SYNTHESIS AND REACTIONS OF TERTIARY PHOSPHINES
CONTAINING HETEROCYCLIC SUBSTITUENTS WITH
TRANSITION METAL CARBONYL COMPLEXES

A thesis submitted in partial fulfillment of the requirements for the degree of
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by

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This thesis describes an examination of the synthesis and coordination chemistry of tertiary phosphines, PPh$_2$R, containing the 2-substituted heterocyclic substituents R = pyridyl, thienyl and furyl and the 2- and 3- substituted heterocycle, pyrrolyl, based on the dinuclear and trinuclear metal carbonyls, [M$_2$(CO)$_{10}$] (M = Mn, Re) and [Os$_3$(CO)$_{12}$], respectively.

For each of the ligands, substitution of up to two axial carbonyl ligands in [Mn$_2$(CO)$_{10}$] and up to two equatorial carbonyl ligands in [Os$_3$(CO)$_{12}$] occurs, to give simple phosphorus-bound monosubstitution compounds. Analogous compounds are not observed with [Re$_2$(CO)$_{10}$]. Other simple compounds, formed from the reaction of [Mn$_2$(CO)$_{10}$] with the furan and pyrrole ligands, include [Mn$_2$(μ-H)(μ-PPh$_2$)(CO)$_8$], which contains a hydride and a diphenyphosphido bridge and a related substitution compound, [Mn$_2$(μ-H)(μ-PPh$_2$)(PPh$_2$(2-C$_5$H$_4$X))(CO)$_8$] (X = O, NH).

Compounds involving coordination of the heterocyclic substituent of the ligand, via the heteroatom, the carbon atoms, or both, have also been characterised.

The bis and tris pyridylphosphines bridge dimanganese compounds via the phosphorus atom and the nitrogen atoms of two pyridyl units, to yield the related compounds, [Mn$_2$(μ-PR(2-C$_5$H$_4$N)$_2$)(CO)$_8$] (R = Ph, 2-C$_5$H$_4$N).

Diphenyl-2-thienylphosphine reacts thermally with [Mn$_2$(CO)$_{10}$] to give [Mn$_2$(μ-PPh$_2$)[μ-η$^0$-(C$_5$H$_4$S)](CO)$_8$], a complex derived from P-C bond cleavage which contains bridging diphenyphosphido and 2-thienyl units. This latter bridge coordinates to one Mn atom via the 2-carbon atom and to the other Mn atom via all
the ring atoms. A related Re compound is formed thermally; it differs in that only the S atom of the cleaved thienyl unit coordinates to the second Re atom. A precursor to this, which does not contain a cleaved thienyl unit, is formed photochemically. The ligand bridges the two Re atoms via the phosphorus and sulfur atoms. Diphenyl-2-pyrrolylphosphine gives a trimanganese compound in which the ligand bridges two of the Mn atoms via the phosphorus and nitrogen atoms and the other Mn atom is coordinated as a tricarbonylmanganese unit to all the atoms of the 2-pyrrolyl unit.

\[\text{[Os}_3(\text{CO})_{12}\text{]}\] reacts with the ligands to give clusters containing a hydride bridge and a $\sigma, \eta^2$-vinyl group, which as expected, exchange between metal centres at a slower rate than their Ru analogues. These clusters have a high thermal stability and only react at a high temperature to give an open trinuclear cluster which contains $\mu_2$-heterocyclic and phenylphosphido units on opposite faces of the triangle and which are derived from the loss of benzene. Two forms of this cluster can be visualised for diphenyl-3-pyrrolylphosphine which are not distinguishable by spectroscopic techniques. With diphenyl-2-pyrrolylphosphine a cluster containing the ligand bridging the Os atoms via a P-N bridge and the 2-carbon atom is also formed.
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Chapter 1

Introduction

This thesis examines the coordination of the tertiary phosphines which contain up to three of the heterocycles: pyridine, thiophene, furan and pyrrole, with the dinuclear metal carbonyl complexes \([M_2(CO)_{10}]\) (\(M = \text{Mn, Re}\)) and the trinuclear metal carbonyl complex \([\text{Os}_3(CO)_{12}]\). Therefore, as a pertinent introduction, a brief review of the transition metal complexes involved and a brief but not exhaustive review of the coordination of tertiary phosphines and related ligands to these transition metals has been included.

It is likely that these phosphines, which contain heterocyclic units, will initially substitute a CO ligand in the transition metal carbonyl complex and coordinate as simple tertiary phosphines through the phosphorus atom. However a second coordinating site, through \(\text{activation of}\) the heteroatom and/or a C-H bond on the heterocyclic unit at an adjacent metal centre in these dinuclear and trinuclear clusters is potentially available. These ligands are therefore potentially bidentate or even multidentate. This is analogous to the diphosphine ligands of the type \(\text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\) which are also discussed in this introduction, especially dppe (\(n = 1\)) which is the most analogous to these ligands. Except for the 2-pyridylphosphines where coordination to the metal through P and N atoms in dinuclear systems has also been achieved, these ligands previously have only been coordinated to mononuclear systems as simple tertiary phosphines with bonding through the
phosphorus atom only. This is discussed in more detail for each ligand in the relevant chapter which includes reports on reactions of these ligands with triruthenium clusters and of 2-pyridylphosphines with \([M_n(CO)_x]\) \((M = Mn, Re)\) and \([M_n(CO)_y]\) \((M = Ru, Os)\), work which has been carried out recently by others in these laboratories.

1.1 Diphosphines as Ligands

1.1.1 Coordination chemistry

The related bidentate diphosphine ligands \(\text{Ph}_2\text{P(CH}_2)\text{nPPH}_2\), especially dppm \((n = 1)\), have been studied extensively with transition metal complexes. Coordination of these diphosphine ligands to transition metal complexes occurs through the phosphorus atom in monodentate, chelate and bridging forms.\(^{12}\) However, for \(n = 0\), an oxidative cleavage of the \(P-P\) bond occurs with dinuclear complexes and the ligand coordinates as two bridging phosphido units. Complexes with monodentate dppm, which relate to tertiary phosphines such as \(\text{PPH}_3\), are formed with metal halide, metal carbonyl and several organometallic derivatives.\(^1\) Metal carbonyl derivatives include \([\text{Fe}(CO)_3(n^1\text{-dppm})]\),\(^3\) and \([\text{Cr}(CO)_6(n^1\text{-dppm})]\).\(^4\)

In forming chelate complexes, the optimum ring size where the natural bond angle at the metal centre is five. It is for this geometrical reason that dppe \((n = 2)\) is an excellent chelating ligand. Chelate complexes of dppm are known such as with the zerovalent carbonyl complexes of group 6, including the complete series, \(\text{cis-}[\text{Mo}(CO)_x(n^2\text{-dppm})]\) \((x = 2, 4, 6)\),\(^5\) and
with metal complexes of other groups. However, the four-membered ring so formed is strained and therefore the ligand usually acts as a monodentate ligand or more often as a bridging ligand.

1.1.2 Bond cleavage reactions of coordinated bridging diphosphines

When dppm (L) bridges a complex, two sites are available for activation by the metal centre. These are the methylene carbon and the phenyl rings. Normally it is the methylene carbon that is activated such that when complexes of the type $[\text{Fe}_2(\mu-L)_x(\mu-CO)(CO)_{y+z}] (x = 1, 2)$ are heated, CO loss followed by P-C bond cleavage occurs to yield $[\text{Fe}_2(\mu-L)_x(\mu-P\text{Ph}_2)(\mu-P\text{Ph}_2\text{CH}_2)(CO)_{y+z}] (x = 0, y = 4; x = 1, y = 2)$. However, if the P-C bond cleavage is prevented by the substitution of a methyl group for hydrogen on the methylene carbon of dppm, an orthometallation together with a P-Ph bond cleavage are observed.

1.2 Decacarbonyldimanganese

1.2.1 Synthesis and physical properties

The simple metal carbonyls of the elements adjacent to manganese such as $[\text{Cr}(CO)_5]$, $[\text{Fe}(CO)_5]$, $[\text{Co}_2(CO)_8]$ and $[\text{Ni}(CO)_4]$ were discovered in the late 1800's and early 1900's. In contrast
decacarboxyldimanganese, $[\text{Mn}_2(\text{CO})_{10}]$, was the first organometallic compound of manganese to be isolated and characterised, but the last of the first-row metal carbonyls to be discovered (reported in 1949). Conditions for synthesis were based on the earlier synthesis of $[\text{Cr}(\text{CO})_6]$.\(^9\) Carbonylation of a mixture of MnI\(_2\) and an unspecified Grignard reagent yielded $[\text{Mn}_2(\text{CO})_{10}]$ as a yellow crystalline solid. Mass spectra suggested a dinuclear species although the parent molecular ion was not observed.

Full characterisation was not achieved until 1954. Carbonylation of an ethereal solution of MnI\(_2\) synthesised from manganese and copper iodide gave $[\text{Mn}_2(\text{CO})_{10}]$ in 1% yield.\(^1\) The product was characterised mainly by IR spectroscopy and mass spectrometry. Synthetic methods for $[\text{Mn}_2(\text{CO})_{10}]$ have improved, the best method is the reduction of MnI\(_2\) by LiAlH\(_4\) in the presence of CO under pressure. Most researchers, including ourselves, use $[\text{Mn}_2(\text{CO})_{10}]$ supplied commercially.

$[\text{Mn}_2(\text{CO})_{10}]$ is a diamagnetic yellow crystalline material; its melting point (154 °C) was measured in a sealed tube because it decomposes at 110 °C. The molecular structure was determined by single-crystal X-ray diffraction and is shown in Figure 1.1. Two square-pyramidal Mn(CO)\(_5\) units are linked together through a metal-metal bond distance of 2.895(1) Å, the carbonyls being in a staggered ($D_{4d}$) arrangement.\(^1\)\(^2\)\(^3\)

Three major $\nu$(CO) absorption's at 2045.8, 2014.7 and 1983.8 cm\(^{-1}\) are observed in its IR spectrum in hexane,\(^4\) as well as weak bands at lower wavenumbers associated with isotopomers containing \(^{15}\)CO in natural abundance.\(^4\)\(^-\)\(^6\) The $\nu$(Mn-C) and $\delta$(MCO) bands in the far IR spectrum have
been assigned, as well as the $\nu$(Mn-Mn) which is observed at 160 cm$^{-1}$ in the Raman spectrum. The mass spectrum shows a low intensity parent ion peak with fragmentation to form dinuclear [Mn$_x$(CO)$_y$]$^+$ (when $x = 1$, $y = 1-5$; $x = 2$, $y = 1-10$) species.

![Molecular structure of [Mn$_2$(CO)$_{10}$]](image)

**Figure 1.1** Molecular structure of [Mn$_2$(CO)$_{10}$]
1.2.2 Reactivity with simple phosphines and related ligands

Generally one or two carbonyls in \([\text{Mn}_2(\text{CO})_{10}]\) can be displaced by simple tertiary phosphines and related ligands (L) under either thermal or photochemical conditions.\(^{21}\) Originally, it was thought (incorrectly) that the only substitution mechanism involved was the facile cleavage of the Mn-Mn bond in \([\text{Mn}_2(\text{CO})_{10}]\) under mild conditions to form the 17-electron species \(\text{Mn}(\text{CO})_5\). This reactive intermediate is readily substituted by an associative mechanism to yield \(\text{Mn}(\text{CO})_5\) radicals. Recombination of \(\text{Mn}(\text{CO})_5\) and \(\text{Mn}(\text{CO})_5\) radicals occurs with no strong thermodynamic preference for particular products, leading to \([\text{Mn}_2(\text{CO})_{10}], [\text{Mn}_2(\text{CO})_9\text{L}], [\text{Mn}_2(\text{CO})_8\text{L}_2], \) [eqn(1.1)], which can be readily separated chromatographically. The easy cleavage of the Mn-Mn bond in \([\text{Mn}_2(\text{CO})_{10}]\) can be understood by thermal or photochemical induced transitions into the lowest excited singlet state (\(\sigma \rightarrow \sigma^*\) transitions) which reduce the Mn-Mn bond order from 1 to 0 and result in the ready formation of \(\text{Mn}(\text{CO})_5\) radicals.

\[
\begin{align*}
\text{[Mn}_2(\text{CO})_{10}] & \quad \underset{\text{\text{Mn}(\text{CO})_5}}{\longrightarrow} \quad 2 \quad \text{Mn}(\text{CO})_5 \\
\text{Mn}(\text{CO})_5 + \text{L} & \quad \longrightarrow \quad \text{Mn}(\text{CO})_4\text{L} + \text{CO} \\
\text{Mn}(\text{CO})_4\text{L} & \quad \text{Mn}(\text{CO})_5 \\
\text{Mn}(\text{CO})_4\text{L} & \quad [\text{Mn}_2(\text{CO})_9\text{L}] \\
\text{Mn}(\text{CO})_4\text{L} & \quad [\text{Mn}_2(\text{CO})_8\text{L}_2]
\end{align*}
\]

Equation 1.1
As techniques for studying mechanisms and observing intermediates were refined, it became apparent that there was a concurrent substitution process for $[\text{Mn}_2(\text{CO})_{10}]$. This process involves a dissociative loss of CO and formation of the transient species $\text{Mn}_2(\text{CO})_9$. Subsequent reaction with an appropriate ligand yields the substituted compound, [(eqn(1.2)].

$$[\text{Mn}_2(\text{CO})_{10}] \xrightarrow{-\text{CO}} [\text{Mn}_2(\text{CO})_9] \xrightarrow{+\text{L}} [\text{Mn}_2(\text{CO})_9\text{L}] \quad (1.2)$$

The transient species, $\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_9$, the products of photolysis, have been detected in the gas phase using time-resolved spectroscopic techniques. Eximer laser photolysis of $[\text{Mn}_2(\text{CO})_{10}]$ at 350 nm (the energy required for the $\sigma \rightarrow \sigma^*$ transition) gave products of both photoprocesses but at shorter wavelengths (193 and 248 nm) only the product resulting from CO loss was observed. Photolysis of $[\text{Mn}_2(\text{CO})_{10}]$ has been studied more intensively in the condensed phase (matrix). Conventional flash-photolysis experiments provided spectra of radical intermediates and kinetic data for their rapid recombination. Flash-photolysis experiments in ethanol and cyclohexane established the presence of a second long-lived intermediate which was assumed to be $[\text{Mn}_2(\text{CO})_9(\text{EtOH})]$ in ethanol while $[\text{Mn}_2(\text{CO})_9]$ persists in cyclohexane. A separate matrix-isolation experiment at 77 K led to a structure for $\text{Mn}_2(\text{CO})_9$ shown in Figure 1.2, based on a carbonyl stretch at 1760 cm$^{-1}$ for the $\mu_1\eta^2$-CO group.
Ligand substitution in $[\text{Mn}_2(\text{CO})_{10}]$ under thermal conditions was shown to occur without homolytic Mn-Mn bond cleavage. The absence of build-up of $[\text{Mn}_2(\text{CO})_{14}(^{13}\text{CO})_{4}]$ in the carbonylation of $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Mn}_2(^{13}\text{CO})_{10}]$ confirmed that Mn-Mn bond cleavage was not a significant process.\textsuperscript{28}

![Figure 1.2](image) Structure of the intermediate $[\text{Mn}_2(\text{CO})_{10}]^f$

Occasionally tri and tetrasubstituted complexes are formed with monodentate ligands containing strong $\pi$-acceptors such as PF$_3$.\textsuperscript{29} This formation can be understood by referring to the formation of Mn(CO)$_5$ radicals and the associative CO substitution of these yielding Mn(CO)$_4$L radicals. Further associative CO substitution of Mn(CO)$_4$L radicals, to yield Mn(CO)$_3$L$_2$ radicals, followed by random recombination results in tri and tetrasubstituted complexes. Attempts to substitute more than two carbonyl ligands with other ligands such as PPh$_3$ yielded the metal-hydride species $[\text{MnH(CO)}_3L_2]$, the hydride being derived from the solvent.\textsuperscript{21} Extensive substitution can occur with bidentate ligands and complexes such as $[\text{Mn}_2(\mu\text{-dppm})_2(\text{CO})_6]$ have been prepared.\textsuperscript{30}
Several different geometries can be visualised for mono and disubstituted complexes of \([\text{Mn}_2\text{(CO)}_{10}]\) with monodentate ligands and these are shown in Figure 1.3. It is generally possible to identify geometries based on IR \(\nu(\text{CO})\) data and some structures were confirmed by X-ray crystallography.\(^3\) Most compounds of the formula \([\text{Mn}_2\text{(CO)}_6\text{L}]\) are substituted in the axial position and for this symmetry \((C_4v)\) five IR bands in the \(\nu(\text{CO})\) region are expected and usually observed.\(^2\) There are a few equatorially substituted \([\text{Mn}_2\text{(CO)}_6\text{L}]\) complexes with the smallest phosphine ligand \(\text{PH}_3\) being an example.\(^3\) With disubstituted complexes, \([\text{Mn}_2\text{(CO)}_6\text{L}_2]\), again there is a strong preference for axial substitution. The high molecular symmetry \((D_{4h})\) results in a simple IR \(\nu(\text{CO})\) spectrum with a very weak and very strong band only observed.\(^4\) The related arsine complexes can have differing geometries. The \(\text{AsPh}_3\) compound retains diaxial geometry,\(^5\) while \(\text{AsMe}_3\), \(\text{AsEt}_3\) and \(\text{AsPhMe}_2\) result in diequatorial symmetry,\(^2\) the latter being confirmed crystallographically.\(^6\) A case for steric crowding in diaxial geometries can be made but cannot be fully justified due to the diaxial geometry observed with \(\text{AsPh}_3\). GC revealed a mixture of products from the reaction of \([\text{Mn}_2\text{(CO)}_{10}]\) with \(\text{PF}_3\), the geometries of which have been worked out.\(^7\)

Bidentate phosphine ligands (P\(^2\)P) give di and tetrasubstitution products with \([\text{Mn}_2\text{(CO)}_{10}]\) in which the ligands coordinate to the equatorial positions on adjacent metals, to give the bridging species shown in Figure 1.4. Two isomers of \([\text{Mn}_2\text{(\mu-dppm)}_2\text{(CO)}_6]\) are formed, \textit{mer},\textit{mer} and \textit{mer},\textit{fac} isomers.\(^8\) The latter is less stable and slowly converts to the former isomer.
Figure 1.3

Figure 1.4
Steric repulsions in these complexes leads to ready CO loss to give $[\text{Mn}_2(\mu\text{-dppm})_2(\text{CO})_6]$ which contains a rare, four-electron donating, CO group which is designated as a $\mu,\eta^1:\eta^2-$CO ligand. This complex relates structurally to the transient species $\text{Mn}_2(\text{CO})_6$.

A different geometry is found with the nitrogen bidentate ligands bipy and phen $(\text{N}^\text{N})$ shown in Figure 1.5. These ligands substitute at a single metal atom. This different geometry can be explained by the smaller bite-size, that is the distance apart of the donor atoms, in bipy and phen than in the diphosphines. They are unable to span adjacent metals but form highly stable chelate rings.

Figure 1.5
1.3 Decacarbonyldirhenium

1.3.1 Synthesis and physical properties

Decacarbonyldirhenium, \([\text{Re}_2\text{(CO)}_{10}]\), was first synthesised by the reaction of \(\text{Re}_2\text{O}_7\) or \(\text{KReO}_4\) at 250 °C under a carbon monoxide atmosphere.\(^{41}\) It is now best prepared by heating the heptoxide with \(\text{CO}\) under pressure.

\([\text{Re}_2\text{(CO)}_{10}]\) is a white crystalline material (m.p. 177 °C) which is structurally isomorphic to \([\text{Mn}_2\text{(CO)}_{10}]\). The molecule consists of two staggered, square-pyramidal \(\text{Re(CO)}_5\) units joined together with a \(\text{Re-Re}\) bond of 3.0413 Å, resulting in \(D_4h\) symmetry.\(^{12}\) Assignments of the \(v(\text{CO})\) bands in IR and Raman spectra have been made,\(^{13}\) and the \(v(\text{Re-Re})\) has been measured at 122 cm\(^{-1}\) by Raman spectroscopy.\(^{42}\)

1.3.2 Reactivity with simple phosphines and related ligands

As with \([\text{Mn}_2\text{(CO)}_{10}]\), two possible CO substitution mechanisms for \([\text{Re}_2\text{(CO)}_{10}]\) with simple phosphines and related ligands (L) have been proposed. One involves reversible homolytic fission of the \(\text{Re-Re}\) bond to form two \(\text{Re(CO)}_5\) radicals, followed by rapid associative CO substitution at the 17-electron species. Radical recombination yields \([\text{Re}_2\text{(CO)}_{10}]\), \([\text{Re}_2\text{(CO)}_5\text{L}]\) and \([\text{Re}_2\text{(CO)}_6\text{L}_3]\) and indeed photolysis of a mixture of
[\textsuperscript{185}Re \textsubscript{2}(CO)\textsubscript{10}] and [\textsuperscript{187}Re \textsubscript{2}(CO)\textsubscript{10}] leads to the rapid and complete scrambling of rhenium isotopes.\textsuperscript{43}

However, from a kinetic study of the photochemical substitution of the mixed metal species, [MnRe(CO)\textsubscript{10}], Atwood and Sonnenberger made three observations which they believed were inconsistent with a free-radical mechanism.\textsuperscript{44} These were the predominance of the rhenium substituted isomer, the failure of the manganese substituted isomer, [L(CO)\textsubscript{4}MnRe(CO)\textsubscript{5}] to isomerise to the rhenium substituted isomer, [(CO)\textsubscript{5}MnRe(CO)\textsubscript{L}] and the lack of isomerisation to homodinuclear species. They proposed dissociative CO loss to form [MnRe(CO)\textsubscript{5}], which contains a 4-electron donating CO group. Solution\textsuperscript{45} and gas-phase\textsuperscript{46} spectroscopy provide evidence that CO loss competes with Re-Re bond cleavage as the primary photochemical event.

As with [Mn\textsubscript{2}(CO)\textsubscript{10}], thermal substitution reactions do not involve homolytic bond cleavage of the Re-Re bond as the primary activation step.\textsuperscript{47} Crossover of rhenium isotopes is not observed in the reactions of [\textsuperscript{185}Re\textsubscript{2}(CO)\textsubscript{10}] and [\textsuperscript{187}Re\textsubscript{2}(CO)\textsubscript{10}] with \textsuperscript{15}CO at 150 °C and similarly reaction of [\textsuperscript{185}Re\textsubscript{2}(CO)\textsubscript{10}], [\textsuperscript{187}Re\textsubscript{2}(CO)\textsubscript{10}] and PPh\textsubscript{3} to yield [Re\textsubscript{2}(CO)\textsubscript{9}(PPh\textsubscript{3})] under a CO atmosphere proceeds with essentially no crossover.\textsuperscript{43}

As for [Mn\textsubscript{2}(CO)\textsubscript{9}L], there are two possible isomers for [Re\textsubscript{2}(CO)\textsubscript{9}L]. It seems that steric factors are important in determining the geometry. Bulky ligands such as PPh\textsubscript{3} and PMePh\textsubscript{2} have a strong preference for axial geometry,\textsuperscript{48,49} although an equatorially substituted PPh\textsubscript{3} complex has been synthesised.\textsuperscript{50} Whereas smaller ligands such as PMe\textsubscript{2}Ph and pyridine
Disubstituted complexes, \([\text{Re}_2(\text{CO})_6L_2]\), are obtained only as the diaxial substitution product with ligands such as \(\text{PPh}_3\) and \(\text{P}(\text{OPh})_3\).\(^{50,51}\) Whereas ligands such as \(\text{PMe}_2\text{Ph}, \text{AsMe}_2\text{Ph}, \text{PMePh}_2\) and pyridine yield only diequatorial disubstituted products.\(^{50,51}\) Trisubstitution has been achieved for several more complexes than for \([\text{Mn}_2(\text{CO})_{10}]\) and the three isomers that have been observed are shown in Figure 1.6.\(^{48,50}\)

\([\text{Re}_2(\text{CO})_{10}]\) is generally more inert than \([\text{Mn}_2(\text{CO})_{10}]\) and various catalysts and agents have been used in its thermal and photochemical CO substitution. As with many transition metal carbonyls, amine-\(N\)-oxides facilitate the loss of carbonyl ligands by the formation and subsequent expulsion of carbon dioxide.\(^{49}\) The resulting coordinated amine is more labile than CO and easily displaced. Transition metal complexes such as \([\text{Pt}(\text{PPh}_3)_4]\),\(^{52}\) are also observed to catalyse substitution reactions of \([\text{Re}_2(\text{CO})_{10}]\) with phosphines.

![Figure 1.6](image-url)
1.4 Dodecacarbonyltriosmium

1.4.1 Synthesis and physical properties

Dodecacarbonyltriosmium, [Os$_3$(CO)$_{12}$], was first reported in 1943 as [Os$_2$(CO)$_6$].$^{53}$ Reaction of [OsO$_4$] with HI led to an oxyiodide, which on carbonylation in benzene at 150 °C yielded [Os$_3$(CO)$_{12}$] in poor yield. Today it is synthesised by high-pressure carbonylation of the tetroxide at 175 °C in an alcoholic solvent.$^{54}$

[Os$_3$(CO)$_{12}$] is an air-stable yellow crystalline material with a limited solubility in organic solvents at room temperature. In solution and in the crystal it is composed of a triangle of osmium atoms linked together with an average Os-Os distance of 2.877(3) Å. There are six axial CO ligands perpendicular to, and six equatorial CO ligands in the plane of the Os$_3$ triangle, giving rise to a molecule with essentially D$_{3h}$ symmetry but with slight distortion to D$_s$.$^{55}$ The average axial Os-C distance [1.946(6) Å] is greater than the average equatorial Os-C distance [1.912(7) Å], the longer Os-C bond distance is a consequence of competition between axial CO ligands for metal π-electron density. Four ν(CO) peaks are observed in IR spectrum,$^{56}$ and two ν(Os-Os) at 158.9 and 113 cm$^{-1}$ are observed in the Raman spectrum.$^{57}$ The EI mass spectrum shows the parent molecular ion and successive loss of carbonyl ligands. High abundances of [Os$_3$(CO)$_{10}$]$^{12+}$ ions are also observed, but mono and dinuclear ions are not.$^{58}$
Dynamic NMR studies on [Os₃(CO)₁₂], and in particular $^{12}$C-NMR of [Os$_{3}^{18}$O$_{3}^{15}$CO] (I = 1/2 for $^{18}$Os), are of particular interest in understanding the fluxional exchange of the axial and equatorial CO ligands. In the static low temperature spectrum an axial and an equatorial doublet are observed at $\delta$ 182.3 and 170.4, with $J$(OsC) of 90 ± 2 and 115 ± 2 Hz, respectively. This difference between axial and equatorial CO signals is a consequence of the longer axial Os-C bond length. At around 70 °C these signals coalesce and at 150 °C a 1:3:3:1 quartet is observed at $\delta$ 176.4 with a $J$(OsC) of 33 ± 1 Hz, indicative of intramolecular exchange of axial and equatorial CO ligands over all three osmium atoms. Exchange of axial and equatorial CO ligands by a localised turnstile rotation within each Os(CO)$_{4}$ unit would not explain these results. A delocalised carbonyl scrambling process involving exchange between a $D_{3h}$ and a $C_{2v}$ structure containing two bridging carbonyls as seen in [Fe$_{3}$CO]$_{12}$] is one process among others occurring.

1.4.2 Reactivity with simple phosphines and related ligands

Thermal reaction of [Os$_{3}$(CO)$_{12}$] with simple phosphines and related ligands (L) requires a minimum temperature of around 100 °C. Presumably, the rate is limited by the rate of unimolecular CO dissociation. The direct reaction of many of ligands, such as PPh$_{3}$, PMe$_{3}$, PEt$_{3}$, PMe$_{2}$Ph, AsMe$_{2}$Ph, and PEt$_{2}$Ph with [Os$_{3}$(CO)$_{12}$] in solvents such as toluene leads to a mixture of the mono, di and trisubstituted products, which are separable by chromatography. This suggests that the rates of the second
and the third substitutions are not very different from that of the first. This is in contrast to $[\text{Ru}_3(\text{CO})_{12}]$, where the rate of the first substitution is significantly slower than the rates of the second and third substitutions and only the trisubstituted product is obtained.\(^{65}\)

The substitution of the more labile acetonitrile ligand in $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ and $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ complexes with a range of ligands, including the ones mentioned above and also $\text{PPh}_2\text{Me}$,\(^{66}\) $\text{P(OMe)}_3$,\(^{67}\) $\text{PBu}^\prime\text{NH}_2$,\(^{68}\) and $\text{AsMe}_2\text{Ar}$ ($\text{Ar} =$ substituted phenyl groups),\(^{69}\) leads to mono and disubstitution products, respectively. Mixed ligand disubstitution products, $[\text{Os}_3(\text{CO})_{10}L^L]\ [L = \text{P(OMe)}_3, L^L = \text{P(p-tolyl)}_3]$, have been obtained by controlled addition of the ligands to the bis-acetonitrile complex.\(^{66}\)

Carbonyl substitution reactions have also been catalysed by the radical anion reducing agent, $[\text{Ph}_2\text{CO}]^\cdot$,\(^{70}\) and by $[\text{PPN}]X$, ($X$ = cyanide, halide or acetate), which coordinates to the metal and is itself replaced.\(^{71}\) Photochemical reactions are not generally used in triosmium clusters as Os-Os bond cleavage and fragmentation of the cluster into mono and dinuclear osmium complexes occurs.

During a thermal substitution reaction of $[\text{Os}_3(\text{CO})_{12}]$, one CO ligand at each Os atom is usually replaced. It follows that more forcing conditions are required to substitute more than one CO on each Os atom. However, high temperatures commonly leads to cyclometallation of the ligand or other oxidative-addition reactions, and no tetrasubstituted complexes of $[\text{Os}_3(\text{CO})_{12}]$ have been prepared with simple monodentate ligands.
As with many substituted transition metal carbonyls, the geometry of the products of substitution of \([\text{Os}_3(\text{CO})_9]\) with these simple ligands, can in principle be identified from their IR \(\nu(\text{CO})\) spectra. Axial substitution is only observed with small ligands or with rod-like ligands such as acetonitrile.\(^{72}\) The vast majority of simple ligands only coordinate equatorially for example, this has been confirmed crystallographically for \(\text{PPh}_3\)\(^{73}\) and \(\text{P(OMe)}_3\)\(^{74}\). At first sight, this is a somewhat perplexing result for two reasons. The axial \(\text{CO}\) ligands in \([\text{Os}_3(\text{CO})_9]\) have longer Os-C bonds, are more weakly coordinated and are expected to be more readily substituted than equatorial \(\text{CO}\) ligands. Also, axial substitution is more favoured electronically, leaving a \(\text{fac}\) tricarbonyl unit. The more dominant steric effects in axial substitution explain why there is a strong preference for equatorial substitution. The average axial-axial C-C bond distance is 2.875 Å compared to the average equatorial-equatorial C-C bond distance of 3.424 Å, across the Os-Os bonds. Therefore only small or rod-like ligands can be accommodated axially.

Substitution of more than one \(\text{CO}\) ligand per osmium atom, and the generation of isomers has been achieved via the use of acetonitrile and butadiene \(\text{Os}_3\) complexes. Reactions of ligands such as \(\text{PMe}_2\text{Ph}\) with the \(\text{bis-}\)acetonitrile complex or the 1,1- and 1,2-isomers of \([\text{Os}_3(\text{CO})_{10}(\text{butadiene})]\) gives two separable isomers; 1,1- and 1,2- \([\text{Os}_3(\text{PMe}_2\text{Ph})_2(\text{CO})_9]\).\(^{75}\) Dynamic \(^1\text{H},\)\(^{13}\text{C}\) and \(^{31}\text{P}\) NMR show there to be two rapidly interconverting 1,2- isomers which do not interchange with the 1,1-isomer up to its decomposition at \(105^\circ\) to \([\text{Os}_3(\mu-\text{H})(\mu-\text{PMe}_2\text{C}_6\text{H}_2})(\text{PMe}_2\text{Ph})(\text{CO})_{10}\)], in which the phosphorus atoms
are still coordinated to the same osmium atoms. A third possible isomer of the 1,2-complex in which the two phosphines are cis has not been observed for monodentate complexes. Isomers have also been observed in the [Os₃(PMe₂Ph)₃(CO)]₇. The 1,2,3-isomer in which the ligands avoid adjacent positions on adjacent metal centres, is the major product but a 1,1,2-isomer is observed by NMR spectroscopy.

Diphosphine, Ph₂P(CH₂)nPPh₂ (n = 1-4), substituted complexes of [Os₃(CO)] have also been prepared. Substitution of acetonitrile from [Os₃(CO)₃(MeCN)] by dppm yields the complex, [Os₃(CO)₃(μ₃-dppm)]. The rate of decarbonylation of this complex to give [Os₃(CO)₃(μ₃-dppm)] is independent of the concentration of dppm or CO. Also, the rate is not retarded by CO, suggesting that reversible CO dissociation is not rate-determining and that bridge closure is associative. A negative ΔS° value further supports this. In comparison a positive ΔS° value for the reaction of L with [Os₃(CO)₃,L] is observed.

Some complexes of the type [Os₃(CO)₃(μ-diphosphine)] have been confirmed by X-ray crystallography, for example with dppe. There is a strong preference again for equatorial substitution, with the phosphorus donor atoms occupying cis coordination sites. As with monodentate phosphines, the availability of 1,1- and 1,2-isomers of [Os₃(CO)₃(butadiene)] has allowed 1,1- and 1,2-isomers of [Os₃(CO)₃(diphosphine)] to be prepared; crystal structures have only been determined for the bridging (1,2-) and not the chelating (1,1-) isomers. The dppm complex is only found in the bridging form because four-membered rings are unfavourable. [Os₃(CO)] and
dppm also give rise to a nonacarbonyl complex, \([\text{Os}_3(\mu-\text{dppm})(\eta^1-\text{dppm})(\text{CO})_3]\).  

Figure 1.7 shows the geometries of the substitution products of \([\text{Os}_3(\text{CO})_{12}]\) with diphosphines.
Chapter 2

Coordination Chemistry of the 2-Pyridylphosphines with Decacarbonyldimanganese

2.1 Introduction

2.1.1 Coordination chemistry of the 2-pyridylphosphines with transition metal complexes

The three 2-pyridylphosphines; PPh$_2$(2-C$_5$H$_4$N), PPh(2-C$_5$H$_4$N)$_2$ and P(2-C$_5$H$_4$N)$_3$ have up to two, three and four potential coordination sites respectively, through the P and N atoms. Of these three ligands the coordination of PPh$_2$(2-C$_5$H$_4$N) to transition metal complexes is by far the most extensive, this is probably as a result of its comparison to the ligand dppm, the chemistry of which has been briefly discussed in Section 1.1. PPh$_2$(2-C$_5$H$_4$N) differs from dppm in two main ways. These are the unsymmetrical nature of the ligand i.e the affinity of different metals or the same metals in different oxidation states towards the P and N atoms and also its smaller bite-size, that is the distance between the donor atoms. Bearing in mind the extensive chemistry of PPh$_2$(2-C$_5$H$_4$N) this discussion has been split into three sections: the chemistry of PPh$_2$(2-C$_5$H$_4$N), the chemistry of PPh(2-C$_5$H$_4$N)$_2$
and \( P(2-C_5H_4N)_3 \), and also the chemistry of all three ligands with \([\text{Re}_2(\text{CO})_{10}]\), \([\text{Ru}_3(\text{CO})_{12}]\) and \([\text{Os}_3(\text{CO})_{12}]\).

(a) Diphenyl-2-pyridylphosphine: Monodentate, chelating and bridging are the three different modes of coordination of the ligand \( \text{PPh}_2(2-C_5H_4N) \) to transition metal complexes that have been observed.\(^8^0\) Two possibilities for the monodentate coordination of \( \text{PPh}_2(2-C_5H_4N) \) to transition metal complexes are available. Through the P and the N donor sites. Monodentate complexes of \( \text{PPh}_2(2-C_5H_4N) \) are observed to bind through the P atom only and no monodentate complexes with binding through the pyridyl N atom have been observed. This is a consequence of the P atom being a stronger \( \pi \)-acceptor. \( \text{PPh}_2(2-C_5H_4N) \) is similar to \( \text{PPh}_3 \), with a CH unit being replaced with a N atom.\(^8^1\) Monodentate P-bound complexes can be synthesised by ligand substitution,\(^8^2\) which includes an example of substitution of \( \text{PPh}_3 \) itself,\(^8^7\) and also with the use of amine-N-oxides.\(^8^0\)

The 2-pyridyl N atom in P-monodentate \( \text{PPh}_2(2-C_5H_4N) \) complexes is positioned such that it can bind to a second identical or different metal atom to yield homo and heterobinuclear complexes, respectively. Being a rigid ligand with a short bite-size it has little flexibility and so can stabilise these complexes, often by the formation of a metal-metal bond. In a heterobimetallic complex each metal centre may undergo reactions observed in the mononuclear species and also due to the close proximity of the centres, novel modes of reactivity can be observed.
A series of *heterobinuclear* complexes have been prepared by methods such as conproportionation reactions, \(^{81,85,88-95}\) and coordination by an organometallic, multidentate ligand such as *trans*-\([Fe\{PPh_2(2-
C_5H_4N)\}_2(CO)_3]\).\(^96\) Conproportionation reactions give rise to head-to-head [HH] and head-to-tail [HT] isomers. In fact, up to three isomers are possible with a heterobinuclear complex as shown in Figure 2.1. Homobinuclear complexes can also be synthesised by conproportionation reactions. Complexes without metal-metal bonds are fewer, but are also formed.\(^97,98\) The rigidity of the pyridyl ring means the ligand may have difficulty in accommodating larger metal-metal separations.

Formation of a four-membered chelate ring from a monodentate P-bound complex with coordination through the pyridyl N atom may occur if no additional metal atom is present.\(^98,97,99,100\) As with chelate complexes of dppm, strains are great in these four-membered chelate rings and there is a high degree of angular distortion at the central metal atom as well as within the chelate ring. Hence PPh\(_2\)(2-C\(_5\)H\(_4\)N) chelate complexes are unstable and the ring is opened up easily, more often than not at the N atom to form either a P-monodentate complex,\(^99\) or a bridged binuclear complex if another metal atom is available.\(^97\)

(b) *Bis- and tris-2-pyridylphosphines:* The coverage of these two phosphines in the literature is very limited. However, the observed P-bound coordination in \([Mo(CO)_{6\pm}\{PPh(2-C_5H_4N)\}_2]\) (\(x = 1,2\)),\(^101\) and the N and N,N' bound coordination in \([CoCl_2\{PPh(2-C_5H_4N)\}_2]\),\(^102\) and \([Mo(n^3-C_3H_5)(CO)_2\{PPh(2-\)
Figure 2.1  Isomers of dibridged heterobinuclear complexes of PPh₃(2-C₅H₄N)
respectively, as shown in Figure 2.2, shows the competitive binding with respect to the P and N atoms. For soft Mo(0) centres preferential binding is to the soft P atom and with the hard Co(II) and Mo(II) centres preferential binding is to the hard N atom.

Figure 2.3 Structures of [CoCl₃(η²-PPh(2-C₅H₄N)₂)] and [Mo(η²-PPh(2-C₅H₄N)₂)(CO)₃] showing the N,N'- bonding nature of the ligand PPh(2-C₅H₄N)₂ to "hard" metal centres.¹⁰¹,¹⁰²
Results obtained with $[\text{Re}_2(\text{CO})_{12}]$ and $[\text{M}_2(\text{CO})_{12}]$ ($\text{M} = \text{Ru}, \text{Os}$):

The complexes obtained from the reaction of $[\text{Re}_2(\text{CO})_{12}]$ with the 2-pyridylphosphines are shown in Figure 2.3. They include axially and diaxially P-bound monosubstitution products (not shown),\textsuperscript{82,103} as well as a complex in which the ligand bridges the dimer through the P and N donor atoms,\textsuperscript{103} with $\text{PPh}_2(2\text{-C}_5\text{H}_4\text{N})$. With the bis- and tris-2-pyridylphosphines two analogous complexes were synthesised which contain the ligand bridging the dimer with P coordinated to one of the metal centres and both N atoms of two pyridyl groups coordinated to the other. The molecular structure of one of these, $[\text{Re}_2(\mu-\text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2)(\text{CO})_8]$ has been determined by single-crystal X-ray diffraction and is shown in Figure 2.4.

Under thermal and photochemical conditions, $[\text{Ru}_3(\text{CO})_{12}]$, gives a trisubstituted trinuclear cluster and a disubstituted mononuclear complex, respectively, with $\text{PPh}_2(2\text{-C}_5\text{H}_4\text{N})$.\textsuperscript{89} The products derived from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with the 2-pyridyl phosphines (L) with the use of catalysts for CO displacement such as $[\text{PPN}]\text{Cl}$ are shown in Figure 2.5.\textsuperscript{104,105} These clusters are thought to be derived from the clusters, $[\text{Ru}_3(\text{CO})_{12}(\mu-\text{L})]$, in which the ligand is bridging. With $\text{PPh}_2(2\text{-C}_5\text{H}_4\text{N})$, the ultimate complex is $[\text{Ru}_3(\mu-\text{PhCO})(\mu_3-\text{PPh}(2\text{-C}_5\text{H}_4\text{N}))(\text{CO})_8]$. This cluster is thought to be derived from $[\text{Ru}_3\text{Ph}(\mu_3-\text{PPh}(2\text{-C}_5\text{H}_4\text{N}))(\text{CO})_{12}]$ in which a phenyl group has migrated from P to Ru atoms. A further migration of Ph to CO atoms yields the desired cluster. With $\text{P}(2\text{-C}_5\text{H}_4\text{N})_3$, only 2-pyridyl groups are available for migration following P-C bond cleavage and hence $[\text{Ru}_3(\mu-\text{C}_5\text{H}_4\text{N})(\mu_3-\text{P}(2\text{-C}_5\text{H}_4\text{N})_2)(\text{CO})_8]$ is formed.
Figure 2.3  Structure of the products of the reaction of the 2-pyridylphosphines with [Re₂(CO)₁₃].

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Figure 2.4  Molecular structure of [Re₂{μ-PPh(2-C₅H₄N)₃}₂(CO)] as determined by single-crystal X-ray diffraction.\textsuperscript{103}
For PPh(2-C₅H₄N)₂ there is a competitive transfer of phenyl and 2-pyridyl groups from the proposed intermediate bridged species to give the clusters [Ru₄(μ-PhCO)(μ₃-P(2-C₅H₄N)](CO)₆ and [Ru₄(μ-C₃H₄N)(μ₃-PPh(2-C₅H₄N)](CO)₆, respectively. These clusters are respectively related to the clusters formed with PPh₃(2-C₅H₄N) and P(2-C₅H₄N).₃₉

From [Os₃(CO)₁₀L₂] (L = CO, MeCN) and the 2-pyridylphosphines (PAN) the clusters [Os₃(μ-(PAN))(CO)₁₀] have been synthesised and isolated.¹⁰⁶,¹⁰⁷ The analogous Ru clusters have been proposed as intermediates in the formation of clusters derived from P-C bond cleavage. This would account for the lack of 2-pyridyl migration from the PPh₃(2-C₅H₄N) clusters and competitive phenyl and 2-pyridyl migration from the PPh₃(2-C₅H₄N)₃ clusters. Thermolysis of the PPh₃(2-C₅H₄N) bridged cluster leads to the P-C bond cleaved products; [Os₃(η¹-Ph)(μ₃-PPh(2-C₅H₄N))(CO)₆], [Os₃(μ-PhCO)(μ₃-PPh(2-C₅H₄N))(CO)₆], [Os₃(μ-C₃H₄N)(μ-PPh₃)(CO)₆] and [Os₃(μ-C₃H₄N)(μ-PPh₃)(CO)₆] shown in Figure 2.6. The first of these clusters is similar to the proposed intermediate in the mechanism for the formation of the ultimate cluster from the reaction of [Ru₄(CO)₁₀] and PPh₃(2-C₅H₄N), prior to migration of the Ph group from Ru to CO atoms. The isolation of the clusters which are proposed intermediates for ruthenium can be explained by the relative M-C bond strengths in ruthenium and osmium carbonyl complexes.
Figure 2.5  Structure of products of reaction of the 2-pyridylphosphines with [Ru₃(CO)₁₂].¹⁰⁴,¹⁰⁵
Figure 2.6  Structures of the products of thermolysis of [Os(μ-PPh₂(2-C₅H₄N))(CO)₆].
2.2 Results and Discussion

2.2.1 Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with diphenyl-2-pyridylphosphine

The thermal reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with the ligand PPh$_2$(2-C$_5$H$_4$N) had been carried out previously in this group, but was repeated to establish consistency and reproducibility. The reaction time was reduced from nine to 4.5 hours and the solvent was modified to refluxing heptane (b.p. 96 °C), compared to the analogous reaction of $[\text{Re}_2(\text{CO})_{10}]$ for which refluxing decane (b.p. 180 °C) was used. Work-up of the resultant deep orange-red solution and small amount of brown solid using TLC separation on silica gave products 1 to 4, which were characterised against authentic samples, and a trace of unreacted $[\text{Mn}_2(\text{CO})_{10}]$. Two of the products were characterised as $[\text{Mn}_2(\text{CO})_6(\text{PPh}_2(2-\text{C}_5\text{H}_4\text{N}))]$ 1 (5%) (yellow solid) and $[\text{Mn}_2(\text{CO})_6(\text{PPh}_2(2-\text{C}_5\text{H}_4\text{N}))_2]$ 2 (2%) (yellow solid) analytically and by comparison of IR spectroscopic data with complexes of the type $[\text{Mn}_x(\text{CO})_{10-x}(\text{PR}_3)_x]$ ($x = 1,2; R = \text{alkyl, aryl}$). These IR data suggest that these complexes have one or two axially coordinated P-bound monodentate ligands, respectively, the latter having one on each metal atom. NMR spectra for these complexes were not possible to interpret due to broadness, possibly caused by traces of paramagnetic impurities.

The compound $[\text{Mn}_2(\mu-\text{PPh}_2(2-\text{C}_5\text{H}_4\text{N}))(\text{CO})_3]$ 3 (42%) (orange microcrystalline solid) which was formed in a relatively high yield, was characterised analytically, by IR spectroscopy and by multinuclear NMR
spectroscopy. Here the ligand bridges the Mn-Mn bond, with coordination through P and N atoms. There is the possibility that the ligand in fact chelates at just one of the Mn atoms. However, comparison of IR data with those of bidentate ligand complexes of [Mn$_2$(CO)$_{10}$], and also the NMR data (especially $^{13}$C($^1$H) NMR data) of the analogous rhenium complex [Re$_2$($\mu$-PPh$_2$(2-C$_5$H$_4$N))(CO)$_6$], suggest the ligand is bridging rather than chelating.

Formed in a low yield is [Mn$_2$($\mu$-PPh$_2$($\mu$-C$_5$H$_4$N))(CO)$_4$] (3%) (orange crystals) which was characterised analytically, by IR spectroscopy, by multinuclear NMR spectroscopy and ultimately by single-crystal X-ray diffraction. Compound 4 seems to be derived from compound 3 in that the pyridyl moiety has cleaved from the P atom and migrated so as to bridge the Mn-Mn bond. The thermolysis of compound 3 in a sealed tube to give a relatively high yield formation of compound 4 proved that this is the most likely route to 4. This conversion was performed at 150 °C, resulting in a red-brown solution which indicated some decomposition as well as decarbonylation to 4. A lower temperature would probably yield more of compound 4, however, this was not attempted.

The same two reagents were also reacted in equimolar quantities in a sealed tube in heptane at 125 °C. Yields of compounds 1 (12%) and 3 (55%) were increased, the yield of compound 4 (2%) decreased and none of compound 2 was observed. The formation of compound 4 in a sealed tube is probably hindered by a CO atmosphere since we have shown that it forms readily from compound 3 at this temperature in the absence of CO. This might indicate that the formation of compound 4 from compound 3
is reversible or that there is a reversible loss of CO from compound 3 before a reaction step involving P-C bond cleavage.

Also, the same two reagents were reacted in equimolar quantities, under UV irradiation at room temperature in toluene. An orange solution results after 15 hours from the original golden yellow solution. Work-up of this solution using TLC separation on silica gave compounds 1 (7%), 2 (3%) and 3 (43%) in similar yields to those of the thermal reaction in refluxing heptane. The non-formation of compound 4 is further evidence that this is a product of thermal decarbonylation of compound 3. Photochemical conditions are commonly appropriate for the displacement of CO from a complex, but P-C bond cleavage apparently needs elevated temperatures and therefore does not appear to occur photochemically.

2.2.2 Reaction of $[{\text{Mn}_2(\text{CO})_{10}}]$ with the bis- and tris-2-pyridyolphosphines

The reactions of $[{\text{Mn}_2(\text{CO})_{10}}]$ with the bis- and tris-2-pyridyolphosphines, PPh$(2$-$\text{C}_9\text{H}_5\text{N})_2$ and P$(\text{C}_9\text{H}_5\text{N})_3$, were initially performed in heptane in sealed tubes at 130 °C. A red suspension gradually formed from the initial golden yellow solution. Work-up of this suspension using column chromatographic separation on neutral alumina gave some unreacted $[{\text{Mn}_2(\text{CO})_{10}}]$ and the compounds $[{\text{Mn}_2(\mu-\text{PR}(2$-$\text{C}_9\text{H}_5\text{N})_2)_{(\text{CO})_2}}] \{R = \text{Ph} 5 (27\%), \text{2-pyridyl} 6 (25%)\}$ isolated as dark-red crystals.

Spectroscopic analysis of these compounds show that they contain the ligands bridging the Mn-Mn bond, coordinating to one Mn atom.
through the P atom and to the other Mn atom through the N atoms of two 2-pyridyl groups. The two compounds differ only with respect to the non-metallated ring at phosphorus which is a phenyl group for compound 5 and a 2-pyridyl group for compound 6. The IR spectra of these complexes are similar to those for the analogous rhenium complexes, including the rhenium analogue of compound 5 which has been characterised ultimately by single-crystal X-ray diffraction, so we can be moderately sure of the structures.

Unfortunately, as with several dimanganese complexes already discussed, $^1$H NMR spectra were not possible to interpret due to line broadened spectra, possibly caused by traces of paramagnetic impurities. However, some information for the characterisation of these two complexes can be gained by comparison of these line broadened $^1$H and $^{13}$C($^1$H) NMR spectra with that of their rhenium analogues. For compound 6, lowfield signals at $\delta$ 9.37 of intensity two and $\delta$ 8.94 of intensity one are observed in the $^1$H NMR spectrum. These correspond to the $H^6$ signals of the two coordinated and one non-coordinated 2-pyridyl groups. Similar signals are observed in the analogous rhenium complex at $\delta$ 9.40 and 8.94. The $H^6$ signal of a non-coordinated 2-pyridyl group is expected to give a signal in the range $\delta$ 8.0-8.8. Other signals corresponding to those of the Re analogue are also observed in the $^1$H NMR spectrum of compound 6 which is shown in Figure 2.7 along with the spectrum for its rhenium analogue for comparison. These include a signal barely resolving into a triplet at $\delta$ 8.52 corresponding to the $H^6$ signal of the uncoordinated 2-pyridyl group in the analogous rhenium complex where the signal is observed at $\delta$ 8.53, a singlet signal at $\delta$ 8.17
Figure 2.7 ¹H NMR spectra of compound 6 and [Re₂(μ-P(2-C₅H₄N)₂)(CO)₆].
corresponding to the H⁴ signal of the uncoordinated 2-pyridyl group in the analogous rhenium complex where the signal is observed at δ 8.20 and two signals at δ 7.63 and 7.56 (the latter being of intensity two) corresponding to the H³ and H⁴ signals of the uncoordinated and coordinated 2-pyridyl groups, respectively, in the analogous rhenium complex which are observed at δ 7.60 and 7.58, respectively. The remaining signals are obscured by the line broadened signal due to the residual chloroform in the NMR solvent. The ¹³C[^H] NMR spectrum of compound 6 shows signals at δ 171.8, 156.4, 135.0, 127.4 and 123.5 and at δ 149.7, 137.9, 132.1 and 125.5 due to two equivalent and one non-equivalent 2-pyridyl groups, respectively. These correspond to the five independent carbon sites of the two coordinated 2-pyridyl groups and of the one non-coordinated 2-pyridyl group.

The 'H and ¹³C NMR spectra of compound 5 are very broad, however a signal at δ 9.42 of intensity two in the 'H NMR spectrum corresponds to the H⁶ signal of the two equivalent coordinated 2-pyridyl groups. The corresponding signal is observed at δ 9.46 in the analogous rhenium complex.

The El mass spectra of compounds 5 and 6 which are shown in Figures 2.8 and 2.9, respectively, were further evidence for the formation of these heptacarbonyl complexes. The El mass spectrum of compound 5 showed the parent molecular ion and the loss of the seven carbonyl ligands from this ion with significant peaks due to the loss of three, five and seven carbonyl ligands. After the loss of a Mn atom (m/z = 319) a peak equivalent to the loss of a phenyl group was observed (m/z = 242). A subsequent loss
of the second Mn atom (m/z = 187) left a peak for the [P(2-CsH^N)]^+ ion. The El mass spectrum for compound 6 again firstly showed the parent molecular ion and the loss of the seven carbonyl ligands, but this time significant peaks are observed for the loss of firstly three carbonyl ligands and then for the subsequent loss of the remaining carbonyl ligands. A loss of a Mn atom (m/z = 320) is followed by the loss of a 2-pyridyl group (m/z = 242). This is probably the uncoordinated 2-pyridyl group as in the bis 2-pyridylphosphine complex, compound 5, the uncoordinated phenyl group was lost at the same stage. Losses of the second Mn atom (m/z = 187), a 2-pyridyl group (m/z = 109) and a P atom (m/z = 78) leave just a peak for the [CgH^N] ion and completes the mass spectrum.

A yellow band was also observed by column chromatography following these dark red bands, which in each case at first was thought to be another simple product. However these uncharacterised bands are actually thought to be products of the reaction of compounds 5 and 6 with the dichloromethane solvent used in the column chromatographic work-up. Compounds 5 and 6 react with chlorinated solvents such as dichloromethane to give yellow compounds by a reaction that is very fast in sunlight and also, as expected, faster in tetrachloromethane. Therefore the yields of compounds 5 and 6 should be significantly higher, but some of the complex is lost in the work-up procedure. This reaction may be one of the reasons for the broadness of the spectral lines associated with the NMR spectra of compounds 5 and 6, chlorinated reaction products are quite likely to be paramagnetic. However this is not the only reason as the ^1H NMR spectrum
Figure 2.8  EI mass spectrum of \([\text{Mn}_2\{\mu-\text{PPh(2-C_5H_4N)\}_2\}(\text{CO})_2]^-\)
Figure 2.9  El mass spectrum of $[\text{Mn}_2(\mu-P(2-\text{C}_5\text{H}_4\text{N})_3(\text{CO}))_6]$
The reactions of $[\text{Mn}_2\text{(CO)}_{10}]$ with the same two ligands were also carried out thermally, under reflux in xylene. The reaction with the bis-2-pyridylphosphine was monitored by IR spectroscopy of the solution. After five hours a spectrum corresponding to only compound 5 was observed. Indeed, work-up of the deep red solution using column chromatographic separation on neutral alumina gave a high yield of compound 5 (63%). With the tris-2-pyridylphosphine decomposition occurred yielding no carbonyl complexes.

Additionally, $[\text{Mn}_2\text{(CO)}_{10}]$ was irradiated under UV light at room temperature with the bis-2-pyridylphosphine. A deep red solution resulted after about one hour and there was no change in the IR spectrum after about two hours, indicating that the reaction had ceased. Work-up of the solution using column chromatography separation on neutral alumina gave some unreacted $[\text{Mn}_2\text{(CO)}_{10}]$ and compound 5 (26%).

The bis- and the tris-2-pyridylphosphines react with $[\text{Mn}_2\text{(CO)}_{10}]$ to give the same products, independent of the reaction conditions. This is unlike the reaction of diphenyl-2-pyridylphosphine, where compound 4, a complex derived from P-C bond cleavage, resulting in the cleavage, migration and insertion of the 2-pyridyl moiety between the Mn atoms, is only formed thermally. No bond cleavage products are observed for the bis- and tris-2-pyridylphosphines.

2.2.3 Possible routes to products
The formation of compound 4 from compound 3 has been discussed in Section 2.2.1. It has been shown that compound 4 is formed readily from the thermal decarbonylation of compound 3 in a sealed tube. However, thermolysis of the reagents \([\text{Mn}_2(\text{CO})_{10}]\) and \(\text{PPPh}_{2}(2-\text{C}_3\text{H}_4\text{N})\) under the same conditions does not yield any of compound 4, indicating that the formation of this complex is hindered by increasing CO concentration. Two possible routes for the formation of compound 4 from compound 3 which may account for the observed results are shown in Schemes 2.1 and 2.2. The first route suggests that the formation of compound 4 from compound 3, that is CO loss, P-C bond cleavage and insertion of the cleaved 2-pyridyl moiety is a reversible process. The second route, which has been observed for bridging complexes of dppm (see Section 1.1.2), which is more likely to be the case, involves the reversible loss of CO from compound 3 to yield an unobserved coordinatively unsaturated 32 electron intermediate, \([\text{Mn}_2(\mu-\text{PPPh}_{2}(2-\text{C}_3\text{H}_4\text{N}))\text{(CO)}_2]\). A subsequent reaction step involving P-C bond cleavage and intramolecular insertion of the cleaved 2-pyridyl moiety yields the 34 electron complex, compound 4. Both of these routes account for the non-formation of compound 4 with increasing CO concentrations as they both contain a step which involves the reversible loss of CO, which is obviously hindered by higher concentrations of this ligand. In any case, the conversion of 3 to 4 requires a step which involves decarbonylation which is less facile for rhenium carbonyl complexes than for manganese carbonyl complexes. This accounts for a rhenium complex analogous to that of complex 4, not being observed.
The formation of compounds 5 and 6 which are shown in Scheme 2.3 may occur via a similar route. An unobserved coordinatively unsaturated 32 electron intermediate, \([\text{Mn}_2(\mu-\text{PR}(2-\text{C}_5\text{H}_4\text{N}))_2(\text{CO})_6]\) (R = Ph, 2-pyridyl), which contains only one of the two pyridyl groups attached to manganese through nitrogen, may be formed by decarbonylation of an equally unobserved complex, \([\text{Mn}_2(\mu-\text{PR}(2-\text{C}_5\text{H}_4\text{N}))_2(\text{CO})_6]\) (R = Ph, 2-pyridyl), which again only contains one bridge and is similar to compound 3. The similarities to Scheme 2.2, in the possible routes to the formation of the products ends here. An extra nitrogen donor atom from the free 2-pyridyl group in the 32 electron intermediate is available and coordination of this to the same manganese atom as the other 2-pyridyl moiety, to yield compounds 5 and 6 occurs, rather than P-C bond cleavage followed by insertion of a 2-pyridyl group.

These manganese and rhenium complexes of the type \([\text{M}_2(\mu-\text{PR}(2-\text{C}_5\text{H}_4\text{N}))_2(\text{CO})_6]\) (R = Ph, 2-C_5H_4N) are stable at up to 140 °C for the former and up to at least 180 °C for the latter. No products derived from P-C bond cleavage and subsequent insertion of a 2-pyridyl group are observed as observed for \([\text{Mn}_2(\mu-\text{PPPh}_2(2-\text{C}_5\text{H}_4\text{N}))(\text{CO})_6]\) 3 which gave \([\text{Mn}_2(\mu-\text{CO})(\mu-\text{PPPh}_2)(\mu-\text{C}_5\text{H}_4\text{N})(\text{CO})_6]\) 4 or the fragmentation of bridging complexes of dppm as seen in Section 1.1.2. The tight rigid bridges observed in the complexes \([\text{M}_2(\mu-\text{PR}(2-\text{C}_5\text{H}_4\text{N}))_2(\text{CO})_6]\) (M = Mn, Re; R = Ph, 2-C_5H_4N) which is illustrated in the crystal structure of \([\text{Re}_2(\mu-\text{PPPh}(2-\text{C}_5\text{H}_4\text{N}))_2(\text{CO})_6]\) (Figure 2.4) do not allow easy P-C bond cleavage and insertion of the cleaved group.
Scheme 2.1

\[
\text{Ph}_2\text{P}-\text{C bond cleavage}
\]

\[
\text{CO}
\]
Scheme 2.2

3

Ph₂P

PhgP N

(CO)₄Mn

(CO)₄Mn

Mn(CO)₃

Mn(CO)₃

P-C bond cleavage

(CO)₃Mn

(CO)₃Mn

5

55
Scheme 2.3

P-C bond cleaved product

5 (R = Ph)
6 (R = 2-pyridyl)
2.3 Experimental

The ligands \( \text{PPh}_2(2\text{-C}_5\text{H}_4\text{N}) \), \(^{109} \) \( \text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2 \), and \( \text{P}(2\text{-C}_5\text{H}_4\text{N})_3 \), \(^{87} \) were synthesised and characterised as reported previously. For \( \text{PPh}_2(2\text{-C}_5\text{H}_4\text{N}) \), this initially involved the synthesis of lithium diphenylphosphide by the dropwise addition of a THF solution of butyl lithium to a cold (-78 °C) THF solution of diphenylphosphine. Subsequent addition of a THF solution of 2-chloropyridine to the salt and work-up yielded the required phosphine. For \( \text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2 \) and \( \text{P}(2\text{-C}_5\text{H}_4\text{N})_3 \), the 2-lithiopyridine salt was initially prepared by the dropwise addition of an ethereal solution of butyl lithium to a cold (-78 °C) ethereal solution of pyridine. Subsequent addition of an ethereal solution of dichlorophenylphosphine or phosphorus trichloride, respectively, to the salt followed by work-up yielded the phosphine.

2.3.1 Reaction of \([\text{Mn}_2(\text{CO})_10]\) with \( \text{PPh}_2(2\text{-C}_5\text{H}_4\text{N}) \)

(a) Reaction in refluxing heptane: The compound \([\text{Mn}_2(\text{CO})_10]\) (0.404 g, 1.04 mmol) and the tertiary phosphine \( \text{PPh}_2(2\text{-C}_5\text{H}_4\text{N}) \) (0.307 g, 1:1 mol/mol carbonyl complex) were heated under reflux in heptane (40 cm\(^3\)) for 4.5 hours. The IR spectrum of the solution was recorded periodically to monitor the conversion of the carbonyl. The resulting deep orange-red solution and small amount of brown solid was evaporated to dryness under reduced pressure to yield a dark-orange solid. TLC work-up [SiO\(_2\); eluent, light petroleum spirit (b.p. 30-40 °C)-dichloromethane (5:3 v/v)] gave five
bands extracted with dichloromethane, which were characterised against authentic samples. A trace of yellow material eluting fast was found to be unreacted \([\text{Mn}_2(\text{CO})_9]\). An orange band gave compound 4 as orange crystals (0.016 g, 3%) by crystallisation from a cool dichloromethane-hexane mixture (Found: C, 50.2; H, 2.7; N, 2.45. \(\text{C}_{24}\text{H}_{14}\text{NO}_8\text{PMn}_2\) requires C, 50.65; H, 2.5; N, 2.45%); \(\nu(\text{CO})/\text{cm}^{-1}\): 2057m, 2022vs, 2013sh, 1988m, 1978s, 1969m, 1950m, 1876w; a yellow band gave compound 1 as a yellow solid (0.022 g, 5%) from evaporation of a dichloromethane solution (Found: C, 49.6; H, 2.35; N, 2.3; P, 5.35. \(\text{C}_{25}\text{H}_{14}\text{NO}_8\text{PMn}_2\) requires C, 49.95; H, 2.25; N, 2.25; P, 4.95%); \(\nu(\text{CO})/\text{cm}^{-1}\): 2091m, 2018m, 1997vs, 1973m, 1965w, 1943m; an orange band gave compound 3 as an orange microcrystalline solid (0.243 g, 42%) by crystallisation from a cool dichloromethane-hexane solution (Found: C, 50.4; H, 2.65; N, 2.3; P, 5.2. \(\text{C}_{40}\text{H}_{22}\text{NO}_8\text{P}_2\text{Mn}_2\) requires C, 50.3; H, 2.35; N, 2.35; P, 5.2%); \(\nu(\text{CO})/\text{cm}^{-1}\): 2064m, 2001s, 1979vs, 1959m, 1946m, 1923s; and a weak yellow band gave compound 2 as a yellow solid (0.013 g, 2%) from evaporation of a dichloromethane solution (Found C, 57.2; H, 3.25; N, 3.3. \(\text{C}_{40}\text{H}_{22}\text{NO}_8\text{P}_2\text{Mn}_2\) requires C, 57.45; H, 3.35; N, 3.35%); \(\nu(\text{CO})/\text{cm}^{-1}\): 1962vs; \(\nu(\text{CO})(\text{CHCl}_3)/\text{cm}^{-1}\): 2061w, 2036w, 2027w, 1984sh, 1958vs, 1919w.

(b) **Reaction in a sealed Carius tube:** The same two compounds, \([\text{Mn}_2(\text{CO})_9]\) (0.505 g) and the tertiary phosphine, \(\text{PPh}_2(2-\text{C}_5\text{H}_4\text{N})\) (0.348 g) in an equimolar quantity (1.29 mmol) were introduced into a 40 cm³ Pyrex glass Carius tube along with heptane (15 cm³). The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum using a torch and placed in
an oven at 125 °C. After 24 hours there had been a gradual change from a yellow to a red suspension. The tube was opened and the red suspension was evaporated to dryness under reduced pressure to yield an orange-red residue. TLC work-up [SiO₂; eluent, light petroleum spirit (b.p. 30-40 °C)-dichloromethane (5:3 v/v)] of the residual orange-red solid gave four bands which corresponded to unreacted \([\text{Mn}_2(\text{CO})_10]\), compound 4 (0.014 g, 2%), compound 1 (0.093 g, 12%) and compound 3 (0.387 g, 55%).

(c) Photochemical reaction: The same two compounds, \([\text{Mn}_2(\text{CO})_10]\) (0.169 g) and \(\text{PPh}_2(2-\text{C}_6\text{H}_5\text{N})\) (0.122 g), in equimolar quantities (0.433 mmol) were photolysed at room temperature under UV irradiation in toluene (60 cm³). The conversion of the carbonyl was monitored by IR spectroscopy of the solution which showed no further change after 15 hours indicating that the reaction had ceased. TLC work-up [SiO₂; eluant, light petroleum spirit (b.p. 30-40 °C)-dichloromethane (5:2 v/v)] gave a trace of unreacted \([\text{Mn}_2(\text{CO})_10]\) (0.005 g), and compounds 1 (0.018 g, 7%), 3 (0.112 g, 43%) and 2 (0.010 g, 3%)

(d) Thermal treatment of compound 3: The bridged dimanganese complex, compound 3 (0.228 g, 0.393 mmol) was introduced into a 20 cm³ Pyrex glass Carius tube along with heptane (8 cm³). The tube was degassed as in (b) above, sealed under vacuum using a torch and placed in an oven at 150 °C. A red-brown solution, resulted from the initial orange-red solution which on evaporation to dryness under reduced pressure yielded a dark-
orange solid. Work-up as previous yielded a series of very minor uncharacterised bands (~ 1-2 mg) and compound 4 (0.040 g, 15%).

2.3.2 Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with $\text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2$

(a) Reaction in a sealed Carius tube: $[\text{Mn}_2(\text{CO})_{10}]$ (0.490 g, 1.26 mmol) and the bis tertiary phosphine, $\text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2$ (0.341 g, 1:1 mol/mol carbonyl complex), were introduced into a 40 cm$^3$ Pyrex glass Carius tube along with heptane (10 cm$^3$). The tube was degassed by three freeze-thaw-pump cycles, sealed under vacuum using a torch and placed in an oven at 130 °C. A dark red suspension resulted from the initial golden yellow suspension which on evaporation to dryness under reduced pressure yielded a red solid. Column chromatographic work-up [neutral $\text{Al}_2\text{O}_3$; eluant, light petroleum spirit (b.p. 30-40 °C)-dichloromethane (5:2 v/v)] gave two bands. A fast moving yellow band gave unreacted $[\text{Mn}_2(\text{CO})_{10}]$ (0.064 g) and a dark-red band gave compound 5 as a dark-red crystalline material (0.191 g, 27%) by crystallisation from a cool dichloromethane-heptane mixture (Found: C, 47.8; H, 2.2; N, 4.7. $\text{C}_{22}\text{H}_{13}\text{N}_2\text{O}_7\text{PMn}_2$ requires C, 48.45; H, 2.3; N, 4.9 %); $\nu(\text{CO})$/cm$^{-1}$: 2034m, 1971m, 1956w, 1947m, 1922w, 1887w; parent molecular ion ($M^* = 570$), $[M^*-n(\text{CO})]$ [n = 3 (m/z = 486), 5 (m/z = 430), 7 (m/z = 374)], $[\text{Mn}[\text{PPh}(2\text{-C}_5\text{H}_4\text{N})_2]]^+$ (m/z = 319), $[\text{Mn}[\text{P}(2\text{-C}_5\text{H}_4\text{N})_2]]^+$ (m/z = 242) and $[\text{P}(2\text{-C}_5\text{H}_4\text{N})]^+$ (m/z = 187) observed in the El mass spectrum.
(b) Reaction in refluxing xylene: The same two compounds in equimolar quantities (0.487 g Mn complex, 0.348 g phosphine; 1.25 mmol) were also heated under reflux in xylene (100 cm$^3$). Over 4 hours there was a gradual colour change to a deep red solution and the IR spectrum of the solution indicated peaks for compound 5 only. Column chromatographic work-up as previously on the resultant dark-red residue after evaporation of the solvent under reduced pressure gave compound 5 (0.450 g, 63%) only.

(c) Photochemical reaction: The same two compounds in equimolar quantities (0.161 g Mn complex, 0.110 g phosphine; 0.413 mmol) were irradiated under UV light at room temperature in toluene (60 cm$^3$). A dark red solution resulted after about one hour and there was no change in the IR spectrum of the solution after about five hours. Column chromatographic work-up as previous gave some unreacted $[\text{Mn}_2(\text{CO})_{10}]$ (0.017 g) and compound 5 (0.062 g, 26%).

2.3.3 Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with P(2-C$_5$H$_4$N)$_3$

$[\text{Mn}_2(\text{CO})_{10}]$ (0.488 g) and the tris tertiary phosphine, P(2-C$_5$H$_4$N)$_3$ (0.338 g), in equimolar quantities (1.25 mmol), were introduced into a 40 cm$^3$ Pyrex glass Carius tube along with heptane (10 cm$^3$). The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum using a torch and placed in an oven at 130 °C. A dark red oily solution resulted which on evaporation to dryness under reduced pressure gave an oily red solid.
Column chromatographic work-up [neutral Al₂O₃; eluant, light petroleum spirit (b.p. 30-40 °C)-dichloromethane (5:2 v/v)] gave unreacted [Mn₂(CO)₁₀] (0.062 g) and a red band yielded compound 6 as a red microcrystalline solid (0.182 g, 25%) by crystallisation from a dichloromethane-hexane mixture (Found: C, 44.8; H, 2.2; N, 7.0; P, 5.4. C₂₂H₁₂₂N₃O₅PMn₂ requires C, 46.3; H, 2.1; N, 7.4; P, 5.4 %); ¹³C[¹H] NMR: δ 171.8 (d, J = 62.3 Hz, ipso Ph), 156.4 (d, ³J = 11.6 Hz, pyridyl ring), 149.7 (d, J = 8.8 Hz, meta Ph), 137.9 (d, J = 12.2 Hz, ortho Ph), 135.0 (d, ³J = 4.5 Hz, pyridyl ring), 132.1 (d, ¹J = 37.9 Hz, ipso pyridyl ring), 127.4 (d, ³J = 9.4 Hz, pyridyl ring), 125.5 (s, para Ph), 123.5 (s, C¹ pyridyl ring); ν(CO)/cm⁻¹: 2033w, 1971w, 1956vw, 1946w, 1880w; parent molecular ion (M⁺ = 571), [M⁺-n(CO)]⁺ {n = 3 (m/z = 487), 4 (m/z = 459), 5 (m/z = 431), 6 (m/z = 403), 7 (m/z = 375)}, [Mn{P(2-C₉H₇N)₃}]⁺ (m/z = 320), [Mn{P(2-C₉H₇N)₂}]⁺ (m/z = 242), [P(2-C₉H₇N)₃]⁺ (m/z = 187), [P(2-C₉H₇N)]⁺ (m/z = 109) and [C₉H₇N]⁺ (m/z = 78) observed in the El mass spectrum.
Chapter 3.

Coordination Chemistry of 2-Thienylphosphines with Group 7 and Group 8 Transition Metal Carbonyl Complexes

3.1 Introduction

3.1.1 Coordination of thiophene and related compounds to transition metal complexes

Until recently, little was known about the coordination of thiophene to transition metal complexes, mainly because it is a weakly coordinating ligand. An interest in understanding the mechanisms of the catalytic hydrodesulfurisation (HDS) of organosulfur compounds in petroleum feedstocks [eqn (3.1)], led to the exploration of the various possible modes of coordination of thiophenes to transition metal complexes. 

\[
C_xH_yS + 2H_2 \xrightarrow{\text{catalyst}} C_xH_{y+z} \ (z = 2, 4, 6) + H_2S \quad (3.1)
\]

These modes represent possible types of thiophene adsorption at metal centres of heterogeneous HDS catalysts which are industrially based on MoS$_2$. 
(Scheme 3.1), although the models do not necessarily relate closely to the catalytic systems.

Scheme 3.1 One possible hydrogenation mechanism for thiophene HDS

The focus of HDS studies has been on thiophenes. This is a consequence of these being the most difficult compounds to desulfurise out of the complex mixture of organosulfur compounds, such as mercaptans, thioethers and thiols, found in petroleum feedstocks. Mechanisms for the catalytic HDS of thiophenes have now been proposed, based on the modes of bonding of thiophenes to transition metal complexes and also their reactivity.

Thiophenes have been observed to be not particularly good ligands with transition metals, even with soft metals such as the heavier late d-block metals that normally bond strongly to sulfur ligands such as thiols and thioethers.

Bond lengths of thiophene determined by microwave spectroscopic studies show π-electron density to be concentrated between
the C(2)-C(3) and the C(4)-C(5) bonds. Therefore, in addition to coordination through a lone pair at the sulfur atom, there is the alternative coordination through the \( \pi \)-electrons in thiophene.

However, few S-bound thiophene complexes are known since thiophene is a weak donor ligand through sulfur, in contrast to other organosulfur compounds such as thiols. The ruthenium cation, \([\text{Ru}(\text{PPh}_3)_2(\text{C}_5\text{H}_5\text{SCH}_2\text{C}_5\text{H}_4)]^+\), was the first S-bound compound of this type to be structurally characterised. An important feature of its structure, and others containing S-bound thiophene such as \([\text{Cp}^*\text{Re}(\text{C}_5\text{H}_5\text{S})(\text{CO})_3]\), is that the metal atom lies out of the thiophene plane such that the sulfur has tetrahedral geometry and can be considered to be approximately \( \text{sp}^3 \) hybridised. Previously, it was assumed that when coordinated to thiophene, the metal would lie in the plane of the ring, as is the case for pyridine.

As well as coordination to a single metal atom through sulfur alone, thiophene can alternatively coordinate to metal complexes by \( \pi \)-coordination through carbon and sulfur atoms. The most common and first reported of these is the pentahapto mode, where all five atoms coordinate in the complex. The chromium complex, \([\text{Cr}(\eta^5\text{-C}_5\text{H}_5\text{S})(\text{CO})_3]\), was the first reported with such a structure in which thiophene is a 6-electron donor. However, the rhodium cation, \([\text{Rh}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5\text{S})]^+\), was the first complex of this type for which the structure was obtained with accurate bond distances. This structure showed that the ring is not exactly planar, with the sulfur being slightly out of the plane of the four carbons and away from the metal centre, a common feature in pentahapto thiophene complexes. A less common form of
π-complexation is the tetrahapto mode, where the sulfur atom is not coordinated to the metal atom. The first reported structure of a complex containing a thiophene in the tetrahapto mode of coordination is the iridium complex, [Cp*Ir(η⁴-2,5-Me₂C₆H₂S)]. Here the thiophene ligand is significantly non-planar with the sulfur atom bent out of the plane of the four carbon atoms, away from the iridium atom, much more so than for η⁵-coordination. Dihapto coordination of thiophene through two carbon atoms has yet to be confirmed crystallographically, but is thought to occur in the osmium cation, [Os(η²-C₄H₂S)(NH₃)₃]⁺, based on ¹H NMR data.

Thiophene can also coordinate to transition metal complexes through a mixture of tetrahapto π-coordination to one metal atom and bonding through the sulfur atom to another, which is observed in [(CO)₅Fe(η⁴-S-μ₂-C₄H₂S)ReCp(CO)₅] shown in Figure 3.1. A summary of the S- and π-coordination modes of thiophene to transition metal complexes is shown in Figure 3.2.

As well as mixtures of modes of bonding to transition metal atoms when two or more are present, isomers with different types of thiophene attachment are sometimes found in equilibrium. In the case of the rhenium-benzothiophene complex, [Cp*Re(benzothiophene)(CO)₃], the S-bound mode is in equilibrium with the dihapto mode.

Thiophene can also bind to transition metal complexes as the product of oxidative addition, of which there are two observed possibilities. The first involves C-H bond cleavage leading to 2-thienyl hydrido complexes, while the second involves C-S bond cleavage to yield
metallasulfacyclohexadiene systems. These oxidative addition products can exist as mixtures of isomers, such as observed for the two rhodium...

Figure 3.1: Structure of $[(\text{CO})_3\text{Fe}(\eta^1-\text{S}_2\text{C}_6\text{H}_4\text{S})\text{ReCp(CO)}_2]$.
Figure 3.2  Observed coordination modes of thiophene to transition metal complexes (M)

Figure 3.3  Structure of [Cp*Rh(PMe₃)(C₅H₅S)]
complexes, [Cp*Rh(PMe₃)(C₄H₄S)] shown in Figure 3.3. Also, isomers can exist in equilibrium involving other different coordination modes of thiophene, such as the two isomers of the iridium complex, [Cp*Ir(2,5-dimethylthiophene)] in which the thiophene coordination is via the η⁵ mode and through C-S bond cleavage.

Thiophene has been coordinated to clusters, in particular of the iron subgroup. One of the modes has thiophene coordinated to an edge of a closed trinuclear cluster through a C-C double bond in the heterocycle, in a σ+π coordination mode, that is as a μ₁η² thiényl ligand. Other modes of coordination of thiophene in trinuclear clusters include the thiophyne (μ₃) mode, and the ring opened form.

As can be seen from these studies, there is considerable variety in the ways thiophene can coordinate and it is not obvious how any of these ways is relevant to the HDS process.

3.1.2 Coordination of ligands containing both phosphorus and sulfur atoms to transition metals

Two types of ligand containing both phosphorus and sulfur atoms are the phosphine-thioethers and the phosphine-thiols. Phosphine-thioethers of the type, PPh₂(CH₂)ₙSR, (n = 1,2; R = Me, Et, Ph) coordinate to M' (M = Rh, Ir) and M'' (M = Pt, Pd) centres through phosphorus alone or through both phosphorus and sulfur atoms. Dissociation at the sulfur end of the hemilabile ligand to generate coordinatively unsaturated species occurs
when small molecules such as oxygen are incorporated. This concept has been utilised in the catalysis of reactions such as the oxidation of terminal alkenes and secondary alcohols to methyl ketones and ketones, respectively. Similarly, the phosphine-thiols exhibit coordination through phosphorus and sulfur atoms,\textsuperscript{133} however a sulfur coordinated titanium complex, \([\text{Cp}^*\text{Ti}\{\text{PPh}_2(\text{CH}_2)\text{SH}\}]\), is known.\textsuperscript{134}

The 2-thienylphosphines contain both phosphorus and sulfur atoms, but, in contrast to the phosphine-thioethers and the phosphine-thiols, before our research they had yet to show any other coordination behaviour than that of a simple tertiary phosphine with coordination through phosphorus atoms only.\textsuperscript{135-136} Diphenyl-2-thienylphosphine, \(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})\), has been observed to coordinate in this way to \(\text{Mo}^6\), \(\text{Rh}^1\) and \(\text{M}^8\) (\(\text{M} = \text{Pt}, \text{Pd}\)) centres such as the cation \([\text{Rh}\{\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})\}_2(\text{COD})]\)\textsuperscript{+} which is shown in Figure 3.4.

![Figure 3.4](image-url)
The molybdenum complex, *cis*-\([\text{Mo}\{\text{PPh}_2(2-C_4H_3S)\}^2\{(\text{CO})_4\}^2]\) which contains two pendant thiophene rings, reacts with \([\text{PdCl}_2(\text{COD})]\) or \([\text{PtCl}_2(\text{PhCN})]\) to give the monometallic molybdenum complexes, *trans*-\([\text{Mo}\{\text{PPh}_2(2-C_4H_3S)\}_2\{(\text{CO})_4\}^2]\) and \([\text{Mo}\{\text{PPh}_2(2-C_4H_3S)\}_2\{(\text{CO})_4\}^2]\) which may form via an unstable, phosphorus-sulfur bridging bimetallic complex as intermediate.\(^{138}\)

Recently, our group has shown that the ligand can substitute for CO in \([\text{Ru}_3(\text{CO})_{12}]\), leading to coordination of the thienyl moiety via oxidative addition of an ortho C-H bond, to give the complexes, \([\text{Ru}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-C_4H_2S)\}^2\{(\text{CO})_4\}^2\}^2\) \([L = \text{CO}, \text{PPh}_2(2-C_4H_2S)]\) which are shown in Figure 3.5.\(^{139}\)

Thermolysis of the first of these complexes (when \(L = \text{CO}\)) with excess \([\text{Ru}_3(\text{CO})_{12}]\) yields two tetranuclear clusters, \([\text{Ru}_4(\mu_4-C_4H_2S)(\mu_4-\text{PPh})(\text{CO})_{11}]\) and the previously characterised \([\text{Ru}_4(\mu_4-C_6H_4)(\mu_4-\text{PPh})(\text{CO})_{11}]\),\(^{140}\) which are shown in Figure 3.6, in which either a phenyl group or thienyl moiety is cleaved from phosphorus and lost probably as benzene or thiophene, respectively.

Our research objectives were to use 2-thienylphosphines with metal carbonyls to coordinate initially through phosphorus and then to explore the reactions of the thiophene ring of the coordinated ligand with a metal centre.
Figure 3.5  Structures of \([\text{Ru}^\text{II}(\mu-H)(\mu_2-\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S}))(\text{CO})_L](L = \text{CO, PPh}_2(2-\text{C}_4\text{H}_2\text{S}))\).^{139}

Figure 3.6  Structures of \([\text{Ru}^\text{II}(\mu_4-X)(\mu_4-\text{PPh})(\text{CO})_1](X = \text{C}_4\text{H}_2\text{S}, \text{C}_6\text{H}_4)\)
3.2 Results and Discussion

3.2.1 Thermal reaction of [Mn₂(CO)₁₀] with diphenyl-2-thienylphosphine

The reaction of [Mn₂(CO)₁₀] with diphenyl-2-thienylphosphine was carried out in refluxing xylene since little chemistry was observed at temperatures below 130 °C. The gradual colour change from a golden-yellow to an orange-brown solution and no further change in the IR spectrum after ten hours showed that the reaction had ceased. Work-up of the solution using TLC separation on silica gave two new complexes and some unreacted [Mn₂(CO)₁₀].

The first product is the axially monosubstituted, phosphorus bound complex [Mn₂(CO)₆{PPh₂(2-C₅H₅S)}] 7 (40%) (yellow solid) which was characterised analytically and by IR spectroscopy. It gave a spectrum around 2000 cm⁻¹ that was very similar to that of [Mn₂(CO)₆(PPh₂)]. Characterisation by ¹H and ¹³C{¹H} NMR spectroscopies was hindered by the problem of line broadening, probably due to paramagnetic impurities.

The second product of this reaction, [Mn₂(μ-PPh₂)(μ-η¹,η²-C₅H₅S)(CO)₆] 8 (20%) (orange yellow crystals), was characterised analytically, by IR spectroscopy, by ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies and ultimately by single-crystal X-ray diffraction. The ¹H and ¹³C{¹H} NMR spectra both show there to be two non-equivalent phenyl groups and π-coordination of the thienyl moiety, with a wide spread of thiophene signals shifted about 2 ppm and 35 ppm upfield of the phenyl ¹H and ¹³C{¹H} NMR resonances,
respectively. Thiophene signals in these spectra show lack of coupling to the $^{31}$P nucleus, suggesting P-C bond cleavage has occurred.

The molecular structure of 8 is shown in Figure 3.7 and selected bond lengths and angles are in Table 3.1. The structure confirms conclusions derived from the NMR spectra. The phosphido group and thienyl moiety are both bridging in a dimanganese complex with no formal Mn-Mn bond. The complex is a 36-electron system with the thienyl bridge as a 7-electron donor and the phosphido bridge as a 3-electron donor and therefore no Mn-Mn bond is expected [Mn---Mn 3.505(1) Å]. The thienyl bridge is characterised by monohapto coordination to Mn(2) and pentahapto coordination to Mn(1). The distances of the thienyl carbons to Mn(1) ranges from 2.132(3) to 2.178(3) Å and the sulfur to Mn(1) distance is 2.307(1) Å. The ring is not exactly planar and the sulfur is slightly out of the plane of the four carbons by 0.117 Å. This compares directly to many pentahapto complexes of thiophene. Mn(2) is observed to be out of the plane of the four carbon atoms and of the thienyl ring by 0.653 Å for the latter. The fact that the thienyl ligand is $\sigma$-bonded to Mn(2) has not led to an observable disturbance of normal pentahapto coordination of the thienyl ligand at Mn(1).

The coordination at the atom Mn(1) is related to that of the well known complex [CpMn(CO)$_3$]. However, in this case a carbonyl has been removed and replaced with a phosphido which is a 1-electron donor to Mn(1) and a 2-electron donor to Mn(2). This is supported by the two Mn-P bond lengths. That to Mn(1) is 2.292(1) Å which is shorter than 2.375(1) Å for the Mn(2)-P length.
Table 3.1  Selected bond lengths (Å) and angles (°) for compound \([\text{Mn}_2(\mu^-\text{PPh}_2)(\mu^-\eta^1, \eta^s-C_4H_2S)(\text{CO})_6] 8\)

<table>
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<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
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<td>P-Mn(2)-C(24)</td>
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<td>C(1)-S-C(4)</td>
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</table>
Other interesting features of this structure include some of the increased M-CO bond lengths which display the trans effect. The Mn(2)-C(21) bond length of 1.819(3) Å is relatively long compared to the Mn(1)-C(11) and Mn(1)-C(12) bond lengths of 1.776(4) Å and 1.786(3) Å, respectively. This arises because the Mn(2)-C(21) bond is trans to a carbon atom whereas the other two are trans to a more weaker bound sulfur atom. The Mn(2)-C(23) and Mn(2)-C(24) bond lengths at 1.842(4) Å and 1.840 Å, respectively, are significantly longer than any other M-C bond lengths. This arises because these carbonyl groups are trans to each other. These increased M-C bond lengths are coupled with shortened C-O bond lengths.

3.2.2 Photochemical reaction of [Mn₂(CO)_₁₀] with diphenyl-2-thienylphosphine

[Mn₂(CO)_₁₀] reacts differently with diphenyl-2-thienylphosphine under UV irradiation in toluene, giving an orange-brown solution after 10 hours photolysis. Work-up of the solution by TLC separation on silica gave unreacted [Mn₂(CO)_₁₀] and the product 7 described above (47%) identified by IR spectroscopy; full characterisation is again hindered by line broadening in the H and C{H} NMR spectra. Another product is the diaxially disubstituted, phosphorus bound complex [Mn₂(CO)_₆{PPh₂(2-C₄H₃S)}₂] 9 (19%) (orange solid) again identified analytically and by IR spectroscopy.²⁹ Like product 7, full characterisation of complex 9 is hindered by line
broadening in the relevant NMR spectra, again possibly due to traces of paramagnetic impurities.

3.2.3 Thermolysis of $[\text{Mn}_2(\text{CO})_6\{\text{PPh}_3(2-\text{C}_7\text{H}_5\text{S})\}]$ 7

After two hours reflux of compound 7 in xylene, there was no further change in the IR spectrum of the solution. The reaction mixture was separated by TLC work-up on silica. Unreacted starting material, compound 7 (22%), and the compound 8 (59%) derived from P-C bond cleavage and loss of CO were found to be the only products. These were characterised by comparison of their spectra with those of authentic samples.

3.2.4 Photochemical reaction of $[\text{Re}_2(\text{CO})_{10}]$ with diphenyl-2-thienylphosphine

$[\text{Re}_2(\text{CO})_{10}]$ reacts with diphenyl-2-thienylphosphine under UV irradiation; a colourless starting solution gradually changes colour to a pale yellow solution and there is no further change in the IR spectrum after 5 hours, suggesting the reaction has gone to completion. Work-up of the solution using TLC separation on silica gave $[\text{Re}_2(\mu-\text{PPh}_3(2-\text{C}_7\text{H}_5\text{S}))(\text{CO})_{10}]$ 10 (35%) (yellow crystals) as the only isolated product, which was characterised analytically, by IR spectroscopy, by $^1\text{H}$, $^{13}\text{C}(^1\text{H})$ and $^{31}\text{P}(^1\text{H})$ NMR spectroscopies and ultimately by single-crystal X-ray diffraction. The IR spectrum of compound 10 is similar to that of the bridging diphenyl-2-
pyridylphosphine dimanganese compound, \([\text{Mn}_2\{\mu-\text{PPh}_3(\text{C}_5\text{H}_4\text{N})\}(\text{CO})_6]\) 3. Unlike compound 8, the \(^1\text{H}\) and \(^{13}\text{C}\{'^1\text{H}\}\) NMR signals of the thienyl ring show coupling to the \(^{31}\text{P}\) nucleus, suggesting there is no fragmentation of the ligand. Also there are no signs of \(\pi\)-coordination, and a lack of any hydride signal suggests there is no coordination of the thienyl ring via orthometallation and the phenyl groups are equivalent.

From these data, a structure based on the intact ligand bridging the Re-Re bond was deduced. This was confirmed by the X-ray structure, shown in Figure 3.8 with selected bond lengths and angles in Table 3.2, which has the ligand bridging the Re-Re bond through phosphorus and sulfur atoms. The coordination geometry at the sulfur atom in the crystal is pyramidal, which would require the phenyl groups to be inequivalent. However, inversion at this sulfur atom must be extremely rapid since it leads to a time-averaged plane of symmetry, making the phenyl groups appear to be equivalent, even at -85 °C. This pyramidal geometry at sulfur compares directly to many sulfur bound complexes of thiophene,\(^{116}\) although there seems to be no evidence for rapid S-inversion in reported cases of monodentate S-bonded complexes. S-inversion would not be easy to detect in simple thiophene complexes. The longer M-C bond lengths due to carbonyl ligands lying \(\text{trans}\) to each other can be observed in this structure. The \(\text{trans}\) influence of a tertiary phosphine and thiophene can be compared from this structure. The Re(1)-C(14) \((\text{trans} \text{ to phosphine})\) bond length at 1.945(14) Å is significantly longer than the Re(2)-C(22) \((\text{trans} \text{ to thiophene})\) bond length at 1.893(13) Å and so the two ligands can be discriminated.
Figure 3.8
Molecular structure of [Re₂(μ-η⁵-CH₅)](CO)₄
Table 3.2  Selected bond lengths (Å) and angles (°) for compound [Re$_2$(μ-PPh$_2$(2-C$_4$H$_2$S))](CO)$_8$] 10

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3.2.5 Thermal Reaction of $[\text{Re}_2(\text{CO})_{10}]$ with diphenyl-2-thienylphosphine

$[\text{Re}_2(\text{CO})_{10}]$ also reacts with diphenyl-2-thienylphosphine, thermally, but only under the relatively harsh conditions of refluxing decane. The reaction is relatively fast at 180 °C and after approximately 30-45 minutes, the solution is a dark yellow colour. However, spot TLC analysis reveals the presence of a fair quantity of unreacted $[\text{Re}_2(\text{CO})_{10}]$. There is virtually no unreacted carbonyl after two hours. Work-up of the solution using TLC on silica gave $[\text{Re}_2(\mu-C_6H_3S)(\mu-\text{PPh}_2)(\text{CO})_8]$ 11 (35%) (pale yellow crystals) as the only product, which was characterised by IR spectroscopy, by $^1\text{H}$, $^{13}\text{C}({^1\text{H}})$ and $^{31}\text{P}({^1\text{H}})$ NMR spectroscopies and ultimately by single-crystal X-ray diffraction. The $^1\text{H}$ NMR spectrum of compound 11 is slightly broadened, and this is possibly due to paramagnetic impurities. However, from this and the $^{13}\text{C}({^1\text{H}})$ NMR spectra it can be seen that the phenyl groups are non-equivalent with separate sets of resonances for each of the ortho, meta and para carbon and hydrogen atoms.

The X-ray structure of compound 11 is shown in Figure 3.9 with selected bond lengths and angles in Table 3.3. The molecule contains separate thienyl and phosphido units, each bridging the two rhenium atoms with no formal Re-Re bond [Re---Re $4.231(1)$ Å]. The phosphido and thienyl bridges are both 3-electron donors which along with eight carbonyl ligands in an eclipsed arrangement, give a 36-electron complex. The thienyl bridge is bonded via the S-Re(1) and C(1)-Re(2) bonds. As with other sulfur bound
complexes of thiophene, the geometry at the sulfur atom is approaching tetrahedral.\textsuperscript{116}

This type of coordination of thiophenes has been observed in triosmium clusters.\textsuperscript{142} The reaction of 2-bromobenzothiophene with [Os\textsubscript{3}(CO)\textsubscript{10}(MeCN)\textsubscript{2}] affords the cluster [Os\textsubscript{3}(\mu-Br)(\mu-C\textsubscript{6}H\textsubscript{5}S)(CO)\textsubscript{10}] containing a benzothienyl ligand formed by the oxidative addition of the C-Br bond of 2-bromobenzothiophene to the cluster. The benzothienyl ligand and the bromine atom coordinate across opposite faces of the open edge of an open triosmium cluster, the benzothienyl ligand coordinating through sulfur and the adjacent carbon atom. The Re----Re distance of 4.231(1) Å in 11 may be compared with the Os----Os distance of 3.742(1) Å in this triosmium cluster.

A related triosmium cluster is [Os\textsubscript{3}(\mu-H)(\mu-C\textsubscript{6}H\textsubscript{5}S)(CO)\textsubscript{10}]. However, the benzothiophene ligand in this case is $\eta^2$-C\textsubscript{2} bonded to a closed triosmium cluster. This change of coordination mode is associated with the formation of an Os-Os bond and a shortening of the Os-Os distance from 3.742(1) Å to 2.843(1) Å. This compares to the shortening of the Re----Re distance from 4.231(1) Å to 3.034(1) Å in compounds 11 and 10, respectively, with the formation of a Re-Re bond. We believe that the mode of bonding of the $\mu$-thienyl ligand will depend upon the M-M distance, large distances requiring C,S coordination.

The structure for this complex differs from that for complex 8, which also contains a cleaved thienyl ring in that the ring is essentially planar with the sulfur atom being just 0.069 Å out of the plane of the four carbon atoms. However, the trans influence of the coordinating sulfur and carbon
Figure 3.9: Molecular structure of $\text{Re}^+\text{(C}_2\text{H}_5)\text{(PPh}_3\text{(CO)}_3\text{)}_2$.
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<td>C(1)-S-C(4)</td>
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</tr>
<tr>
<td>Re(2)-C(1)-S</td>
<td>118.8(6)</td>
</tr>
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</table>

**Selected bond lengths (Å) and angles (°) for compound [Re₂(μ-
C₄H₃S)(μ-PPh₂)(CO)₆]**
atoms of the cleaved thiophene fragment can be made by comparing the Re(1)-C(12) \( (\text{trans to S}) \) and Re(2)-C(23) \( (\text{trans to C}) \) bond lengths which are significantly different at 1.904(17) Å and 1.974(13) Å, respectively. The shorter/stronger Re(1)-C(12) bond is due to the \text{trans} sulfur atom being more weakly bound than C(1).

At room temperature, the carbonyl region of the \(^{13}\text{C}[^{1}\text{H}]\) NMR spectrum of 11 from δ 200-185 shows a sharp doublet at δ 197.9 which has been assigned to the C\(^2\) signal of the thiënyl ring (Re-C) and also broad signals from approximately δ 195-185. These broad signals indicate fluxional behaviour of all of the carbonyl ligands in complex 11. The variable temperature \(^{13}\text{C}[^{1}\text{H}]\) NMR spectrum of 11 in this region is shown in Figure 3.10, ranging from -50 to 55 °C - the temperature range limit for CDCl\(_3\).

The spectrum at -50 °C is consistent with the static molecular structure found in the crystal, with all eight CO ligands in distinguishable sites. As expected, there are two signals with large \( J_{PC} \) values of 38.6 and 32.9 Hz at δ 188.6 and δ 185.3, respectively, which can be assigned to the CO ligands \text{trans} to the diphenylphosphido bridge. The remainder are CO ligands \text{cis} to this phosphido unit, with much reduced coupling constants. This includes a multiplet at δ 193.2 which is the accidental overlap of two CO ligands. As the temperature is raised all CO signals broaden indicating a fluxional process which involves all of the CO ligands.
Figure 3.10 Variable temperature $^{13}$C($^1$H) NMR spectrum of $[\text{Re}_2(\mu-C_2\text{H}_2\text{S})(\mu-\text{PPh}_2)(\text{CO})_6]$ 11 from approximately $\delta$ 200-180 (carbonyl region)
A possible process which involves exchange of the CO ligands is exchange of the sulfur and carbon bonding in the thienyl bridge between the two rhenium atoms. This relates to the exchange processes that occur in complexes of the type \([\text{Re}_2(\mu-\text{H})(\mu-\text{X})(\text{CO})_j]\) (\(\text{X} = \text{alkynyl},^{143,144}\) alkenyl. \(^{145,146}\)). Here, the \(\sigma\) and \(\pi\) bonds of the \(\mu\)-alkenyl or \(\mu\)-acetylide ligand are rapidly interchanged between the bridged rhenium atoms.

A possible mechanism for the exchange of sulfur and carbon bonding between the two rhenium atoms is shown in Figure 3.11. This mechanism involves firstly the recoordination of the thienyl bridge so that a double bond of the ring and not the sulfur and carbon atoms coordinate to the two rhenium atoms through a \(\sigma\) and a \(\pi\) bond. An interchange of the \(\sigma\) and \(\pi\) bonds of this \(\mu\)-alkenyl bridge as for the alkenyl and alkynyl dirhenium complexes, followed by recoordination through the sulfur and carbon atoms yields complex 11. This process involves the exchange of all eight CO ligands, as observed in the variable temperature \(^{13}\text{C}(^1\text{H})\) NMR spectrum of 11. At the higher temperature, signals in the ratio 4:2:2 would be expected for CO ligands a-d, e and g, and f and h. The CO ligands \textit{trans} to the diphenylphosphido bridge, e and g, would coalesce into a doublet with an averaged chemical shift and P-C coupling constant. This is possibly observed for 11 at 55 °C - two fairly broad signals at approximately \(\delta\) 189 and 187.5 in an approximately 1:2 ratio along with possibly a doublet at \(\delta\) 186.6 with a \(J_{\text{pc}}\) value of 36.4 Hz. This is not the expected values for this doublet (\(\delta\) 187.0, \(J_{\text{pc}} = 35.8\) Hz), however, the high temperature limit has yet to be reached (55 °C is the temperature limit
for the CDCI₃ solvent. Therefore, this process may explain the variable temperature \(^{13}C(\text{H})\) NMR spectrum of 11 in the carbonyl region.

Figure 3.11 Diagram showing a possible mechanism for the observed fluxionality observed in \([\text{Re}_2(\mu-C_5H_5S)(\mu-PPh_3)(CO)]_{11}\)
3.2.6 Thermolysis of \([\text{Re}_2(\mu-\text{PPh}_2(2-C_4H_3S))(\text{CO})_6] 10\)

After heating compound 10 for four hours under reflux in toluene, there was only a little change in the IR spectrum. Work-up of the solution using TLC separation on silica gave unreacted starting material, compound 10 (90%) and its isomer, compound 11 (10%) as the only products, by spectroscopic characterisation with authentic samples. Thermal isomerisation of compound 10 to compound 11 is a very slow process at 110 °C.

3.2.7 A proposed mechanism for the observed reactivity

It seems likely that, in the conversion of \([\text{Mn}_2(\text{CO})_6(\text{PPh}_2(2- C_4H_3S))] 7\) to \([\text{Mn}_2(\mu-\text{PPh}_2)(\mu-\eta^5-\text{C}_4\text{H}_3\text{S})(\text{CO})_6] 8\), there are two unobserved manganese intermediates which are analogues to the rhenium complexes 10 and 11. However, isomerisation and rapid decarbonylation with conversion of the 3-electron donating thienyl to a 7-electron donating \((\eta^1:\eta^5-)\) bridge must occur, possibly via an 5-electron donating \((\eta^1:\eta^3-)\) bridge.

Scheme 3.2 shows the possible route, with intermediates, for the conversion of compound 7 to compound 8 for a \([\text{M}_2(\text{CO})_{10}]\) complex (M = Mn, Re). Only the manganese analogue of complex 7 is observed. The rhenium analogue of this complex may be formed but is not observed due the formation of complex 10 which is stable. However, as stated, the manganese analogue of this complex may be formed but rapidly isomerises, possibly to
the manganese analogue of complex 11. Again, this unobserved complex is unstable and spontaneously decarbonylates to give complex 8. As seen in Section 3.2.6 the isomerisation of complex 10 to 11 is slow at 110 °C. Also decarbonylation of complex 11, which is stable at temperatures up to 180 °C, to give the rhenium analogue of complex 8 does not occur. The use of catalysts such as amine-N-oxides may facilitate this decarbonylation although without using these we have been unable to remove CO from 11 to generate the analogue of compound 8 for rhenium.

These results may be discussed in terms of the relative bond strengths in manganese and rhenium carbonyl complexes. The isomerisation of \([\text{M}_2\{\mu-\text{PPh}_3(\text{2-C}_2\text{H}_5\text{S})\}(\text{CO})_3\}]\) to \([\text{M}_2\{\mu-\text{PPh}_3\}(\mu-\text{C}_2\text{H}_5\text{S})(\text{CO})_3\}]\) requires a M-M and a P-C bond cleavage and also the formation of a M-P and a M-C bond. Although the Mn-Mn bond strength is likely to be weaker than that for Re-Re in the non-cleaved bridging complex, this isomerisation is believed to be thermodynamically more favoured for the rhenium complex. However, these complexes are not observed for manganese which may be due to the activation parameters for this isomerisation being lower than for the rhenium complex. Another reason may be that this isomerisation occurs via another process which may initially involve a loss of CO, followed by a rearrangement and finally a regaining of CO. The more facile M-C bond cleavage in manganese carbonyl complexes compared to rhenium carbonyl complexes would account for these complexes not being observed. It would also account for the rhenium analogue of complex 8 not being observed as the formation of this complex requires the loss of a further two CO ligands.
Scheme 3.2
3.2.8 Reaction of $[\text{Os}_3(\text{CO})_{12}]$ with diphenyl-2-thienylphosphine

The reaction of $[\text{Os}_3(\text{CO})_{12}]$ with diphenyl-2-thienylphosphine (L) was first carried out under reflux in heptane. This temperature was selected as it was thought that the mono, the di and the trisubstituted P-bound complexes $[\text{Os}_x(\text{CO})_{12-x}L_x]$ ($x = 1, 2, 3$) would be formed and then could easily be separated utilising chromatographical techniques. The gradual colour change from a yellow solution to an orange solution and no further change in the IR spectrum after seventeen hours, showed that the reaction had ceased. Work-up of the solution using TLC separation gave two clear yellow bands corresponding to products and some unreacted cluster, $[\text{Os}_3(\text{CO})_{12}]$.

The first TLC band gave a yellow microcrystalline solid, which yielded a complex IR spectrum, with a number of peaks seeming to have shoulders or overlapping signals. As well as this, complex $^1\text{H}$ and $^{13}\text{C}(^1\text{H})$ NMR spectra suggested a mixture of two or more compounds or addition of more than one ligand per osmium compound. Two non-associated signals of differing intensity at $\delta$ -5.9 and -17.8 in the $^{31}\text{P}(^1\text{H})$ NMR spectrum again suggested a mixture of at least two compounds. The highest mass molecular ion peak at $M^+ = 1153$, in the FAB mass spectrum (based on $^{195}\text{Os}$) $\text{Cl}$ to the conclusion that there were only trinuclear species present as we expected for reaction at 98 °C. The above molecular ion peak in the FAB mass spectrum corresponded to $[\text{Os}_3\text{H(CO)}_{11}\{\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}]^+$ and hence one of the compounds in the mixture may be the monosubstituted product, $[\text{Os}_3(\text{CO})_{11}\{\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}]$. Note that the FAB technique normally shows the
parent molecular ion [MH]$^+$ by protonation from the medium used, in this case $m$-nitrobenzylalcohol. Further evidence for this cluster came from comparison of the complex IR spectrum with other clusters of the same type, such as $[\text{Os}_3(\text{CO})_{11}(\text{PR}_3)]$ ($R = \text{alkyl, aryl}$). A hydride signal at $\delta -18.06$ in the broad $^1H$ NMR spectrum suggested that there had been oxidative addition with C-H bond cleavage at either the thienyl group or a phenyl group, in one of the compounds in the mixture.

Separation of the compounds by TLC was unsuccessful, so attempts were made to selectively crystallise each compound, from a cold dichloromethane-hexane mixture. This led to yellow crystals suitable for single-crystal X-ray diffraction. The crystal selected for study contained very unusually two quite different co-crystallised triosmium clusters in the unit cell, the structures of which are shown in Figures 3.12 and 3.13, with selected bond lengths and angles in Tables 3.4 and 3.5, respectively.

As suggested above, one was indeed the phosphorus-bound monosubstitution product, $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_2(2-C_5H_5S))]$ 12. The non-coordinated thienyl substituent in this cluster was found to be disordered over two orientations related by a $180^\circ$ rotation about the P-thienyl bond. Figure 3.12 shows only one of these disordered forms, but Figure 3.14 shows both. But other than this effect, the structure was exactly as expected with the tertiary phosphine in an equatorial site. The other cluster, $[\text{Os}({\mu}-\text{H})\{\mu_3-\text{PPh}_2(2-C_5H_5S)](\text{CO})_9\}$ 13, is the analogue of a known ruthenium cluster. The $\mu_3,\eta^1,\eta^2$-cyclometallated ligand is coordinated to all three osmium atoms. The atom P(1) is bonded to Os(3), as a tertiary phosphine donor. There is a
σ-bond between Os(2) and C(2) and an η²-interaction between C(1), C(2) and Os(1), which result in a σ,η²-vinyl type bridge between
Table 3.4  Selected bond lengths (Å) and angles (°) for compound 

\[\text{[Os}_3(\text{CO})_7\text{(PPh}_2(2-\text{C}_4\text{H}_7\text{S})]) \ 12\]

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<thead>
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<th>Bond</th>
<th>Distance (Å)</th>
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<td>Os(4)-Os(5)</td>
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<td>2.877(2)</td>
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<tr>
<td>Os(4)-Os(6)-Os(5)</td>
<td>60.5(1)</td>
</tr>
<tr>
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<td>Os(6)-Os(4)-P(2)</td>
<td>164.6(2)</td>
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</tbody>
</table>
Figure 3.13  Molecular structure of $[\text{Os}_3\text{(µ-H)}_2\text{PPh}_3\text{]}_3\text{]}\text{(CO)}_{13}$
Table 3.5  Selected bond lengths (Å) and angles (°) for compound [Os₃(μ-H)[μ₃-PP₃(2-C₅H₅)](CO)₃] 13

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<td>C(1)-S(1)-C(4)</td>
<td>89(1)</td>
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Figure 3.14  Diagram showing the disorder over two orientations related by a 180° rotation about the P-thienyl bond in [Os₁₂(CO)₁₂(PPh₃)(2-C₆H₃S)]₁₂
the osmium atoms Os(2) and Os(3). The structure corresponds closely to that of its ruthenium analogue and that of [Os₃(μ-H)(μ₃-PMePhC₆H₄)(CO)₉]₁⁴⁷.

The second TLC band, gave an orange microcrystalline solid on extraction and crystallisation from a cool dichloromethane-hexane solution. Again the crystalline sample yielded a complex IR spectrum and complex ¹H and ¹³C(¹H) NMR spectra, suggesting that it was a mixture. The highest mass molecular ion peak was observed at M⁺ = 1393, in the FAB mass spectrum (based on ¹⁸⁵Os) corresponding to [Os₃H(CO)₁₀{PPh₂(2-C₆H₅S)}₂]⁺, the protonated form of the bisphosphine derivative. It seems to be clear from this that one component of the mixture is the disubstituted cluster, [Os₃(CO)₁₀(PPh₂(2-C₆H₅S))₂] 14. Two other pieces of data supported the evidence for this cluster. One came from comparison of the complex IR spectrum with other clusters of the same type, such as [Os₃(CO)₁₀(PR₃)] (R = alkyl, aryl).⁶² Another came from the ³¹P(¹H) NMR spectrum, in which broad signals are observed at room temperature from approximately δ -18 to -25. This is indicative of the equilibrium, at room temperature, of the two isomers of the 1,2-phosphorus bound disubstituted clusters.⁷⁵ The variable temperature ³¹P(¹H) NMR spectrum at -40 °C showed that this was the case. At this temperature the equilibrium between the symmetrical and unsymmetrical 1,2-bisphosphine is expected to be frozen out. Separate signals are expected for each of these two isomers which are two peaks for the two inequivalent phosphorus nuclei in the unsymmetrical cluster and one peak for the two equivalent phosphorus nuclei in the symmetrical cluster. This is observed and the two peaks at δ -20.8 and -21.2 are due to the
unsymmetrical cluster and also the single peak at δ -24.6 is due to the symmetrical cluster. In addition to the above signals two doublet resonances at δ -2.5 and -3.0 in the $^{31}$P{'H} NMR spectrum ($J = 16.7$ Hz) suggest that there is another, non-fluxional, cluster containing two of the original ligands. A hydride signal at δ -17.46 in the $^1$H NMR spectrum suggests that, as with the previous band, there has been oxidative-addition of either the thienyl group or a phenyl group. The double-doublet pattern of the hydride signal is consistent with there being two non-equivalent phosphorus groups in the molecule and there is a close resemblance to the spectrum of $[\text{Ru}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}\{\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}{\text{CO}}]$, a cluster derived by substitution of a carbonyl group by diphenyl-2-thienylphosphine from $[\text{Ru}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}]{\text{CO}}]$. This suggests the second cluster in the mixture is the osmium analogue, $[\text{Os}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}\{\text{PPh}_2(2-\text{C}_4\text{H}_2\text{S})\}{\text{CO}}]$. 15.

Thus carrying out the reaction at 96 °C lead to a mixture of metallated and non-metallated phosphine clusters and to avoid this the reaction was repeated at the elevated temperature of refluxing octane (b.p. 130 °C). A gradual colour change occurred from a yellow to an orange solution and there was no further change in the IR spectrum. TLC work-up gave two products and some unreacted $[\text{Os}_3(\text{CO})_{12}]$.

The first product, a yellow microcrystalline solid, was characterised analytically, by IR spectroscopy, by $^1$H, $^{13}$C{'H} and $^{31}$P{'H} NMR spectroscopies and ultimately by single-crystal X-ray diffraction. The crystal structure is shown in Figure 3.15 with selected bond lengths and angles in Table 3.6. The crystal contains pure cluster 13 (54% yield). The $^1$H NMR
Figure 3.15  Molecular structure of [Os₅(μ-H)(μ₃-PPh₃(2-C₅H₅S))(CO)₉] 13
Table 3.6  Selected bond lengths (Å) and angles (°) for compound [Os₃(µ-
H)ₜraits-PPh₂(2-C₅H₂S)](CO)₃] 13

<table>
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spectrum of cluster 13 was as expected except that the two signals for the two C-HgS proton signals were not observed. Since the signal for CHCl₃ of the solvent is relatively broad and strong it is likely that it overlies the thienyl proton signals.

The variable temperature ¹H and ¹³C(¹H) NMR spectra of cluster 13 differ from those of its ruthenium analogue. For cluster 13 the room temperature ¹H and ¹³C(¹H) NMR data are consistent with the static structure found in the crystal. Two sets of ortho proton signals at δ 7.12 and 7.89 and two sets of meta and para multiplets at δ 7.59 and 7.30, show there to be non-equivalent phenyl groups as observed in the static structure. Non-equivalent phenyl groups can also be observed in the room temperature ¹³C(¹H) NMR spectrum. For the ruthenium analogue, low temperature (-20 °C) ¹H and ¹³C(¹H) NMR spectra are consistent with the static structure. The two sets of each ortho, meta and para signals which are broad at room temperature, coalesce at around 35 °C, and give single coalesced signals at around 90 °C. Coalescence of the ipso phenyl resonances, from two sets of doublets at -70 °C to a single doublet at 90 °C, with an averaged Jₑₑ value, shows that the coalescence of the phenyl signals is not the result of restricted rotation about the P-Ph bond but from phenyl exchange. The proposed mechanism requires a hydride shift between M-M edges as well as oscillation of the σ, π²-vinyl group between two metal centres (σ-π flip), to give a time averaged plane of symmetry as shown in Figure 3.16. This was further confirmed by variable temperature ¹³C(¹H) NMR spectroscopic data in the carbonyl region.
Figure 3.16
The variable temperature $^1$H NMR spectroscopy of $^{13}$ in toluene-$d_6$, which is shown in Figure 3.17 shows that the same but slower process occurs. At room temperature separate resonances for the non-equivalent phenyl groups are observed, ortho signals at $\delta$ 8.06 and 7.35, meta signals at $\delta$ 7.35 and 7.12 and para signals at $\delta$ 7.27 and 7.03. These signals broaden and approach coalescence as the temperature approaches 95 °C, the maximum temperature we could use. This suggests, as expected, that for the osmium cluster, either or both of the two processes that give rise to a time-averaged plane of symmetry, that is the hydride shift and the $\sigma$-$\pi$ flip, are slower than in the analogous ruthenium cluster.

Single-crystal X-ray diffraction confirmed that clusters 12 and 13 were present in the first TLC band from the reaction mixture derived from $\text{[Os}_3(\text{CO})_{12}]$ with diphenyl-2-thienylphosphine in refluxing heptane. The IR spectra of this mixture, of pure cluster 13 and that derived by subtraction of the IR spectrum of pure cluster 13 from that of the mixture are shown in Figure 3.18. The subtracted spectrum is similar to that of other monosubstituted phosphorus bound triosmium clusters, such as $\text{[Os}_3(\text{CO})_{11}(\text{PR}_3)]}$ (R = alkyl, aryl). This further confirms that cluster 12 is one products of the first TLC band, from the reaction in refluxing heptane.

The second product of the reaction in octane, an orange-yellow microcrystalline solid, was characterised analytically, by IR spectroscopy and by $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR as cluster 15 (14%), a substituted derivative of cluster 13. The IR spectrum of this cluster is similar to that of its ruthenium analogue. $^1$H and $^{13}$C($^1$H) NMR spectra are complex, but similarities with the
Figure 3.17 Variable temperature $^1$H NMR spectrum of [Os$_3$(μ-H)(μ$_3$-PPh$_2$(2-C$_4$H$_2$S))(CO)$_3$] 13 in toluene-$d_6$ ($\bullet$ = solvent) (★ = thieryl)
spectra for cluster 13 are observed, for example, an ortho signal at around δ 7.85 is observed in both spectra. A hydride signal in the 1H NMR spectrum at δ -17.46 is a double-doublet consistent with there being two non-equivalent phosphorus nuclei in the molecule. Therefore as expected the 31P(1H) NMR spectrum contains two coupled signals at δ -2.30 and -2.80. In retrospect, these data help confirm that cluster 15 was one of the products in the second TLC band from the reaction of [Os₃(CO)₁₂] with diphenyl-2-thienylphosphine in refluxing heptane.

The IR spectrum of this second band, together with that of pure cluster 15 and the subtraction of the IR spectrum of pure cluster 15 from that of the mixture of products in the second band, are shown in Figure 3.19. This difference spectrum is similar to those of other 1,2-disubstituted phosphorus bound trosmium clusters, such as [Os₃(CO)₁₀(PR₃)₂] (R = alkyl, aryl). This confirms that the mixture contains cluster 14.

The reaction between [Os₃(CO)₁₂] and PPh₂(2-C₆H₃S) was also carried out in refluxing nonane (b.p. 155 °C) with a 3:2 excess of cluster, in an attempt to see if clusters of higher nuclearity could be synthesised. After six hours the resulting orange solution was separated by TLC on silica. Unreacted cluster [Os₃(CO)₁₂], cluster 13 (64%) and cluster 15 (14%) were obtained. Hence even under these forcing conditions we did not obtain clusters corresponding [Ru₄(μ₄-PPh)(μ₄-C₆H₃S)(CO)]₄ and [Ru₄(μ₄-PPh)(μ₄-C₆H₅)₄(CO)]₄ as formed with ruthenium.
(a) IR spectrum of a mixture of clusters 12 and 13

(b) IR spectrum of cluster 13

(c) IR spectrum derived from the subtraction of spectrum 3.18(b) from 3.18(a)

Figure 3.18
(a) IR spectrum of a mixture of clusters 14 and 15

(b) IR spectrum of cluster 15

(c) IR spectrum derived from the subtraction of spectrum 3.19(b) from 3.19(a)

Figure 3.19
3.2.9 Thermolysis of a mixture of $[\text{Os}_3(\text{CO})_{11}\{\text{PPh}_2(2-C_4H_2S)\}]$ and $[\text{Os}_3(\mu-H)(\mu_3-PPh_2(2-C_4H_2S))(\text{CO})_3]$

The inseparable mixture of the two clusters 12 and 13 formed in the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with diphenyl-2-thienylphosphine in refluxing heptane was treated at higher temperatures to see if cluster 12 was an intermediate in the formation of cluster 13. After five hours of heating in refluxing toluene there was no further change in the IR spectrum of the solution. Also the spot for cluster 12 had disappeared from the spot-TLC plate, leaving only the spot for cluster 13. Cluster 12 had fully converted to cluster 13. This was confirmed by the isolation and characterisation of cluster 13 from TLC separation on silica.

Under the conditions of refluxing heptane, cluster 12 is formed and converts relatively slowly to cluster 13. At elevated temperatures this conversion is proportionally faster. The ruthenium analogues of clusters 12 and 13 are readily interconvertible; $[\text{Ru}_3(\mu-H)(\mu_3-PPh_2(2-C_4H_2S))(\text{CO})_3]$ reacts with carbon monoxide to give the cluster $[\text{Ru}_3(\text{CO})_{11}\{\text{PPh}_2(2-C_4H_2S)\}]$, facile decarbonylation of this at room temperature gives the cluster with the metallated ligand, as expected as the second and third decarbonylations from $[\text{Ru}_3(\text{CO})_{11}(\text{PR})_3]$ are fast compared to the first. However, treatment of cluster 13 with CO (1 atm) failed to give cluster 12 or any other product, suggesting that the conversion of cluster 13 to cluster 12 either does not occur or is much slower than for the ruthenium analogue, as expected.
3.2.10 Reactivity of \([\text{Os}_3(\mu-H)][\mu_3-\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})](\text{CO})_3] 13\)

Thermolysis of the mixture of clusters 12 and 13, formed from the reaction of \([\text{Os}_3(\text{CO})_{12}]\) and diphenyl-2-thienylphosphine in refluxing heptane, gave cluster 13 as the only product, showing that cluster 12 is an intermediate in the formation of cluster 13. Cluster 13 was reacted with the ligand, \(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})\), to ascertain whether it was an intermediate in the formation of cluster 15. After five hours of heating under reflux in octane there was a significant change in the IR spectrum of the solution, but peaks due to cluster 13 were still observable. The new peaks closely corresponded to those of cluster 15. Spot TLC analysis of the solution, on silica, showed there to be a new compound with an \(R_f\) closely corresponding to that of cluster 15. TLC separation on silica gave clusters 13 and 15 in ca. 1:1 ratio.

Cluster 13 was shown to be an intermediate in the formation of cluster 15, but it is a slow reaction with only ca. 50% conversion after five hours under reflux in octane. A mixture of clusters 12 and 13 gave only cluster 13 when heated at a temperature greater than 100 °C and cluster 13 is the only the only product of the two, of the reaction of \([\text{Os}_3(\text{CO})_{12}]\) with \(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})\) under reflux in octane or nonane. The fact that clusters 14 and 15 are formed from the same reaction in refluxing heptane and cluster 15 is the only product of the two, of the reaction in octane or nonane, suggests that as well as cluster 13, cluster 14 is an intermediate in the formation of cluster 15.

Cluster 13 has a high thermal stability with neither fragmentation or build-up in the nuclearity of the cluster at temperatures of up
to refluxing nonane (b.p. 152 °C). The cluster also has low chemical reactivity, in its reaction with PPh₃(2-C₆H₅S) to give cluster 15 which is slow even under reflux in octane.

Elevated temperatures were used to thermolyse the cluster in the absence of reagent, achieved by heating the cluster in nonane at 175 °C in a sealed Pyrex tube. TLC separation on silica of the resultant orange-brown solution gave only one product (73%) for which the ¹H NMR spectrum showed two outstanding features. One was the loss of hydride signal, the other was that integration showed the compound to contain 7 protons of the original 13 protons in cluster 13. This suggested that one of the groups on the phosphine had been cleaved and lost, along with the hydridic hydrogen. A thienyl signal could be observed at δ 7.36, suggesting that the group cleaved from the phosphine and subsequently lost was a phenyl group, which along with the hydridic hydrogen was lost as benzene. This was confirmed by resonances integrating for only one phenyl group being observed in the ¹H and ¹³C(¹H) NMR spectra. A highest mass ion peak at M⁺ = 1018 (based on ¹⁸⁵Os) further confirmed the loss of benzene and a formula C₆₂H₅₇O₇PSO₃. The lack of coupling to ³¹P in the thienyl resonance at δ 7.36 in the ¹H NMR spectrum confirmed the cleavage of the thienyl group from the P atom.

The IR spectrum of the compound is similar to those of two other triosmium clusters, [Os₃(μ₃-S)(μ₃-CHCФc)(CO)]₃ (Fc = ferrocene),¹⁴⁸ and [Os₃(μ₃-PR)(μ₃-C₆H₅)(CO)]₃ (R = Me, Ph).¹⁴⁷,¹⁴⁹ Both clusters contain a triangular Os₃ unit with an open Os—Os edge, with either the sulfur atom or the PR moiety capping one face of the Os₃ triangle. The geometry's of
coordination of the ethynylferrocene or the benzyne ligands on the opposite faces of the Os₃ triangle are however, quite different as shown in Figure 3.20. The ethynylferrocene ligand spans the open Os—Os edge through two carbon atoms via σ-bonds and there is an η²-interaction to the other osmium atom. The benzyne ligand does not span the open Os—Os edge but instead it is coordinated via σ-Os-C bonds to two osmium atoms through one carbon atom, and to the other osmium atom through the other carbon atom, predominantly via π-orbitals.

The product of the reaction could now be characterised by IR spectroscopy, by ¹H and ¹³C(¹H) NMR spectroscopy and by mass spectroscopy as [Os₃(µ₃-PPh)(µ₃-C₄H₄S)(CO)₉] 16 (73%), which contains a thiophyne unit. However, we could not confirm from the spectra whether the coordination is like ethynylferrocene or benzyne in the above complexes. Figure 3.21 shows the two possible structures of cluster 16.

Figure 3.20 Structures of [Os₃(µ₃-X)(µ₃-PPh)(CO)₉] (X = S, C₆H₄)

Figure 3.21 Structures of [Os₃(µ₃-X)(µ₃-PPh)(CO)₉] (X = S, C₆H₄)
3.2.11 Conclusions

As stated in Section 3.1.2, the 2-thienylphosphines have previously only shown the coordination behaviour of a simple tertiary phosphine with coordination through phosphorus atoms only.

With the group 7 dinuclear metal carbonyls, \([M_2(CO)_3] (M = Mn, Re)\), a rich chemistry has been developed with coordination of the thienyl ring through the sulfur atom only and also with up to all four of the carbon atoms. The differences between the two metal systems has been discussed in terms of activation parameters for reactions and also the relative strengths of the M-C and other bonds in manganese and rhenium carbonyl complexes.
Scheme 3.3 shows the reaction of the trinuclear metal carbonyl clusters \([M_3(CO)_{12}]\) (M = Ru, Os) with PPh\(_2\)(2-C\(_4\)H\(_3\)S) and any subsequent reactivity of the complexes formed. With these group 8 trinuclear metal carbonyl clusters again there has been coordination of the thienyl ring as well as through phosphorus atoms, as a simple tertiary phosphine. However, with these metal systems the sulfur atom of the thienyl ring is not coordinated nor is the P-C bond to the thiophene cleaved but instead initially the ortho C-H bond is broken leading to the related oxidative-addition products \([M_3(\mu-H)(\mu_3-\text{PPh}_2(2-C_4H_3S))(CO)_6L]\) (M = Ru, Os; L = CO, PPh\(_2\)(2-C\(_4\)H\(_3\)S)). The more rapid formation of the ruthenium clusters compared to the analogous osmium clusters can be accounted for due to the relative strengths of the M-M and M-C bonds in ruthenium and osmium carbonyl complexes.

When L = CO in these clusters, an exchange process occurs which leads to NMR coalescence and a time-averaged plane of symmetry. Unsurprisingly, this process which was found to be an interchange between the \(\sigma\) and \(\eta^2\) interactions of the thienyl group as well as a hydride shift between M-M bonds, was observed to be more rapid in the corresponding ruthenium cluster.

Prolonged thermolysis of \([\text{Ru}_3(\mu-H)(\mu_3-\text{PPh}_2(2-C_4H_3S))(CO)_6]\) leads to the tetranuclear clusters \([\text{Ru}_4(\mu_4-\text{PPh})(\mu_4-C_4H_3S)(CO)]_4\) and \([\text{Ru}_4(\mu_4-\text{PPh})(\mu_4-C_6H_4)(CO)]_4\). No such cluster build-up occurs for the analogous triosmium cluster which is stable in refluxing nonane (b.p. 155 °C) and even with an excess of parent carbonyl cluster at 175 °C. Again this can be accounted for by the relative strengths of the M-M and M-C bonds in
ruthenium and osmium carbonyl clusters. Temperatures of around 190 °C were required for the thermolysis of the Os cluster, yielding an open trinuclear cluster \([\text{Os}_3(\mu_3-\text{PPh})(\mu_3-\text{C}_4\text{H}_2\text{S})(\text{CO})_9]\) which would be a precursor in the formation of the as yet unobserved tetrannuclear osmium cluster analogous to \([\text{Ru}_4(\mu_4-\text{PPh})(\mu_4-\text{C}_4\text{H}_2\text{S})(\text{CO})_{14}]\).

The thienyl substituent on the ligand \(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{S})\) has been shown to have a different coordination behaviour between the group 7 and the group 8 metal carbonyl complexes. With the group 7 metal carbonyls the sulfur atom and up to all four carbon atoms on the thienyl ring can be involved in coordination whereas with the group 8 metal carbonyls the ortho C-H bond is activated via oxidative-addition. Other carbon atoms of the ring may be activated, which is the case in the tetrannuclear ruthenium cluster and the open triosmium cluster, however, the sulfur atom is not activated in these clusters.
Scheme 3.3

Numbers correspond to $M = Os$
3.3 Experimental

The ligand diphenyl-2-thienylphosphine was synthesised and characterised as reported previously. This synthesis initially involves the formation of 2-lithiothiophene from the dropwise addition of an ethereal solution of butyl lithium to a cooled ethereal solution of thiophene. Subsequent reaction with an ethereal solution of chlorodiphenylphosphine and a work-up involving washing with Na\textsubscript{2}SO\textsubscript{4} solution and a vacuum distillation at 130 °C and 0.05 mm Hg, yielded the desired ligand as a thick yellow oil which solidified on standing to yield an off-white solid.

3.3.1 Thermal reaction of [Mn\textsubscript{2}(CO)\textsubscript{10}] with PPh\textsubscript{2}(2-C\textsubscript{6}H\textsubscript{5}S)

The compound [Mn\textsubscript{2}(CO)\textsubscript{10}] (0.168 g, 0.430 mmol) and PPh\textsubscript{2}(2-C\textsubscript{6}H\textsubscript{5}S) (0.124 g, 1:1 mol/mol carbonyl) were heated under reflux in xylene (20 cm\textsuperscript{3}) for ten hours. The IR spectrum of the solution was recorded periodically to monitor the conversion of the carbonyl. The resulting orange-brown solution was evaporated to dryness under reduced pressure to yield an orange-brown solid. TLC work-up [SiO\textsubscript{2}; eluent, hexane-dichloromethane (5:2 v/v)] gave three bands. A yellow material eluting fast was found spectroscopically to be unreacted carbonyl. A second yellow band yielded [Mn\textsubscript{2}(CO)\textsubscript{10}(PPh\textsubscript{2}(2-C\textsubscript{6}H\textsubscript{5}S))\textsubscript{7}] as a yellow solid (0.109 g, 40%) from evaporation of a dichloromethane solution (Found: C, 48.1; H, 2.95; P, 6.4; S, 4.9. C\textsubscript{25}H\textsubscript{13}O\textsubscript{5}PSMn\textsubscript{2} requires C, 47.6; H, 2.1; P, 4.9; S, 5.1%); \textsuperscript{1}H and \textsuperscript{13}C{[\textsuperscript{1}H]}
NMR spectra are broadened and not easy to report; $^3$P($^1$H) NMR: $\delta$ 65.5 (s); $\nu$(CO)/cm$^{-1}$: 2093m, 2013m, 1995vs, 1974m, 1963w, 1941s. An orange-yellow band gave $[\text{Mn}_2(\mu-\eta^1,\eta^2-C_8H_8S)(\mu-\text{PPh}_3)(\text{CO})_6]_8$ as an orange-yellow crystalline solid (0.047 g, 20%) by crystallisation from a cool dichloromethane-heptane solution (Found: C, 48.2; H, 2.6; P, 5.6; S, 5.4. $C_{20}H_{13}O_6PSMn_2$ requires C, 48.4; H, 2.4; P, 5.7; S, 5.9%); $^1$H NMR: $\delta$ 7.74 (ddd, $J = 1.1, 7.4, 10.4$ Hz, 2H, ortho Ph), 7.58 (ddd, $J = 1.6, 7.9, 10.8$ Hz, 2H, ortho Ph), 7.36-7.23 (m, 6H, meta/para Ph), 6.15 (t, $J = 2.4$ Hz, 1H, thienyl), 5.83 (d, $J = 3.1$ Hz, 1H, thienyl), 5.75 (t, $J = 3.1$ Hz, thienyl); $^{13}$C($^1$H) NMR: $\delta$ 134.2 (d, $J = 9.2$ Hz, ortho Ph), 133.1 (d, $J = 9.5$ Hz, ortho Ph), 128.6 (d, $J = 2.2$ Hz, para Ph), 128.1 (d, $J = 9.1$ Hz, meta Ph), 127.8 (d, $J = 3.1$ Hz, para Ph), 127.7 (d, $J = 8.6$ Hz, meta Ph), 105.3 (d, $J = 2.1$ Hz, thienyl), 98.1 (s, thienyl), 97.1 (s, thienyl), CO and ipso signals not observed; $^3$P($^1$H) NMR: $\delta$ -25.7 (s); $\nu$(CO)/cm$^{-1}$: 2067s, 1991m, 1978s, 1970s, 1959s, 1922s; parent molecular ion observed in the El mass spectrum.

3.3.2 Photochemical reaction of $[\text{Mn}_2(\text{CO})_6]$ with $\text{PPh}_3(2-C_8H_8S)$

The same two compounds in a 1:1 mol ratio {0.188 g $[\text{Mn}_2(\text{CO})_6]$, 0.141 g $\text{PPh}_3(2-C_8H_8S)$ (0.476 mmol)}, were photolysed with UV irradiation in toluene (100 cm$^3$) for ten hours. The resulting orange-brown solution was evaporated to dryness by vacuum distillation to yield an orange-brown solid. TLC work-up [$\text{SiO}_2$; eluent, hexane-dichloromethane (5:2 v/v)] gave three bands, the first of which was found spectroscopically to be
unreacted carbonyl. A yellow band yielded compound 7 (0.143 g 47%), characterised spectroscopically. An orange-yellow band gave [Mn₄(CO)₆(PPh₃(2-C₆H₃S))] 9 as an orange solid (0.082 g, 19%) from evaporation of dichloromethane (Found: C, 52.4; H, 3.3; P, 6.3; S, 6.7. C₄₀H₂₀O₆P₂S₂Mn₂ requires C, 55.2; H, 3.0; P, 7.1; S, 7.4%); ¹H and ¹³C(¹H) NMR spectra are broad and are not reported; v(CO)/cm⁻¹: 1995vw, 1963vs; parent molecular ion peak observed in the EI mass spectrum.

3.3.3 Thermolysis of [Mn₄(CO)₆(PPh₃(2-C₆H₃S))] 7

Compound 7 (0.031 g, 0.05 mmol) was heated under reflux in xylene (8 cm³) for two hours, the reaction being monitored by IR spectroscopy. The darker orange solution was evaporated to dryness under reduced pressure to yield an orange solid. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:2 v/v)] gave unreacted compound 7 (0.02 g, 22%) and compound 8 (0.061 g, 59%), characterised spectroscopically with authentic samples.

3.3.4 Photochemical reaction of [Re₂(CO)₁₀] with PPh₃(2-C₆H₃S)

The compound [Re₂(CO)₁₀] (0.108 g, 0.166 mol) and the tertiary phosphine PPh₃(2-C₆H₃S) (0.053 g. 1:1 mol/mol carbonyl) were photolysed with UV irradiation in toluene (100 cm³) for five hours; the IR spectrum of the solution was recorded periodically to monitor the conversion of the carbonyl.
The resulting pale yellow solution was evaporated to dryness by vacuum distillation to yield a pale yellow solid. TLC work-up [SiO₂; eluent, hexanedichloromethane (5:3 v/v)] gave two bands. The first, a colourless band, was found to be unreacted carbonyl. A second yellow band gave [Re₂(μ-PPh₂(2-C₄H₅S))(CO)₆] 10 as a yellow crystalline solid (0.046 g, 32%) by crystallisation of a cool dichloromethane-heptane solution (Found: C, 33.4; H, 1.7; P, 3.0; S, 3.8. C₂₄H₁₉O₆PRe₂ requires C, 33.3; H, 1.5; P, 3.6; S, 3.7%); ¹H NMR: δ 7.71 (m, 1H, thienyl), 7.74-7.44 (m, 10H, Ph), 7.33 (m, 1H, thienyl), 6.67 (m, 1H, thienyl); ¹³C(¹H) NMR: δ 146.8 (d, ³J = 3.4 Hz, thienyl), 135.7 (d, ³J = 5.3 Hz, thienyl), 133.1 (d, ²J = 7.8 Hz, thienyl), 132.1 (d, J = 12.2 Hz, ortho Ph), 131.1 (d, J = 2.1 Hz, para Ph), 128.9 (d, J = 10.9 Hz, meta Ph), CO and ipso signals not observed; ³¹P(¹H) NMR: δ -10.6 (s); ν(CO)/cm⁻¹: 2108w, 2081m, 2029s, 2012s, 1990sh, 1983s, 1966w, 1951m, 1930s; parent molecular ion observed in the EI and FAB mass spectra.

3.3.5 Thermal reaction of [Re₂(CO)₁₀] with PPh₂(2-C₄H₅S)

The same two compounds in a 1:1 mole ratio {0.211 g [Re₂(CO)₁₀], 0.088 g PPh₂(2-C₄H₅S) (0.324 mmol)} were heated under reflux in decane (10 cm³) for two hours. The resulting yellow solution was evaporated to dryness by vacuum distillation to yield a yellow oily solid. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:2 v/v)] gave only one compound, [Re₂(μ-C₄H₅S)(μ-PPh₂)(CO)₆] 11 as a yellow crystalline solid (0.097 g, 35%) by crystallisation from a cool dichloromethane-heptane solution; ¹H NMR: δ 7.72

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(d, J = 5.0 Hz, 1H, thienyl), 7.58 (dd, J = 7.7, 10.8 Hz, 2H, ortho Ph), 7.47-7.42 (m, 4H, two ortho and two para Ph), 7.34 (dt, J = 1.7, 7.9 Hz, 2H, meta Ph), 7.24 (dt, J = 1.3, 7.5 Hz, 2H, meta Ph), 7.07 (m, 1H, thienyl), 7.05 (m, 1H, thienyl); $^{13}$C($^1$H) NMR: $\delta$ 197.9 (d, J = 5.4 Hz, Re-C), broad CO signals in range ~195-185, 168.1 (s, thienyl), 142.4 (d, J = 27.5 Hz, ipso Ph), 137.8 (d, J = 54.3 Hz, ipso Ph), 135.2 (s, thienyl), 133.5 (d, J = 10.3 Hz, meta Ph), 131.2 (d, J = 12.0 Hz, ortho Ph), 130.5 (d, J = 2.3 Hz, para Ph), 128.5 (s, thienyl), 128.5 (d, J = 2.6 Hz, para Ph), 128.45 (d, J = 10.7 Hz, ortho Ph), 128.1 (d, J = 9.1 Hz, meta Ph); CO region at -50 °C: $\delta$ 193.3-193.1 (m, 2CO), 190.8 (d, J = 7.8 Hz, 1CO), 188.6 (d, J = 38.6 Hz, 1CO trans to PPh$_2$), 188.4 (d, J = 7.2 Hz, 1CO), 187.7 (d, J = 6.4 Hz, 1CO), 186.3 (d, J = 6.4 Hz, 1CO), 185.3 (d, J = 32.9 Hz, 1CO trans to PPh$_2$). $^3$P($^1$H) NMR: $\delta$ -21.5 (s); $\nu$(CO)/cm$^{-1}$: 2106w, 2084m, 2012s, 1999vs, 1978m, 1967s, 1956s, 1945m; low intensity parent molecular ion observed in the EI mass spectrum.

3.3.6 Thermolysis of [Re$_2$(μ-PPh$_2$(2-C$_4$H$_8$S))(CO)$_3$] 10

Compound 10 (0.078 g, 0.090 mmol) was heated under reflux in toluene (15 cm$^3$) for four hours, whilst being monitored by IR spectroscopy. The yellow solution was evaporated to dryness under reduced pressure to yield a yellow solid. TLC work-up [SiO$_2$; eluent, hexane-dichloromethane (5:2 v/v)] gave unreacted starting material, compound 10 (0.070 g, 90%) and compound 11 (0.005 g, 7%) as a minor product.
3.3.7 Thermal reaction of $[\text{Os}_3(\text{CO})_{12}]$ with $\text{PPh}_2(2\text{-C}_4\text{H}_5\text{S})$

(a) Reaction in refluxing heptane: The cluster $[\text{Os}_3(\text{CO})_{12}]$ (0.131 g, 0.145 mmol) and $\text{PPh}_2(2\text{-C}_4\text{H}_5\text{S})$ (0.045 g, 1:1 mol/mol) were heated under reflux in heptane ($20 \text{ cm}^3$) for ten hours. The conversion of the cluster was monitored by solution IR spectroscopy and spot-TLC [$\text{SiO}_2$; eluent, hexane-dichloromethane (5:2 v/v)]. The resulting orange solution was evaporated to dryness under reduced pressure to yield an orange solid. TLC work-up [$\text{SiO}_2$; eluent, hexane-dichloromethane (5:2 v/v)] gave four bands, the first being unreacted cluster, $[\text{Os}_3(\text{CO})_{12}]$. A second yellow band gave a mixture of $[\text{Os}_3(\text{CO})_{12}\{\text{PPh}_2(2\text{-C}_4\text{H}_5\text{S})\}]$ 12 and $[\text{Os}_3(\mu-\text{H})\{\mu_3\text{-PPh}_2(2\text{-C}_4\text{H}_5\text{S})\}](\text{CO})_3$ 13 as a yellow microcrystalline solid (0.081 g) by crystallisation from a dichloromethane-hexane solution; $^1\text{H}$ NMR: $\delta$ 7.92-7.87 (m, 3H), 7.69 (m, 1H), 7.59 (m, 5H), 7.44-7.40 (m, 10H), 7.36-7.13 (m, 6H), -18.07 (d, $J = 13.8$ Hz, 1H); $^{31}\text{P}[^1\text{H}]$ NMR: $\delta$ -4.98 (s), -17.83 (s); $\nu(\text{CO})/\text{cm}^{-1}$: 2109w, 2088s, 2059s, 2033vs, 2020vs, 2002w, 1989s, 1984m, 1073w, 1964m; parent molecular ion $[\text{M}]^+$ and $[\text{M-2CO}]^+$ observed for both 12 and 13 in the EI and FAB mass spectra. A second orange-yellow band gave a mixture of $[\text{Os}_3(\text{CO})_{10}\{\text{PPh}_2(2\text{-C}_4\text{H}_5\text{S})\}_2]$ 14 and $[\text{Os}_3(\mu-\text{H})\{\mu_3\text{-PPh}_2(2\text{-C}_4\text{H}_5\text{S})\}\{\text{PPh}_2(2\text{-C}_4\text{H}_5\text{S})\}](\text{CO})_3$ 15 as an orange microcrystalline solid (0.060 g) by crystallisation from a cool dichloromethane-hexane solution; $^1\text{H}$ NMR: complex signals in the range $\delta$ 7.84-6.33, -17.46 (dd, $J = 10.4$, 15.4 Hz, 1H); $^{31}\text{P}[^1\text{H}]$ NMR: $\delta$ -2.5 (d, $J_{pp} = 16.7$ Hz), -3.0 (d, $J_{pp} = 16.7$ Hz), broad signals from approximately $\delta$ -18 to -25; (-40 °C): sharp signals observed at room temperature are unchanged but
in addition there are sharp peaks at -20.8 (s), -21.2 (s), -24.6 (s); v(CO)/cm⁻¹: 2088w, 2074s, 2056w, 2033vs, 2025sh, 2015vs, 2003s, 1980m, 1976m, 1968m, 1957m, 1949vw; parent molecular ion [M]⁺ and [M-2CO]⁺ observed for both 14 and 15 in the El and FAB mass spectra.

(b) Reaction in refluxing octane: The reaction was also carried out in a 1:1 mole ratio {0.110 g [Os₃(CO)₁₂], 0.032 g PPh₂(2-C₅H₂S) (0.121 mmol)} for nine hours under reflux in octane (20 cm³). The resulting orange solution was evaporated to dryness under reduced pressure to yield an orange solid. TLC work-up of this orange solid [SiO₂; hexane-dichloromethane (5:3 v/v)] gave three bands, the first being unreacted [Os₃(CO)₁₂] (ca. 20 mg). A second yellow band gave [Os₃(μ-H)(μ₃-PPh₂(2-C₅H₂S))(CO)]₁₃ as a yellow crystalline solid (0.071 g, 55%) by crystallisation from a dichloromethane-hexane solution (Found: C, 27.4; H, 1.2; P, 3.1; S, 2.2. C₉₃H₁₆O₅P₂O₅ requires C, 27.5; H, 1.2; P, 2.9; S; 2.9%); 'H NMR: δ 7.89 (ddd, J = 1.7, 7.5, 11.0 Hz, 2H, ortho Ph), 7.63-7.55 (m, 3H, meta/para Ph), 7.36-7.25 (m, 3H, meta/para Ph), 7.24 (s, 2H; thienyl resonances obscured by CHCl₃ peak), 7.12 (ddd, J = 1.4, 8.0, 11.0 Hz, 2H, ortho Ph), -18.06 (d, J = 13.9 Hz, 1H, OsH₂Os); (toluene-d₅, 22 °C): δ 8.06 (ddd, J = 1.4, 7.8, 11.8 Hz, 2H, ortho Ph), 7.40-7.32 (m, 4H, ortho/meta Ph), 7.27 (ddd, J = 1.7, 6.5, 8.4 Hz, 1H, para Ph), 7.16* (dd, J = 1.4, 5.0 Hz, 1H, thienyl ring; *estimated as part of resonance is obscured by peak due to residual toluene), 7.12 (td, J = 2.3, 7.4 Hz, 2H, meta Ph), 7.03 (ddd, J = 2.0, 6.4, 8.4 Hz, 1H, para Ph), 6.65 (dd, J = 0.9, 5.0 Hz, 1H, thienyl); ¹³C{¹H} NMR: δ 176.1 (d, J = 91.7 Hz, OsC), 150.4 (d, J = 33.9 Hz, ipso thienyl), 144.4 (d, J = 12.5 Hz, thienyl), 136.2 (s, thienyl), 134.0 (d, J = 38.0
Hz), 132.6 (d, J = 11.2 Hz, ortho Ph), 131.9 (d, J = 10.5 Hz, meta Ph), 131.5 (d, J = 2.5 Hz, para Ph), 131.3 (d, J = 2.2 Hz, para Ph), 128.9 (d, J = 10.8 Hz, ortho Ph), 128.2 (d, J = 10.3 Hz, meta Ph), CO signals not observed; $^{31}$P($^1$H) NMR: $\delta$ -4.8 (s); v(CO)/cm$^{-1}$: 2088s, 2060s, 2033vs, 2018s, 1995m, 1982s, 1984m, 1973w, 1964w; parent molecular ion observed in the EI and FAB mass spectra. The final band gave [Os$_4$(μ-H)(μ$_2$-PPh$_2$(2-C$_4$H$_3$S))]$(CO)_6$ as an orange microcrystalline solid (0.022 g, 14%) by crystallisation from a dichloromethane-hexane solution (Found: C, 36.2; H, 2.1; P, 4.7; S, 4.0. C$_{48}$H$_{28}$O$_6$P$_2$S$_2$O$_3$ requires C, 36.1; H, 1.8; P, 4.65; S, 4.8%);

$^1$H NMR: $\delta$ 7.81 (dd, J = 7.0, 11.6 Hz, 2H), 7.68 (t, J = 3.1 Hz, 1H), 7.52-7.39 (m, 4H), 7.27-7.03 (m, 10H), 6.92 (d, J = 5.0 Hz, 1H), 6.85-6.74 (m, 4H), 6.71-6.61 (broad, 2H), 6.34 (d, J = 4.8 Hz, 1H), -17.46 (dd, J = 10.6, 15.7 Hz, 1H, OsHOs); $^{13}$C($^1$H) NMR: $\delta$ 144.5 (d, J = 13.5 Hz), 137.6 (d, J = 10.9 Hz), 133.8 (s), 133.6 (d, J = 12.0 Hz), 133.2 (d, J = 11.9 Hz), 132.9 (d, J = 2.7 Hz), 132.0 (d, J = 10.3 Hz), 131.6 (d, J = 11.9 Hz), 130.8 (d, J = 2.1 Hz), 130.2 (s), 129.8 (s), 128.5 (d, J = 10.7 Hz), 128.3 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.9 (d, J = 2.7 Hz), 127.7 (s), CO and ipso signals not observed; $^{31}$P($^1$H) NMR: $\delta$ -2.3 (d, $J_{pp}$ = 17.7 Hz), -2.8 (d, $J_{pp}$ = 17.7 Hz); v(CO)/cm$^{-1}$: 2074s, 2032s, 2015s, 1995w, 1981m, 1968m, 1957m, 1945w; parent molecular ion observed in the EI and FAB mass spectra.

(c) **Reaction in refluxing nonane:** The same reaction was also carried out with an excess of parent carbonyl cluster compared to the ligand (0.142 g [Os$_4$(CO)$_{12}$], 0.036 g PPh$_2$(2-C$_4$H$_3$S), 3:2 mol/mol) and at an elevated
temperature (under reflux in nonane (20 cm³)). TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:3 v/v)] of the residual orange solid after six hours reflux gave cluster 13 (0.095 g, 64%) and cluster 15 (0.025 g, 14%), characterised spectroscopically against authentic samples.

3.3.8 Thermolysis of the mixture of [Os₃(CO)₁₂][PPh₃(2-C₆H₃S)] and [Os₃(μ-H)(μ₋PPh₃(2-C₆H₃S))(CO)₆] A mixture of the two compounds (0.051 g), formed from the reaction of [Os₃(CO)₁₂] and PPh₃(2-C₆H₃S) in heptane was heated under reflux in toluene (20 cm³) for five hours. TLC work-up [SiO₂, eluent, hexane-dichloromethane (5:2 v/v)] of the residual dark-yellow solid gave cluster 13 (0.037 g), characterised spectroscopically against authentic samples, as the only product.

3.3.9 Reactivity of [Os₃(μ-H)(μ₋PPh₃(2-C₆H₃S))(CO)₆] 13

(a) Reaction with PPh₃(2-C₆H₃S): Cluster 13 (0.017 g, 0.015 mmol) and the ligand PPh₃(2-C₆H₃S) (ca. 5 mg, ~ 1:1 mol/mol) were heated under reflux in octane (8 cm³). The conversion of the cluster was monitored by solution IR spectroscopy and spot TLC [SiO₂, eluent, hexane-dichloromethane (5:2 v/v)]. After five hours the reaction was ceased and work-up of the residual yellow solid using TLC [SiO₂, eluent, hexane-
dichloromethane (5:2 v/v)] gave unreacted cluster 13 and cluster 15 in ca. 1:1 mole ratio.

(b) **Thermal treatment at 175 °C:** Cluster 13 (0.080 g, 0.073 mmol) was charged into a 10 cm³ Carius tube along with 5 cm³ of nonane. The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum and placed in an oven at 175 °C. After 20 hours the yellow suspension had become an orange-brown solution. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:3 v/v)] of the dark-orange solid remaining after removal of the solvent gave only one compound, a pale-yellow solid of [Os₃(µ₃-PPh)(µ₃-C₄H₂S)(CO)₉] (0.054 g, 73%) from evaporation of a dichloromethane solution; 'H NMR: δ 7.57-7.51 (m, 3H, ortho Ph and thienyl), 7.45-7.38 (m, 3H, meta/para Ph), 7.36 (d, J = 2.5 Hz, 1H, thienyl ring); 'C('H) NMR: δ 152.7 (d, J = 2.1 Hz, thienyl), 143.6 (d, J = 5.1 Hz, thienyl), 142.0 (s, para Ph), 141.7 (d, J = 17.0 Hz, thienyl), 132.9 (d, J = 11.8 Hz, ortho Ph), 131.0 (d, J = 2.8 Hz, thienyl), 128.3 (d, J = 10.7 Hz, meta Ph), CO and ipso signals not observed; ν(CO)/cm⁻¹: 2091w, 2068s, 2053s, 2010s, 1999s, 1992m; parent molecular ion observed in the EI and FAB mass spectra.
4.1 Introduction

4.1.1 Coordination of furan and related compounds to transition metal complexes

Unlike thiophene, where a great deal of its coordination chemistry to transition metal complexes is by $\pi$-complexation, furan does not seem to form $\pi$-complexes even though it is a $\pi$-heterocycle. This is a result of furan being an almost non-aromatic heterocycle.\textsuperscript{151} However, it can still coordinate as a 1,3-diene in a $\pi$-manner.\textsuperscript{152}

2-Furyl complexes have been realised with cyclopentadienyl zirconium complexes.\textsuperscript{153} These complexes oxidise into metalla-oxo-cyclohexadiene products at elevated temperatures. Furan has been observed to add by oxidative-addition to triosmium clusters (Scheme 4.1). Coordination \textit{via} orthometallation and $\eta^g$ coordination of the furyl group leads to the $\mu$-2-furyl cluster $[\text{Os}_3(\mu-H)(\mu-C_4H_3O)(\text{CO})_{12}]$ which decarbonylates to yield $[\text{Os}_3(\mu-H)(\mu_3-C_4H_2O)(\text{CO})_{12}]$.\textsuperscript{154}
Scheme 4.1
4.1.2 Coordination of 2-furylphosphines to transition metals

As with the 2-thienylphosphines, before our research the 2-furylphosphines had yet to show any other coordination behaviour than that of a simple tertiary phosphine with coordination through phosphorus atoms only.\textsuperscript{155} As with diphenyl-2-thienylphosphine, diphenyl-2-furylphosphine has also been substituted for CO in [Ru\textsubscript{3}(CO)\textsubscript{12}] leading to the analogous trinuclear clusters, [Ru\textsubscript{3}(μ-H)\{μ-3\textsubscript{1}PPh\textsubscript{2}(2-C\textsubscript{4}H\textsubscript{2}O)(CO)\textsubscript{2}L\}] \(L = \text{CO}, \text{PPh}_2(2-\text{C}_4\text{H}_2\text{O})\) shown in Figure 4.1, which contain coordination of the furyl group via oxidative addition of an ortho C-H bond.\textsuperscript{156} No tetranuclear clusters were observed in this short synthesis, but these may be formed on prolonged thermolysis.

Our research objectives with this ligand were the same as for the 2-thienylphosphines. This was to react this ligand with metal carbonyls to initially coordinate through phosphorus and then explore the reactions of the furyl group with a metal centre. In light of the limited coordination behaviour of furan compared to thiophene, our expectations of a rich chemistry were lower.
4.2 Results and Discussion

4.2.1 Thermal reaction of [Mn$_2$(CO)$_{10}$] with diphenyl-2-furylphosphine

[Mn$_2$(CO)$_{10}$] was reacted with diphenyl-2-furylphosphine under reflux in toluene. A resultant red-orange solution formed from the original golden-yellow solution and no further change in the IR spectrum of the solution after 7 hours suggested that the reaction had ceased. Work-up using
TLC separation on silica gave three products and some unreacted [Mn₂(CO)₁₀] (0.010 g), characterised spectroscopically.

The first product, [Mn₂(μ-H)(μ-PPh₂)(CO)]₁₇ (10%), contains a bridging hydride and a bridging phosphido group. Characterisation was achieved analytically, by IR spectroscopy, by ¹H and ¹³C{¹H} NMR spectroscopies and ultimately by single-crystal X-ray diffraction. The aromatic region of the ¹H NMR spectrum is very simple with only two multiplets at δ 7.85 and 7.35 in a 1:2 intensity ratio, assigned to the ortho and the meta and para phenyl protons. The same conclusion can be drawn from the aromatic region of the ¹³C{¹H} NMR spectrum with only three resonances at δ 133.1, 129.8 and 128.7. There are no ¹H or ¹³C{¹H} NMR signals for the furyl group, confirming that it has been cleaved from the phosphine and lost. A ¹H NMR doublet at δ -16.28 is for a hydride ligand coupled to phosphorus. A compound with a hydrido and diphenylphosphido bridges, as suggested by the multinuclear NMR, was confirmed by the crystal structure of compound 17 which is shown in Figure 4.2 with selected bond lengths and angles in Table 4.1. Compound 17 has been synthesised previously, and its crystal structure has been solved previously but we were unaware of this at the time of our work. The bond lengths and angles from our structure compare with those of the previously solved structures, however for all three, crystallisation has occurred in different space groups. A high yield synthesis of compound 17, by the reaction of [Mn₂(CO)₁₀] with diphenylphosphine in decalin, has been reported. In this synthesis undried decalin was used, since the use of dried decalin reduced the yield. This suggested that the
Figure 4.2 Molecular structure of $[\text{Mn}_2(\mu-\text{H})(\mu-\text{PPh})_2(\text{CO})_8]$
Table 4.1 Selected bond lengths (Å) and angles (°) for compound [Mn₂(μ-
H)(μ-PPh₃)(CO)₆] 17

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
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<tbody>
<tr>
<td>Mn(1)-Mn(1A)</td>
<td>2.940(1)</td>
</tr>
<tr>
<td>Mn(1)-P(1)</td>
<td>2.281(1)</td>
</tr>
<tr>
<td>P(1)-Mn(1A)</td>
<td>2.281(1)</td>
</tr>
<tr>
<td>C(11)-O(11)</td>
<td>1.146(4)</td>
</tr>
<tr>
<td>C(12)-O(12)</td>
<td>1.124(6)</td>
</tr>
<tr>
<td>C(13)-O(13)</td>
<td>1.126(6)</td>
</tr>
<tr>
<td>C(14)-O(14)</td>
<td>1.138(4)</td>
</tr>
<tr>
<td>P(1)-Mn(1)-H(1)</td>
<td>82(2)</td>
</tr>
<tr>
<td>P(1)-Mn(1)-Mn(1A)</td>
<td>49.9(1)</td>
</tr>
<tr>
<td>H(1)-Mn(1)-Mn(1A)</td>
<td>32(2)</td>
</tr>
<tr>
<td>Mn(1)-P(1)-Mn(1A)</td>
<td>80.3(1)</td>
</tr>
<tr>
<td>Mn(1)-H(1)-Mn(1A)</td>
<td>116(3)</td>
</tr>
</tbody>
</table>
solvent was the source of the hydride ligand, and this may be the case in our synthesis.

The second product is the axially monosubstituted, tertiary phosphine complex, \([\text{Mn}_2(\text{CO})_9(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{O})))\] 18 (11\%), which was characterised analytically and by IR spectroscopy.\(^{49}\) \(^1\text{H}\) and \(^{31}\text{C}('\text{H})\) NMR spectra are broad, as observed in compounds 7 and 9, hindering further characterisation.

The final product of this reaction, \([\text{Mn}_2(\mu-\text{H})(\mu-\text{PPh}_3)(\text{PPh}_2(2-\text{C}_4\text{H}_3\text{O}))(\text{CO}))\] 19 (28\%), was characterised analytically, by IR spectroscopy and by \(^1\text{H}, \; ^{13}\text{C}('\text{H})\) and \(^{31}\text{P}('\text{H})\) NMR spectroscopies. The \(^1\text{H}\) NMR spectrum of compound 19 has signals at \(\delta 7.71, 6.55\) and 6.40 for the furyl group. These signals correspond very closely to those of the furyl substituent of the parent ligand. Fine coupling to the \(^{31}\text{P}\) nucleus suggests that the furyl group has not cleaved from the parent ligand. The remaining signals in the aromatic region of the \(^1\text{H}\) NMR spectrum correspond to two sets of ortho signals at \(\delta 7.96-7.92\) and 7.61-7.56 and two sets of meta/para signals at \(\delta 7.45-7.41\) and 7.38-7.23. The \(^{13}\text{C}('\text{H})\) NMR spectrum has corresponding signals with phosphorus-coupled resonances due to one furyl group and two sets of phenyl resonances. These NMR data suggest that the two phenyl resonances could be due to two phosphido bridges. But phosphorus coupling in the furyl resonances suggest that one phenyl NMR set is due to a phosphido bridge where a furyl group has been lost, and the other set is due to an intact ligand. This is further confirmed by the \(^{31}\text{P}('\text{H})\) NMR spectrum with two resonances at \(\delta 167.2\) and 55.6. These signals may be coupled but
the spectrum is broad and coupling is not detected. The structure of compound 19 is based on that of compound 17 with one CO ligand substituted by a diphenyl-2-furylphosphine ligand. Three isomers of this are possible (A, B and C in Figure 4.3). A hydride signal at δ -16.12 shows approximately equal coupling to two phosphorus nuclei. The similarities in the J(\text{PH}) values suggests that as well as the phosphido bridge, the intact phosphine ligand is cis to the hydride, favouring isomers B or C in Figure 4.3. This argument was also used for the analogous PPh₃ substituted complex, [Mn₂(\mu-H)(\mu-PPh₂)(PPh₃)(CO)$_4$]²⁺ which has a similar IR spectrum. 

\[ ^{13}C(^1H) \]
NMR data in the CO region was used further to distinguish the two remaining possible isomers in the analogous PPh₃ substituted complex; five signals in a 1:1:1:2:2 ratio were observed in this part of the spectrum. A similar pattern was observed in the \[^{13}C(^1H)\] NMR spectrum for compound 19 favouring isomer B in Figure 4.3.

[Mn₂(CO)$_{10}$] also reacts with diphenyl-2-furylphosphine under UV irradiation in toluene to yield an orange solution. Work-up of this solution using TLC separation on silica gave unreacted [Mn₂(CO)$_{10}$] (0.004 g), compounds 17 (2%), 18 (30%) and 19 (3%) characterised spectroscopically against authentic samples. Another product is the diaxially substituted phosphine complex, [Mn₂(CO)$_{8}$[PPh₂(2-C₄H₃O)]₂] 20 (17%), again only identified analytically and by IR spectroscopy due to broad multinuclear NMR.⁴⁹
Figure 4.3  Three possible isomers of $[\text{Mn}_2(\mu-\text{H})(\mu-\text{PPh}_2)\text{P(CO)}_2] \{\text{P = PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}$ 19
4.2.2 Thermal reaction of \([\text{Os}_3(\text{CO})_{13}]\) with diphenyl-2-furylphosphine

The chemistry of \([\text{Os}_3(\text{CO})_{13}]\) with diphenyl-2-furylphosphine is essentially the same as the chemistry with the thiophene analogue of the ligand. When the two compounds were heated under reflux in heptane, TLC work-up of the solution on silica gave two bands and some unreacted cluster.

The first band was characterised by IR, \(^1\text{H}, \ ^{13}\text{C}(\ ^1\text{H}), \ ^{31}\text{P}(\ ^1\text{H})\) NMR and mass spectroscopies, as an inseparable mixture of the clusters; \([\text{Os}_3(\text{CO})_{11}\{\text{PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}]\) \(21\) and \([\text{Os}_3(\mu-\text{H})\{\mu_3-\text{PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}(\text{CO})_3]\) \(22\). The IR spectrum of a solution of this mixture is similar to that for a mixture of the analogous thiophene compounds, clusters \(12\) and \(13\), which were characterised ultimately by X-ray diffraction of a single mixed compound crystal. Coincidental peaks in this IR spectrum compared to other triosmium clusters of the type \([\text{Os}_3(\text{CO})_{11}(\text{PR}_3)]\) \(R = \text{alkyl, aryl}\),\(^{69}\) and also cluster \(13\) further confirmed the formation of clusters \(21\) and \(22\), respectively. Other evidence for these furyl clusters came from the mass spectral data with amongst others, a highest mass molecular ion peak at \(M^+ = 1136\) (based on \(^{193}\text{Os}\)) which corresponds to cluster \(21\) and also a high intensity peak at \(M^+ = 1080\) (based on \(^{193}\text{Os}\)) which probably corresponds to the parent molecular ion peak for cluster \(22\) and also the \([M-2(\text{CO})]^+\) peak for cluster \(21\).

Corresponding peaks for the analogous thiényl clusters, \(12\) and \(13\), were observed at \(M^+ = 1152\) and 1096, respectively. The \(^1\text{H}\) NMR spectrum of the mixture is a lot clearer than for the mixture of the thiophene analogues, with no overlapping signals. In fact, signals for the two clusters are easily
distinguishable. For cluster 21 there is a multiplet at δ 7.39-7.27 for the phenyl groups, and at δ 7.64, 6.54 and 6.37 for the furyl protons. These are at a similar δ due to those of the uncoordinated ligand. For cluster 22 there are two ortho multiplets at δ 7.94 and 6.96, two meta and para multiplets at δ 7.52-7.44 and 7.22-7.14, furyl resonances at δ 7.23 and 6.20 and a hydride doublet at δ -18.97 with the same J(PH) of 12.8 Hz as for cluster 13. Separate signals for the two clusters can also be observed in the $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR spectra. The former has some overlapping signals, whereas signals are observed at δ -14.5 and -19.5 in the latter for clusters 22 and 21, respectively.

The second band was also characterised by IR, $^1$H, $^{31}$P($^1$H) NMR and mass spectroscopies as a mixture of the clusters $[\text{Os}_3(\text{CO})_{10}\{\text{PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}]_{23}$ and $[\text{Os}_3(\mu-\text{H})\{\mu_3-\text{PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}\{\text{PPh}_2(2-\text{C}_6\text{H}_3\text{O})\}]_{24}$. The solution IR spectrum of this mixture resembled that for a mixture of the analogous, partially characterised thiophene compounds, clusters 14 and 15. Peaks in this IR spectrum had similarities to triosmium clusters of the type $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_3]_2$ (R = alkyl, aryl),$^{62}$ and also to cluster 15. The highest mass molecular ion peak at M$^+ = 1376$ (based on $^{195}$Os) in the mass spectrum corresponds to the parent molecular ion peak for cluster 23 and a high intensity peak at M$^+ = 1320$ (based on $^{195}$Os) corresponds to the M$^+$ ion for cluster 24 and the [M-2(CO)]$^+$ ion for cluster 23. The $^1$H NMR spectrum of the mixture is very complicated and interpretation difficult. However, a multiplet at δ -18.40 showing coupling to two non-equivalent phosphorus groups, supports cluster 24. This is further quantified by two
doublet of doublets with the same $J(P^1P^3)$ at $\delta$ -9.3 and -13.5 in the $^{31}P(^1H)$ NMR spectrum. Similar hydride and phosphorus signals were observed for the analogous thiophene compound, cluster 15. Broad signals would be expected for cluster 23 in the $^{31}P(^1H)$ NMR spectrum because of the equilibrium between the two isomers of this 1,2-triosmium cluster. These are observed between approximately $\delta$ -20 and -25. The $^{31}P(^1H)$ NMR spectrum of 23 at -40 °C is similar to that for cluster 14 at the same temperature, in that sharp signals are observed instead of the broad signals which represent the equilibrium between the symmetrical and unsymmetrical isomers of the 1,2-bisphosphine. For cluster 23 the unsymmetrical isomer gives two signals of equal intensity at $\delta$ -22.1 and -22.2 and the symmetrical isomer gives a single signal at $\delta$ -26.0.

Partial separation of the two clusters in this mixture was achieved by crystallisation from a cold dichloromethane-hexane solution of this mixture. Orange crystals and large red crystals were formed and shown to be highly enriched in 23 and 24, respectively. These were characterised spectroscopically against triosmium clusters of the type $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_2]$ ($R = \text{alkyl, aryl}$),^2 and cluster 15, respectively.

Like its reaction with diphenyl-2-thienylphosphine, the reaction of $[\text{Os}_3(\text{CO})_{13}]$ with diphenyl-2-furylphosphine was repeated in refluxing octane. TLC work-up of the orange solution after ten hours reflux gave two bands and some unreacted $[\text{Os}_3(\text{CO})_{13}]$. These bands were characterised analytically, by IR spectroscopy and by $^1H$, $^{13}C(^1H)$ and $^{31}P(^1H)$ NMR spectroscopies as clusters 22 (42%) and 24 (7%). The IR spectrum of cluster
22 is nearly exactly the same as its thiophene analogue, cluster 13, which was characterised ultimately by single-crystal X-ray diffraction. In addition to IR evidence for 22, its ¹H NMR spectrum shows two multiplets at δ 7.94 and 6.96 for the ortho phenyl protons, two multiplets at δ 7.48 and 7.18 for the meta and para phenyl protons, signals at δ 7.23 and 5.19 for the furyl protons which are not obscured by the peak due to the residual CHCl₃ in the solvent as for the thiophene analogue and a hydride doublet at δ -18.97. These data and the ¹³C{¹H} NMR data, showing non-equivalent phenyl groups are consistent with a cluster corresponding to the non-dynamic cluster 13. Note that the ruthenium analogues of clusters 13,¹³⁸ and 22,¹⁵⁶ are highly fluxional.

A hydride shift and oscillation of the σ,η²-vinyl groups lead to a time-averaged plane of symmetry in clusters [Ru₅(μ-H)(μ₃-PPh₂(2-C₆H₄X))(CO)₅] (X = S, O).

The variable temperature ¹H NMR spectra of cluster 22 in toluene-d₆ is shown in Figure 4.4. Non-equivalent phenyl groups of the static molecular structure are observed at room temperature. Thus at 27 °C there is an ortho phenyl signal at δ 8.03, an ortho and meta phenyl multiplet from δ 7.15-7.07, two meta phenyl multiplets at δ 7.21 and 6.90 and the remaining para phenyl signal is at δ 6.81. Broadening of these signals occurs at between 70 and 90 °C and coalescence is anticipated at even higher temperatures. As for cluster 13 the process(es) that lead to a time-averaged plane of symmetry are much slower, as expected, than for the analogous ruthenium clusters. The furyl proton signals are unaffected in the variable temperature NMR spectrum.
Figure 4.4 Variable temperature $^1$H NMR spectrum of $[\text{Os}_3(\mu-H)(\mu_3-PPh_3)(2-\text{C}_7\text{H}_5\text{O})(\text{CO})_3]^{22}$ in toluene-$d_6$ (* = solvent) (● = furyl)
Thermolysis in refluxing toluene of a mixture of clusters 21 and 22 (assumed to be the compounds in the first band from the reaction in heptane) gave cluster 22 only. Cluster 21 is therefore believed to be an intermediate in the formation of cluster 22, as observed for the thiophene analogues.

Similar arguments can be used for cluster 24. The IR spectrum and multinuclear NMR spectra of this cluster closely resemble those of cluster 15. In particular, there is a hydride multiplet with coupling to two non-equivalent phosphorus groups at $\delta$ -18.41 in the $^1$H NMR spectrum, and two doublets at $\delta$ -8.5 and -12.6 ($J(PP) = 17.8$ Hz) in the $^{31}$P[1H] NMR spectrum.

As for diphenyl-2-thienylphosphine, the reaction was also performed at even higher temperature in refluxing nonane, with a 3:2 excess of cluster over ligand, in an attempt to synthesise clusters of higher nuclearity. This did not occur as work-up of the solution using TLC separation on silica gave unreacted [Os$_3$(CO)$_{12}$], cluster 22 (61%) and cluster 24 (15%).

4.2.3 Reactivity of [Os$_3$(μ-H)(μ$_3$-PPh$_3$(2-C$_6$H$_4$O))(CO)$_d$] 22

Cluster 22 was shown to be the most likely intermediate in the formation of cluster 24, by its reaction with diphenyl-2-furylphosphine. After five hours under reflux in nonane in the presence of the tertiary phosphine, the IR spectrum of the reaction solution and the spot TLC analysis showed only cluster 24. TLC work-up on silica gave unreacted cluster 22 in traces
and mostly cluster 24. Cluster 23 may also be an intermediate in the formation of cluster 24, by analogy with corresponding thiophene chemistry.

Cluster 22 has a high thermal stability, like its thiophene analogue, 13, and only reacts when heated in nonane at 175 °C in a sealed tube. TLC work-up of the resultant suspension on silica gave $[\text{Os}_3(\mu_3-C_4H_2O)(\mu_3-PPh)(CO)]_9$ 25 as the only product, which was characterised by IR and $^1\text{H}$ NMR spectroscopies and mass spectrometry. The IR and $^1\text{H}$ NMR spectra of clusters 25 and 16 are very similar, the outstanding features being the lack of any hydride signal and integration for only seven protons. The molecular formula has been established by MS; it is most likely that the hydrogen and phenyl groups have been lost as benzene. As for cluster 16 we cannot show without an X-ray structure whether a structure of the type for $[\text{Os}_3(\mu_3-S)(\mu_3-\text{CHFc})(CO)]_9$, or $[\text{Os}_3(\mu_3-\text{PR})(\mu_3-C_6H_4)(CO)]_9$ ($R = \text{Me, Ph}$) is adopted. Figure 4.5 shows the two possible structures of cluster 25.

![Figure 4.5: Two possible structures for $[\text{Os}(\mu_3-C_4H_2O)(\mu_3-PPh)(CO)]_9$ 25](image-url)
4.2.4 Discussion

The chemistry of \([\text{Mn}_{2}(\text{CO})_{10}]\) and \([\text{Re}_{2}(\text{CO})_{10}]\) with \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O})\) differs very much to the chemistry observed with \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{S})\) and in the fact the only similarities are when the ligands act as simple tertiary phosphines, in the formation of the complexes \([\text{Mn}_{2}(\text{CO})_{10} L] (x = 1, 2)\). For the thienyl ligand all five atoms of the heterocycle, including the heteroatom, can be coordinated to form the complex \([\text{Mn}_{2}(\mu-\eta^3\text{C}_4\text{H}_3\text{S})(\mu-\text{PPh}_{2})(\text{CO})_8] 8\), which also requires a P-C bond cleavage, possibly via the unobserved complexes \([\text{Mn}_{2}(\mu-\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{S}))(\text{CO})_8]\), \([\text{Mn}_{2}(\mu-\text{C}_4\text{H}_3\text{S})(\mu-\text{PPh}_{2})(\text{CO})_8]\) and \([\text{Mn}_{2}(\mu-\eta^3\text{C}_4\text{H}_3\text{S})(\mu-\text{PPh}_{2})(\text{CO})_8]\), the first two of which were observed in the rhenium chemistry. P-C bond cleavage is the only form of bond activation of the ligand \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O})\) achieved by \([\text{Mn}_{2}(\text{CO})_{10}]\) yielding the related complexes \([\text{Mn}_{2}(\mu-H)(\mu-\text{PPh}_{2})(\text{CO})_8 L] (L = \text{CO} 17, L = \text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O}) 19\) in which the furyl group has cleaved from the rest of the ligand and is lost, most likely as furan. Non-coordination of the furyl group (even in 19) is not too surprising considering the reluctance of furan to form complexes with transition metal complexes (see Section 4.1.1). Note that no products were isolated on reaction of \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O})\) with \([\text{Re}_{2}(\text{CO})_{10}]\) even with the use of trimethylamine-N-oxide as a CO displacement reagent.

As stated earlier, the chemistry of \([\text{Os}_{3}(\text{CO})_{12}]\) with \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O})\) is essentially similar to that with \(\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{S})\), with C-H bond activation giving rise to the related clusters \([\text{Os}_{3}(\mu-H)(\mu_3-\text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O}))(\text{CO})_8 L] (L = \text{CO} 22, L = \text{PPh}_{2}(2-\text{C}_4\text{H}_3\text{O}) 24\) with further C-H bond
activation being achieved upon thermolysis of 22 at elevated temperatures (175 °C in a sealed tube) to give [Os₃(μ₃-PPh)(μ₃-C₄H₂O)(CO)₉] 25, a step which also requires a P-C bond cleavage. These results can be attributed to the similarities in the observed coordination of thiophene and furan to [Os₃(CO)₁₉] an the non-involvement of the heteroatoms O and S in this chemistry.

4.3 Experimental

The ligand diphenyl-2-furylphosphine was synthesised and characterised as reported previously. The synthesis is as for diphenyl-2-thienylphosphine except that furan is used instead of thiophene.

4.3.1 Reaction of [Mn₂(CO)₁₀] with PPh₃(2-C₄H₅O)

(a) Reaction in refluxing toluene: The compound [Mn₂(CO)₁₀] (0.183 g, 0.469 mmol) and the tertiary phosphine, PPh₃(2-C₄H₅O) (0.129 g, 1:1 mol/mol carbonyl) were heated under reflux in toluene (40 cm³) for 9 hours. The IR spectrum of the solution was recorded periodically to monitor the conversion of the carbonyl. The resulting orange-brown solution was evaporated to dryness under reduced pressure to yield a dark-orange solid. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:3 v/v)] gave four bands, a yellow band eluting fast was found to be unreacted carbonyl (0.010
g) spectroscopically. A second lime-yellow band yielded [Mn₂(µ-H)(µ-
PPh₂)(CO)]₆ as a yellow solid (0.024 g, 10%) from evaporation of a
dichloromethane solution (Found: C, 45.8; H, 2.5; P, 6.4. C₂₉H₁₈O₈P₂Mn₂
requires C, 46.2; H, 2.1; P, 5.95 %); 'H NMR: δ 7.85 (m, 4H, ortho Ph), 7.35
(m, 6H, meta/para Ph), -16.12 (d, Jₚₙ = 35.5 Hz, 1H, MnHMn); ¹³C[{¹H}] NMR: δ
133.1 (d, J = 9.0 Hz, meta Ph), 129.8 (d, J = 2.2 Hz, para Ph), 128.7 (d, J =
9.7 Hz, ortho Ph), CO and ipso signals not observed; ν(CO)/cm⁻¹: 2093w,
2063m, 2010vs, 2000m, 1965s; parent molecular ion observed in the FAB
mass spectrum. The third yellow band yielded [Mn₂(CO)₆(PPh₂(2-C₅H₃O))] as
an orange-yellow microcrystalline solid (0.031 g, 11%) by crystallisation from
a cool dichloromethane-heptane solution (Found: C, 49.5; H, 2.7; P, 4.95.
C₂₅H₁₃O₁₀P₂Mn₂ requires C, 48.9; H, 2.13; P, 5.0 %); 'H and ¹³C[{¹H}] NMR
spectra are broad and not reported; ν(CO)/cm⁻¹: 2092m, 2014s, 1996vs,
1973s, 1943m; weak parent molecular ion observed in the FAB mass
spectrum. The final orange band yielded [Mn₂(µ-H)(µ-PPh₂)(PPh₂(2-
C₅H₃O))(CO)] as an orange microcrystalline solid (0.098 g, 28%) by
crystallisation from a cool dichloromethane-hexane solution (Found: C, 56.6;
H, 3.5; P, 8.1. C₃₅H₄₄O₈P₂Mn₂ requires C, 56.5; H, 3.25; P, 8.3 %); 'H NMR: δ
7.96-7.92 (m, 4H, ortho Ph), 7.71 (s, 1H, furyl), 7.61-7.56 (m, 4H, ortho Ph),
7.45-7.41 (m, 6H, meta/para Ph), 7.38-7.23 (m, 6H, meta/para Ph), 6.55 (d, J =
3.4 Hz, 1H, furyl), 6.40 (m, 1H, furyl), -16.12 (t, Jₚₙ = 31.3 Hz, 1H, MnHMn);
¹³C[{¹H}] NMR: δ 151.5 (d, J = 75.3 Hz, ipso furyl), 148.2 (d, J = 4.9 Hz, furyl),
142.3 (d, J = 28.7 Hz, ipso Ph), 135.5 (d, J = 44.7 Hz, ipso Ph), 133.3 (d, J =
8.9 Hz, meta Ph), 132.3 (d, J = 11.1 Hz, ortho Ph), 130.3 (s, para Ph), 129.0
(s, para Ph), 128.6 (d, $J = 10.1$ Hz, ortho Ph), 128.3 (d, $J = 9.6$ Hz, meta Ph),
121.5 (d, $J = 12.7$ Hz, furyl), 111.1 (d, $J = 5.6$ Hz, furyl), broad resonances between $\delta$ 224-210 in ~ 1:1:1:2:2 ratio; $^{31}$P($^1$H) NMR: broad resonances at $\delta$
167.2 (s), 55.6 (s); $\nu$(CO)/cm$^{-1}$: 2074m, 2030m, 1995vs, 1951s, 1920m;
strong parent molecular ion peak in FAB mass spectrum.

(b) Photochemical reaction: The two starting compounds were also
photolysed under UV irradiation in a 1:1 mole ratio (0.204 g [Mn$_2$(CO)$_{10}$], 0.138
g PPh$_2$(2-C$_4$H$_3$O)$_2$(0.523 mmol}) in toluene (100 cm$^3$) for 7 hours. The
resulting orange solution was evaporated to dryness by vacuum distillation to
yield an orange solid. TLC work-up [SiO$_2$; eluent, hexane-dichloromethane
(5:3 v/v)] gave five bands, the first of which was found to be unreacted
carbonyl (0.004 g), spectroscopically. A lime-yellow band, a yellow band and
an orange band yielded compounds 17 (0.006 g, 2%), 18 (0.095 g, 30%) and
19 (0.010 g, 3%), respectively, characterised spectroscopically against
authentic samples. The final orange band yielded [Mn$_2$(CO)$_{10}$PPh$_2$(2-
C$_4$H$_3$O)$_2$] as an orange microcrystalline solid (0.074 g, 17%) by evaporation of
a dichloromethane solution (Found: C, 57.1; H, 3.5; P, 7.4. C$_{46}$H$_{30}$O$_8$P$_2$Mn$_2$
requires C, 57.3; H, 3.1; P, 7.4 %); $^1$H and $^{13}$C($^1$H) NMR spectra are broad and
not reported; $\nu$(CO)/cm$^{-1}$: 1963 vs; weak parent molecular ion peak observed
in the FAB mass spectrum.
4.3.2 Thermal reaction of $[\text{Os}_3(\text{CO})_{12}]$ with $\text{PPh}_2(2-\text{C}_6\text{H}_5\text{O})$

(a) Reaction in refluxing heptane: The cluster $[\text{Os}_3(\text{CO})_{12}]$ (0.103 g, 0.114 mmol) and the tertiary phosphine $\text{PPh}_2(2-\text{C}_6\text{H}_5\text{O})$ (0.031 g, 1:1 mol/mol) were heated under reflux in heptane for 24 hours. The conversion of the cluster was monitored by solution IR spectroscopy and spot-TLC [SiO$_2$; eluent, hexane-dichloromethane (5:2 v/v)]. The resulting dark-orange solution was evaporated to dryness under reduced pressure to yield a dark-orange solid. TLC work-up [SiO$_2$; eluent, hexane-dichloromethane (5:2 v/v)] gave two bands. The first yellow band gave a mixture of $[\text{Os}_3(\text{CO})_{12}[\text{PPh}_2(2-\text{C}_6\text{H}_5\text{O})]]$ and $[\text{Os}_3(\mu-\text{H})[\mu_3-\text{PPh}_2(2-\text{C}_6\text{H}_5\text{O})](\text{CO})_{12}]$ as a yellow microcrystalline solid (0.055 g) by crystallisation of a dichloromethane-heptane solution; $^1$H NMR: δ 7.94 (ddd, $J = 1.6$, 7.9, 12.2 Hz, 2H, ortho Ph), 7.64 (d, $J = 2.0$ Hz, 1H, furyl), 7.52-7.44 (m, 3H, meta/para Ph), 7.39-7.27 (m, 10H, Ph), 7.23 (d, $J = 1.9$ Hz, 1H, coordinated furyl ring), 7.22-7.14 (m, 3H, meta/para Ph), 6.96 (ddd, $J = 1.6$, 7.6, 11.6 Hz, 2H, ortho Ph), 6.54 (d, $J = 1.4$ Hz, 1H, furyl), 6.37 (m, 1H, furyl), 6.20 (d, $J = 3.5$ Hz, 1H, coordinated furyl ring), -18.97 (d, $J_{\text{OsO}} = 12.8$ Hz, OsHOS); $^{13}$C($^1$H) NMR: δ 152.5 (s), 148.1 (d, $J = 6.1$ Hz), 134.3 (d, $J = 58.7$ Hz), 132.8 (d, $J = 10.9$ Hz), 132.3 (d, $J = 11.7$ Hz), 131.8 (d, $J = 11.5$ Hz), 131.6 (d, $J = 2.4$ Hz), 131.2 (d, $J = 2.1$ Hz), 131.0 (d, $J = 2.5$ Hz), 128.8 (d, $J = 11.5$ Hz), 128.6 (d, $J = 11.2$ Hz), 128.4 (s), 127.7 (d, $J = 8.4$ Hz), 121.0 (d, $J = 12.8$ Hz), 111.4 (d, $J = 6.0$ Hz), CO signals not observed; $^{31}$P($^1$H) NMR: δ -14.5 (s), -19.5 (s); ν(CO)/cm$^{-1}$: 2109w, 2089m, 2078w, 2060s, 2055s, 2034s, 2020s, 2001m, 1990s, 1983m, 1979m, 1966w; parent molecular ion
[M]* and [M*-2(CO)] observed in the El and FAB mass spectra. A second orange-yellow band gave a mixture of [Os₃(CO)₁₀{PPh₃(2-C₆H₅O)}₂] and [Os₃(μ-H){PPh₃(2-C₆H₅O)}{PPh₂-C₆H₅O}(CO)] as an orange-yellow microcrystalline solid (0.077 g) by crystallisation from a dichloromethane-heptane solution; 'H NMR: complex signals in the range δ 7.92-6.43, -18.40 (dd, Jₚₚ = 11.0, 14.0 Hz, 1H, OsHOs); ³¹P('H) NMR: δ -10.9 (dd, Jₚₚ = 2.9 Hz, Jₚₚ = 17.8 Hz), -14.4 (dd, Jₚₚ = 4.5 Hz, Jₚₚ = 17.8 Hz) broad resonances between δ -22 and 28, (-40 °C) sharp signals mentioned previous unchanged and sharp signals observed also at δ -22.1 (s), -22.2 (s), -26.1 (s); ν(CO)cm⁻¹: 2088w, 2074m, 2068w, 2056w, 2033vs, 2015s, 1976m, 1968m, 1958m, 1951sh; parent molecular ion [M]* and [M*-2(CO)] observed in the El and FAB mass spectra. Cluster 24; ν(CO)/cm⁻¹: 2089m, 2060s, 2034s, 2018m, 1997m, 1990s, 184m, 1974w, 1966w. Cluster 23; ν(CO)/cm⁻¹: 2088vW, 2034m, 2017w, 2002s, 1975m 1957w.

(b) Reaction in refluxing octane: The reaction was also carried out in a 1:1 mole ratio (0.102 g [Os₃(CO)₁₀], 0.034 g PPh₃(2-C₆H₅O) (0.123 mmol)) under reflux in octane (20 cm³) for nine hours. The resulting orange solution was evaporated to dryness under reduced pressure to yield an orange solid. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:2 v/v)] gave three bands, the first being unreacted cluster (0.016 g). A second yellow band yielded [Os₃(μ-H){PPh₃(2-C₆H₅O)}(CO)] as a yellow crystalline solid (0.052 g, 42%) by crystallisation from a dichloromethane-heptane solution (Found: C, 28.1; H, 1.2; P, 2.9. C₂₅H₁₀O₁₀P₃Os₃ requires C, 27.9; H, 1.2; P, 2.9
%); 'H NMR: δ 7.94 (ddd, J = 1.6, 7.9, 12.2 Hz, 2H, ortho) Ph, 7.52-7.44 (m, 3H, meta/para Ph), 7.23 (s, 1H, furyl), 7.22-7.14 (m, 3H, ortho/meta Ph), 6.96 (ddd, J = 1.6, 7.6, 11.6 Hz, 2H, ortho Ph), 5.19 (s, 1H, furyl), -18.97 (d, Jp = 12.8 Hz, 1H, OsHOs); (toluene-d6, 22 °C): δ 8.03 (ddd, J = 1.2, 7.2, 12.1 Hz, 2H, ortho Ph), 7.21 (td, J = 2.5, 7.7 Hz, 2H, para Ph), 7.15-7.07 (m, 3H, meta/para Ph), 6.90 (td, J = 1.9, 7.5 Hz, 2H, meta Ph), 6.81 (td, J = 1.4, 7.4 Hz, 1H, para Ph), 6.61 (d, J = 1.9 Hz, 1H, furyl), 6.29 (dd, J = 1.3, 1.9 Hz, 1H, furyl); 13C{'H} NMR: δ 152.5 (s, furyl), 133.8 (d, J = 36.2 Hz, ipso furyl), 132.8 (d, J = 11.0 Hz, meta Ph), 131.8 (d, J = 11.6 Hz, ortho Ph), 131.6 (d, J = 2.5 Hz, para Ph), 131.2 (d, J = 2.4 Hz, para Ph), 130.7 (d, J = 68.7 Hz, ipso phenyl), 128.8 (d, J = 11.4 Hz, ortho Ph), 128.5 (d, J = 10.3 Hz, meta Ph), 127.3 (d, J = 8.4 Hz, furyl), CO signals not observed; 31P{'H} NMR: δ -14.0 (s); ν(CO)/cm⁻¹: 2089m, 2060s, 2034s, 2018m, 1997m, 1990s, 1984m, 1974w, 1966w; parent molecular ion observed in the El and FAB mass spectra. The final orange band gave [Os₃(µ-H){µ₂-PPh₂(2-C₅H₅)O}{PPh₂(2-C₅H₅)O}](CO)₃ 23 as an orange microcrystalline solid (0.010 g, 7%) by crystallisation from a dichloromethane-heptane solution (Found: C, 37.2; H, 1.9; P, 4.5; C₆₀H₆₀P₂Os₃ requires C, 37.0; H, 2.0; P, 4.8 %); 'H NMR: δ 7.91 (ddd, J = 1.2, 7.1, 11.8 Hz, 2H), 7.68 (s, 1H), 7.52-7.36 (m, 8H), 7.24-7.07 (m, 3H), 6.97 (td, J = 2.33, 7.8 Hz, 2H), 6.81-6.74 (m, 4H), 6.62 (d, J = 3.3 Hz, 1H), 6.47 (s, 1H), 6.35 (dd, J = 7.6, 12.5 Hz, 2H), 5.60 (s, 1H), -18.41 (dd, Jp = 10.7, 14.4 Hz, 1H, OsHOs); 13C{'H} NMR: δ 150.8 (d, J = 73.9 Hz), 150.8 (s), 148.0 (d, J = 5.2 Hz), 144.5 (d, J = 44.0 Hz), several low intensity signals in the range 135.5-133.1, 133.9 (d, J = 12.1 Hz), 132.6 (d, J = 10.8 Hz), 131.9
(d, J = 12.2 Hz), 131.4 (d, J = 11.9 Hz), 130.8 (d, J = 15.0 Hz), 130.2 (s), 129.7 (s), 128.4 (d, J = 11.0 Hz), 127.9 (d, J = 21.0 Hz), 127.9 (s), 126.6 (d, J = 9.2 Hz), 122.2 (d, J = 16.9 Hz), 111.0 (d, J = 7.0 Hz), CO signals not observed; $^3$P[$^1$H] NMR: $\delta$ -8.5 (d, $J_{pp} = 17.8$ Hz), -12.6 (d, $J_{pp} = 17.8$ Hz); v(CO)/cm$^{-1}$: 2074s, 2032s, 2016s, 1995w, 1981m, 1968m, 1957m, 1945w; parent molecular ion observed in the EI and FAB mass spectra.

(c) Reaction in refluxing nonane: The reaction was also carried out with an excess of parent carbonyl cluster compared to the ligand (0.139 g [Os$_3$(CO)$_{12}$], 0.031 g PPh$_2$(2-C$_4$H$_3$O) 3:2 mol/mol) and at an elevated temperature (under reflux in nonane (20 cm$^3$)). TLC work-up [SiO$_2$; eluent, hexane-dichloromethane (5:2 v/v)] of the residual dark-orange solid after seven hours reflux gave cluster 22 (0.082 g, 61%) and cluster 24 (0.024 g, 15%), characterised spectroscopically against authentic samples.

4.3.3 Thermolysis of a mixture of [Os$_3$(CO)$_{11}$PPh$_2$(2-C$_4$H$_3$O)] and [Os$_2$(µ-H)$_5$(µ$_3$-PPh$_3$(2-C$_4$H$_3$O))(CO)$_{12}$]

A mixture of the two clusters (0.073 g) formed from the reaction of [Os$_3$(CO)$_{12}$] and PPh$_2$(2-C$_4$H$_3$S) in heptane, were heated under reflux in heptane (20 cm$^3$). After 10 hours there was little further change in the IR spectrum of the solution. The solvent was removed under reduced pressure and the reaction was continued, under reflux in toluene (20 cm$^3$) for four hours. TLC work-up of the residual yellow solid gave cluster 22 (0.059 g),
characterised spectroscopically against authentic samples, as the only product.

4.3.4 Reactivity of [Os₃(µ-H)(µ-J-PPh₃(2-C₅H₅O))(CO)]_22

(a) Reaction with PPh₃(2-C₅H₅O): Cluster 22 (0.027 g, 0.025 mmol) and the ligand PPh₃(2-C₅H₅S) (ca. 5 mg, ~1:1 mol/mol) were heated under reflux in nonane (8 cm³). The reaction was monitored by IR spectroscopy of the solution and by spot-TLC [SiO₂; eluent, hexane-dichloromethane (5:2 v/v)]. After five hours the reaction was ceased and work-up of the residual yellow solid using TLC [SiO₂; eluent, hexane-dichloromethane (5:2 v/v)] gave a small amount of unreacted cluster 22 (0.004 g) and cluster 24 (0.029 g), characterised spectroscopically against authentic samples.

(b) Thermal treatment at 175 °C: Cluster 22 (0.037 g, 0.034 mmol) was added to a 20 cm³ Carius tube containing nonane (5 cm³). The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum and placed in an oven at 175 °C. After 20 hours the yellow suspension had become an orange solution. TLC work-up of [SiO₂; eluent, hexane-dichloromethane (5:3 v/v)] gave only one compound, [Os₃(µ-J-C₅H₅O)(µ-J-PPh)(CO)]₃, as a pale-yellow solid (0.023 g, 68%) by evaporation of a dichloromethane solution; ¹H NMR: δ 7.53-7.48 (m, 3H, ortho Ph and furyl), 7.43-7.36 (m, 3H, meta/para Ph), 6.51 (d, J = 2.1 Hz, 1H, furyl); ν(CO)/cm⁻¹:
2093w, 2071vs, 2065s, 2052vs, 2019s, 2010s, 1998br; parent molecular ion observed in the EI and FAB mass spectra.
5.1 Introduction

5.1.1 Coordination of pyrrole and related compounds to transition metal complexes

Pyrrole can be compared with benzene as a 6-electron donor and the deprotonated pyrrolyl ligand can be compared as a 5-electron donor to cyclopentadienyl. Many \( \eta^5 \)-complexes of pyrrole are known such as \([\text{Cr}(\eta^5-C_5H_4NR)(CO)](R = H, Me, Ph)\), \([\text{Mn}(\eta^5-C_5H_4N)(CO)]\), \([\text{CpM}(\text{CO})_2(\eta^5-C_5H_4N[Mn(\text{CO})_3])] (M = Mn, Re)\), and azaferrocene.\(^{141,165}\) Other modes of coordination are available for pyrrole. With \([\text{Os}_3(\text{CO})_{10}L_2] (L = \text{CO, MeCN}, C_2H_4NR (R = H, Me)\) gives the monohydride complex \([\text{Os}_3(\mu-H)(\mu-C_4H_2NR)(\text{CO})_{10}]\) which decarbonylates to the dihydride complex \([\text{Os}_3(\mu-H)_2(\mu_3-C_4H_2NR)(\text{CO})_9]\) which can subsequently isomerise to \([\text{Os}_3(\mu-H)_2(\mu_3-C_4H_2N)(\text{CO})_9]\) for \(R = H\) (see Figure 5.1).\(^{166,167}\) Non-aromatic pyrrole can be generated with \(\text{Os}_3\) which contains a tetrahedral ring atom and its coordination has been proposed tentatively from the alternatives shown in Figure 5.2.
Figure 5.1 Structures of the isomers $\text{[Os}_3(\mu-H)_6(\mu_3-X)(\text{CO})_6]$ ($X = \text{C}_6\text{H}_5\text{NH}, \text{C}_6\text{H}_3\text{N}$)

Figure 5.2 Alternative structures for $\text{[Os}_3(\mu-H)_6(\mu_3-C_6H_5N)(\text{CO})_6]$ and for $\text{[Os}_3(\mu-H)(\mu-C_6H_5N)(\text{CO})_{10}]$
Complexes with pyrrolyl coordinated solely through the nitrogen atom are known such as \[M(C_8H_7Me_2N)(PPh_3)_2CO]\ (M = Rh, Ir).\(^{168}\)

5.1.2 Coordination of the diphenyl-n-pyrrolylphosphines (n = 2 or 3) to transition metal complexes

There are no examples in the literature for coordination of these ligands to transition metal complexes, however, the 1-isomer has coordinated as a simple tertiary phosphine through the phosphorus atom.\(^{169}\)

The reactivity of these ligands with \([\text{Ru}_3(\text{CO})_{12}]\) has been carried out recently in these laboratories.\(^{170}\) With the 2-isomer, the cluster \([\text{Ru}_3(\text{CO})_{11}\{\text{PPh}_2(2-C_6H_4NH)\}]\) in which the ligand acts as a tertiary phosphine has been isolated and characterised as well as the related clusters \([\text{Ru}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-C_6H_4NH)\}(\text{CO})_8L]\ \(L = \text{CO}, \text{PPh}_2(2-C_6H_4NH)\) which are similar to the trinuclear ruthenium clusters isolated on reaction with \(\text{PPh}_2(2-C_4H_3X)\ \(X = \text{S}, \text{O}\)\). Tetranuclear ruthenium clusters derived from \([\text{Ru}_3(\mu-H)\{\mu_3-\text{PPh}_2(2-C_6H_4NH)\}(\text{CO})_9]\) by addition of \(\text{Ru}(\text{CO})_4\), P-C bond cleavage and displacement of either benzene or pyrrole have also been isolated and characterised. These are the previously characterised cluster \([\text{Ru}_4(\mu_2-C_6H_5)(\mu_2-PPh)(\mu-\text{CO})(\text{CO})_{10}]\)\(^{160}\) and the two isomeric clusters \([\text{Ru}_4(\mu_4-X)(\mu_4-PPh)(\mu-\text{CO})(\text{CO})_{13}]\ \(X = C_6H_5N, C_6H_5NH\) shown in Figure 5.3. The first isomer is coordinated perpendicular to the ruthenium rectangle through the nitrogen atom and the ortho carbon atom whereas the second is coordinated in a diagonal through the ortho and meta carbon atoms.
Figure 5.3  Structures or $[\text{Ru}_2(\mu_4-X)(\mu_4-\text{PPh})(\mu-\text{CO})(\text{CO})_{10}]$ ($X = \text{C}_2\text{H}_3\text{N}, \text{C}_4\text{H}_2\text{NH}$)
The 3-isomer also gives the related trinuclear clusters \([\text{Ru}_3(\mu-H)\{\mu_3-P\text{Ph}_2(3-C_2H_3NH)\}(\text{CO})_8L}\) \((L = \text{CO}, \text{PPh}_2(3-C_2H_3NH))\) which are comparable to those for \(\text{PPh}_2(2-C_2H_3X)\) \((X = S, O, NH)\) except that there are two non-equivalent ortho sites that could be metallated and zwitterionic or non-zwitterionic structures might be considered for each product as shown in Figure 5.4 for \(L = \text{CO}\). The second structure was proposed tentatively by means of X-ray crystallography. Tetranuclear clusters similar to those for the 2-isomer have also been isolated.

Our research objectives with these ligands are the same as for the other phosphines. This was to react them with metal carbonyls to achieve initial coordination through phosphorus and then to explore, if any, the reactivity of the pyrrolyl unit with the metal centre(s). Also, for these two isomeric ligands, reactivity with the metal centre could be compared with the expectation of different chemistries for the 2-pyrrolyl and 3-pyrrolylphosphines.
Figure 5.4 Non-zwitterionic and zwitterionic forms of the two possible structures of \([\text{Ru}(\mu-H)\{\mu_3-P\text{Ph}_2(3-C_6H_4NH)\})(\text{CO})_6]\)
5.2 Results and Discussion

5.2.1 Synthesis of the diphenyl-n-pyrrolylphosphines (n = 2 or 3)

The ligand diphenyl-2-pyrrolylphosphine was synthesised from a pyrrolyl-Grignard reagent and PPh₂Cl according to the literature. Vacuum distillation of the washed ethereal layer of the reaction mixture yielded a yellow oil which solidified on standing. Three singlet resonances at δ 12.0, -26.0 and -27.5 in the $^{31}$P$\{^1$H$\}$ NMR spectrum indicated that there were three phosphorus compounds in this oil and the close proximity of two of these suggested that they may be isomers. TLC or column chromatographic separation on silica yielded three colourless bands. The first fast-moving air-sensitive band was characterised spectroscopically as ethyldiphenyphosphine (EtMgBr was used in the synthesis). The second band was characterised spectroscopically as diphenyl-2-pyrrolylphosphine, which had been synthesised and characterised previously. The third band was the 3-substituted isomer of the same ligand, which was not reported as a product from this preparation when first published. However, as well as by $^{31}$P$\{^1$H$\}$ NMR, the two isomers can be distinguished by the pyrrolyl resonances in the $^1$H NMR spectrum. The 2-substituted isomer has one relatively lowfield resonance at δ 6.96 and two higher field resonances at δ 6.51 and 6.31 in the $^1$H NMR spectrum. In contrast the 3-substituted isomer has two relatively lowfield overlapping resonances at δ 6.87 and one higher field resonance at δ 6.20 in the
corresponding spectrum. The broad N-pyrrolyl proton signals also differ at δ 8.10 and 8.42 for the 2- and 3-substituted isomers, respectively.

5.2.2 Reaction of [Mn₂(CO)₁₀] with diphenyl-n-pyrrolylphosphine (n = 2 or 3)

[Mn₂(CO)₁₀] has been reacted both thermally and photochemically with the two isomers of diphenylpyrrolylphosphine. Reaction with the 2-isomer was carried out under reflux in toluene. The conversion of the carbonyl was monitored by IR spectroscopy of the solution at around 2000 cm⁻¹, which indicated the formation of a compound corresponding to the axially phosphorus-bound monosubstitution complex, [Mn₂(CO)₆{PPh₂(2-C₄H₃NH)}] after about one hour. Signals in the IR spectrum due to this complex slowly (ca. 3 hours) began to disappear and there was no further change in the IR spectrum after seven hours indicating that reaction was complete. Work-up of the dark-orange solution using TLC separation on silica gave four bands. A fast moving yellow band gave a substantial quantity of unreacted [Mn₂(CO)₁₀]. A second lime-yellow band was characterised spectroscopically as [Mn(μ-H)(μ-PPh₂)(CO)₆] 17 (4%).

The third yellow band was characterised from its IR spectrum and to some extent from its ¹H and ¹³C NMR spectra as the complex which was thought to be formed initially, the axially phosphorus-bound monosubstitution product [Mn₂(CO)₆{PPh₂(2-C₄H₃NH)}] 26 (7%). The IR spectrum around 2000 cm⁻¹ of 26 closely resembles that of analogous dimanganese complexes of the type, [Mn₂(CO)₆(PR₃)] (R = alkyl, aryl). 19
Although broadened, possibly by paramagnetic impurities, the $^1$H and the
$^{13}$C($^1$H) NMR spectra of 26 are not broadened as much of those of other
complexes of this type such as 1 and 2. Some structural information was
available from these spectra which are similar to those of the free ligand,
indicating that coordination via the phosphorus atom only is likely. Four
pyrrolyl proton signals at $\delta$ 7.88, 6.98, 6.94 and 6.38 and phenyl proton
signals at $\delta$ 7.45-7.35 can be observed in the $^1$H NMR spectrum. There is no
orthometallation of the pyrrolyl or phenyl groups.

The fourth orange-red complex gave a complicated IR
spectrum with 11 signals in the carbonyl region, which suggested a build-up
in the nuclearity of the complex. This was somewhat further confirmed by a
highest mass molecular ion peak in the FAB mass spectrum ($M^+ = 723$),
which suggested a trimanganese complex. The multinuclear NMR spectra
were broad and of little use for structure determination. Single red crystals
suitable for X-ray diffraction were grown from a cool hexane-dichloromethane
solution and the result was the trimanganese complex, $[\text{Mn}_3(\mu-PPh}_3][2-C_6H_5N-
\eta^5-Mn(CO)_3][(CO)_3] 27$ (21%) which is shown in Figure 5.5 with selected bond
lengths and angles in Table 5.1. Complex 27 contains the ligand bridging two
manganese atoms via the phosphorus atom and the nitrogen atom of the
pyrrolyl ring with a P(1)-Mn(1)-Mn(2)-N(1) torsional angle of 24.8°, the N-
pyrrolyl hydrogen is presumably lost, possibly as hydrogen gas. The third
manganese atom is coordinated as a tricarbonylmanganese unit to all the
atoms of the pyrrolyl ring, in an $\eta^5$ mode as observed for complexes of the
type $[\text{Mn(}\eta^5-C_6H_5N)(CO)_3]^{141,163}$ $[\text{CpM(CO)}_3(C_6H_5N)Mn(CO)_3]$ (M = Mn, Re)$^{164}$
and \([\text{Os}_2(\mu-H)[\mu-\text{C}_2\text{H}_4\text{N}[\eta^3-\text{Mn(CO)}_2]](\text{CO})_d]\). The Mn(3)-pyrrolyl C distances vary from 2.122(4) Å to 2.165(4) Å, the Mn(3)-N(1) distance is 2.156(3) Å and the Mn(3)-carbonyl C \{C(31), C(32) and C(33)\} distances vary from 1.739(5) Å to 1.804(5) Å. The eight carbonyl ligands on Mn(1) and Mn(2) are between
Table 5.1 Selected bond lengths (Å) and angles (°) for compound [Mn₂(µ-
PPh₂[2-C₆H₃N-η⁵-Mn(CO)₃](CO)₆] 27

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</table>
the staggered and the eclipsed conformation with C(14)-Mn(1)-Mn(2)-C(21), C(13)-Mn(1)-Mn(2)-Mn(3)-C(24) and C(11)-Mn(1)-Mn(2)-C(22) torsional angles of 32.1°, 32.1° and 31.1°, respectively, this 52-electron system requires one Mn-Mn bond (2.913(3) Å) to achieve an electron-precise EAN.

\[
\text{[Mn}_2\text{(CO)}_{10}] \text{ also reacts with diphenyl-2-pyrrolylphosphine under UV irradiation. The conversion of the metal carbonyl was monitored by IR spectroscopy of the solution which showed no further change after 20 hours indicating that the reaction had ceased. Work-up of the resultant orange solution using TLC separation on silica gave a high yield synthesis of compound 17 (52%). The second bright yellow band was characterised analytically, by IR spectroscopy and by } ^1\text{H, } ^{13}\text{C[^1H]} \text{ and } ^{31}\text{P[^1H]} \text{ NMR spectroscopy as [Mn}_2(\mu-\text{H})(\mu-\text{PPh}_2)[\text{PPh}_2(2-C_4\text{H}_5\text{NH})](\text{CO})_2] \text{ 28 (20%). The highest mass molecular ion peak at } M^+ = 743 \text{ in the FAB mass spectrum supports this formula, which corresponds to that of the furyl complex 19. A triplet at } \delta \text{ -16.03 in the hydride region of the } ^1\text{H NMR spectrum with } J(\text{PH}) = 31.3 \text{ Hz further suggested that compound 28 was isostructural with the previously described compound 19 (see first isomer in Figure 4.3). Signals at } \delta \text{ 8.20, 7.02, 6.81 and 6.38 for the pyrrolyl ring in the } ^1\text{H NMR spectrum do not significantly differ from those of the parent ligand. Corresponding signals at } \delta \text{ 123.6, 121.2 and 110.5 can be observed in the } ^{13}\text{C[^1H]} \text{ NMR spectrum. Remaining signals in the } ^1\text{H and } ^{13}\text{C[^1H]} \text{ NMR spectra are due to two non-equivalent phenyl groups of the PPh}_2 \text{ and PPh}_2(2-C_4\text{H}_5\text{NH}) \text{ ligands. The } ^{31}\text{P[^1H]} \text{ NMR spectra for compounds 28 and 19 are similar with two broad resonances at } \delta \text{ 167.2 and 48.9, for the former.} \]
The reactivity of this ligand with $[\text{Mn}_2(\text{CO})_{10}]$ differs somewhat to that of diphenyl-2-furylphosphine in that compound 28 is yielded photochemically whereas the analogous furyl complex is yielded thermally. Also, there is no analogous complex to compound 27 in the furylphosphine chemistry, which is unsurprising as unlike the pyrrolyl unit, the furyl unit does not have an ionisable NH proton.

The thermal and photochemical reactions of $[\text{Mn}_2(\text{CO})_{10}]$ with diphenyl-3-pyrrolylphosphine differ markedly to those of the 2-substituted isomer. When heated under reflux in toluene a red-orange suspension was formed after eight hours. The conversion of the carbonyl was monitored by IR spectroscopy of the solution and like the 2-substituted isomer signals corresponding to the axially phosphorus-bound monosubstitution complex, $[\text{Mn}_2(\text{CO})_5\{\text{PPh}_2(3-\text{C}_6\text{H}_3\text{NH})\}]$ appeared. However, precipitation of this complex on formation seems to prevent further reaction. Work-up of the solution using TLC separation on silica bears out this postulate, with unreacted $[\text{Mn}_2(\text{CO})_{10}]$ (11 %) and compound 17 (9%) being characterised spectroscopically against authentic samples and $[\text{Mn}_2(\text{CO})_5\{\text{PPh}_2(3-\text{C}_6\text{H}_3\text{NH})\}]$ 29 (19%) being characterised analytically and by IR spectroscopy.\(^6\)

The reaction of the same two compounds under UV irradiation in toluene is similar in that precipitation of products occurs. Again the use of IR spectroscopy of the solution to monitor the conversion of the carbonyl indicates the formation of compound 29 which subsequently precipitates. Work-up of the solution using TLC separation on silica yields only unreacted
[Mn₃(CO)₁₀] and compound 29 (25%) characterised spectroscopically against authentic samples.

The chemistry of the two isomers with [Mn₃(CO)₁₀] differs and this is initially the result of the precipitation of compound 29 in the case of the 3-substituted isomer under both thermal and photochemical conditions, although a small amount of 17 is formed thermally. The analogous complex with the 2-substituted isomer, compound 26, remains soluble in the reaction solvent and continues to react further. Thermally compound 27 is observed predominantly over compound 17, a process which requires activation of the NH bond in the ligand and also a Mn-Mn bond cleavage to yield the Mn(CO)₃ unit, a step which probably only occurs for [Mn₃(CO)₁₀] and compound 26. Photochemically, compounds 17 and 28, which are related products of P-C bond cleavage, are yielded predominantly. In any case an analogous N-bound complex to the trimanganese complex, compound 27, could not be formed by the 3-substituted isomer due to its inability to form a sterically favoured five-membered ring with bonding through nitrogen.

5.2.3 Reaction of [Re₃(CO)₁₀] with diphenyl-2-pyrrolylphosphine

Several attempts to react this ligand with [Re₃(CO)₁₀] were carried out. Thermal reactions in high boiling solvents or in the presence of trimethylamine-N-oxide in situ as a reagent for CO displacement or photochemical reactions yielded yellow and dark-orange solutions,
respectively. However, work-up of these solutions yielded no characterisable products.

A reaction of the two compounds to yield an isolatable product was achieved at a high temperature in a sealed tube. A colourless decane suspension yielded a dark-orange suspension after 24 hours. Work-up of the solution using TLC separation on silica gave \([\text{Re}_2(\mu-H)(\mu-\text{PPh}_3)(\text{CO})_8] \) 30 (37%) as the only product. The IR spectrum of compound 30 is similar to that of compound 17, as are the \(^1\text{H}\) and \(^{13}\text{C}\{'\text{H}\}\) NMR spectra which have signals due to the phenyl protons only. A hydride signal at \(\delta -15.02\) further confirms the formation of compound 30. The complex is derived from P-C bond cleavage and loss of the pyrrolyl ring, the hydride ligand is probably from the solvent as suggested for compound 17. No heptacarbonyl substitution compounds of the type, \([\text{Re}_2(\mu-H)(\mu-\text{PPh}_3)[\text{PPh}_2(2-\text{C}_4\text{H}_5\text{NH})](\text{CO})_8]\), as found in the analogous manganese chemistry are observed. This is a consequence of the relatively stronger M-C bond strengths in rhenium carbonyl complexes compared to that of manganese carbonyl complexes.

5.2.4 Reaction of [Os\(_3\)(CO)\(_{12}\)] with diphenyl-n-pyrrolylphosphine (\(n = 2\) or 3)

The reaction of [Os\(_3\)(CO)\(_{12}\)] with the 2- and 3-substituted isomers of diphenylpyrrolylphosphine were only performed under reflux in octane. This was to avoid mixtures of related clusters, as observed for
reactions involving the analogous 2-substituted thienyl and furyl ligands with \([\text{Os}_3(\text{CO})_{12}]\) under reflux in heptane.

The reaction of \([\text{Os}_3(\text{CO})_{12}]\) with the 2-substituted isomer of diphenylpyrrolylphosphine, yielded an orange-red solution after five hours. There was no further change after this time in the IR spectrum of the solution, which had been recorded periodically to monitor the conversion of the cluster, and spot TLC analysis on silica revealed the same four products that had been observed an hour previously. Work-up of the solution using TLC separation on silica gave four bands, the first one of which was unreacted \([\text{Os}_3(\text{CO})_{12}]\) (4%).

The third yellow band was characterised as \([\text{Os}_3(\mu-H)(\mu_3-PPh_3(2-C_6H_4NH)(\text{CO})_6)]\) 31 (18%), which is cyclometallated at the pyrrolyl ring in an \(\mu_1,\pi^-\eta^2\)-vinyl mode. This compares to the analogous thienyl and furyl clusters, compounds 13 and 22 and its IR spectrum is similar. Also, like the analogous thienyl and furyl clusters, the \(^1\text{H}\) and \(^{13}\text{C}(^1\text{H})\) NMR spectra show resonances for two non-equivalent phenyl groups indicating that the static molecular structure is retained in solution a room temperature. A degree of line broadening is associated with the \(^1\text{H}\) NMR spectrum of cluster 31, however two \textit{ortho} phenyl signals are observed at \(\delta\) 7.81 and 7.08 and two \textit{meta} and \textit{para} phenyl signals at \(\delta\) 7.53 and 7.23. The static structure NMR spectrum is observed at low temperature (-25 °C) for the analogous thienyl, furyl, and 2-pyrrolyl ruthenium clusters. Exchange of the hydride ligand and the cyclometallated \textit{heterocyclic} unit between metal centres, leading to a time-averaged plane of symmetry occurs at around 30 °C for these analogous
ruthenium clusters. The same process for the analogous thienyl and furyl osmium clusters and probably cluster 31 is thought to occur, but leads to coalescence at an elevated temperature of around 70 °C.

IR and multinuclear NMR data for the first yellow band (0.027 g from 0.106 g starting complex) indicated that it was a mixture of two or more inseparable products. Two signals at δ -8.0 and -18.9 in the $^{31}\text{P}[^1\text{H}]$ NMR spectrum suggested that the mixture contained two clusters. A highest mass molecular ion peak at $M^+ = 1080$ (based on $^{190}\text{Os}$) is equivalent to that for cluster 31. However, cluster 31 has a different Rf value than the mixture and separates on a different area of the TLC plate and has already been isolated and characterised, suggesting that at least one of the clusters is an isomer of cluster 31. In any case there are no corresponding spectroscopic data for the mixture and cluster 31. The two clusters in the mixture contain the ligand metallated at either the pyrrolyl or one of the phenyl rings as two hydride signals at δ -13.08 and -14.45 with $J(\text{PH}) = 5.8$ and 12.3 Hz, respectively, are observed in the $^1\text{H}$ NMR spectrum. The metal hydride signal for 31 is observed at δ -17.83 with $J(\text{PH}) = 12.7$ Hz. Attempts to separate these two clusters using further TLC separation on silica with modified eluents failed.

Fortunately, single crystals suitable for diffraction by X-rays were grown from a cool dichloromethane-methanol mixture. Yellow needle-like crystals were yielded which suggested that either the crystals for two components in the mixture were non-distinguishable or that the two clusters had co-crystallised in the unit cell. One crystal from those most suitable for X-ray diffraction was selected and the IR and $^1\text{H}$ NMR spectra recorded of the
remaining good crystals which indicated that these were the same as the mixture above. However, this structure determination yielded just one of the clusters, suggesting that the crystals for the two clusters are non-distinguishable visually.

The structure that was determined is for [Os₃(µ-H)(µ₃-PPh₂(2-C₆H₃N))(CO)₆] 32, which is shown in Figure 5.6 with selected bond lengths and angles in Table 5.2. This cluster is isomeric with cluster 31. However, the coordination of the ligand to the metal atoms is quite different. For cluster

Figure 5.6 Molecular structure of [Os₃(µ-H)(µ₃-PPh₂(2-C₆H₃N))(CO)₆] 32
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</tbody>
</table>
the hydrogen atom on the ortho carbon atom on the pyrrolyl ring is activated, and the pyrrolyl ring is coordinated in a \( \mu_{\eta^1}:\eta^2 \)-vinyl mode. For cluster 32 it is the hydrogen atom on the nitrogen atom of the pyrrolyl ring that is activated and the ligand bridges one of the sides of a closed triosmium cluster through P and N atoms. The ligand is also coordinated to the third Os atom through C(1) and not through P or N atoms. If the parent ligand is considered as diphenylphosphinopyrrole, i.e. a substituted pyrrole rather than a tertiary phosphine, then it is coordinated as a diphenylphosphinopyrrolyl ligand with donation through a lone pair on the N atom. This would require the C(2)-C(3) and N(1)-C(4) bonds to be formally double and also it would require \( sp^3 \) hybridisation at the C(1) atom. This is observed in the molecular structure. The C(2)-C(3) and N(1)-C(4) bond lengths at 1.35(2) and 1.32(2) Å, respectively, are considerably shorter than the C(1)-(2) and C(3)-C(4) bond lengths at 1.47(2) and 1.40(2) Å, respectively. Also, the N(1)-C(1)-C(2) bond angle at 105.0(9) ° is smaller than those for the rest of the ring with C(1)-C(2)-C(3), C(2)-C(3)-C(4), C(3)-C(4)-N(1) and C(4)-N(1)-C(1) having bond angles of 107.8(10), 107.9(12), 111.4(11) and 107.9(9) °, respectively.

The hydride was located in this cluster as bridging the same two Os atoms \{Os(2) and Os(3)\} that are bridged by the pyrrolyl ring through the N(1) and C(1) atoms, respectively. This hydride is not bonded to the same Os atom as the tertiary phosphine and is therefore expected to have a lower phosphorus coupling constant than for its isomer, cluster 31. The two hydride signals in the \(^1\)H NMR of the mixture show very different phosphorus coupling constants. The signal at \( \delta = -14.45 \) shows phosphorus coupling (12.3
Hz) comparable to that observed in cluster 31, whereas the signal at \( \delta -13.08 \) has a much reduced phosphorus coupling constant (5.8 Hz). This suggests that this minor signal (in ~ 2:3 ratio with signal at \( \delta -14.45 \)) is the hydride signal for cluster 32.

Two sets of two associated pyrrolyl ring signals with comparable signal intensity ratios to the hydride signals at \( \delta -14.45 \) and -13.08 are observed at \( \delta 7.81 \) and 6.48 and \( \delta 6.87 \) and 6.40, respectively, in the \(^1\)H NMR spectrum of the mixture. However, three signals for the pyrrolyl ring are expected for cluster 32 and probably the other cluster in the mixture. The signals associated with cluster 32 are a triplet at \( \delta 6.40 \) (probably H') and a doublet at \( \delta 6.87 \) (probably either H\(^3\) or H\(^5\)). The two pyrrolyl ring signals for the other cluster are both doublets. The missing signals for both of the clusters, which is probably a doublet or a doublet of doublets for cluster 32, are obscured by the phenyl hydrogen signals from \( \delta 7.60-7.05 \).

Decoupling difference (DD) spectroscopy was employed in an attempt to fully assign the spectrum, and some selected irradiation spectra are shown in Figure 5.7. However, this only managed to confirm what was already known. Irradiation of the signal at \( \delta 6.48 \) caused a loss in coupling of the signal at \( \delta 7.81 \) which collapsed into a singlet and vice versa. Irradiation of the signal at \( \delta 6.40 \) caused the signal at \( \delta 6.87 \) to collapse into a singlet, indicating that they were associated. However, irradiation of the signal at \( \delta 6.87 \) caused the triplet signal at \( \delta 6.40 \) to collapse into a doublet, indicating again that they were associated, but also that this signal is coupled with
Figure 5.7  Selected \(^1\)H DD NMR spectra for \([\text{Os}_{3}(\mu-\text{H})(\mu_{3}-\text{PPh}_{2}(2-\text{C}_2\text{H}_3\text{N}))](\text{CO})_{32}\].
another hydrogen. This is further evidence for the triplet signal being assigned as the H⁺ proton of the pyrrolyl ring. One new piece of data was gained from the DD spectrum. Irradiation of the signals at δ 6.40 and 6.87 caused a collapse in the multiplet signal based around δ 7.08, irradiation of which only affected the triplet signal at 6.40 which collapsed into a doublet. 

So, the missing pyrrolyl ring proton signal for cluster 32 occurs at between δ 7.10-7.05 and is obscured by signals due to phenyl protons. The fact that irradiation of the signal at δ 6.87 and this multiplet based around δ 7.08 affects only the triplet signal at δ 6.40, is conclusive evidence that the triplet signal is due to the H⁺ proton of the pyrrolyl ring.

The last orange-yellow band was formulated as C₄₀H₂₉O₆N₂P₂Os₃ from its FAB mass spectrum and has an IR spectrum around 2000 cm⁻¹ which correlates to \([\text{Os}_3(\mu-H)(\mu_3\text{PPPh}_2(2-C_4H_2NH))\{\text{PPh}_2(2-C_4H_2NH)}\text{CO}_{12}\] 33A by comparison with the analogous thienyl and furyl clusters. However substitution of CO with \text{PPh}_2(2-C_4H_2NH) in the isomeric clusters 31 and 32 are probably both possible and so another isomer, the N-bound cluster which is related to 32, \([\text{Os}_3(\mu-H)(\mu_3\text{PPPh}_2(2-C_4H_2NH))\{\text{PPh}_2(2-C_4H_2NH)}\text{CO}_{12}\] 33B is available. A doublet of doublets in the hydride region of the ¹H NMR spectrum is expected by analogy to the related thienyl and furyl clusters. This signal is observed at no more than ± 0.5 ppm than for the analogous thienyl and furyl nonacarbonyl osmium and ruthenium clusters. However it is observed at δ -14.16 for this cluster, which is more than 1 ppm away from that for cluster 32 and more than 3 ppm away from that for cluster 31. Furthermore, the pyrrolyl signals in the aromatic region of the ¹H NMR
spectrum from δ 8.48-5.91 do not correspond to the pyrrolyl signals for clusters 31 and 32. For this cluster the three pyrrolyl signals (excluding the NH signal) of the non-coordinated pyrrolyl group are observed at δ 6.76, 6.50 and 6.42 which correspond to that for the free ligand. The signals for the coordinated pyrrolyl group are at δ 8.47, 6.56 and 5.91 which do not correspond to clusters 31 (δ 7.17 and 6.49) or 32 (δ 7.08, 6.87 and 6.40). Also there is only one NH signal which further suggests a cluster related to 32.

There are some coincidences between the spectral data for this cluster and that for the unknown cluster which has the same Rf value as cluster 32. This unknown cluster has signals at δ 7.81, 6.48 and -14.45 and possibly at δ 7.41, however this is not fully convincing.

Another feature of the 1H NMR spectrum of the unknown octacarbonyl osmium cluster is that the signals due to the coordinated pyrrolyl group show only hydrogen coupling to each other and no coupling to phosphorus. This suggests that the pyrrolyl group has cleaved from phosphorus and recoordinated, yielding also a phosphido bridge. This mode of coordination of the pyrrolyl group may be similar to that observed in [Os₃(μ-H)(μ₃-C₄H₃N)(CO)₄],¹⁶⁶,¹⁶⁷ or like one of the two modes observed in the tetraruthenium clusters with PPh₂(2-C₄H₃NH).¹⁷⁰

Heating [Os₃(CO)₁₂] and the 3-substituted isomer under reflux in octane for five hours resulted in an orange suspension. Work-up of the suspension using TLC separation on silica gave two bands and some unreacted [Os₃(CO)₁₂] (17 %). The first yellow band was characterised
analytically, by IR spectroscopy and by $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR spectroscopies as $[\text{Os}_3(\mu-H)[\mu_3-P\text{Ph}_3(3-C_2H_4NH)])(\text{CO})_6]$ 34 (45%). The IR spectrum of cluster 34 closely resembles those of clusters 13, 22 and 31, the analogous thienyl, furyl and 2-pyrrolyl clusters. Further justification for the formation of cluster 34 which is cyclometallated at the pyrrolyl ring is a doublet signal at $\delta -17.83$ in the hydride region of the $^1$H NMR spectrum and a parent molecular ion at $M^+ = 1079$ (based on $^{185}$Os) in the FAB mass spectrum. The $^1$H and $^{13}$C($^1$H) NMR spectra of cluster 34 are similar to those for clusters 13, 22 and 31 in that they show signals for two inequivalent phenyl groups. Two ortho phenyl signals are observed at $\delta$ 7.83 and 7.08 and two meta and para phenyl signals at $\delta$ 7.29-7.21 in the $^1$H NMR spectrum. The pyrrolyl signals are observed at $\delta$ 7.49 in the same spectrum. This suggests that the static structure of this cluster is retained in solution at room temperature. A similar conclusion was drawn from the $^1$H and $^{13}$C($^1$H) NMR spectra of the analogous thienyl, furyl and 2-pyrrolyl clusters but from the ruthenium analogues where exchange of the hydride ligand and the cyclometallated heterocyclic unit between metal centres leading to a time-averaged plane of symmetry occurs at room temperature. These exchanges do occur in the osmium clusters, but as expected, at a elevated temperature. Coalescence of the phenyl signals begins to occur at between 70 and 90 °C, in the $^1$H NMR spectrum of clusters 13 and 22. Cluster 34 differs from its thienyl and furyl analogues in that there are two possible isomers involving cyclometallation of the pyrrolyl ring, which are comparative to those shown in
Figure 5.4. The structure of the analogous ruthenium cluster has been tentatively solved using single-crystal X-ray diffraction.

Spectroscopic data for the second band were complicated, indicating that it was a mixture of two or more products. A doublet of doublets at $\delta$ -17.34 in the hydride region of the $^1$H NMR spectrum, two doublets at $\delta$ -10.9 and -12.9 with the same coupling constant and broad resonances between approximately $\delta$ -22 and -28 in the $^{31}$P($^1$H) NMR spectrum suggested that the mixture may contain $[\text{Os}_3(\mu-H)\{\mu_3-P\text{Ph}_3(3-C_6H_3\text{NH})\}]\{\text{PPh}_3(3-C_6H_3\text{NH})\}$ [CO]$_2$ 35, a cluster related to cluster 34 by substitution of one carbonyl ligand for a phosphine, and $[\text{Os}_3(\text{CO})_6\{\text{PPh}_3(3-C_6H_3\text{NH})\}]$ 36. Further work-up of this band using TLC separation on silica and a modified eluent led to separation into two bands.

The first minor band was characterised by IR, $^1$H, $^{31}$P($^1$H) NMR and mass spectroscopecies as cluster 35 (12%). The IR spectrum of this cluster is similar to that for the analogous clusters containing thienyl, furyl and 2-pyrrolyl groups, clusters 15, 24 and 32. Also a parent molecular ion peak at $M^+ = 1302$ (based on $^{192}$Os) is observed in the FAB mass spectrum. The $^1$H NMR spectrum of cluster 35 is complicated but some of the signals can be assigned including the hydride multiplet at $\delta$ -17.34. Others include unsurprisingly the NH signal of the non-cyclometallated pyrrolyl unit at $\delta$ 8.50, surprisingly the two para phenyl protons of the cyclometallated pyrrolyl unit at $\delta$ 7.12 and 7.04 and one of the ortho phenyl protons of the cyclometallated pyrrolyl unit at $\delta$ 7.73. The remaining signals cannot be fully assigned due to
mutual overlap. Similarly to cluster 34, there are two possible isomers for cluster 35.

The second major band was characterised analytically, by IR spectroscopy and by $^1$H, $^{13}$C($^1$H) and $^{31}$P($^1$H) NMR spectroscopies as cluster 36 (35%). The IR spectrum of this cluster is similar to triosmium clusters of the type $[\text{Os}_3\text{(CO)}_{12}(\text{PR})_2]$ ($R = \text{alkyl, aryl}$). The $^1$H and $^{13}$C($^1$H) NMR spectra of this cluster do not significantly differ from the spectra due to the ligand with signals in the $^1$H NMR spectrum at $\delta$ 8.42 6.86-6.82 and 6.14 and from $\delta$ 7.47-7.43 and 7.38-7.31 due to the four pyrrolyl protons and two equivalent phenyl groups, respectively. This suggests that there has been no orthometallation of the pyrrolyl unit or either of the two phenyl groups. A parent molecular ion peak at $M^+ = 1358$ (based on $^{185}$Os) and broad signals between $\delta$ -22 and -28 in the $^{31}$P($^1$H) NMR spectrum are further evidence for the formation of this cluster. The broad signals in this spectrum represent the equilibrium between the two known types of isomer of the $1,2$-disubstituted cluster. As for the clusters $[\text{Os}_3\text{(CO)}_{12}(\text{PPh})_{2}(2-\text{C}_6\text{H}_3\text{X})_2] \ (X = \text{S} 14, \text{O} 23)$, sharp signals are observed in the $^{31}$P($^1$H) NMR spectrum at -40 °C, representing the freezing out of the equilibrium between the two known geometric isomers. Instead, sharp singlet signals are observed at $\delta$ -26.4 and -26.9 for the unsymmetrical isomer and at $\delta$ -30.5 for the symmetrical isomer.

The chemistry of this 3-substituted isomer differs from that of the 2-substituted isomer and the 2-thienyl and 2-furyl ligands in that cluster 36 is a high yield product of the reaction under reflux in octane. Analogous clusters containing thienyl and furyl ligands, clusters 14 and 23 are formed in
the reaction with \([\text{Os}_3(\text{CO})_{12}]\) in heptane but not in octane. This suggests that
they are intermediates in the formation of clusters 15 and 24, the only
disubstituted triosmium clusters formed in the reaction in octane. Indeed
cluster 32 is the only disubstituted triosmium cluster formed by the reaction of
the 2-substituted isomer of diphenylpyrrolylphosphine with \([\text{Os}_3(\text{CO})_{12}]\) in
octane. However, similarly to the thermal and photochemical reactions of
\([\text{Mn}_2(\text{CO})_{10}]\) with diphenyl-3-pyrrolylphosphine where a suspension forms,
cluster 36 probably does not react further due to its insolubility in and
subsequent precipitation from the reaction medium. Hence the high yield of
cluster 36 in this reaction. Cluster 34, which is probably one of the
intermediates in the formation of cluster 35 as suggested by the reaction of
clusters 13 and 22 with the free ligand, does not react further to give more of
cluster 35 due to the non-availability of the free ligand. The reaction is being
carried out in a 1:1 \(\text{mol ratio} \) and cluster 36 requires a 1:2 \(\text{mol ratio} \) of cluster to
ligand for its formation.

The reactivity of this ligand with \([\text{Os}_3(\text{CO})_{12}]\) does have
similarities to that for \(\text{PPh}_2(2-\text{C}_6\text{H}_3\text{X})\) \((\text{X} = \text{S}, \text{O})\) in that the C-H bond \(\text{ortho}\) to
the \(\text{heteroatom}\) is activated yielding the related clusters, 34 and 35, the
second albeit in a low yield. A similar activation of the \(\text{ortho} \) C-H bond occurs
for the ligand \(\text{PPh}_2(2-\text{C}_6\text{H}_3\text{NH})\) to yield cluster 31 (and possibly 33A), but
unlike the 3-isomer, the N-H bond is also activated in this ligand to give
cluster 32 (and possibly 33B) which is isomeric to 31, as shown in Scheme 5.1. This difference can be explained by the ability of \(\text{PPh}_2(2-\text{C}_6\text{H}_3\text{NH})\) to form
a relatively favoured 6-membered ring on bridging the triosmium unit through
the phosphorus, *ipso* carbon and nitrogen atoms of the ligand - ring formation for the 3-isomer of the ligand is sterically unfavoured. The thienyl and furyl do not form the analogous *heteroatom* bound clusters which is due to the lower preference for S-bound and O-bound thienyl and furyl complexes with group 8 metal complexes.

Scheme 5.1
5.3 Experimental

5.3.1 Synthesis of the diphenyl-n-pyrrolylphosphines (n = 2 or 3)

Diphenyl-2-pyrrolylphosphine (45%) as a white solid by evaporation of a dichloromethane solution (Found: C, 76.2; H, 5.8; N, 5.6; P, 12.7. \(\text{C}_{15}\text{H}_{14}\text{NP}\) requires C, 76.5; H, 5.6; N, 5.6; P, 12.3%); \(^1\text{H}\) NMR: \(\delta\) 8.10 (broad s, NH), 7.33-7.26 (m, 10H, Ph), 6.96 (dd, \(J = 2.5, 3.9\) Hz, \(H'\) pyrrolyl), 6.51 (m, \(H''/H''\) pyrrolyl), 6.31 (m, \(H''/H''\) pyrrolyl); \(^13\text{C}(\{'\text{H}\}\) NMR: \(\delta\) 132.8 (d, \(J = 18.7\) Hz, \(\text{ortho}\) Ph), 128.6 (s, \(\text{para}\) Ph), 128.5 (d, \(J = 6.3\) Hz, \(\text{meta}\) Ph), 122.5 (d, \(J = 2.3\) Hz, pyrrolyl), 119.3 (d, \(J = 23.4\) Hz, pyrrolyl), 110.0 (d, \(J = 6.9\) Hz, pyrrolyl), \(\text{ipso}\) signals not observed; \(^31\text{P}(\{'\text{H}\}\) NMR: \(\delta\) -27.5 (s); parent molecular ion observed in the FAB mass spectrum; was prepared according to literature techniques and characterised analytically and spectroscopically against authentic samples. Column chromatographic or TLC work-up [SiO\(_2\); eluent, hexane-dichloromethane (5:3 v/v)] of the distillate also gave firstly PEtPh\(_2\) (10%) as an air-sensitive colourless liquid by evaporation of a dichloromethane solution, characterised spectroscopically against authentic samples and finally diphenyl-3-pyrrolylphosphine (40%) as a colourless oil by evaporation of a dichloromethane solution, which solidified to yield a white oil on standing (Found: C, 76.6; H, 5.6; N, 5.55; P, 12.3. \(\text{C}_{15}\text{H}_{14}\text{NP}\) requires C, 76.5; H, 5.6; N, 5.6; P, 12.3 %); \(^1\text{H}\) NMR: broad signals at \(\delta\) 8.42 (broad s, NH), 7.36 (m, 4H, \(\text{ortho}\) Ph), 7.32-7.25 (m, 6H, \(\text{meta/para}\) Ph), 6.86 (m, 2H, \(H''/H''\) pyrrolyl), 6.20 (m, 1H, \(H''\) pyrrolyl); \(^13\text{C}(\{'\text{H}\}\) NMR: \(\delta\) 133.0 (d, \(J = 18.8\) Hz,
ortho Ph), 128.8 (d, \( J = 6.8 \) Hz, meta Ph), 128.0 (s, para Ph), 125.2 (d, \( J = 37.1 \) Hz, pyrrolyl), 119.6 (d, \( J = 5.3 \) Hz, pyrrolyl), 113.1 (d, \( J = 8.6 \) Hz, pyrrolyl), ipso signals not observed; \(^{31}\)P(\(^1\)H) NMR: \( \delta = 26.0 \) (s); parent molecular ion observed in the FAB mass spectrum.

5.3.2 Reaction of \([\text{Mn}_2(\text{CO})_10]\) with \(\text{PPh}(2-\text{C}_6\text{H}_3\text{NH})\)

(a) Reaction in refluxing toluene: The compound \([\text{Mn}_2(\text{CO})_10]\) (0.197 g, 0.506 mmol) was heated under reflux in toluene (40 cm\(^3\)) with the 2-substituted isomer of the tertiary phosphine, diphenylpyrrolylphosphine (0.136 g, 1:1 mol/mol carbonyl), for eight hours. The IR spectrum of a hexane solution of the reaction medium was recorded periodically to monitor the conversion of the carbonyl. During the reaction, peaks for the axially substituted phosphorus bound monosubstitution product, \([\text{Mn}_2(\text{CO})_3\{\text{PPh}_2(2-\text{C}_6\text{H}_3\text{NH})\}]\) \(26\), appeared after about 90 minutes, began to disappear after about two hours and were not observed after about three hours. The resulting dark-orange solution was evaporated to dryness under reduced pressure to yield an orange-brown solid. TLC work-up [SiO\(_2\); eluent, hexane-dichloromethane (5:3 v/v)] gave four bands which included unreacted \([\text{Mn}_2(\text{CO})_10]\) (0.053 g) and compound \(17\) (0.010 g, 4%), characterised spectroscopically against authentic samples. An orange band yielded \([\text{Mn}_2(\text{CO})_6\{\text{PPh}_2(2-\text{C}_6\text{H}_3\text{NH})\}]\) \(26\) as an orange solid (0.021 g, 7%) by evaporation of a dichloromethane solution; \(^1\)H NMR: broad resonances at \(\delta = 7.88\) (broad s, NH), 7.45-7.35 (m, 10H, Ph), 6.98/6.94 (s, 1H, H\(^7\)/H\(^8\) pyrrolyl),

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6.38 (s, 1H, H\textsuperscript{\textprime} pyrrolyl); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR: \(\delta\) 131.5 (d, \(J = 10.8\) Hz, \textit{ortho} Ph), 130.4 (s, \textit{para} Ph), 128.9 (d, \(J = 10.0\) Hz, \textit{meta} Ph), 124.0 (d, \(J = 4.5\) Hz, pyrrolyl), 121.7 (d, \(J = 17.0\) Hz, pyrrolyl), 110.6 (d, \(J = 9.5\) Hz, pyrrolyl), CO and \textit{ipso} signals not observed; \(\nu\)(CO)/cm\(^{-1}\): 2091w, 2012m, 1995vs, 1973m, 1962vw, 1942m; weak parent molecular ion observed in the FAB mass spectrum. The final dark-orange band gave \([\text{Mn}_2\mu\text{-PPh}_2(2-C_3H_3N(\eta^5-Mn(CO))_2})_2\) \(27\) as a red microcrystalline solid (0.077 g, 21%) by crystallisation from a cool dichloromethane-hexane solution; multinuclear NMR broadened and not easy to report; \(\nu\)(CO)/cm\(^{-1}\): 2067w, 2049m, 2000s, 1991w, 1980m, 1967s, 1955w, 1942vw, 1926sh, 1899m; parent molecular ion observed in the FAB mass spectrum.

\textbf{(b)} \textit{Photochemical reaction:} The same two starting materials were also photolysed under UV irradiation in a 1:1 mole ratio (0.240 g [Mn\(_2\)(CO)]\(_{10}\), 0.161 g PPh\(_2\)(2-C\(_3\)H\(_3\)NH) (0.614 mmol)) in toluene (100 cm\(^3\)) for 20 hours. An orange solution resulted which was evaporated to dryness by vacuum distillation to yield an orange solid. TLC work-up [SiO\(_2\); eluent, hexane-dichloromethane (5:3 v/v)] gave two bands, the first of which was compound \(17\) (0.168 g, 52%), characterised spectroscopically against authentic samples. A second orange band gave \([\text{Mn}_2(\mu-H)(\mu-PPh)_2(PPh_2(2-C_3H_3NH))(CO)]_2\) \(28\) as an orange crystalline solid (0.091 g, 20%) from evaporation of a dichloromethane solution (Found: C, 55.9; H, 3.5; N, 1.8; P, 8.6. C\(_{58}\)H\(_{55}\)O\(_7\)NPMn\(_2\) requires C, 56.55; H, 3.4; N, 1.9; P, 8.3 %); \textsuperscript{1}H NMR: \(\delta\) 8.20 (broad s, NH), 7.93 (dd, \(J = 7.9, 10.2\) Hz, 4H, \textit{ortho} Ph), 7.52-7.48 (m,
4H, ortho Ph), 7.42 (broad s, 6H, meta/para Ph), 7.38-7.25 (m, 6H, meta/para Ph), 7.02 (s, 1H, pyrrolyl), 6.81 (d, J = 4.5 Hz, 1H, pyrrolyl), 6.38 (s, 1H, pyrrolyl), -16.03 (t, J_pMn = 31.3 Hz, 1H, MnH Mn); \(^1^3\)C\(^{1}\)H NMR: \(\delta\) 142.1 (d, \(J = 29.1\) Hz, ipso Ph), 136.5 (d, \(J = 42.7\) Hz, ipso Ph), 133.2 (d, \(J = 8.9\) Hz, meta Ph), 131.9 (d, \(J = 10.8\) Hz, ortho Ph), 130.1 (s, para Ph), 129.0 (d, \(J = 1.9\) Hz, para Ph), 128.6 (d, \(J = 9.9\) Hz, ortho Ph), 128.3 (d, \(J = 9.7\) Hz, meta Ph), 123.6 (d, \(J = 4.5\) Hz, pyrrolyl), 121.2 (d, \(J = 14.8\) Hz, pyrrolyl), 110.5 (d, \(J = 9.0\) Hz, pyrrolyl), CO and ipso pyrrolyl signals not observed; \(^31\)P\(^{1}\)H NMR: broad resonances at \(\delta\) 167.2 and 48.9; \(\nu\)(CO)/cm\(^{-1}\): 2074m, 2027m, 1992s br, 1952s, 1945sh, 1935sh, 1921m, 1896w; parent molecular ion observed in FAB mass spectrum.

5.3.3 Reaction of [Mn\(_2\)(CO)\(_{10}\)] with PPh\(_2\)(3-C\(_3\)H\(_3\)NH)

(a) Reaction in refluxing toluene: [Mn\(_2\)(CO)\(_{10}\)] (0.105 g, 0.270 mmol) was also heated under reflux in toluene (40 cm\(^3\)) with the 3-substituted isomer of diphenylpyrrolylphosphine (0.069 g, 1:1 mol/mol carbonyl). A red-orange suspension resulted after eight hours which was evaporated to dryness under reduced pressure to yield a dark-orange solid. TLC work-up [SiO\(_2\); eluent, hexane-dichloromethane (1:1 v/v)] gave three bands which included unreacted [Mn\(_2\)(CO)\(_{10}\)] (0.012 g) and compound 17 (0.013 g, 9%). The third orange band gave [Mn\(_2\)(CO)\(_6\){PPh\(_2\)(3-C\(_3\)H\(_3\)NH)}] 29 as an orange solid (0.031 g, 19%) by evaporation of a dichloromethane solution (Found: C, 50.0; H, 2.8; N, 2.4; P, 5.5. \(C_{29}H_{14}O_{9}NP\)Mn\(_2\) requires C, 49.0; H, 2.3; N, 2.3; P, 5.05 %);
multinuclear NMR are broadened and not easy to report; ν(CO)/cm⁻¹: 2089m, 2010s, 1993vs, 1970s, 1959vw, 1937s; weak parent molecular ion observed in the FAB mass spectrum.

(b) **Photochemical reaction**: The same two compounds were also photolysed under UV irradiation in a 1:1 mole ratio {0.198 g [Mn₂(CO)₁₀] 0.133 g PPh₃(3-C₆H₅NH) (0.507 mmol)} in toluene (100 cm³) for 10 hours. The resultant orange suspension was evaporated to dryness under vacuum distillation to yield an orange solid. TLC work-up [SiO₂; eluent, hexane-dichloromethane (1:1 v/v)] gave two bands, characterised spectroscopically against authentic samples as, unreacted [Mn₂(CO)₁₀] (0.007 g) and compound 29 (0.077 g, 25%).

5.3.4 Reaction of [Re₅(CO)₁₀] with PPh₃(2-C₆H₅NH)

The compound [Re₅(CO)₁₀] (0.199 g, 0.305 mmol) and the tertiary phosphine PPh₃(2-C₆H₅NH) (0.077 g, 1:1 mol/mol carbonyl) were charged into a 20 cm³ Carius tube along with 5 cm³ of decane. The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum and placed in an oven at 190 °C. After 24 hours the colourless suspension had become an orange suspension. TLC work-up [SiO₂; eluent, hexane-dichloromethane (5:3 v/v)] gave only a very pale yellow solid of [Re₅(μ-H)(μ-PPh₃)(CO)₃] 30 (0.088 g, 37%) by evaporation of a dichloromethane solution; ¹H NMR: δ 7.82 (ddd, J = 1.5, 7.3, 11.5 Hz, 4H, ortho Ph), 7.80-7.28 (m, 6H,
meta/para Ph), -15.02 (d, J_{\text{ph}} = 4.6 Hz, 1H, ReHRe); $^{13}$C[$^1$H] NMR: \( \delta 185.1 \) (d, \( J = 28.0 \) Hz, 2CO trans to PPh\(_3\)), 183.7 (d, \( J = 3.1 \) Hz, 2CO), 182.3 (d, \( J = 6.7 \) Hz, 4CO), 138.8 (d, \( J = 40.3 \) Hz, ipso Ph), 134.5 (d, \( J = 11.7 \) Hz, ortho Ph), 129.8 (s, para Ph), 128.8 (d, \( J = 10.6 \) Hz, meta Ph); $^3$P[$^1$H] NMR: \( \delta 42.9 \) (s);

\( \nu(\text{CO})/\text{cm}^{-1} \): 2108m, 2084s, 2076sh, 2014vs, 1998vs, 1983vw, 1964vs; parent molecular ion observed in the FAB mass spectrum.

5.3.5 Reaction of $[\text{Os}_3(\text{CO})_{12}]$ with PPh\(_3\)(2-C\(_6\)H\(_5\)NH)

The cluster $[\text{Os}_3(\text{CO})_{12}]$ (0.106 g, 0.117 mmol) and the 2-substituted isomer of the tertiary phosphine, diphenylpyrrolylphosphine (0.034 g, 1:1 mol/mol cluster), were heated under reflux in octane (20 cm\(^3\)) for five hours. The resultant red-orange solution was evaporated to dryness under reduced pressure to yield an orange-brown solid. TLC work-up [SiO\(_2\); eluent, hexane-dichloromethane (5:3 v/v)] gave three bands and some unreacted $[\text{Os}_3(\text{CO})_{12}]$ (0.017 g). The first yellow band yielded a mixture of compounds as yellow crystals (0.027 g) by crystallisation from a dichloromethane-methanol solution; \( \nu(\text{CO})/\text{cm}^{-1} \): 2086s, 2064s, 2057s, 2036sh, 2029vs, 2013ms, 2006s, 1992s, 1987s, 1973m, 1963w, 1956m, 1949w; one of which included $[\text{Os}_3(\mu-H)(\mu-P\text{Ph}_3(2-C\(_6\)H\(_5\)N))(\text{CO})_9]$ 32 (identified crytallographically);

\( ^1 \)N NMR: pyrrolyl signals at \( \delta 7.07 \) (obscured by phenyl signals), 6.87, 6.40; hydride signal at \( \delta - 13.08 \) (d, \( J = 5.8 \) Hz, 1H, OsHOs). The second yellow band yielded $[\text{Os}_3(\mu-H)(\mu-P\text{Ph}_3(2-C\(_6\)H\(_5\)NH))(\text{CO})_9]$ 31 as a yellow microcrystalline solid (0.025 g, 18%) by crystallisation from a
dichloromethane-heptane solution); $^1$H NMR: slightly broadened resonances at δ 7.81 (m, 2H, ortho Ph), 7.56-7.51 (m, 3H, meta/para Ph), 7.25-7.22 (m, 3H, meta/para Ph), 7.17 (m, 1H, pyrrolyl), 7.08 (m, 2H, ortho Ph), 6.49 (m, 1H, pyrrolyl), -17.83 (d, J$_{pp}$ = 12.7 Hz, 1H, OsHOs); $^{31}$C($^1$H) NMR: δ 132.5 (d, J = 7.1 Hz, pyrrolyl), 132.2 (d, J = 10.1 Hz, meta Ph), 131.8 (d, J = 11.3 Hz, ortho Ph), 131.1 (d, J = 2.3 Hz, para Ph), 130.7 (d, J = 2.5 Hz, para Ph), 128.7 (d, J = 10.8 Hz, ortho Ph), 128.2 (d, J = 10.1 Hz, meta Ph), 120.4 (s, pyrrolyl), CO and ipso signals not observed; $^{31}$P($^1$H) NMR: δ -16.8 (s); v(CO)/cm$^{-1}$: 2085vs, 2055vs, 2029vs, 2014vs, 1992s, 1983s, 1979s, 1967m, 1955m; parent molecular ion observed in the EI and FAB mass spectra. A second orange-yellow band yielded [Os$_3$(μ-H)(μ$_2$-PPh$_2$(2-X))(PPh$_2$(2-C$_6$H$_5$NH))(CO)$_6$]$_n$ (X = C$_6$H$_5$NH 33A, C$_6$H$_3$N 33B) as an orange-yellow microcrystalline solid (0.029 g, 19%) by crystallisation from a dichloromethane-heptane solution; $^1$H NMR: δ 8.47 (d, J = 4.6 Hz, 1H, coordinated pyrrolyl), 7.69-7.47 (m, 13H), 7.38 (td, J = 3.1, 6.9 Hz, 1H, para Ph), 7.27 (broad s, 1H, NH), 7.07 (td, J = 1.8, 7.2 Hz, 2H, meta Ph), 7.02 (ddd, J = 3.0, 7.8, 9.3 Hz, 2H, ortho Ph), 6.76 (s, 1H, uncoordinated pyrrolyl), 6.67 (dd, J = 7.6, 11.5 Hz, 2H, ortho Ph), 6.56 (d, J = 4.7 Hz, 1H, coordinated pyrrolyl), 6.50 (s, 1H, uncoordinated pyrrolyl), 6.42 (s, 1H, uncoordinated pyrrolyl), 5.91 (s, 1H, coordinated pyrrolyl), -14.16 (dd, J = 10.8, 14.8 Hz, 1H, OsHOs); $^{31}$P($^1$H) NMR: δ -9.8 (s), -17.1 (s), J(PP) not observed; v(CO)/cm$^{-1}$: 2070s, 2030vs, 2010s, 1994w, 1972m, 1963m, 1945m, 1936w; parent molecular ion observed in the EI and FAB mass spectra.
5.3.6 Reaction of $[\text{Os}_3(\text{CO})_{13}]$ with $\text{PPh}_3(3-$C$_2\text{H}_2\text{NH})$

$[\text{Os}_3(\text{CO})_{13}]$ (0.096 g, 0.105 mmol) was also heated under reflux in octane (20 cm$^3$) in a 1:1 ratio, with the 3-substituted isomer of diphenylpyrrolylphosphine (0.038 g). An orange suspension resulted after five hours which was evaporated to dryness under reduced pressure to yield an orange solid. TLC work-up$[\text{SiO}_2$; eluent, hexane-dichloromethane (3:5 v/v)] gave two bands and some unreacted $[\text{Os}_3(\text{CO})_{13}]$ (0.016 g). The first yellow band yielded $[\text{Os}_3(\mu-H)(\mu_3-\text{PPh}_3(3-\text{C}_2\text{H}_2\text{NH}))\text{(CO)_{13}}]$ 34 as a yellow microcrystalline solid (0.051 g, 45%) by crystallisation from a dichloromethane-heptane solution; $^1\text{H}$ NMR: $\delta$ 7.83 (m, 3H, 2 ortho Ph and an NH), 7.58-7.42 (m, 3H, meta/para Ph), 7.29-7.21 (m, 3H, meta/para Ph), 7.14 (dd, $J$ = 2.0, 3.2 Hz, 1H, pyrrolyl), 7.08 (ddd, $J$ = 1.8, 7.6, 11.1 Hz, 2H, ortho Ph), 6.49 (t, $J$ = 1.6 Hz, 1H, pyrrolyl), -17.83 (d, $J_{pp}$ = 13.08 Hz, 1H, OsHOs); $^{13}\text{C}(^1\text{H})$ NMR: $\delta$ 177.1 (s), 176.2 (s), 173.7 (d, $J$ = 8.6 Hz), 173.1 (d, $J$ = 8.5 Hz), 144.8 (d, $J$ = 46.4 Hz, ipso Ph), 136.8 (d, $J$ = 37.9 Hz, ipso Ph), 132.5 (d, $J$ = 7.3 Hz, pyrrolyl), 132.4 (d, $J$ = 66.2 Hz, ipso pyrrolyl), 132.2 (d, $J$ = 10.1 Hz, meta Ph), 131.8 (d, $J$ = 11.4 Hz, ortho Ph), 131.1 (d, $J$ = 2.4 Hz, para Ph), 130.1 (d, $J$ = 2.1 Hz, para Ph), 128.7 (d, $J$ = 10.7 Hz, ortho Ph), 128.2 (d, $J$ = 10.3 Hz, meta Ph), 120.4 (s, pyrrolyl), not all CO signals observed; $^{31}\text{P}(^1\text{H})$ NMR: $\delta$ -13.3 (s); v(CO)/cm$^{-1}$: 2085s, 2055vs, 2028vs, 2014s, 1992m, 1983m, 1979m, 1967w, 1955w; parent molecular ion observed in the FAB mass spectrum. The second band, a mixture, was separated with further TLC work-up $[\text{SiO}_2$; eluent, hexane-dichloromethane (2:5 v/v)] to give two clusters.
The first orange-yellow band gave \([\text{Os}_3(\mu-\text{H})_3\{\mu_3-\text{PPh}_2(3\text{-C}_4\text{H}_3\text{NH})\} \{\text{PPh}_2(3\text{-C}_4\text{H}_3\text{NH})\} \{\text{CO}\}_3]\) as an orange-yellow microcrystalline solid (0.015 g, 12%) by crystallisation from a dichloromethane-heptane solution; \(^1\text{H}\) NMR: \(\delta\) 8.50 (br s, \text{NH}), 7.73 (ddd, \(J = 1.5, 7.0, 11.6\) Hz, 2H), 7.48-7.43 (m, 3H), 7.12 (td, \(J = 1.7, 7.5\) Hz, 1H), 7.04 (td, \(J = 1.9, 7.5\) Hz), 6.95-6.89 (m, 3H), 6.82 (br d, \(J = 1.5\) Hz, 1H), 6.78-6.71 (m, 3H), 6.70-6.66 (m, 2H), 6.47-6.40 (m, 3H), 6.27 (br s, 1H), 6.07 (br s, 1H), -17.34 (dd, \(J_{\text{pp}} = 9.9, 14.8\) Hz, OsH\(\text{Os}\)); \(^{31}\text{P}(^1\text{H})\) NMR: \(\delta\) -10.9 (d, \(J_{\text{pp}} = 17.8\) Hz), -12.9 (d, \(J_{\text{pp}} = 17.8\) Hz). The second orange band gave \([\text{Os}_3(\text{CO})_{10}\{\text{PPh}_2(3\text{-C}_4\text{H}_3\text{NH})\}_2]\) as an orange solid (0.050 g, 35%) from evaporation of a dichloromethane solution (Found: C, 37.3; H, 2.0; N, 2.0; P, 4.9. \(\text{C}_{68}\text{H}_{14}\text{O}_{20}\text{NPO}_{3}\) requires C, 37.3; H, 2.1; N, 2.1; P, 4.6 %); \(^1\text{H}\) NMR: slightly broadened resonances at \(\delta\) 8.42 (broad s, \text{NH}), 7.47-7.43 (m, 4H, \text{ortho Ph}), 7.38-7.31 (m, 6H, meta/para Ph), 6.86-6.82 (s, 2H, \(\text{H}^3/\text{H}^6\) pyrrolyl), 6.14 (s, 1H, \(\text{H}^4\) pyrrolyl); \(^{13}\text{C}(^1\text{H})\) NMR: \(\delta\) 137.5 (d, \(J = 55.2\) Hz, ipso Ph), 132.3 (d, \(J = 11.2\) Hz, \text{ortho Ph}), 129.7 (s, \text{para Ph}), 127.9 (d, \(J = 10.8\) Hz, meta Ph), 126.2 (d, \(J = 21.5\) Hz, pyrrolyl), 119.7 (d, \(J = 10.4\) Hz, pyrrolyl), 117.4 (d, \(J = 71.5\) Hz, ipso pyrrolyl), 113.4 (d, \(J = 8.5\) Hz, pyrrolyl), CO signals not observed; \(^{31}\text{P}(^1\text{H})\) NMR: broad resonances between approximately \(\delta\) -22 and -28; (-40 °C): sharp signals at -26.4 (s), -26.9 (s), -30.5 (s); \(\nu(\text{CO})/\text{cm}^{-1}\): 2084w, 2070w, 2027s, 2010m, 1999s, 1971m, 1956w; parent molecular ion observed in the FAB mass spectrum.
Appendix 1

1. General Experimental

Decacarbonyldimanganese and decacarbonyldirhenium were both purchased from Strem and used without any further purification, although the manganese carbonyl was stored under nitrogen. Dodecacarbonyltriosmium was purchased as osmium tetroxide and converted to the trinuclear carbonyl compound according to literature preparations. All solvents used in TLC separations were dried according to normal techniques, reaction solvents were used straight from the bottle of freshly purchased solvents.

TLC separations were performed on either laboratory prepared plates with a thickness of approximately 1 mm or pre-prepared plates with a thickness of 0.5 mm using SiO\(_2\) (HF\(_{254}\)-type 60, E. Merck, Germany).

2. IR Spectroscopy

Unless otherwise stated, all IR spectra were recorded for cyclohexane solutions using calcium fluoride solution IR cells. In Chapter 2, the IR spectra were ran using a Perkin-Elmer 983 spectrometer and workstation. A Nicolet 254 FT-IR spectrometer was used in the subsequent chapters.
3. **NMR Spectroscopy**

All NMR spectra were recorded in CDCl$_3$, unless otherwise stated, using a Varian VXR-400 FT-NMR spectrometer (400 MHz for $^1$H). $^{31}$P($^1$H) NMR spectra were recorded using 85% phosphoric acid as an external standard. Spectra were recorded by the author and Gill Maxwell. Further assistance was provided by Dr Graeme Hogarth, Mr Chris Cooksey and Marc Schtedroff.

4. **Mass Spectrometry**

All EI and FAB (using meta-nitrobenzylalcohol as matrix) mass spectra were recorded on a VG ZAB F-1 high resolution mass spectrometer using the service at UCL provided by Mr Jon Hill, Mr Steve Corker and Dr Margaret Mruszek.

5. **Analysis**

All analyses were performed by the UCL microanalysis laboratory as a service provided by Mr Alan Stones and Gill Maxwell.
Appendix 2

1. General Crystallographic Experimental

All crystallographic experiments were performed by Professor A. J. Deeming.

Data collection. Data was collected on a Nicolet R3v/m diffractometer (Mo-Kα radiation; λ = 0.71073 Å) at room temperature, corrections were applied for Lorentz and polarisation effects and for small variations in intensity based on three standard reflections. An empirical absorption correction based on a Ψ-scan method was also applied in each case.

Structure solution and refinement. Structures were solved by direct methods and the structures refined using difference Fourier techniques. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms bonded to carbon were included in the model in idealised positions (C-H distances at 0.96 Å, Uiso = 0.008 Å²). \[ R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \] and \[ R_w = \left( \frac{\sum w |F_o|^2 - |F_c|^2}{\sum |F_o|^2} \right)^{1/2}, \] where \( w = \left[ \sigma^2(F_o) + g(F_o^2) \right]^{-1} \).

All calculations were carried out on a MicroVax II computer running SHELXTL-PLUS.\(^{173}\)

2.1 Structure Determination for \([\text{Mn}_2(\mu-\text{PPh}_2)(\mu-\eta^1:\eta^5-C_4H_3S})(\text{CO})_8]\)
Crystal data: Orange crystal, 0.25 x 0.38 x 0.50 mm³, C₁₀H₁₃O₆PSMn₃, 
\( M = 546.26 \text{ g mol}^{-1} \), monoclinic, \( a = 16.317(3), b = 9.101(1), c = 16.280(3) \text{ Å}, \beta = 112.08(1)° \). The unit cell was determined from 35 orientation reflections (16 ≤ 2θ ≤ 30°).

Data collection: 4404 data were collected, 3997 unique, \( \omega-2\theta \) scan mode, hkl range 0, 0, -22 to 12, 12, 22 (5 ≤ 2θ ≤ 55°).

Structure solution and refinement - P2₁/n, \( Z = 4, F(000) = 1096, D_c = 1.63 \text{ g cm}^{-3}, 289 \) parameters, 3474 data with \( I_0 ≥ 1.5σ(I_0), R = 0.0332, R_w = 0.0388, g = 0.000808 \) Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 0.26 eÅ⁻³.

2.2 Structure Determination for \( \left[ \text{Re}_2(\mu\text{-PPh}_2(2\text{-C}_3\text{H}_3\text{S}))(\text{CO})_8 \right] \)

Crystal data: Yellow crystal, 0.14 x 0.28 x 0.48 mm³, C₉H₁₃O₆PSRe₂, \( M = 864.80 \text{ g mol}^{-1} \), orthorhombic, \( a = 14.781(5), b = 16.863(5), c = 20.407(7) \text{ Å}, \ U = 2226.3(6) \text{ Å}^3 \). The unit cell was determined from 33 orientation reflections (12 ≤ 2θ ≤ 27°).

Data collection: 4847 data were collected, 4392 unique, \( \omega-2\theta \) scan mode, hkl range 0, 0, 0 to 10, 21, 25 (5 ≤ 2θ ≤ 55°).

Structure solution and refinement: Pcab, \( Z = 8, F(000) = 3216, D_c = 2.26 \text{ g cm}^{-3}, 325 \) parameters, 3536 data with \( I_0 ≥ 1.5σ(I_0), R = 0.0461, R_w = 0.0420, g = 0.000808 \) Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 0.26 eÅ⁻³.
2.3 Structure Determination for \([\text{Re}_2(\mu-C_4H_9S)(\mu-\text{PPh}_3)(\text{CO})_6]\) 11

Crystal data: Colourless crystal, 0.25 x 0.32 x 0.45 mm\(^3\), 
\(C_{24}H_{18}O_8\text{PSRe}_2\), \(M = 864.80\) g mol\(^{-1}\), monoclinic, \(a = 9.367(2)\), \(b = 30.24(1)\), \(c = 9.481(3)\) Å, \(\beta = 105.37(2)\)°, \(U = 2589.0(1.5)\) Å\(^3\). The unit cell was determined from 25 orientation reflections (14 ≤ 2θ ≤ 27°).

Data collection: 4867 data were collected, 4483 unique, ω scan mode, hkl range 0, 0, -12 to 12, 36, 12 (5 ≤ 2θ ≤ 50°).

Structure solution and refinement: P2\(\alpha/a\), \(Z = 4\), \(F(000) = 1608\), \(D_\text{c} = 2.22\) g cm\(^{-3}\), 325 parameters, 3554 data with \(I_\text{o} ≥ 3σ(I_\text{o})\), \(R = 0.0468\), \(R_w = 0.0490\), \(g = 0.000634\). Largest shift-to-error in the final refinement was 0.003 and the largest peak in the final difference Fourier map was 1.73 eÅ\(^{-3}\).

2.4 Structure Determination for the Mixture of Clusters \([\text{Os}_3(\text{CO})_{11}(\text{PPh}_3(2-C_4H_9S))]\) 12 and \([\text{Os}_3(\mu-H)(\mu_2-\text{PPh}_3(2-C_4H_2S))(\text{CO})_6]\) 13

Crystal data: Yellow crystal, 0.20 x 0.28 x 0.35 mm\(^3\), \(C_{24}H_{20}O_8\text{PS}_{12}\text{OS}_{16}\), \(M = 2238.04\) g mol\(^{-1}\), triclinic, \(a = 11.610(2)\), \(b = 13.145(4)\), \(c = 19.852(7)\) Å, \(\alpha = 85.60(3)\), \(β = 82.72(2)\), \(γ = 76.39(2)\)°, \(U = 2917.0(1)\) Å\(^3\). The unit cell was determined from 31 orientation reflections (11 ≤ 2θ ≤ 26°).

Data collection: 7994 data were collected, 7553 unique, ω-2θ scan mode, hkl range 0, -15, -22 to 13, 15, 22 (5 ≤ 2θ ≤ 45°).

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Structure solution and refinement: \( P1, Z = 2, F(000) = 2032, D_\rho = 2.55 \) g cm\(^{-3}\), 380 parameters, 5391 data with \( I_0 \geq 3\sigma(I) \), \( R = 0.0589, R_w = 0.0641, g = 0.00275 \). Largest shift-to-error in the final refinement was 0.008 and the largest peak in the final difference Fourier map was 2.88 eÅ\(^{-3}\).

2.5 Structure Determination for \([\text{Os}_3(\mu-H)(\mu_3-PPh_3(2-C_4H_2S))(CO)]\)

Crystal data: Yellow crystal, 0.40 x 0.48 x 0.58 mm\(^3\), \( C_{25}H_{13}O_gPSO_{29} \), \( M = 1091.01 \) g mol\(^{-1}\), orthorhombic, \( a = 9.963(5), b = 11.191(8), c = 23.859(8) \) Å, \( U = 2659.0(2) \) Å\(^3\). The unit cell was determined from 24 orientation reflections (14 \( \leq \theta \leq 26^\circ\)).

Data collection: 2647 data were collected, 2435 unique, \( \omega \) scan mode, hkl range 0, 0, 0 to 12, 14, 29 (5 \( \leq \theta \leq 50^\circ\)).

Structure solution and refinement: \( Pc2_1n, Z = 4, F(000) = 1976, D_\rho = 2.73 \) g cm\(^{-3}\), 226 parameters, 2194 data with \( I_0 \geq 3\sigma(I) \), \( R = 0.0586, R_w = 0.0637, g = 0.004967 \). Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 3.33 eÅ\(^{-3}\).

2.6 Structure Determination for \([\text{Mn}_2(\mu-H)(\mu-PPh_2(CO)]_8\)

Crystal data: Yellow crystal, 0.24 x 0.75 x 0.80 mm\(^3\), \( C_{22}H_{11}O_gPMn_{g2} \), \( M = 520.16 \) g mol\(^{-1}\), monoclinic, \( a = 19.160(5), b = 8.131(2), c = 16.742(3) \) Å, \( \beta = \ldots \)
\[ \theta = 124.04(2)°, \quad U = 2161.4(8) \text{ Å}^3. \] The unit cell was determined from 32 orientation reflections \((15 \leq 2\theta \leq 29°)\).

**Data collection:** 2954 data were collected, 2030 unique, \(\omega-2\theta\) scan mode, hkl range \(0, 0, -20\) to \(23, 10, 20\) \((5 \leq 2\theta \leq 50°)\).

**Structure solution and refinement:** \(C2c, \quad Z = 4, \quad F(000) = 1040, \quad D_e = 1.60 \text{ g cm}^{-3}\), 142 parameters, 1763 data with \(I_\text{o} \geq 2\sigma(I_\text{o})\), \(R = 0.0373, \quad R_w = 0.0411, \quad g = 0.000390\). Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 0.28 eÅ\(^3\).

2.7 Structure Determination for \([\text{Mn}_2\text{µ-PPh}_2(2-\text{C}_2\text{H}_3\text{N}-\text{η}^5-\text{Mn(CO)}_3)](\text{CO})_2\)

**Crystal data:** Orange-red crystal, \(0.22 \times 0.28 \times 0.30 \text{ mm}^3\), \(C_{27}H_{30}NO_4PMn_3\), \(M = 723.20\) g mol\(^{-1}\), monoclinic, \(a = 12.520(4), \quad b = 14.837(3), \quad c = 15.801(3) \text{ Å}, \quad \beta = 101.86(2)^°, \quad U = 2872.0(1) \text{ Å}^3\). The unit cell was determined from 30 orientation reflections \((16 \leq 2\theta \leq 30°)\).

**Data collection:** 5973 data were collected, 5506 unique, \(\omega-2\theta\) scan mode, hkl range \(0, 0, -20\) to \(16, 19, 20\) \((5 \leq 2\theta \leq 52°)\).

**Structure solution and refinement:** \(P2_{1}/c, \quad Z = 4, \quad F(000) = 1440, \quad D_e = 1.67 \text{ g cm}^{-3}\), 308 parameters, 3956 data with \(I_\text{o} \geq 2\sigma(I_\text{o})\), \(R = 0.0425, \quad R_w = 0.0450, \quad g = 0.000787\). Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 0.323 eÅ\(^3\).

2.8 Structure Determination for \([\text{Os}_3(\text{µ-H})\text{µ-PPh}_2(2-\text{C}_2\text{H}_3\text{N})](\text{CO})_3\)
Crystal data: Yellow crystal, 0.60 x 0.35 x 0.30 mm$^3$, $\text{C}_{20}\text{H}_{14}\text{NO}_{8}\text{PO}_{33}$, $M = 1073.97$ g mol$^{-1}$, triclinic, $a = 9.165(1)$, $b = 9.313(1)$, $c = 16.772(2)$ Å, $\alpha = 101.00(1)$, $\beta = 124.04(1)$, $\gamma = 97.99(1)^\circ$, $U = 1388.8(3)$ Å$^3$. The unit cell was determined from 30 orientation reflections (15 $\leq \theta \leq 30^\circ$),

Data collection: 6457 data were collected, 6089 unique, $\omega-2\theta$ scan mode, hkl range 0, -12, -22 to 12, 13, 22 (5 $\leq 2\theta \leq 55^\circ$).

Structure solution and refinement: $P\overline{1}$, $Z = 2$, $F(000) = 972$, $D_v = 2.66$ g cm$^{-3}$, 352 parameters, 5060 data with $I_o \geq 3\sigma(I_o)$, $R = 0.0429$, $R_w = 0.0422$, $g = 0.000390$. Largest shift-to-error in the final refinement was 0.001 and the largest peak in the final difference Fourier map was 2.56 eÅ$^{-3}$. 

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References


123. H. Selman, J. S. Merba,


