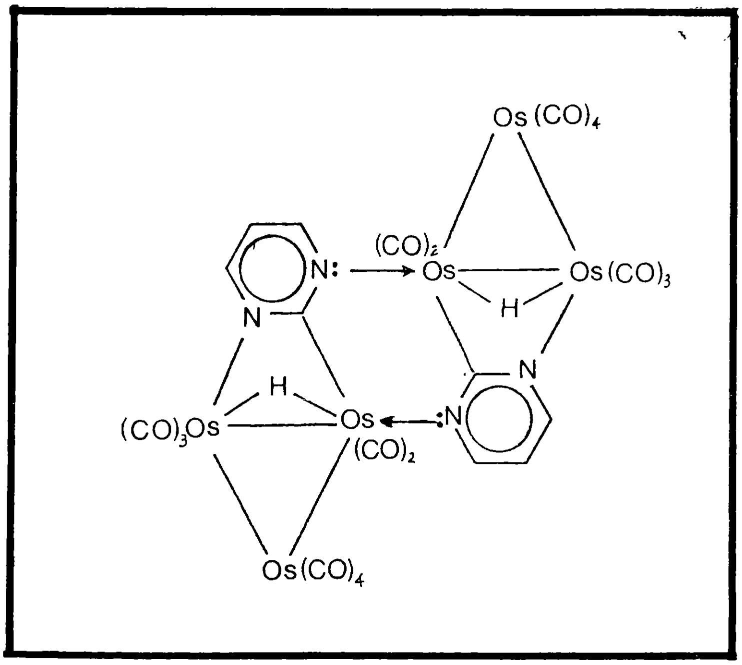


Figure 5.6 Acetonitrile substituted isomers of 1,2- and 1,6- metallated $[Os_3H(C_4H_4N_2)(MeCN)(CO)_9]$

Both the nonacarbonyl isomers were found to be stable as yellow microcrystals at room temperature. Subsequently each isomer was heated to reflux in cyclohexane to attempt dimerization through loss of the labile aceonitrile ligand as occurred in the thermolysis of the N,N bonded isomer of $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$ discussed in the previous chapter. It was thought likely that the 1,2-metallated isomer would be the more likely candidate for dimerization to give a product of the type shown in Figure 5.7



5.7 Possible product of dimerization of 1,2-metallated $[Os_3H(C_4H_4N_2)(MeCN)(CO)_9]$

However, as the reflux was continued, it could be seen from the infrared spectrum of the carbonyl region that a decacarbonyl species was forming gradually at the expense of the nonacarbonyl species. After one hour, the only product was the decacarbonyl starting material. Exactly the same result was obtained using the 1,6-metallated isomer.

It is difficult to see why both these dimerization reactions failed in view of the ease of formation of the dimer from $[Os_3H(C_6H_4N_3)(MeCN)(CO)_9]$. The only obvious difference seems to be in the orientation of the lone pairs on the nitrogen atoms in the rings (Figure 5.8).

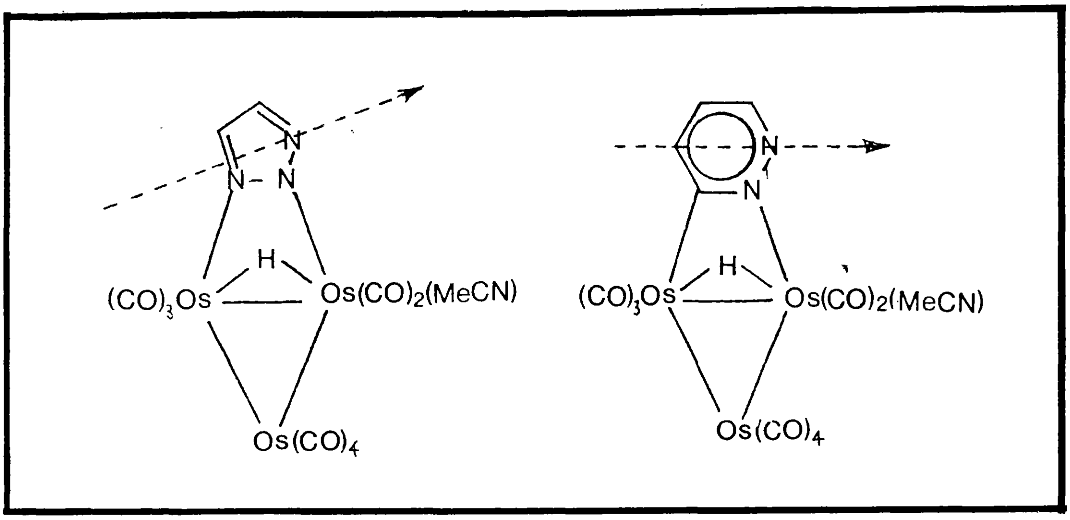


Figure 5.8 Orientation of nitrogen lone pairs in [$Os_3H(C_6H_4N_3)(MeCN)(CO)_9$] and [$Os_3H(C_4H_3N_2)(MeCN)(CO)_9$]

The difference in the orientation of the lone pairs on the nitrogen atoms is then Ø

Other possibilities are that there is interference between the carbonyl ligands disfavouring the formation of the dimer or that the acetonitrile ligand had been introduced at a site unfavourable for the formation of a dimer. The latter seems unlikely because CO ligands are known to redistribute readily according to the requirements of the cluster. Overall, the probability is that during reflux there was some small initial degradation which then provided carbonyl ligands to replace the labile acetonitrile ligands.

5.2.3 Reaction of 1,6 - metallated [$Os_3H(C_4H_3N_2)(CO)_{10}$] and [$Os_3(CO)_{10}(MeCN)_2$]

To test whether the uncoordinated nitrogen atom can coordinate through the remaining lone pair, a clean sample of the 1,6-metallated isomer of [$Os_3H(C_4H_3N_2)(CO)_{10}$] was stirred with [$Os_3(CO)_{10}(MeCN)_2$] at room temperature until the infrared spectrum of the carbonyl stretching frequencies indicated that a major change had occurred. It was thought possible that new products might be the result of coordination of the incoming osmium cluster such that it would lie on the same or on opposite sides of the heterocyclic ring as the original triosmium cluster. Furthermore metallation at different sites is possible as shown in Figure 5.9.

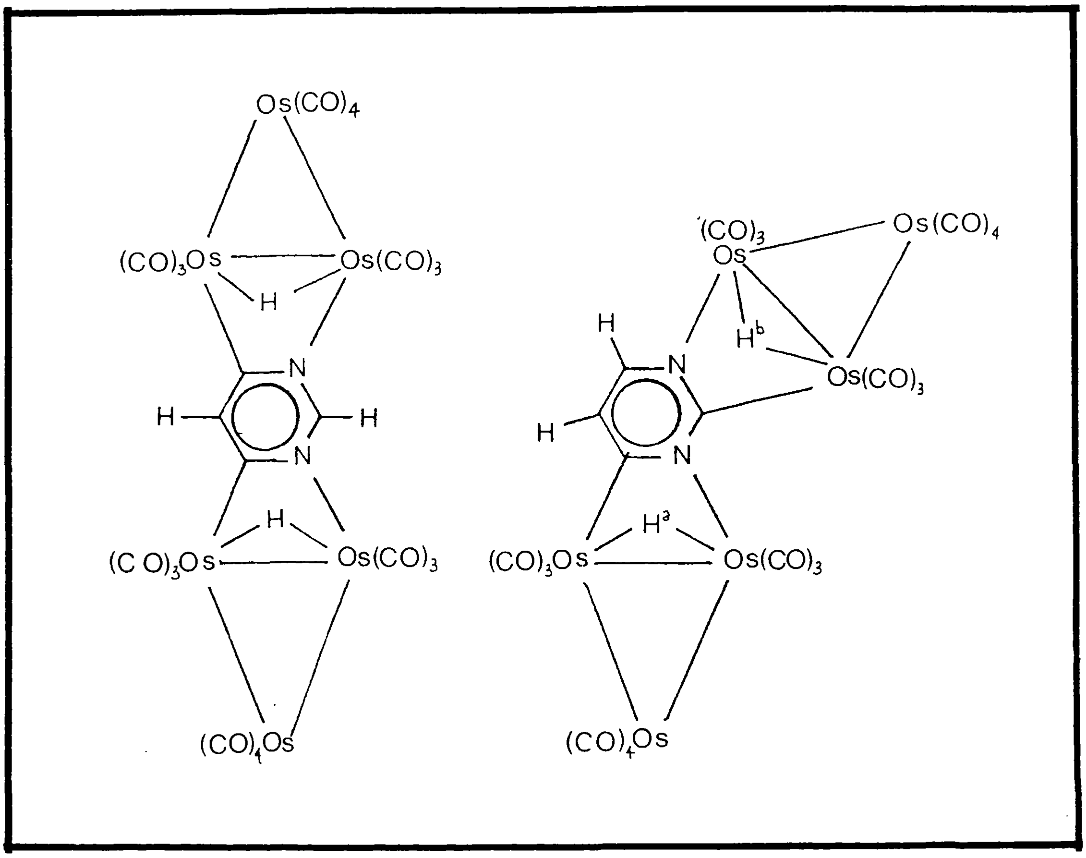


Figure 5.9 Possible products of the reaction of the 1,6-metallated isomer of $[Os_3H(C_4H_3N_2)(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$

The reaction produced a fine yellow precipitate and chromatography of the supernatant liquid gave four yellow bands, two of which were identified as the starting materials. One band had no hydride signal in the ^1H NMR but we believed that the fourth chromatography band and the yellow precipitate contained the 2 isomers shown in Figure 5.9 and ^1H NMR spectra were used to distinguish between the possible structures. The ^1H NMR specturm of the precipitate indicated the presence of two hydride signals (δ -14.37 and -14.50) and two doublet signals (δ 7.15 and

6.63). The chromatography band was analysed after several successive chromatograms had been run in order to clean up the material as much as was possible. Only one hydride signal was apparent in the ^{1}H NMR spectrum of this material but there was too little material available to fully analyse the low-field resonances which were partially obscured by noise on the base line of the spectrum.

Isomer **1** has a mirror plane and it would be expected that only one hydride signal would be observed in the ^{1}H NMR spectrum as the hydride ligands are in identical environments. Isomer **2** does not have this plane of symmetry and the hydride ligands are in dissimilar environments so two hydride signals are expected. Two low-field doublet signals would also be expected for the two hydrogen atoms on the heterocyclic ring for each isomer. Isomer **1** is chiral and is of the point group C_2. This is illustrated in Figure 5.10. The hydrogen atoms on the heterocyclic ring are in very different environments; H_a should have a signal at much lower field than H_b under usual circumstances owing to deshielding of H_a by two adjacent nitrogen atoms.

Our results could indicate that isomer **2** was present in the precipitate as the predicted resonances do appear, so, for cross-reference purposes, the 1,2-metallated isomer was also reacted with $[Os_3(CO)_{10}(MeCN)_2]$. In this case the only possble product is that where the osmium clusters are on the same side of the heterocyclic ring assuming that the lone pair of electrons is the invariable site of initial attack. The ^{1}H NMR spectrum of the minute amount of product of this reaction showed only one hydride signal (δ -15.0) and two doublets for the ring hydrogen atoms (δ 6.71 and 6.68).

Neither of the reactions was clean and all products were separated in very low yield. Although the products were crystalline, it proved impossible to grow

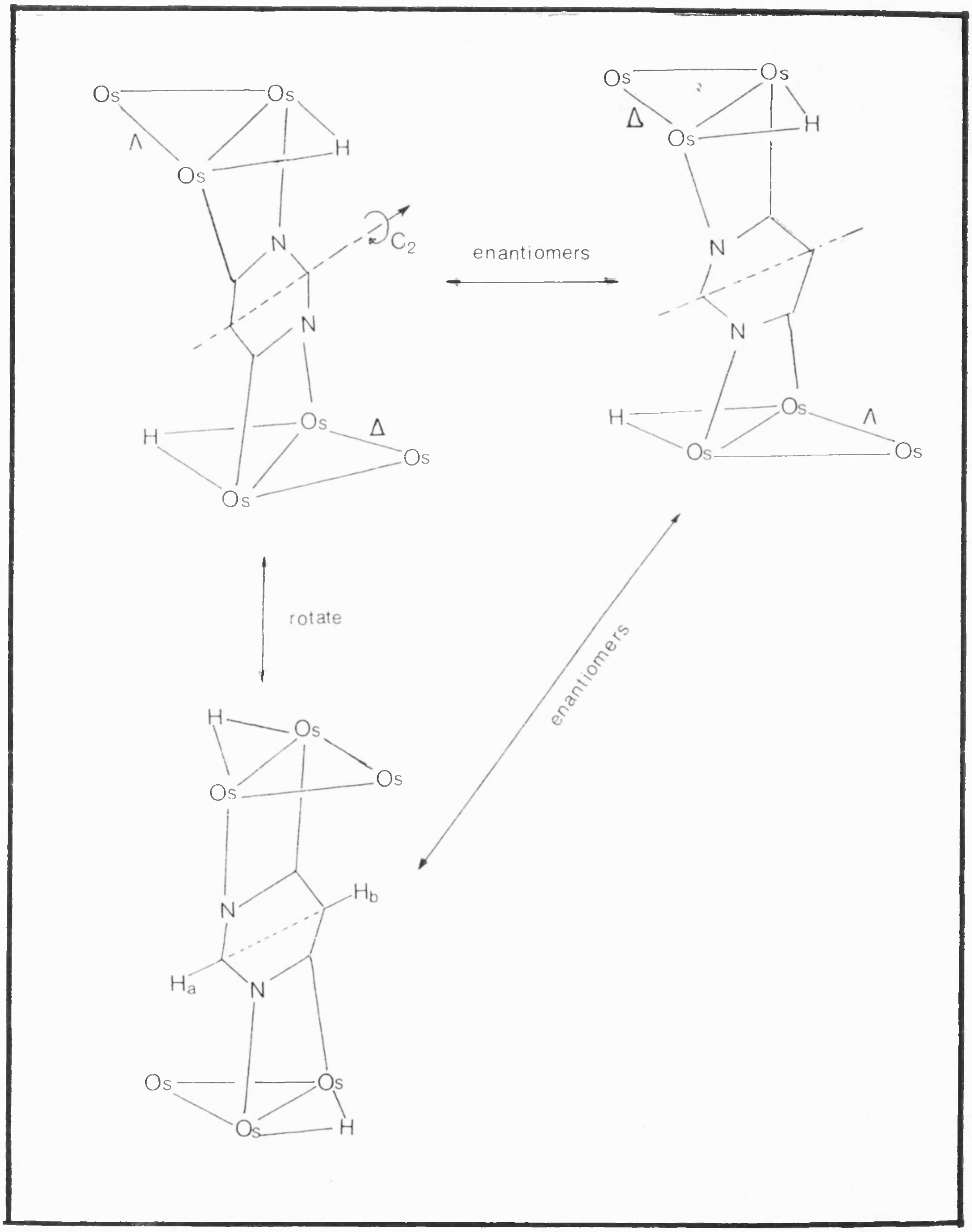


Figure 5.10 Isomer **1** and its enantiomers

cystals suitable for X-ray crystallographic investigation. The ^1H NMR indicated that there was, in fact, cross contamination of the products and when these were rechromatographed insufficient material remained for complete analysis (< 1 mg). A much larger scale preparation might afford products in sufficiently large quantites to make assignment possible but in the current work it is not possible to make any unambiguous statements as to structure of the products.

5.2.4 The reaction of 1,6-metallated and 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ with $AgClO_4$

As an alternative way to link the 1,6- and 1,2-metallated pyrimidine products, we decided to try to produce a silver-linked ionic species as shown in Figure 5.11. 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ immediately formed an intransigent black substance on mixing with $AgClO_4$. This substance resisted all attempts at purification, extraction, separation and crystallization. Mass spectrometry was attempted but no spectrum was obtained.

However, 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ initially formed a bright orange precipitate with $AgClO_4$ in small quantities. This was filtered under gravity but within five minutes it too went black. As the compound formed in both these reactions resisted all attempts at classification no further work was done on the systems.

5.2.5 The reaction of (S)(-) nicotine with triosmium clusters

Some decade ago, $[Os_3H(C_9H_{10}N_2Me)(CO)_{10}]$ was synthesised.[9] Separation of the crude mixture into its component parts had been attempted using thin layer

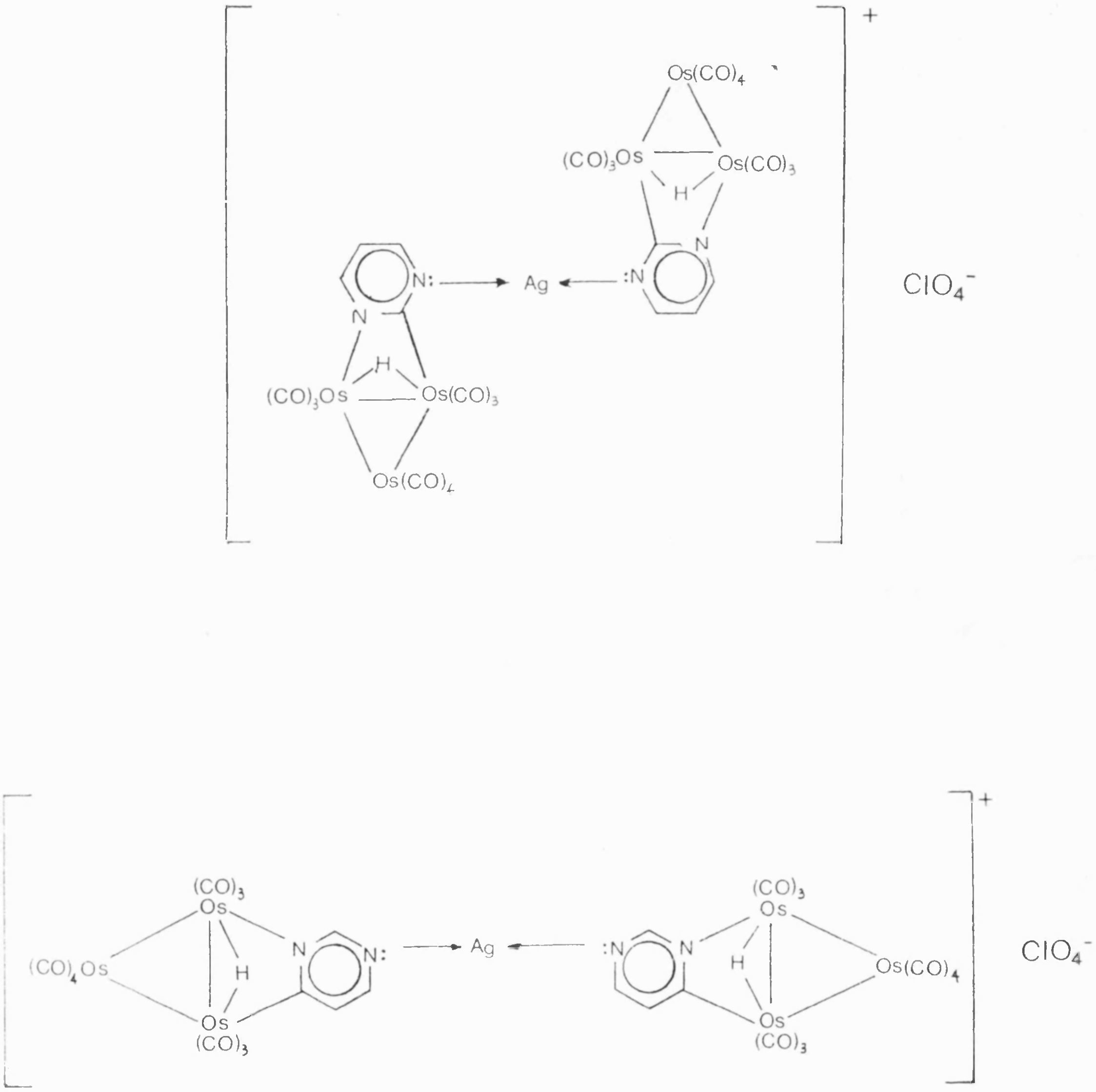


Figure 5.11 Predicted reaction products of $[Os_3H(C_4H_3N_2)(CO)_{10}]$ with $AgClO_4$

chromatography and the results had been analysed using 200 MHz ^1H NMR. The separation was not wholly successful because chromatography bands were overlapping. We have repeated this work so that the more sophisticated analytical methods currently available could be used in order totally to resolve the system.

The conformation of the nicotine used in this work was (S)(-) nicotine and the absolute stereochemistry about the chiral carbon atom is as shown in Figure 5.12.

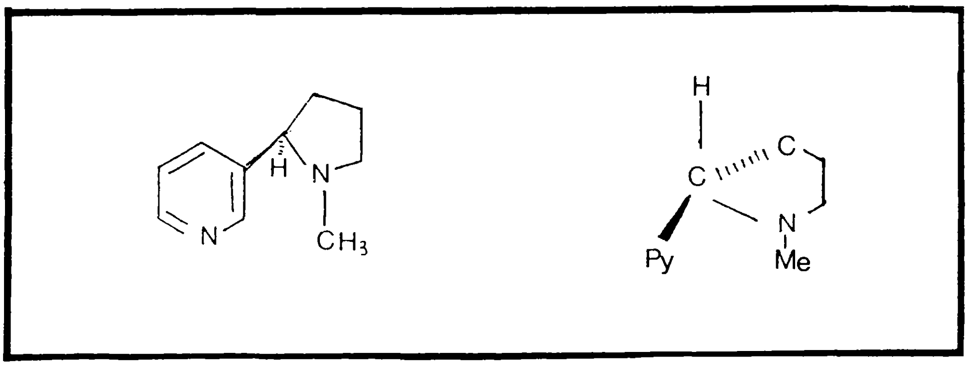


Figure 5.12 Absolute stereochemisty of (S)(-) nicotine

Initial attack at the triosmium cluster is through the lone pair of electrons on the nitrogen atom in the 6-membered ring followed by cleavage of a C - H bond, either C(1) - H or C(5) - H, as a result of which two pairs of diastereoisomers are possible as shown in Figure 5.13.

Positional isomer 1: Λ S Δ S

Positional isomer 2: Λ S Δ S

The crude mixture was chromatographed but no separation of the expected isomers was achieved. Impurities and residual starting material eluted in separate bands but the products appeared slowly as one very broad yellow band. This product was removed carefully from the silica surface and was rechromatographed using increasingly polar eluent mixtures and eventually some separation (into three bands) was visible. These bands were removed from the silica with great care but analysis

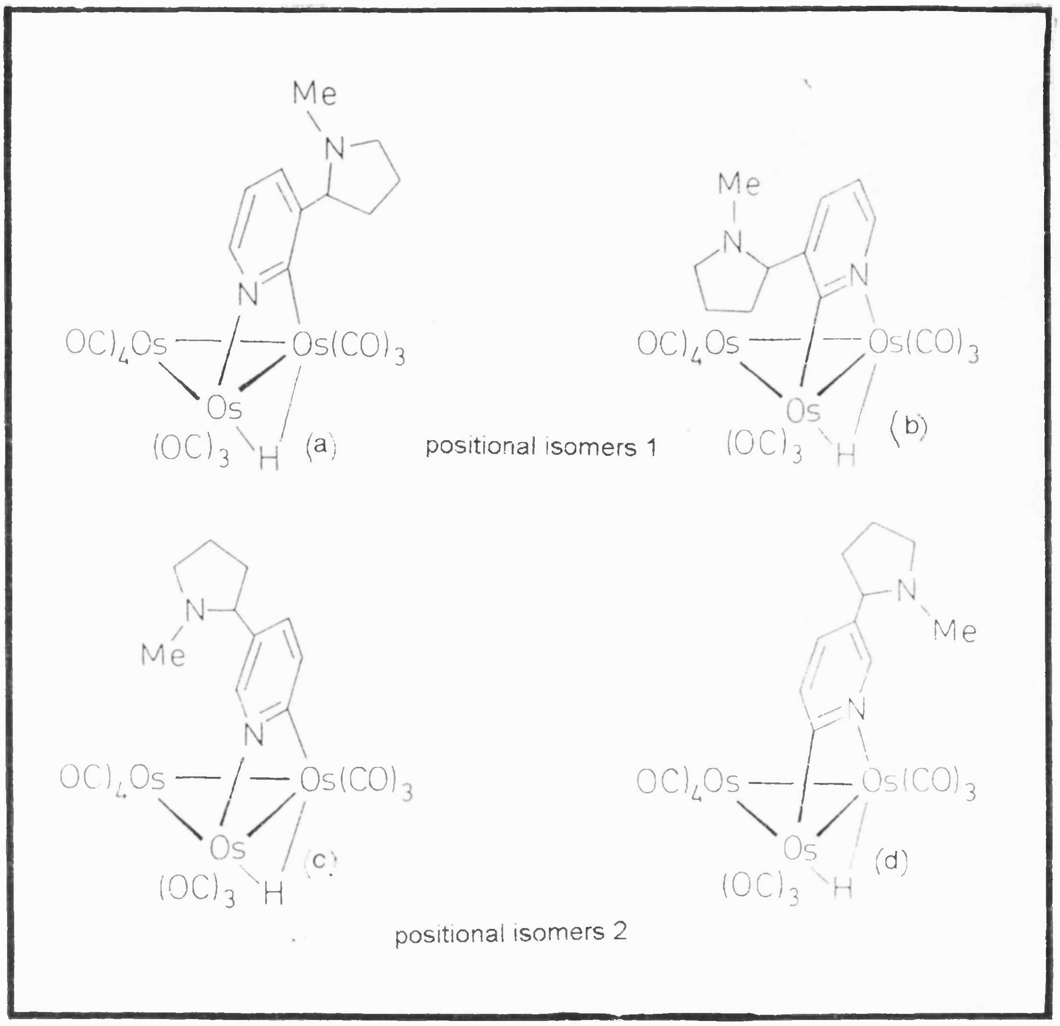


Figure 5.13 The diasteroisomeric pairs of [Os_3(nicotinyl)$(CO)_{10}$]

of the 400 MHz ^1H NMR spectra indicated that the bands still contained a mixture of the components shown in Figure 5.14.

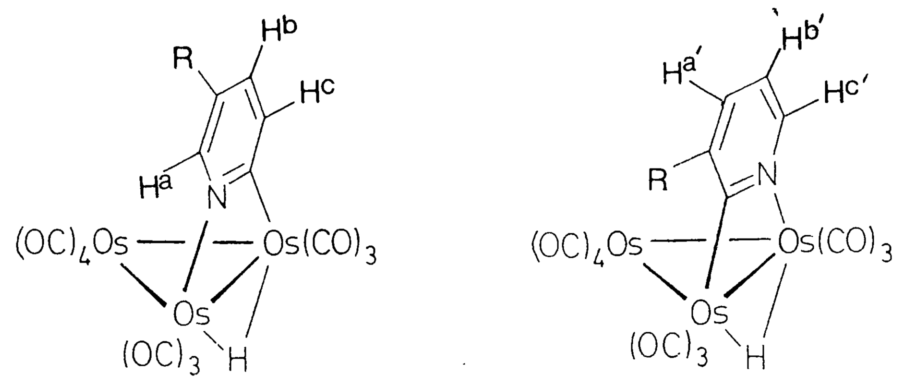
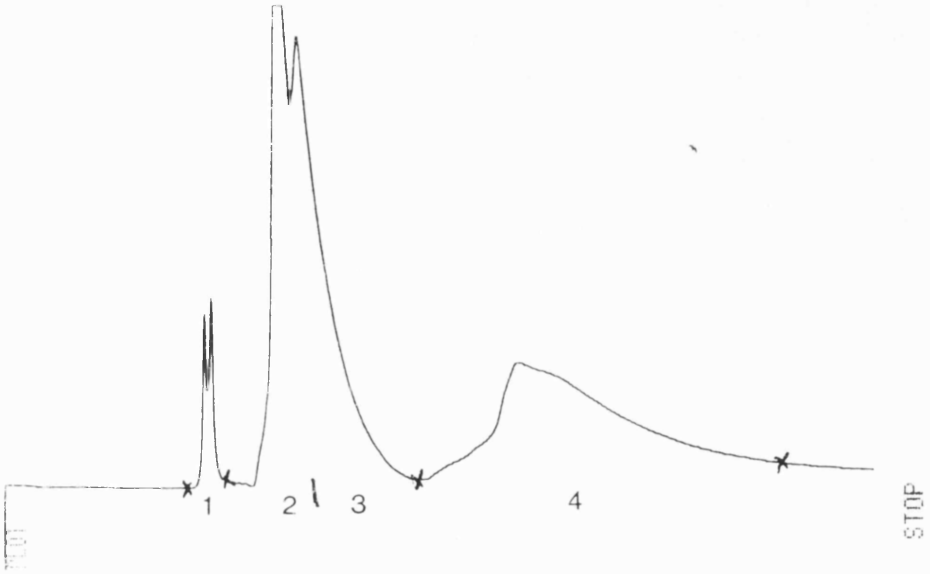


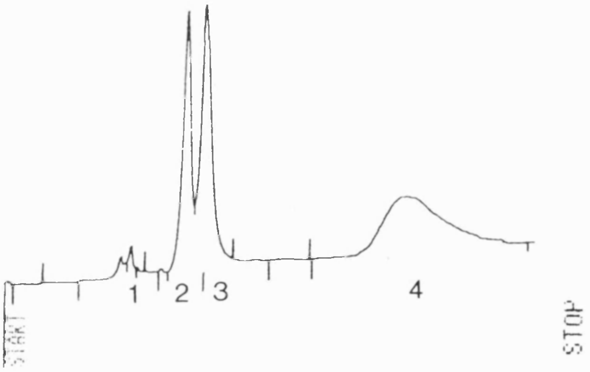
Figure 5.14 Mixture of components in TLC bands

As no pure samples of the expected isomers had been obtained, a pure sample of the mixture of isomers was prepared for separation by high performance liquid chromatography. The resulting chromatograms are shown in Figure 5.15. The fractions obtained from HPLC were extremely dilute, each containing less than 1 mg of product. Analysis by 400 MHz ^1H HMR showed that there was no hydride signal in Fraction 1 so it was not one of the major products expected from the reaction and was discarded. Fraction 2 showed two hydride signals at δ -14.41 and -15.50 which indicated that it was a mixture of isomers. Fractions 3 and 4 each showed one hydride signal at δ -14.41 and -14.83 respectively. The other signals in all the spectra were not unambiguousy assigned as the samples were very dilute and the signals at low field were difficult to interpret.

However, from the infrared spectra together with the ^1H NMR spectra, it was possible to deduce that Fractions 2 and 3 contained the isomeric pair shown in Figure 5.16.



Semi-preparative separation
250 x 10 mm Nucleosil silica gel/5 μm
254 nm
10% methanol/90% ethyl acetate



Analytical chromatogram
250 x 4.5 mm Kromasil silicage/5 μm
254 nm; 0.05 amps
1.0 cm^3/min
100% ethyl acetate

Figure 5.15 High performance liquid chromatograms of the mixture of isomers of $[Os_3(nicotinyl)(CO)_{10}]$

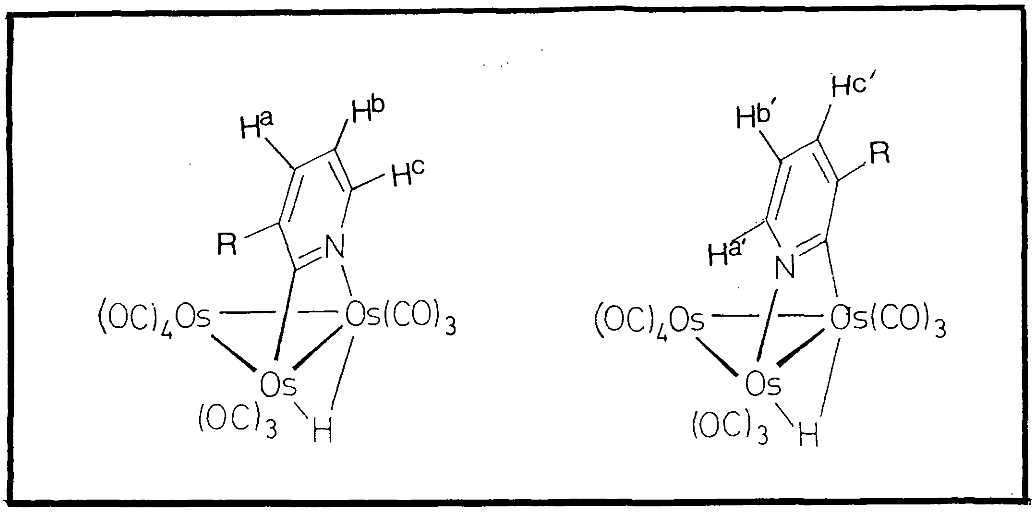
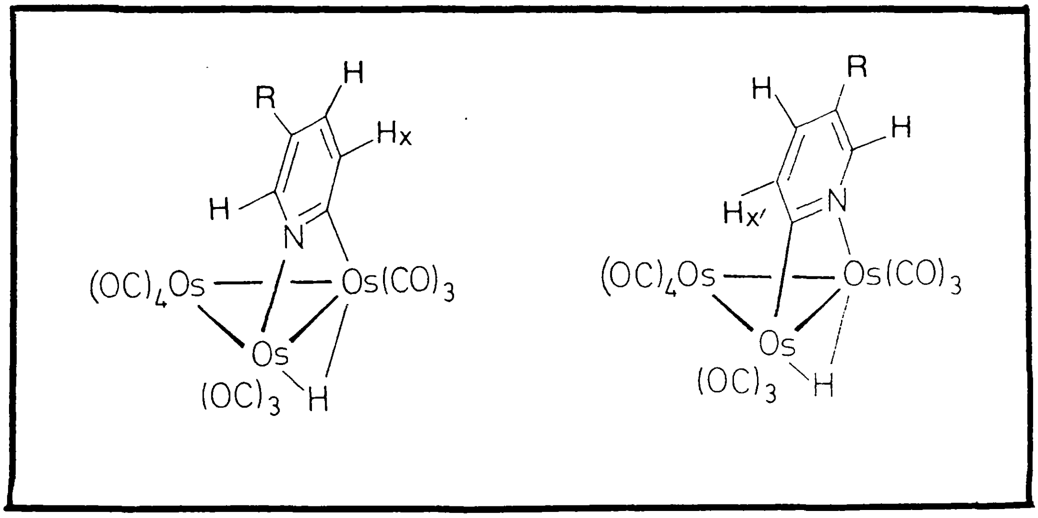


Figure 5.16 Pair of nicotinyl isomers contained in HPLC Fractions 2 and 3

Deductions made from the infrared spectra together with ^{1}H NMR data for Fraction 4 indicated that it was an unresolved mixture of the isomeric pair of compounds shown in Figure 5.17 where the signals for H_x and $H_{x'}$ would be expected to appear at low field due to deshielding by nitrogen:



5.17 Pair of nicotinyl isomers contained in HPLC Fraction 4

It is clear from these results that there are two positions of substitution and that each appears as diastereoisomers resulting from the different orientations of the ligand at the metal cluster. The four isomers could be clearly detected but could not be satisfactorily separated.

5.3 Tables

Table 5.1 ^{1}H NMR data for 6-membered ring heterocyclic compounds*

	δ/ppm	Assignment
$[Os_3H(C_4H_3N_2)(CO)_{10}]$ **1**	8.33 dd, 1H	C(6) or C(4) - H
1,2-metallated pyrimidine	8.14 dd, 1H	C(6) or C(4) - H
	6.88 t, 1H	C(5) - H
	-14.91 s, 1H	Os - H
$[Os_3H(C_4H_3N_2)(CO)_{10}]$ **2**	8.53 d, 1H	C(2) - H
1,6-metallated pyrimidine	7.93 d, 1H	C(5) - H
	7.37 dd, 1H	C(4) - H
	-14.97 s, 1H	Os - H
$[Os_3H(C_4H_3N_2)(CO)_{10}Os_3H(CO)_{10}]$	6.71 d, 1H	H^x
from **1** + $[Os_3(CO)_{10}(MeCN)_2]$	6.68 d, 1H	H^y
	-15.00 s, 1H	Os - H
$[Os_3H(C_4H_3N_2)(CO)_{10}Os_3H(CO)_{10}]$	7.15 d, 1H	H^a
from **2** + $[Os_3(CO)_{10}(MeCN)_2]$	6.63 d, 1H	H^b
	-14.37 s, 1H	Os - H
	-14.50 s, 1H	Os - H

* recorded in deuteriochloroform at 400 MHz and at room temperature

Table 5.2 ^{1}H NMR data for all isomers of [Os_3(nicotinyl)$(CO)_{10}$]

Isomer	Os*H*	H^3	H^4	H^5	H^6	Me
a*	-14.41 s	7.98 dd (J = 1.6, 5.5)	6.00 dd (J = 5.4, 8.1)	7.49 dd (J = 1.6, 7.9)		2.10 s
b*	-14.50 s	7.98 dd (J = 1.6, 5.5)	6.00 dd (J = 5.5, 7.9)	7.49 dd (J = 1.7, 7.9)		2.09 s
c#	-14.84 s	8.14 d (J = 1.4)		7.17 dd (J = 7.7, 1.8)	7.27 d (J = 7.8)	2.09 s
d#	-14.84 s	8.08 d (J = 1.4)		7.16 dd (J = 2.0, 8.0)	7.28 d (J = 8.0)	2.12 s

Spectra recorded at 400 MHz at room temperature. J values in Hz in parentheses.

* recorded in d_8-toluene

\# recorded in deuteriochloroform

Table 5.3 Comparison of ^{1}H NMR resonances in separations

TLC bands *	Os*H*	Assignment
1	-14.41 s	Isomer a
2	-14.50 s	Isomer b
3	-14.82 s	Isomers c and d (unresolved)
HPLC fractions *		
1	none	
2	-14.41 s -14.50 s	Isomers a and b
3	-14.41 s	Isomer a
4	-14.83 s	Isomers c and d

* recorded in d_8-toluene at 400 MHz and at room temperature

5.4 Experimental

Preparation of $[Os_3H(C_4H_3N_2)(CO)_{10}]$

To an off-yellow solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.2800 g, 3.002 x 10^{-4} mol) in dichloromethane (25 cm^3) was added a colourless solution of 1,3-diazine (pyrimidine) (0.07 cm^3). The mixture was stirred at room temperature under a nitrogen atmosphere for one hour and the progress of the reaction was monitored by infrared spectroscopy. The solvent was then removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and chromatographed (eluent, dichloromethane:petrol (b.p. < 40 °C) 9:11 v/v) to give two major and two trace yellow bands. These were extracted into dichloromethane from the silica.

Yields: 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$; 0.0290 g, 10%
1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$; 0.1090 g, 39%

Thermolysis of 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$

A yellow solution of 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ (0.1090 g, 1.171 x 10^{-4} mol) in heptane (80 cm^3) was heated to reflux under a nitrogen atmosphere for four hours. The progress of the reaction was monitored by infrared spectroscopy and at the end of this time the reaction mixture showed no change from the spectrum of the starting material.

Thermolysis of 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$

A yellow solution of 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ (0.0290 g, 3.12 x 10^{-5} mol) in heptane (40 cm^3) was heated to reflux under a nitrogen atmosphere for 4 hours. The progress of the reaction was monitored by infrared spectroscopy and after 4 hours the spectrum of the reaction mixture showed no change from that of the starting material.

Preparation of 1,2-metallated [$Os_3H(C_4H_3N_2)(MeCN)(CO)_9$]

To a bright yellow stirred solution of 1,2-metallated [$Os_3H(C_4H_3N_2)(CO)_{10}$] (0.1090 g, 1.171×10^{-4} mol) in acetonitrile (40 cm^3) was added dropwise over 20 minutes a solution of trimethylamine N-oxide (0.018 g, 1.62×10^{-4} mol) in warmed acetonitrile (16 cm^3). The progress of the reaction was monitored by infrared spectroscopy and a spectrum was taken after each addition of the trimethylamine N-oxide solution. After addition of all of the solution the mixture was allowed to continue stirring at room temperature for 10 minutes. It was then passed down a column (1" diameter, packing; silica gel mesh size 60 - 120, eluent, acetonitrile) to remove trimethylamine N-oxide which is irreversibily adsorbed by the silica. From the assignment of the infrared data it seemed that [$Os_3H(C_4H_4N_2)(MeCN)(CO)_9$] was the major product as the spectrum was characteristic of an acetonitrile-substituted nonacarbonyl species. The solvent was removed under reduced pressure to give a greenish-yellow residue which was used in its crude form as separation by chromatography was not successful.

Attempted preparation of 1,2-metallated [$Os_3H(C_4H_3N_2)(CO)_9$]

A yellow solution of 1,2-metallated [$Os_3H(C_4H_4N_2)(MeCN)(CO)_9$] plus impurities (*ca.* 0.1090 g) in cyclohexane was prepared by gradually warming whilst stirring under a nitrogen atmosphere. When fully dissolved the solution was heated to reflux. After 20 minutes a brown ring had formed on the flask around the liquid interface. The progress of the reaction was monitored by infrared spectroscopy and after this period it was possible to detect the formation of a decacarbonyl species at the expense of the nonacarbonyl species. After 1 hour, only the decacarbonyl species remained and this was subsequently identified as the parent compound.

Preparation of 1,6-metallated [$Os_3H(C_4H_3N_2)(MeCN)(CO)_9$]

To a bright yellow stirred solution of 1,6-metallated [$Os_3H(C_4H_3N_2)(CO)_{10}$] (0.0290 g, 3.12×10^{-5} mol) in acetonitrile (40 cm^3) was added dropwise over 20 minutes a solution of trimethylamine N-oxide (0.0168 g, 1.512×10^{-4} mol) in warmed acetonitrile (16 cm^3). The progress of the reaction was monitored by infrared spectroscopy and a spectrum was taken after each addition of the trimethylamine N-oxide solution. After addition of all of the solution the mixture was allowed to continue stirring at room temperature for 10 minutes. It was then passed down a column (1" diameter, packing; silica gel mesh size 60 - 120, eluent, acetonitrile) to remove trimethylamine N-oxide which is irreversibily adsorbed by the silica. From the assignment of the infrared data it seemed that [$Os_3H(C_4H_4N_2)(MeCN)(CO)_9$] was the major product as the spectrum was characteristic of an acetonitrile-substituted nonacarbonyl species. The solvent was removed under reduced pressure to give a yellow residue which was used in its crude form as separation by chromatography was not successful.

Thermolysis of 1,6-metallated [$Os_3H(C_4H_3N_2)(MeCN)(CO)_9$]

A yellow solution of 1,6-metallated [$Os_3H(C_4H_4N_2)(MeCN)(CO)_9$] (*ca.* 0.1000 g) plus impurities was prepared by stirring under a nitrogen atmosphere in hot toluene (50 cm^3) for 30 minutes. The solution was then heated to reflux. After 5 minutes a fine yellow precipitate formed and after 30 minutes the infrared spectrum indicated that the major product of the reaction was a decacarbonyl species. The solvent was removed under reduced pressure and the product was identified as the decacarbonyl parent compound.

Reaction of 1,6-metallated [$Os_3H(C_4H_3N_2)(CO)_{10}$] with [$Os_3(CO)_{10}(MeCN)_2$]

A bright yellow solution of 1,6-metallated (0.0424 g, 4.56 x 10^{-5} mol) in dichloromethane (30 cm^3) was mixed with an off-yellow solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.0439 g, 4.17 x 10^{-5} mol) in dichloromethane (25 cm^3). The mixture was stirred under a nitrogen atmosphere at room temperature and the progress of the reaction was monitored by infrared scectroscopy. After 4 hours a very fine yellow precipitate started to form. Stirring was continued for 4 days at room temperature. The precipitate was filted under vacuum and the solvent removed from the pale yellow filtrate under reduced pressure. The residue of the filtrate was chromatographed (eluent; dichloromethane: low-boiling petroleum ether 1:1 v/v) to give four major yellow bands which were extracted into dichloromethane from the silica. Two of the bands were identified as being [$Os_3H(C_4H_3N_2)(CO)_{10}$] and [$Os_3(CO)_{10}(MeCN)_2$] and one band did not have a hydride ligand in the ^1H NMR spectrum. The bright yellow precipitate was washed in low-boiling petroleum ether and air dried at room temperature. The remaining band from the chromatographic separation and the precipitate were believed to contain the two isomeric forms of [$Os_6H_2(C_4H_2N_2)(CO)_{20}$]. Unfortunately it proved impossible to grow crystals suitable for structure determination by X-ray crystallography.

Total yield: 0.021 g, 23%

Reaction of 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ with $[Os_3(CO)_{10}(MeCN)_2]$

An off-yellow solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.1080 g, 1.158 x 10^{-4} mol) in dichloromethane (25 cm^3) was added to a bright yellow solution of 1,2-metallated $[Os_3(C_4H_3N_2)(CO)_{10}]$ (0.1016 g, 1.092 x 10^{-4} mol) in dichloromethane (30 cm^3) and the mixture was stirred under a nitrogen atmosphere at room temperature for 4 days. The solvent was removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and chromatographed (eluent; dichloromethane:petroleum ether (b.p. < 40 °C) 4:1 v/v) to give three major yellow bands each of < 0.01 g and several minor bands each of < 0.001 g. Two of the major bands were identified from infrared spectra as being the starting materials. The remaining band was believed to be the required product.

Reaction of 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ with $AgClO_4$

To a yellow solution of 1,2-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ (0.040 g, 4.3 x 10^{-5} mol) in dichloromethane (15 cm^3) was added 2 mole equivalent of silver perchloride (0.0178 g, 8.6 x 10^{-5} mol) in dichloromethane (15 cm^3). The solutions were thoroughly mixed and diethyl ether (*ca.* 0.5 cm^3) was added dropwise. A small amount of orange solid was precipitated (< 0.01 g). This was washed in diethyl ether and air dried. As it dried the orange colour of the solid changed to black. Results from mass spectrometry were inadequate.

Reaction of 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ with $AgClO_4$

To a yellow solution of 1,6-metallated $[Os_3H(C_4H_3N_2)(CO)_{10}]$ (0.04 g, 4.3 x 10^{-5} mol) in dichloromethane (15 cm^3) was added 2 mole equivalent of silver perchloride

(0.0178 g, 8.6×10^{-5} mol) in dichloromethane (15 cm^3). The solutions were mixed and diethyl ether (*ca.* 0.5 cm^3) added dropwise. The solution immediately turned black and no separation process attempted was successful.

Preparation of $[Os_3(nicotinyl)(CO)_{10}]$ from (S)(-) nicotine

To an off-yellow solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.280 g, 3.002×10^{-4} mol) in dichloromethane (80 cm^3) was added (S)(-) nicotine (48.22 µl, 3.002×10^{-4} mol) The solutions were stirred at room temperature. After two hours the solvent was removed under reduced pressure and the residue redissolved in the minimum of dichloromethane and chromatographed (eluent; dichloromethane:petroleum ether (b.p. < 40 °C) 4:1 v/v) for 8 elutions to give one major and one minor yellow band. These were extracted into dichloromethane and the minor band was identified as $[Os_3(CO)_{10}(MeCN)_2]$. The major yellow band was rechromatographed (eluent; dichloromethane:petroleum ether (distilled, b.p. < 40 °C) in the combinations 1:9, 1:7, 1:5, 1:4 and 1:1 v/v succesively) to give three yellow bands which were extracted into dichloromethane and the solvent removed under reduced pressure. It was apparent from the ^1H NMR spectra that the bands were still mixtures of isomers and that one of the bands was not one of the required products as there was no hydride signal. The whole band was then chromatographed using high performance liquid chromatography (eluent; methanol:ethyl acetate 1:9 v/v) to give three bands, one of which was pure but the other two were still a mixture of the isomers of the product $[Os_3H(nicotinyl)(CO)_{10}]$.

5.5 References

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APPENDIX 1 General Experimental Details

Infrared spectra

Infrared spectra were recorded on a Perkin Elmer 257 spectrometer. In the region 2200 - 1800 cm^{-1}, spectra were recorded in soltion using cells made of either sodium chloride or calcium fluoride, with a cell path length of 0.5 mm. Calibration was carried out using the spectrometer on single beam to record a spectrum of atmospheric water, with sample spectra calibrated against the 1846 cm^{-1} absorption of water. The values in this thesis were adjusted in the light of the calibration results.

^{1}H NMR Spectra

^{1}H NMR spectra were recorded at 200 MHz and 400 MHz on a Varian spectrophotometer and at room temperature.

Thin Layer Chromatography

Chromatographic separations were carried out on 1 mm glass thin layer plates using silica gel (HF_{254} (type 60), E. Merck, Germany) prepared as an aqueous slurry which, after coating was allowed to dry at room temperature for 24 hours. The plates were then activated by heating in an oven at > 100 °C for a minimum of two hours.

Analyses

Carbon, hydrogen, nitrogen and phosphorus were determined by the Analytical laboratory, Chemistry Department, University College London.

Chemicals

$[Os_3(MeCN)_2(CO)_{10}]$ was prepared by the literature method cited in the text. Both phosphorus ylides were used as purchased from the Aldrich Chemical Company.