SYNTHESES AND CHARACTERIZATION OF SOME TRIOSMIUM AND TRIRUTHENIUM CLUSTER COMPLEXES CONTAINING UNUSUAL FERROCENYL MOIETIES

by

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ABSTRACT

Series of ferrocenyl ligands, predominantly phosphines, have been prepared: PFcPh₂ (Fc=(η⁵-C₅H₄)Fe(η⁵-C₅H₅)), PFc₂Ph, PET₂Fc, PETFc₂, PFc'iPr₂, PnBuFcPh, PtBu₂Fc, Fc'PPh (Fc'=(η⁵-C₅H₄)₂Fe), Fc'(PPh₂)₂, Fc'(P'iPr₂)₂, AsFc₂Ph, Fc'(SPh)₂, Fc'(SMe)₂, SFcPh, Fc₂S₂, and SbFc₃, and characterized by spectroscopic and analytical techniques.

The reactions of most of the ferrocenylphosphine ligands with M₃(CO)₁₂ (M=Os, Ru) were studied and a series of complexes of general formulae M₃(CO)₁₁L, M₃(CO)₁₀L₂, Ru₃(CO)₉L₃, M₃(CO)₁₀(L-L), Ru₃(CO)₉(L-L)L' were prepared and characterized by spectroscopic and analytical techniques. The disubstituted compounds M₃(CO)₁₀L₂ were found to exist as symmetrical and unsymmetrical isomers. The electronic effects accounting for this phenomenon are discussed. The structure of the unsymmetrical isomer of Os₃(CO)₁₀(PFc₂Ph)₂ (I) was determined.

![Diagram](I)

A large number of pyrolytic reactions of these complexes and/or pyrolytic reactions of M₃(CO)₁₂ (M=Os or Ru) with an appropriate ligand were studied in order to prepare metal cluster complexes containing unusual ferrocenyl moieties.

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These pyrolytic reactions mentioned above have afforded many interesting complexes containing two to five metal atoms with the most common one being three metal atoms. Over a hundred complexes, many of them novel, have been prepared and characterized by spectroscopic and analytical techniques. Over thirty of these have been structurally characterized by using X-ray crystallography, and over thirty await analysis.

The novel ferrocynne and ferrodicyne complexes (II) and (III) have been prepared via the pyrolysis of Os₃(CO)₁₁(PFc₂Ph) and Os₃(CO)₁₀[Fe'PiPr₂]₂ respectively and structurally characterized. Four series of complexes (IV), (V), (VI), and (VII) containing Fe (ferrocene)-M (Os or Ru) bonds have been characterized. Series (IV) and (V) show Fe-Os bond distances from 2.813(1) to 2.858(1) Å. Some other novel complexes include the first cluster naphthyne complex (VIII), the first μ₃-η¹,η¹,η⁶ bonded benzyne complex (VIV), complex (X) resulting from a CO insertion into an Os-R bond, complex (XI) derived from Ph₂S, complex (XII) obtained via i-
Pr and Fc C-H oxidative addition reactions, and complex (XIII) containing a \( \mu-\eta^1,\eta^5 \) bonded \( C_5H_4 \) moiety that is derived from a ferrocenyl group.

![Chemical structures](image)

Detailed reaction sequences have been proposed for the pyrolyses of \( M_3(CO)_{10}[Fe(P^{i}Pr_2)_2] \) (\( M=Os, Ru \)), \( Os_3(CO)_{11}(PFc_2Ph) \), \( Os_3(CO)_{11}(PFc^{i}Pr_2) \), and \( Os_3(CO)_{11}(PEt_2Fc) \). In addition to a common Fe-M bonding involvement, ferrocenyl groups have been found to undergo orthometalation, hetero-annular metalation, or both, and these reactions are more facile than alkyl C-H bond activation of ethyl and i-propyl groups. Ethyl and n-butyl groups
undergo α C-H activation only, while i-propyl groups undergo β C-H activation preferentially. Phenyl and ferrocenyl groups undergo C-P cleavages with the elimination of benzene and ferrocene, i-propyl groups are lost as propene.

In conclusion, this study has demonstrated that phosphine ligands on Ru₃ and Os₃ clusters are not inert to further reactions, and this reactivity has been used successfully to prepare a large number of unprecedented type of complexes.
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List of Abbreviations

Å         angstrom
a, b, c    unit cell dimensions
α, β, γ    unit cell angles
anal.      analysis
atm       standard atmosphere
bm        broad multiplet
bppf      bis(diphenylphosphino)ferrocene Fe(C5H4PPh2)2
BPK       sodium benzophenone ketyl radical anion Na+[PhCOPh]-
bs        broad singlet
nBu       n-butyl -CH2CH2CH2CH3
tBu       tert-butyl -C(CH3)3
Bz        benzyl -CH2C6H5
°C        degrees centigrade (Celsius)
13C       carbon
calc.      calculated
cm        centimeter (10^-2 m)
\( \text{cm}^3 \)  cubic centimeter (milliliter; 10^-6 m^3)
Cp        cyclopentadienyl C5H5 or C5H4 or C5H3
Cp*       pentamethylcyclopentadienyl C5Me5
Cy        cyclohexyl -C6H11
d         doublet
δ         chemical shift
°         degree (angle)
DCI       Desorption Chemical Ionization
dd        doublet of doublet
<table>
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<th>Full Form</th>
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<tr>
<td>dmpm</td>
<td>bis(dimethylphosphino)methane $\text{Me}_2\text{PCH}_2\text{PMe}_2$</td>
</tr>
<tr>
<td>dppa</td>
<td>bis(diphenylphosphino)acetylene $\text{Ph}_2\text{PC}≡\text{CPPPh}_2$</td>
</tr>
<tr>
<td>dpae</td>
<td>bis(diphenylarsino)ethane $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$</td>
</tr>
<tr>
<td>dpam</td>
<td>bis(diphenylarsino)methane $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$</td>
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<tr>
<td>dppb</td>
<td>bis(diphenylphosphino)butane $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$</td>
</tr>
<tr>
<td>dppe</td>
<td>bis(diphenylphosphino)ethane $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$</td>
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<td>cis-dppee</td>
<td>cis-bis(diphenylphosphino)ethylene cis-(Ph$_2$P)CH=CH(PPh$_2$)</td>
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<td>dppm</td>
<td>bis(diphenylphosphino)methane $\text{Ph}_2\text{PCH}_2\text{PPPh}_2$</td>
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<tr>
<td>dppp</td>
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<tr>
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<td>ethyl $-\text{CH}_2\text{CH}_3$</td>
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<tr>
<td>FAB</td>
<td>Fast Atom Bombardment</td>
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<td>Fc</td>
<td>ferrocenyl $(\text{C}_5\text{H}_4)\text{Fe(C}_5\text{H}_5)$</td>
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<tr>
<td>Fc'</td>
<td>ferrocenyl $(\text{C}_5\text{H}_4)\text{Fe(C}_5\text{H}_4)$</td>
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<td>ffars</td>
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</tr>
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<td>Hertz</td>
</tr>
<tr>
<td>IR</td>
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</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
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<td>L</td>
<td>general monodentate phosphine or arsine</td>
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<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>L-L</td>
<td>general bidentate phosphine or arsine</td>
</tr>
<tr>
<td>M</td>
<td>general transition metal</td>
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<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>m</td>
<td>milli</td>
</tr>
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<td>μ</td>
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<tr>
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</tr>
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</tr>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<td>PPN⁺</td>
<td>bis(triphenylphosphino) iminium (Ph₃P)₂N⁺</td>
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</tr>
<tr>
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</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
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</tr>
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<tr>
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<td>-------------------------------</td>
</tr>
<tr>
<td>t</td>
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</tr>
<tr>
<td>td</td>
<td>triplet of doublet</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TMEDA</td>
<td>tetramethylethylenediamine (\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>V</td>
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</tr>
<tr>
<td>X</td>
<td>halogen or halide F, Cl, Br, I</td>
</tr>
<tr>
<td>Z</td>
<td>number of molecules in a unit cell</td>
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DEDICATION

To my beloved Ying-min

Du bist wie eine Blume,
So hold und schon und rein;
Ich schau' dich an, und Wehmut
Schleicht mir ins Herz hinein.

Mir ist, als ob ich die Hande
Aufs Haupt dir legen sollt',
Betend, daß Gott dich erhalte
So rein und schon und hold.

Heinrich Heine
PART ONE: INTRODUCTION
Chapter 1 Benzyne, Ferrocyne, and Their Transition Metal Complexes

1.1 Benzyne

1.1.1 Historical Background

Soon after Kekule [1] and Wurtz [2] discovered the transformation of sodium benzenesulfonate to phenol by molten alkali in the 1860's, the preferred formation of resorcinol from the alkaline fusion of benzene-1,4-disulfonate [3] or 4-bromobenzenesulfonate [4] was reported (Scheme 1-1). It was also found that the action of the N-alkali-derivatives of ammonia or

Scheme 1-1 The preferred formation of resorcinol from benzene-1,4-disulfonate or 4-bromobenzenesulfonate.
amines upon aryl halides leads to substitution with rearrangement [5,6].

The first interpretation of these rearrangements in nucleophilic aromatic substitution reactions appeared in 1902 when Stoermer and Kahlert [7] rationalized the formation of 2-ethoxycoumarone from the reaction of 3-bromocoumarone with sodium ethoxide in terms of the aryne intermediate (1), Scheme 1-2.

\[
\begin{array}{c}
\text{OEt} \\
\text{Br} \\
\end{array} \rightarrow
\begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \rightarrow
\begin{array}{c}
\text{O} \\
\text{Et} \\
\end{array}
\]

Scheme 1-2 The first aryne intermediate proposed in a rearrangement reaction.

In 1927, Bachmann and Clarke [8] ascribed the small amount of triphenylene formed on treating chlorobenzene with sodium to a trimerization of 'phenylene radicals', \( \text{C}_6\text{H}_4 \). Wittig [9] postulated the 'dipolar phenylene' (2) as intermediate in the formation of \( \text{o-lithiobiphenyl} \) from the reaction of fluorobenzene with phenyllithium. He also discussed the structure of a neutral, triply bonded aryne (3). The dipolar phenylene (2) was also used by Morton et al. [10] to interpret the reaction of chlorobenzene with amylysodium.

\[
\begin{array}{c}
\text{C}_6\text{H}_4^+ \\
\text{C}_6\text{H}_4^- \\
\end{array}
\]

(2) (3)
Roberts et al. [11] studied the isotope distribution in aniline obtained from the reaction of chlorobenzene-(1-\(^{14}\)C) with potassium amide in liquid ammonia and coined the name "benzyne" for the proposed intermediate. A related reaction of fluorobenzene-(1-\(^{14}\)C) with phenyllithium, studied by Jenny et al. [12], is shown in Scheme 1-3. The \(^{14}\)C labelled benzyne intermediate (4) reacts in the indicated proportions. The small deviation from a 50:50 product ratio can be attributed to a kinetic isotope effect.

Scheme 1-3 Reaction of fluorobenzene-(1-\(^{14}\)C) with phenyllithium.

Huisgen et al. [13] found that both o- and m-fluoroanisole afford common products (5) and (6) upon treatment with phenyllithium and carbon dioxide. Similar reactions with \(\alpha\)- and \(\beta\)-fluoronaphthalenes yield (7) and (8) in the same ratio ((9) was also obtained from the \(\beta\)-isomer). Bunnett et al [14] and Sauer et al [15] found that lithium piperidide converts 1- and 2-halonaphthalenes to \(\alpha\)- and \(\beta\)-naphthylpiperidines in a constant isomer ratio (Scheme 1-4, \(X=\text{Cl, Br, I}\)). These results indicate a common intermediate 1,2-naphthyne (10).

The involvement of 'free' benzyne in some solution reactions is
implied from the results of a competition experiment [16]. When both furan and cyclohexadiene are present, benzyne generated by several different routes (Section 1.1.2) affords Diels-Alder addition products (11) and (12) in the same ratio.

1.1.2 Preparation of Benzyne

Benzyne may be prepared in a variety of ways. Dehalogenation of halobenzenes with strong bases such as amide ion or phenyllithium, as discussed above, remains a convenient and important route to benzyne.
Treatment of o-dihalobenzenes such as (13) with magnesium also produces benzyne [17].

The action of heat or light upon the zwitterionic salt (14) leads to benzyne [18]. A modification of this method involves the in situ diazotisation of anthranilic acid (15) with i-amyl nitrite in methylene chloride [19]. Photolysis of o-diiodobenzene [20] and of the iodonium salt (16) [21] produces benzyne. Thermolysis of phthalic anhydride [22] and of the benzothiadiazole (17) [23] also affords benzyne.

Benzyne can be generated by the lead tetraacetate oxidation of 1-amino-triazolo (18) [24], and by the reduction of nitroso compounds such as (19) with ethoxydiphenylphosphine [25]. A particularly gentle method
is to cover the salt (20) with tetrahydrofuran at 0°C and to allow the mixture to warm up to room temperature to produce benzyne [26].

1.1.3 Structure and Properties of Benzyne

Earlier descriptions suggest two formulations for benzyne. In the first of these, two carbon atoms have sp hybrid orbitals and there is a true triple bond (21). Severe distortions are necessary to obtain appreciable overlap between the sp$^2$- and sp-hybrid orbitals, accounting for the high reactivity of benzyne. A resonance structure can be written as in (22).

![Resonance structure diagram](image)

In the alternative description, the benzene ring retains its σ-bond skeleton with sp$^2$ hybridization and the geometry of a regular hexagon (23). The two electrons, forming the special bond of benzyne, occupy two sp$^2$ orbitals within the plane of the carbon atoms. The binding overlap of these orbitals will be very weak because they are not parallel but include an angle of 60°. Such a model would also account for the high reactivity of benzyne. If the electrons have parallel spins, a triplet state will result. However, this is an unlikely description for the ground state benzyne since there is no π bonding involved.

The resonance structure (22) has generally been accepted as the ground state representation of benzyne [27]. Benzyne has been subjected to theoretical calculations at various levels of sophistication [28-33].
1.1 shows bond lengths and angles obtained from an \textit{ab-initio} 6-31G*-based calculation [32]; the lengths are corrected values based on the standard C=C and C≡C bond lengths of 1.334 and 1.203 Å, respectively. The acetylenic bond length C1-C2 generally falls in the range 1.22-1.25 Å and is thus only slightly longer than a normal C≡C bond.

![Diagram of benzyne with bond lengths and angles]

Figure 1.1 Calculated bond lengths (Å) and bond angles (°) in benzyne.

The mass and UV spectra of benzyne can be measured by the use of various flash techniques [34,35].

The microwave spectrum of benzyne in the gas phase can be simulated by using the \textit{ab-initio} geometry, and the predicted and observed rotational constants agree to within 1% [36]. The IR spectrum of benzyne, measured in an argon matrix, shows a C≡C stretching band at 2085 cm\(^{-1}\), which is only slightly lower than the value of ca. 2200 cm\(^{-1}\) in acyclic alkynes [37].

1.1.4 Reactions of Benzyne

Benzyne is a short-lived species, and the short lifetime of free benzyne was first demonstrated by passing argon saturated with di-(o-
iodophenyl)mercury through a hot zone at 750°C and observing the ability of the emerging gas to add to furan as a function of the distance from where it was formed [38]. It can be observed by using spectroscopic methods in an argon matrix at low temperatures or at low pressure in the gas phase as mentioned above [36,37,39-41]. In the absence of other reagents, benzyne dimerizes to biphenylene (24) and in some cases trimerizes to triphenylene (25) [34,35,42].

Benzyne often acts as an electron deficient species. A number of addition reactions of metallorganic substances and metal amides to benzyne have already been mentioned (Section 1.1.1). If one of the carbon atoms adjacent to the benzyne triple bond carries an atom or group that is nucleophilic, cyclization readily occurs and a wide variety of heterocyclic compounds can be prepared this way [43]. For example, compounds (26) and (28) can be synthesized from (27) and (29), respectively.
A well studied reaction of benzyne is the Diels-Alder reaction in which benzyne acts as a dienophile. The benzofuran (30), for example, traps benzyne effectively to give 7-oxanorbornadienes such as (31). Pyrroles also react with benzyynes, but the products undergo further reactions to form β-naphthylamines (32) [44]. Tetracyclone (33) is also frequently used to trap benzyynes and the adducts generally split off carbon monoxide rapidly to give 1,2,3,4-tetraphenylnaphthalenes (34). Even benzene [45] and naphthalene [46] react readily with benzyne to give benzo- and dibenzobarrelene, (35) and (36), respectively.

Benzyne can also react with an olefin. A remarkable example is the reaction of o-bromofluorobenzene (13) and 3,4-dichlorotetramethylcyclobutene with lithium amalgam in ether to form (37) [47]. Benzyne can even add to more widely separated centers; tetrachlorobenzyne reacts with norbornadiene to give product (38) together with some [2+2] cycloadDITION product (39) [48]. Benzyne can add to longer conjugated systems; thus, the thermal decomposition of o-benzenediazonium carboxylate (14) in the absence of other trapping reagents gives (40) [49].

Most recently, reactions of benzyne with fullerenes have been studied and a series of compounds of the composition C_{60+}(C_6H_4)_n (n=1, 2, 3, 4) were identified by using mass spectroscopy [50]. The monoaddition
product was isolated by using chromatography and structurally characterized by $^1$H and $^{13}$C NMR spectroscopy [50].

1.2 Transition Metal Complexes of Benzyne

1.2.1 Introduction

During the development of organometallic chemistry, especially that of the transition metals, the ability of metal containing moieties to stabilize highly reactive organic fragments such as carbene, carbyne, and cyclobutadiene, on one hand, and to activate stable molecules towards selective attack, on the other, have been well established and extensively studied. For example, cyclobutadiene is too reactive to be isolated, but coordination to a transition metal fragment stabilizes this molecule. The first complex of unsubstituted cyclobutadiene to be isolated was ($\eta^4$-C$_4$H$_4$)Fe(CO)$_3$ (41), pre-
pared in 1965 as in Equation (1.1) [51]. Cyclobutadiene(cyclopentadienyl) cobalt (42) was later prepared as in Equations (1.2) and (1.3) [52,53]. The most interesting aspect of these compounds is that the cyclobutadiene can be liberated and trapped with various organic substrates. Oxidation of (η⁴-C₄H₄)Fe(CO)₃ (41) with Ce⁴⁺ generates transient, free cyclobutadiene which reacts with alkynes to give Dewar-benzene derivatives, while its treatment with p-quinones opens up an elegant route for the synthesis of cubane as shown in Scheme 1-5 [54].

The first unsuccessful attempts to form transition metal complexes of benzyne made by Wittig and Bickelhaupt [55] involved the treatment of 1,2-dilithiobenzene with various transition metal salts. An attempt to
Scheme 1-5 Synthesis of cubane by using $(\eta^4$-$C_4H_4)$Fe(CO)$_3$ (41) as a source of free cyclobutadiene.

prepare Pt(PPh$_3$)$_2$(C$_6$H$_4$) by treating 1,2-dilithiobenzene with cis-PtCl$_2$(PPh$_3$)$_2$ was also unsuccessful [56] as were other early efforts to trap benzyne, generated from suitable precursors, by zero valent platinum complexes. Thermal decomposition of 1,2-benzenediazonium carboxylate (14) or benzo-1,2,3-thiadiazole-S,S-dioxide (17) in the presence of Pt(PPh$_3$)$_2$(C$_2$H$_4$) or Pt(PPh$_3$)$_4$, Scheme 1-6, are two examples. The metallacyclic platinum(II) complexes (43) and (44) are the final products [57-59]. These are resistant to CO$_2$ or SO$_2$ elimination to give a benzyne complex. UV irradiation of (45) does generate free benzyne which can be trapped with furan or tetracyclone [57,59]. Free benzyne also inserts into the acetylide-metal bond of the nickel(II) complex (46) as in Equation (1.4) [60].
Scheme 1-6 Reaction of benzyne precursors with Pt(0) complexes [27].

Reaction of Ni(CO)₄ with 1,2-diiodobenzene was reported to give a benzyne complex [61], but it was later shown to be a polymeric nickel(IV) complex (47) [62].

The first indication of a benzyne transition metal complex was the reactivity change associated with the presence of silver ion observed for the cycloaddition of benzyne to benzene (Scheme 1-7) [63]. The normal
1,4-cycloaddition to give benzobarrelene (35) is suppressed and the main products become benzocyclooctatetraene and biphenyl. A silver-benzyne complex (48) is thought to be involved. Similar effects are observed in other cycloadditions of benzyne [64-66].

Scheme 1-7 Influence of Ag⁺ on the cycloaddition of benzyne to benzene.

In the course of studying the thermal substitution reactions of PPh₃ with Os₃(CO)₁₂ in 1972, Bradford, Nyholm and coworkers isolated and characterized by X-ray crystallography the first three benzyne complexes (49), (50), and (51) [67-69]. Since then, many transition metal stabilized benzyne complexes have been isolated, both with early and late transition metals. Though the largest number of these complexes contain three metal
atoms like Ru₃ and Os₃, complexes in which benzyne is stabilized by one, two, four, and five metal centers are known.

\[
\begin{align*}
\text{(49)} & \quad \text{(50)} & \quad \text{(51)}
\end{align*}
\]

1.2.2 Mononuclear Metal Complexes of Benzyne

Two limiting modes of coordination of benzyne, (52a) and (52b), to a metal center are possible. The contributions from each depend on the metal center and its ligands.

\[
\begin{align*}
\text{(52a)} & \quad \text{(52b)}
\end{align*}
\]

1.2.2.1 Complexes of early transition metals and actinoid elements

Benzyne complexes are generally implicated as reactive intermediates in the thermal decomposition of perphenyl derivatives of the early transition metals, and of uranium and thorium. A benzyne-chromium complex is probably involved in the hydrolytic σ- to \(\eta^6\)-rearrangement of Cr(C₆H₅)₃(THF)₃ to Cr(C₆H₆)₂⁺ [70]. Heating Cp₂TiPh₂ (53) gives mainly benzene with almost no biphenyl formation. The benzene is formed by elimination of one phenyl group and a hydrogen atom from the ortho-
position of the other phenyl group [71-73]. A benzyne intermediate such as (54) is implied which can be trapped with alkynes [74-76], carbon dioxide [77] or selenium [78], to give the expected titanacycles (55)-(57) as shown in Scheme 1-8. Compound (54) is probably also formed when Cp₂TiCl₂ is treated with 1-bromo-2-fluorobenzene (13) and magnesium because in the presence of diphenyl-acetylene the titanacycle (55) (R=R'-Ph) was isolated [79].

![Scheme 1-8 Generation and trapping of [Cp₂Ti(C₆H₄)] (54).](image)

Heating Cp₂TiPh₂ (53) or its 3- or 4-tolyl analogues in benzene or ether at 80-130°C under nitrogen (100 atm) affords small amounts of aniline or the appropriate toluidine in addition to the main product ammonia [80]. Reaction of Cp₂TiCl₂ with 1-bromo-2-fluorobenzene (13) and magnesium under N₂ (100 atm) also gives aniline. A nitrogen insertion product (58) is believed to derive from (54) and N₂. The aromatic amines are not formed in the corresponding zirconium systems [80].
Zirconium complexes $\text{Cp}_2\text{Zr}(\text{aryl})_2$ on heating in aromatic solvents undergo aryl group exchange with the solvent (Scheme 1-9) [81, 82]. These reactions suggest a 16 electron aryne-metal intermediate (e.g. (59)).

$$\text{Cp}_2\text{Zr}(p-\text{C}_6\text{H}_4\text{Me})(\text{C}_6\text{H}_5)$$

(59)

$$\text{Cp}_2\text{Zr}(m-\text{C}_6\text{H}_4\text{Me})_2$$

(60)

Scheme 1-9 Aryl group exchange in $\text{Cp}_2\text{Zr}(\text{aryl})_2$.

Typical reactions of $[\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_4)]$ (60) are shown in Scheme 1-10. Ethylene inserts to give the zirconaindan (61) [83], and cis- and trans-stilbene insert specifically to give (62) and (63) respectively [84]. Cyanides insert to give azazirconacyclopentenes (68) [85]. The oxophilicity of the $\text{Cp}_2\text{Zr}$ unit of (60) is clearly seen from its reaction with $\text{W(CO)}_6$ to give (69) [86].

Complex (60) can be trapped as a stable trimethylphosphine adduct (70) whose structure was determined by X-ray crystallography [87]. Ready displacement of PMe$_3$ in (70) provides a convenient alternative source of (60). Some insertion reactions of (70) and its methanolysis to give (71) are shown in Scheme 1-11.

The zirconaindan complex (64) obtained from (60) and 1-hexene undergoes olefin exchange on heating with norbornene to give a new zirconaindan complex (65) (Scheme 1-12). This implies that benzyne complexes (66) and (67) are in equilibrium with (64) and (65) respectively [83].
Scheme 1-10 Reactions of \( \text{[Cp}_2\text{Zr(C}_6\text{H}_4\text{)] (60)} \) [27].

Scheme 1-11 Reactions of \( \text{Cp}_2\text{Zr(C}_6\text{H}_4\text{)(PMe}_3\text{)} (70) \).
A more general route to aryne-zirconocene complexes involves the treatment of Cp₂ZrCl(Me) with an aryllithium [88]. The resulting complex Cp₂Zr(aryl)(Me) readily loses methane on heating to give the transient aryne complex (72) which can be trapped with cyanides (Scheme 1-13) or ethylene (Scheme 1-14) [88]. The zirconacycles can be converted into organic products such as aromatic ketones and 2-iodo-phenylketones, isothiazoles (Scheme 1-13) and dihydrocyclobutabenzenes (Scheme 1-14). The high regiospecificity in the reactions in Scheme 1-13 is presumably due to steric hindrance of the substituents X [88].

Phenyl derivatives of bis(pentamethylcyclopentadienyl)zirconium [89,90], -uranium [90], and -thorium [91] also undergo phenyl group exchange with aromatic solvents, and the intermediate benzyne complexes can be trapped with ethylene or diphenylacetylene. A solution of Cp₂*ZrD(Ph) in C₆D₆ incorporates deuterium in both the phenyl ring and in the Cp* methyl groups at room temperature; these processes probably proceed via the benzyne complex (73) (Scheme 1-15). When either Cp₂*ZrPh₂ or Cp₂*ZrH(Ph) is heated in benzene, the cyclometalated complex (74) is formed by hydrogen transfer from a Cp* methyl group to the coordinated benzyne [89,90]. Similar processes occur on heating complexes Zr(η⁵-
Scheme 1-13 Synthesis and reactions of \([\text{Cp}_2\text{Zr}(\text{aryne})]\) (72) [27].
(a) Only one isomer observed for \(X=\text{OMe, Me}\).

Scheme 1-14 Synthesis of dihydrocyclobutabenzenes from (72).
(a) Mixture of regioisomers.
Scheme 1-15 Hydrogen/deuterium exchange in Cp₂²Zr(D)(Ph).

\[ \text{Equation 1.5} \]

\[ \text{C₅H₄CMe₂Ph}_2 \text{Ph}_2 \text{ and Zr}(η⁵-C₅H₄CMe₃)_₂\text{Ph}_2; \text{ the former undergoes a phenyl C-H bond activation of the CMe₂Ph substituent preferentially (Equation 1.5)} [92]. \]

Scheme 1-16 shows the reaction of Ph₃P=CH₂ with [Cp₂Zr(C₆H₄)] (60)
to give the phenylzirconium(IV) complex (75), probably via an intermediate zirconium(II) complex. A hydrogen atom is transferred from the ylide to the coordinated benzyne. The 4-methylbenzyne complex (59) reacts with Ph₃P-CH₂ similarly to give a mixture of 3- and 4-tolyl derivatives [93]. The titanium analogue of (59) behaves similarly, but here a competing reaction also occurs in which PPh₃ is eliminated and CH₂ inserts into the titanium-aryne bond to give (76) and (77) [94].

![Scheme 1-16 Reaction of [Cp₂Zr(C₆H₄)] (60) with Ph₃P-CH₂.](image)

The elimination of benzene or an alkane from appropriate precursor complexes has given benzyne complexes of Nb, Ta, Mo, W, and Re. For example, Cp⁺M(Ph)Me₃ (M=Ta, Nb) lose methane on heating to give benzyne complexes (78) and (79) [95]. Complex (78) was the first
mononuclear benzyne complex to be structurally characterized [95,96]. The reaction of \( \text{Cp}_2^*\text{TaCl}_2 \) with \( \text{PhLi} \) (1:2 molar ratio) also gives benzyne complex \([\text{Cp}_2^*\text{Ta}(C_6H_4)H]\) (81) directly. This compound was shown to be in equilibrium with the \( \sigma \)-phenyl complex \( \text{Cp}_2^*\text{Ta}(C_6H_5) \) [97]. The reaction of \( \text{Ph}_2\text{Zn} \) with \( \text{Cp}^*\text{Ta(CH}_2\text{CMe}_3)\text{Cl}_3 \) (Equation 1.6) gives the benzyne complex (80) without the presumed intermediate being detected [95].

\[
\text{Cp}^*\text{Ta(CH}_2\text{CMe}_3)\text{Cl}_3 + \text{Ph}_2\text{Zn} \rightarrow [\text{Cp}^*\text{Ta(CH}_2\text{CMe}_3)(\text{Ph})\text{Cl}_2] -\text{CMe}_4
\]

A series of benzyne complexes of general formula \([\text{Li(Et}_2\text{O})]_n\text{[M(C}_6\text{H}_4)_2\text{(C}_6\text{H}_5)_4]\) are formed from \( \text{MCl}_5 \) (M=Ta, Nb, W, and Mo) and \( \text{PhLi} \) or aryl\( \text{Li} \) in ether [98-102]. Hexaphenylmetalates of the general formula \([\text{Li(Et}_2\text{O})]_n\text{[M(C}_6\text{H}_5)_6]\) are likely precursors to the bis(benzyne) complexes [98, 99]. Table 1-1 summarizes the compounds described to date with the formal oxidation states and electron configurations of the metal atoms. Benzyne is regarded as a neutral or a dianionic ligand. The products isolated from these reactions are very sensitive to slight changes in experimental conditions and to the reagents used.

Complexes with the empirical formulae (88) and (89) have been structurally characterized [103]. The niobium center in (88) has an approximately trigonal bipyramidal geometry with both \( \eta^2 \)-benzyne ligands in equatorial positions. The tantalum center in (89) is coordinated.
Table 1-1. Anionic bis(aryne) complexes isolated from reactions of early transition metal pentahalides with aryllithium reagents [27].

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products^a</th>
<th>Oxidation state, d^n</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbBr5/PhLi/Et2O</td>
<td>(82)^b Nb(0),d^5 (Nb(IV),d^1)</td>
<td>98,100</td>
<td></td>
</tr>
<tr>
<td>TaBr5/PhLi/Et2O</td>
<td>(83) Ta(0),d^5 (Ta(IV),d^1)</td>
<td>97b,100</td>
<td></td>
</tr>
<tr>
<td>TaBr5/PhLi/Et2O</td>
<td>(84)c Ta(I),d^4 (Ta(V),d^0)</td>
<td>97b,100</td>
<td></td>
</tr>
<tr>
<td>MoCl5/PhLi/Et2O</td>
<td>(85) Mo(0),d^6 (Mo(IV),d^2)</td>
<td>97b</td>
<td></td>
</tr>
<tr>
<td>WBr5/PhLi/Et2O</td>
<td>(86) W(0),d^6 (W(IV),d^2)</td>
<td>98,100</td>
<td></td>
</tr>
<tr>
<td>WBr5/4-tolylLi/Et2O</td>
<td>(87) W(0),d^6 (W(IV),d^2)</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>NbCl5/PhLi/THF</td>
<td>(88)d Nb(-I),d^6 (Nb(III),d^2)</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>TaCl5/PhLi/THF</td>
<td>(89)e Ta(I),d^4 (Ta(V),d^0)</td>
<td>102</td>
<td></td>
</tr>
</tbody>
</table>

a. [Li(Et20)]_4[Nb(C6H4)2(C6H5)4] (82) [Li(Et20)]_4[Ta(C6H4)2(C6H5)4] (83) [Li(Et20)]_3[Ta(C6H4)2(C6H5)4] (84) [Li(Et20)]_4[Mo(C6H4)2(C6H5)4] (85) [Li(Et20)]_4[W(C6H4)2(C6H5)4] (86) [Li(Et20)]_4[W(C6H3Me)2(p-C6H4Me)4] (87) [Li(THF)]_4[Nb(C6H4)2(C6H5)3][C6H5Li(THF)]·0.5THF·0.5C6H14 (88) [Li(THF)]_2[Li4Cl2(THF)_10]Ta(C6H4)2(C6H5)4 (89) b. Thermally unstable.


e. Contains six-coordinated Ta.

in approximately octahedral geometry with two $\eta^2$-benzyne ligands in a cis arrangement. If C6H4 is regarded as dianionic, the coordination geometries of (88) and (89) are approximately pentagonal bipyramidal and square anti-prismatic, respectively. These anions are thought to be stabilized by
extensive secondary interactions between solvated lithium ions and carbon atoms of the \( \text{C}_6\text{H}_4 \) and \( \text{C}_6\text{H}_5 \) moieties.

The benzyne tantalum complex (91) is in equilibrium with the phenyl-substituted metallaspiro complex (90) at 120°C [104, 105]. A hydrogen atom transfers reversibly between the phenyl group and the Ta-CH\(_2\) group (Equation 1.7).

The aryne complex \( \text{Mo(\eta}^2\text{-3-C}_6\text{H}_3\text{Me)(2-MeC}_6\text{H}_4)_2(\text{PMe}_2\text{Ph})_2 \) (92) is formed by the interaction of \( \text{PMe}_2\text{Ph} \) with \( \text{Mo(2-MeC}_6\text{H}_4)_4 \), and the analogous complex \( \text{W(\eta}^2\text{-3,6-C}_6\text{H}_2\text{Me}_2)(2,5-\text{Me}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2 \) (93) is obtained similarly from \( \text{PMe}_3 \) and \( \text{W(2,5-\text{Me}_2\text{C}_6\text{H}_3)_4 \) [106]. Both structures have been determined and they have approximate trigonal bipyramidal geometries around the metal center. Similar reactions of \( \text{Re(2-MeC}_6\text{H}_4)_4 \) with \( \text{PMe}_3 \) or \( \text{PMe}_2\text{Ph} \) afford paramagnetic 3-methylbenzyne complexes (94) [107, 108]. They undergo facile reversible oxidation to the diamagnetic cations (95) (Equation 1.8). X-ray crystallographic analyses of (94) (L-\( \text{PMe}_2\text{Ph} \)) and (95) (L-\( \text{PMe}_3 \), I\(_5^-\) salt) show that both have approximately trigonal bipyramidal structures. Unlike some other benzyne complexes, these two compounds are remarkably inert towards a variety
of substrates such as olefins, acetylenes, acetonitrile, and acetone.

No benzyne complexes of hafnium, vanadium, chromium, manganese and the lanthanides have been observed or implicated as reaction intermediates. Also, the chemistry of benzyne complexes has been largely developed from titanium and zirconium complexes, and relatively little attention has been paid to the complexes of niobium, tantalum, molybdenum, and tungsten.

1.2.2.2 Complexes of Late Transition Metals

The possible involvement of a silver-benzyne complex in the cycloaddition of benzyne to benzene has been mentioned (Section 1.2.1), but no effort has been made to stabilize or isolate such complexes.

Despite early unsuccessful attempts to stabilize benzyne on platinum centers (Section 1.2.1), the first well characterized mononuclear group 8 metal benzyne complex, a nickel(0)-benzyne complex (96), was obtained as shown in Scheme 1-17 and the structure of (96) was determined by X-ray crystallography [109]. Complexes NiL2(C6H4) (L=PCy3, PiPr3) were obtained similarly [27], although the PEt3 complex was assigned a dimeric μ-o-phenylene structure [110].
Compound (96) or its analogues cannot be prepared by using procedures analogous to those used to prepare the zirconocene compounds since on heating, diphenyl- or methyl(phenyl)nickel(II) complexes undergo reductive elimination rather than hydrogen abstraction. Convenient high yield routes to the (2-halogenphenyl)nickel(II) halide precursors are shown in Scheme 1-18 [27].

Scheme 1-17 Preparation of Ni(Cy$_2$PCH$_2$CH$_2$PCy$_2$)(C$_6$H$_4$) (96).

Scheme 1-18 Preparation of (2-halogenphenyl)nickel(II) halide complexes [27].
Mononuclear platinum-benzyne complexes \( \text{PtL}_2(\text{C}_6\text{H}_4) \) (2L = 2PEt\(_3\), 2PCy\(_3\), 2\( \text{P}^{\text{i}}\)Pr\(_3\), Cy\(_2\)PCH\(_2\)CH\(_2\)PCy\(_2\)) have been prepared similarly [27]. Tertiary phosphines in \( \text{M}(\text{P}^{\text{i}}\text{Pr}_3)_2(\text{C}_6\text{H}_4) \) (M = Ni, Pt) can be replaced by less bulky phosphines, thus \( \text{M}(\text{PMe}_3)_2(\text{C}_6\text{H}_4) \) (M = Ni, Pt) and \( \text{Pt}(\text{P}^{\text{i}}\text{Pr}_3)L(\text{C}_6\text{H}_4) \) (L = PMe\(_3\), PEt\(_3\), PPh\(_3\), PMe\(_2\)Ph, PMePh\(_2\)) have been characterized [27].

These benzyne complexes are very sensitive to water, alcohols, and other protic solvents. For example, the nickel complex (96) reacts rapidly with primary and secondary alcohols to give alkoxides; these are unstable at room temperature and form the nickel(0) complexes of aldehyde or ketone with elimination of benzene (Equation 1.9) [109]. The benzyne-nickel bond in (96) is also attacked by other electrophiles such as iodine and methyl iodide and undergoes insertion with CO\(_2\), ethylene, and dimethyl acetylenedicarboxylate to give metallacycles (Scheme 1-19) [109]. Whereas acetonitrile inserts into the benzyne-zirconocene complex (60), it is deprotonated by (96). Also in contrast with \([\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_4)]](60), \(96)\) does not undergo insertion with diphenylacetylene; instead, the benzyne is displaced to give \(\text{Ni}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{Ph-CEC-Ph})\) [109].

A very reactive ruthenium benzyne complex \((\text{PMe}_3)_4\text{Ru}(\eta^2-\text{C}_6\text{H}_4)\) (98) has been reported and structurally characterized [111]. It is generated by heating the cis-diphenyl or the cis-methyl (phenyl) precursors. The ruthenium-benzyne bond in (98) reacts with a wide range of substrates.
Scheme 1-19 Reactions of Ni(Cy2PCH2CH2PCy2)(C6H4) (96) [27].

that are typically inert toward late transition metal-carbon bonds, including those in benzyne complexes [109, 112]. The reactions are summarized in Scheme 1-20. The reaction with C6D6 parallels that in the zirconium system (Scheme 1-9), but with PhCH3 simple exchange does not take place, instead a methyl C-H is also activated to give the 4-membered metallacycle. Benzaldehyde inserts into the ruthenium-benzyne bond just as acetone inserts into the zirconium benzyne trimethylphosphine adduct (70), however, acetone undergoes C-C bond cleavage in reaction with (98) to form the unusual compound (99). Interestingly, the reaction of acetophenone with (98) also gives (99) presumably by way of the phenyl enolate complex (100).

There are no known mononuclear benzyne complexes of iron, osmium, cobalt, rhodium, iridium, copper, gold, zinc, cadmium, mercury,
and most remarkably palladium. The rich chemistry of the ruthenium benzyne complex (98) and the zirconium benzyne complexes (60) and (70) are particularly accessible and general applications of these benzyne complexes in synthesis may be expected.

Scheme 1-20 Preparation and reactions of (PMe₃)₄Ru(η²-C₆H₄) (99).

1.2.2.3 Structure and Bonding of Benzyne in Mononuclear Metal Complexes

Table 1-2 compares the benzyne C-C bond lengths determined by X-ray crystallography in various complexes with those in free benzyne as
obtained by an *ab-initio* calculation [32]. In all cases the "acetylenic" bond (C1-C2) is lengthened on coordination; the remaining C-C bonds are of about the same length as those in free benzyne. The greatest deviation is found in complex (92) where C2-C3 (1.52±0.06 Å) and C6-C1 (1.60±0.06 Å) are much longer and C5-C6 (1.26±0.06 Å) much shorter than the corresponding lengths in free benzyne.

**Table 1-2. Comparison of C-C bond lengths in metal benzyne complexes with those in free benzyne**a [27].

<table>
<thead>
<tr>
<th></th>
<th>C6H4b (70)</th>
<th>(88)</th>
<th>(89)</th>
<th>(78)</th>
<th>(92)c</th>
<th>(93)c</th>
<th>(94)c</th>
<th>(95)c</th>
<th>(98)</th>
<th>(96)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>1.240(1)</td>
<td>1.364(5)</td>
<td>1.276(16)</td>
<td>1.431(33)</td>
<td>1.34(1)</td>
<td>1.39(2)</td>
<td>1.355(3)</td>
<td>1.332(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.410(7)</td>
<td>1.402(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.393(1)</td>
<td>1.389(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.410(5)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.402(1)</td>
<td>1.383(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.362(2)</td>
</tr>
<tr>
<td></td>
<td>1.388(8)</td>
<td>1.380(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.421(1)</td>
<td>1.380(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.403(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.416(7)d</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.404(9)d</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.402(1)</td>
<td>1.377(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.375(6)</td>
</tr>
<tr>
<td>C6-C1</td>
<td>1.393(1)</td>
<td>1.406(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.408(6)</td>
</tr>
</tbody>
</table>

a. Carbon atoms numbered as in Figure 1-1. b. Calculated values from ref. 32. c. The carbon where methyl attaches is numbered 3. d. C4-C5 is the shortest bond.

Benzyne behaves as a two electron donor in (70), (96) and (98) and these are saturated complexes. The nickel complex (96) is similar to other 16 electron ML₂(alkyne) (M-Ni, Pt) complexes. Though the C1-C2 bond
The length of 1.322(6) Å is greater than the value of 1.29 Å typical of most ML₂(alkyne) complexes, the lengthening on coordination relative to the free ligand is about the same [27]. All the other C-C bonds in (70) and (96) are almost equal and show no variation indicating delocalization of the π electrons. Thus a reasonable representation would be structure (101). In complex (98), the C-C bonds do show alternation indicating slight localization of the aromatic π electrons though the average value 1.385 Å does not differ from those of (70) and (96). An appropriate representation is structure (102).

All the other complexes listed in Table 1-2 are unsaturated electronically, and the benzyne most probably donates two to four electrons. The bond lengths of the rhenium complexes (94) and (95) do not show clear alternation, and the authors suggest that these structures be best described as a rhenacyclop propane type with a delocalized aromatic benzyne ring (structure (103)).

The molybdenum and tungsten benzyne complexes (92) and (93) seem to have relatively large deviations in the bond lengths, and structure (104) is possibly the best representation of the benzyne bonding.

The niobium and tantalum complexes (88) and (89) have shorter M-C (aryne) (by 0.07-0.14 Å) bonds than the other complexes in Table 1-2, and these bonds are presumably stronger than the σ-M-C (aryl) bonds. The C1-C2 (aryne) distances in (88) and (89) (average 1.414(8) and 1.393(8) Å respectively) are slightly longer than those in (70) and (78). The remaining
C-C distances in (88) and (89) show very small, if any, variation and the bonding can be represented by structure (103).

Finally the tantalum complex (78) is highly electron-deficient. The C1-C2 distance is similar to those in (70), (89), (94) and (98), but the remaining C-C distances show a similar long-short alternation as found in (92). Also, the benzyne ligand in (78) is oriented perpendicular to the plane of the Cp* ring, whereas in the ethylene complex Cp*TaMe2(C2H4) the olefin is parallel to this ring. These observations led to the suggestion that both sets of orthogonal benzyne π-orbitals are involved in bonding to the metal [94,95]. Thus benzyne bonding in (78) could be represented as in structure (105).

1.2.3 Metal Cluster Complexes of Benzyne

By far the largest number of known benzyne complexes are those based on triruthenium and triosmium carbonyl metal frameworks [27, 113]. No benzyne cluster complexes of other metals have been described. Much attention has been paid to the structures and fluxional behaviour of these benzyne complexes; relatively little attention has been paid to their chemistry [114].

1.2.3.1 Ruthenium Cluster Complexes of Benzyne

The first three ruthenium cluster benzyne complexes Ru3(μ3-C₆H₃R')(PR₂)₂(CO)₇ (R'=H, R=C₆H₅, (106a); R'=Me, R=3-MeC₆H₄, (106e); R'=Me, R=4-MeC₆H₄, (106f)) were isolated following the pyrolysis of Ru₃(CO)₉(PR₃)₃ (R=Ph, 3-MeC₆H₄, 4-MeC₆H₄) in refluxing decalin or mesitylene, and were characterized on the basis of analytical and spectroscopic data [115]. The
crystal structure of (106a) was determined later [116] revealing that it belongs to a structural series known previously for osmium (e.g. structure (49)). Complex (106a) was also obtained from the pyrolysis of Ru$_3$(CO)$_{10}$ (PPh$_3$)$_2$ and Ru$_3$(CO)$_{11}$(PPh$_3$) [117, 118]. The latter starting material also afforded a tetra-nuclear benzyne complex Ru$_4$(CO)$_{10}$($\mu$-CO)($\mu$$_4$-C$_6$H$_4$)($\mu$$_4$-PPh) (107a) and a penta-nuclear benzyne complex Ru$_5$(CO)$_{13}$($\mu$$_5$-C$_6$H$_4$)($\mu$$_4$-PPh) (108a), the structures of both have been determined [117, 118]. Complexes (106e) and (106f) were also obtained from the pyrolysis of Ru$_3$(CO)$_{11}$($\text{PR}_3$) (R=3-MeC$_6$H$_4$, 4-MeC$_6$H$_4$) which in addition afforded the tetra-nuclear benzyne complexes Ru$_4$(CO)$_{10}$($\mu$-CO)($\mu$$_4$-C$_6$H$_3$R')($\mu$$_4$-PR) (R'=Me, R=3-MeC$_6$H$_4$, (107d); R'=Me, R=4-MeC$_6$H$_4$, (107e)) [118]. Pyrolysis of Ru$_3$(CO)$_{11}$($\text{Ph}_2\text{PCH}_2\text{NPh}_2$) afforded the tetra-nuclear benzyne complex Ru$_4$(CO)$_{10}$($\mu$-CO)($\mu$$_4$-C$_6$H$_4$)($\mu$$_4$-P$\text{CH}_2\text{NPh}_2$) (107b) and its structure was determined [117, 118]. Pyrolysis of Ru$_3$(CO)$_{11}$($\text{AsPh}_3$) afforded both the tetra-nuclear Ru$_4$(CO)$_{10}$($\mu$-CO)($\mu$$_4$-C$_6$H$_4$)($\mu$$_4$-AsPh) (107f) and the penta-nuclear benzyne complexes Ru$_5$(CO)$_{13}$($\mu$$_5$-C$_6$H$_4$)($\mu$$_4$-AsPh) (108b), but no analogue of (106a) [118]. Pyrolysis of Ru$_3$(CO)$_{11}$($\text{PPh}_2\text{Me}$) gave a hexa-nuclear bis(benzyne) complex Ru$_6$(CO)$_{12}$($\mu$$_4$-PMe)$_2$($\mu$$_3$-C$_6$H$_4$)$_2$ (109) whose structure was determined [118]. An attempt to trap ferrocyne by pyrolysis of Ru$_3$(CO)$_{10}$($\text{PFcPh}_2$)$_2$ was unsuccessful, instead the benzyne complex (106b) was obtained in good yield [119]. Further effort in this respect involving Ru$_3$(CO)$_{10}$[Fc'($\text{PPh}_2$)$_2$] as a potential source of ferrocyne led to the characterization of a number of products, and while no ferrocyne derivatives were isolated, two benzyne complexes (106c) and (107c) were obtained and characterized by X-ray diffraction studies [120]. A similar attempt to trap (benzyne)chromium tricarbonyl via pyrolysis of Ru$_3$(CO)$_{11}$($\text{PPh}_2[\text{C}_6\text{H}_5\text{Cr(CO)}_3]$) led to the complex (106d) [121].
Remarkably similar structures were found in the series (106a)-(106d). Table 1-3 summarizes some important bonding parameters for these complexes and the numbering scheme is shown in Figure 1.2. In the structures, Ru(1)-Ru(2) and Ru(2)-Ru(3) are asymmetrically bridged by the phosphido groups $P_A$ and $P_B$, respectively. One of the CO groups on Ru(1) is semibridging with Ru(3); all other CO groups are normal terminal carbonyls. Ru(1)-Ru(2) is significantly longer than the other two Ru-Ru bonds with Ru(2)-Ru(3) being slightly longer than Ru(1)-Ru(3). $P_A$ lies above the Ru$_3$ plane on the same side as the benzyne moiety, while $P_B$ is situated below the Ru$_3$ plane.

\[
\begin{align*}
\text{a, } PR_2 &= PPh_2, PPh_2, R' = H \\
\text{b, } PR_2 &= PFcPh, PFcPh, R' = H \\
\text{c, } PR_2 &= PFcPh, PPh_2, R' = H \\
\text{d, } PR_2 &= PPh[(C_6H_5)Cr(CO)_2], PPh[(C_6H_5)Cr(CO)_2], R' = H \\
\text{e, } PR_2 &= P(m-MeC_6H_4)_2, P(m-MeC_6H_4)_2, R' = Me \\
\text{f, } PR_2 &= P(p-MeC_6H_4)_2, P(p-MeC_6H_4)_2, R' = Me
\end{align*}
\]

(106)

\[
\begin{align*}
\text{a, } \text{ER} &= PPh, R' = H \\
\text{b, } \text{ER} &= \text{PCH}_2\text{NPh}_2, R' = H \\
\text{c, } \text{ER} &= \text{PFc}, R' = H \\
\text{d, } \text{ER} &= \text{P}(m-MeC_6H_4), R' = \text{Me} \\
\text{e, } \text{ER} &= \text{P}(p-MeC_6H_4), R' = \text{Me} \\
\text{f, } \text{ER} &= \text{AsPh}, R' = H
\end{align*}
\]

(107)
Though complex (106a) has no possible geometrical isomers, complexes (106b), (106c), and (106d) have at least one other possible isomer (e.g. with the bulky ferrocenyl or (phenyl)chromium tricarbonyl group on \( P_A \) lying on the other side of the \( \text{Ru}_3 \) plane. In both (106b) and (106c), the ferrocenyl group on \( P_A \) points to benzyne side of the \( \text{Ru}_3 \) plane. The (phenyl)chromium tricarbonyl moiety on \( P_A \) in (106d) has the same arrangement. The ferrocenyl and (phenyl)chromium tricarbonyl groups on \( P_B \) in (106b) and (106d), respectively point to the opposite side of the \( \text{Ru}_3 \) plane. No evidence for the existence of these isomers was reported. In both (106e) and (106f), the methyl group is in the 4-position of the benzyne.
Table 1-3. Some important structural parameters for complexes (106)a.

<table>
<thead>
<tr>
<th></th>
<th>(106a)</th>
<th>(106b)</th>
<th>(106c)</th>
<th>(106d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[116]b</td>
<td>[119]b</td>
<td>[120]b</td>
<td>[121]b</td>
</tr>
<tr>
<td>Ru1-Ru2</td>
<td>2.956(1)</td>
<td>2.8983(8)</td>
<td>2.938(1)</td>
<td>2.9227(8)</td>
</tr>
<tr>
<td>Ru2-Ru3</td>
<td>2.776(1)</td>
<td>2.7748(8)</td>
<td>2.794(1)</td>
<td>2.793(1)</td>
</tr>
<tr>
<td>Ru3-Ru1</td>
<td>2.759(1)</td>
<td>2.7420(8)</td>
<td>2.779(1)</td>
<td>2.7248(8)</td>
</tr>
<tr>
<td>PA-Ru1</td>
<td>2.361(2)</td>
<td>2.380(2)</td>
<td>2.378(2)</td>
<td>2.360(2)</td>
</tr>
<tr>
<td>PA-Ru2</td>
<td>2.319(2)</td>
<td>2.321(2)</td>
<td>2.314(2)</td>
<td>2.311(2)</td>
</tr>
<tr>
<td>PB-Ru2</td>
<td>2.334(2)</td>
<td>2.343(2)</td>
<td>2.320(2)</td>
<td>2.340(2)</td>
</tr>
<tr>
<td>PB-Ru3</td>
<td>2.267(2)</td>
<td>2.270(2)</td>
<td>2.251(2)</td>
<td>2.266(2)</td>
</tr>
<tr>
<td>C(semi-bridging)</td>
<td>2.625(6)</td>
<td>2.670(8)</td>
<td>--------</td>
<td>2.696(8)</td>
</tr>
<tr>
<td>CO-Ru3</td>
<td>164.4(6)</td>
<td>165.3(7)</td>
<td>169.8(9)</td>
<td>--------</td>
</tr>
<tr>
<td>Ru1-C-O</td>
<td>2.127(6)</td>
<td>2.123(7)</td>
<td>2.116(8)</td>
<td>2.117(6)</td>
</tr>
<tr>
<td>Ru1-C1</td>
<td>2.135(6)</td>
<td>2.123(7)</td>
<td>2.138(8)</td>
<td>2.132(6)</td>
</tr>
<tr>
<td>Ru2-C2</td>
<td>2.303(6)</td>
<td>2.318(6)</td>
<td>2.374(8)</td>
<td>2.327(6)</td>
</tr>
<tr>
<td>Ru3-C1</td>
<td>2.353(6)</td>
<td>2.360(6)</td>
<td>2.313(8)</td>
<td>2.319(6)</td>
</tr>
<tr>
<td>C6H4 to Ru3c</td>
<td>65.2</td>
<td>64.0(2)</td>
<td>--------</td>
<td>61.5(2)</td>
</tr>
</tbody>
</table>

a. All bond lengths in (Å) and angles in (°). b. These are corresponding references. c. The angle refers to the dihedral angle between the benzyne and Ru3 planes.

This is attributed to reversible hydrogen transfer between the benzyne moiety and the metal cluster [139], a process that also occurs in Os3 complexes [128].

Some degree of bond localization is found in the benzyne ligand. The bond lengths and angles for the benzyne moiety in (106b) are shown in Figure 1.3 as an example. The C(3)-C(4) and C(5)-C(6) bonds are somewhat
benzyne fragment in (106b) indicate that a 180° rotation process is less facile than in related Os₃ systems [119].

![Diagram of benzyne in (106b)](image)

Figure 1.3 Bond lengths (Å) and angles (°) of benzyne in (106b).

The structures (107a)-(107c) contain a square Ru₄ unit capped on one face asymmetrically by a μ₄-phosphinidene ligand, and on the other by a μ₄-benzyne moiety that in this case acts as a six-electron donor to the Ru₄ plane. The important bonding parameters are tabulated in Table 1-4 and the numbering scheme is shown in Figure 1.4. Ru(1)-Ru(2) lies close to the C₆ plane and show Ru-Cσ bond distances that are considerably shorter than the π-bonded Ru(3)-C and Ru(4)-C distances. The η²-interaction of C(2)-C(3) and C(6)-C(1) with Ru(3) and Ru(4), respectively, are rather asymmetric. The flexibility of this bonding mode is reflected in the varying angle between the Ru₄ and C₆ planes. Some bond localization within the benzyne moieties is present with (107b) as an example (Figure 1.5), but the alternation trend is opposite to that shown in Figure 1.3 for (106b), that is, the C(1)-C(2) bond is longer than C(3)-C(4) and C(5)-C(6) which are longer than C(1)-C(6) and C(2)-C(3). The C(4)-C(5) bond is the shortest.
### Table 1-4. Important bonding parameters for complexes (107).\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>107a(^b) [117, 118](^c)</th>
<th>107b [117, 118](^c)</th>
<th>107c [120](^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1-Ru2</td>
<td>2.943(1) (2.932(1))</td>
<td>2.921(1)</td>
<td>2.993(4)</td>
</tr>
<tr>
<td>Ru2-Ru3</td>
<td>2.896(1) (2.918(1))</td>
<td>2.927(1)</td>
<td>2.893(3)</td>
</tr>
<tr>
<td>Ru3-Ru4</td>
<td>2.791(1) (2.805(1))</td>
<td>2.816(1)</td>
<td>2.841(4)</td>
</tr>
<tr>
<td>Ru1-Ru4</td>
<td>2.891(1) (2.910(2))</td>
<td>2.875(1)</td>
<td>2.879(2)</td>
</tr>
<tr>
<td>Ru1-P</td>
<td>2.352(3) (2.344(3))</td>
<td>2.359(1)</td>
<td>2.351(7)</td>
</tr>
<tr>
<td>Ru2-P</td>
<td>2.353(3) (2.354(4))</td>
<td>2.356(1)</td>
<td>2.348(7)</td>
</tr>
<tr>
<td>Ru3-P</td>
<td>2.425(3) (2.444(3))</td>
<td>2.423(1)</td>
<td>2.478(7)</td>
</tr>
<tr>
<td>Ru4-P</td>
<td>2.446(3) (2.432(3))</td>
<td>2.469(1)</td>
<td>2.495(7)</td>
</tr>
<tr>
<td>Ru1-C1</td>
<td>2.108(10) (2.100(11))</td>
<td>2.115(4)</td>
<td>2.10(3)</td>
</tr>
<tr>
<td>Ru2-C2</td>
<td>2.110(10) (2.122(10))</td>
<td>2.117(3)</td>
<td>2.10(2)</td>
</tr>
<tr>
<td>Ru3-C2</td>
<td>2.294(9) (2.309(12))</td>
<td>2.301(4)</td>
<td>2.32(3)</td>
</tr>
<tr>
<td>Ru3-C3</td>
<td>2.656(11) (2.583(12))</td>
<td>2.634(4)</td>
<td>2.61(3)</td>
</tr>
<tr>
<td>Ru4-C1</td>
<td>2.299(10) (2.317(13))</td>
<td>2.292(4)</td>
<td>2.30(3)</td>
</tr>
<tr>
<td>Ru4-C6</td>
<td>2.689(11) (2.619(14))</td>
<td>2.592(4)</td>
<td>------</td>
</tr>
<tr>
<td>C(_6)H(_4)^d to Ru(_4)</td>
<td>54.7 (49.0)</td>
<td>50.9</td>
<td>------</td>
</tr>
</tbody>
</table>

\(^a\) All bond lengths in (Å) and angles in (°). \(^b\) Two crystallographically distinct molecules are found. Data in brackets are for the second molecule. \(^c\) These are the corresponding references. \(^d\) The angle refers to the dihedral angle between the benzyne and Ru\(_4\) planes.

---

**Figure 1.4 Numbering of complexes (107).**
Figure 1.5 Bond lengths (Å) of benzyne in complex (107c).

The Ru₅ complex (108a) may be envisaged as a derivative of (107a) formed by replacing the bridging CO with a Ru(CO)₃ moiety that is η²-bonded to the remaining carbon atoms C(4) and C(5) in the C₆ ring. The numbering is shown with the structure (108a). The μ₄-phosphinidene caps the square Ru₄ unit symmetrically (P-Ru(n) lengths 2.379(1), 2.386(2), 2.378(2), 2.381(2) Å). The Ru(1)-Ru(2) (2.902(1) Å), Ru(2)-Ru(3) (2.905(1) Å) and Ru(4)-Ru(1) (2.897(1) Å) distances are the same and the longest, while Ru(3)-Ru(5) (2.769(1) Å) and Ru(4)-Ru(5) (2.783(1) Å) are the shortest. The Ru(3)-Ru(4)-Ru(5) unit is similar to the Os₃ unit in Os₃(CO)₉(C₆H₆) [122]. As in (107a), Ru(1) and Ru(2) are almost coplanar with the benzyne ring and the Ru(1)-C(1) (2.097(6) Å) and Ru(2)-C(2) (2.116(6) Å) bonds are as expected. The Ru-C bonds involving the η²-bound carbon atoms are longer. Thus, Ru(3)-C(2) (2.334(5) Å) and Ru(4)-C(1) (2.251(6) Å) are longer, Ru(3)-C(3) (2.391(5) Å), Ru(4)-C(6) (2.391(6) Å), Ru(5)-C(4) (2.398(7) Å) and Ru(5)-C(5) (2.427(6) Å) are the longest. The bond length alternation in the benzyne ring is similar to that in (107b) (Figure 1.5). An interesting feature of the structure of (108a) is that the five ruthenium atoms mimic a step-site on a metal (111) surface, thus
Ru(3)Ru(4)Ru(5) would be in one terrace and Ru(1)Ru(2) would be step atoms in the first row of the next terrace. It is attractive to envisage that the approach of a benzene molecule to a metal (111) surface in which there are exposed, low-coordinate, step atoms would result in the activation of two ortho-C-H bonds, to generate benzyne chemisorbed as in (108a) [123].

The Ru₆ complex (109) may be viewed as having a slipped trigonal prismatic Ru₆ core in which two of the quadrilateral faces of the prism are bridged by the µ₄-PPh groups, while the third has a diagonal Ru-Ru bond (Ru(11)-Ru(14)). The Ru atoms each carry two terminal CO groups. The triangular faces of the Ru₆ prism are each capped by a µ₃-benzyne moiety. The Ru(13)-Ru(15) bond is the longest at 3.143(1) Å followed by the diagonal Ru(11)-Ru(14) bond of 2.991(1) Å. In each of the two triangular faces, one Ru-Ru bond (Ru(11)-Ru(13) 2.915(1) Å, Ru(14)-Ru(15) 2.916(1) Å) is longer than the other two which are almost equal and are the shortest (Ru(11)-Ru(12) 2.740(1), Ru(12)-Ru(13) 2.739(1) Å; Ru(14)-Ru(16) 2.731(1), Ru(15)-Ru(16) 2.748(1) Å). Both phosphinidene caps are slightly asymmetric with P-Ru(13) and P-Ru(15) bonds ca. 0.05 Å longer than the others. The benzyne moiety is bonded to the Ru₃ face in a fashion similar to that found in (106a) except that here both the σ (by ca. 0.03 Å) and the π (by ca. 0.12 Å) bonds are shortened. The C-C bond alternation pattern is also similar to that in (106a), and the electron localization is even more profound.

Some reactions of (106a), (107a) and (108a) with CO have been studied [114] and are summarized in Scheme 1-21. Treatment of (106a) with CO at room temperature yields (110) quantitatively and the structure of its PiPr₃ derivative was determined. The Ru₃ triangle is opened and CO
insertion generates a novel orthometalated benzoyl ligand that triply bridges the Ru₃ unit in μ-acyl fashion. The μ₄-benzyne complex (107a) undergoes cluster fragmentation under CO (50 atm) at 60°C to give the

Scheme 1-21 Reactions of benzyne complexes (106a), (107a), and (108).

dinuclear compound (112) in good yield. The μ₅-benzyne complex (108) also undergoes cluster fragmentation under CO (50 atm) at 100°C to give Ru₃(CO)₁₂ and (111), but not (112). The structure of (111) and (112) were
established by X-ray diffraction studies. In both (110) and (111) one CO molecule has been inserted into the cluster-benzyne moiety. In (112) two CO molecules have been inserted into the Ru-benzyne σ-bonds to form a pathaloyl ligand. Under refluxing complexes (110), (111) and (112) reform the starting complexes (106a) and (107a), respectively.

1.2.3.2 Osmium Cluster Complexes of Benzyne

The first three benzyne complexes to be isolated were Os₃ cluster complexes (49), (50) and (51) which have already been mentioned (Section 1.2.1) [67-69]. They were obtained by heating Os₃(CO)₁₂ with PPh₃ or refluxing Os₃(CO)₁₀(PPh₃)₂ in xylene, and all were structurally characterized. The structure of (49) is typical of a range of Os₃ and Ru₃ complexes. All the three structures are closely related. In (51), the benzyne moiety is bonded to the ortho position of a phenyl group on a PPh₂ moiety that is attached to Os(3). This compound shows a rare example of C-C coupling.

Pyrolysis of Os₃(CO)₁₁(PMe₂Ph) produces HOs₃(μ₃-C₆H₄)(PMe₂)(CO)₉ (114a), similarly Os₃(CO)₁₀(PMe₂Ph)₂ affords Os₃(µ₃-C₆H₄)(PMe₂)₂(CO)₇ (113a), an analogue of (49), HOs₃(μ₃-η³-Me₂PC₆H₄C₆H₃)(PMe₂)(CO)₈ (115)
and HOs₃(µ₃-C₆H₄)(PMe₂)(CO)₈(PMe₂Ph) (116) [124, 125]. Pyrolysis of Os₃(CO)₁₁(AsMe₂Ph) affords HOs₃(µ₃-C₆H₄)(AsMe₂)(CO)₉ (114b), and pyrolysis of Os₃(CO)₁₀(AsMe₂Ph)₂ also affords (114b) in addition to Os₃(µ₃-C₆H₄)(AsMe₂)₂(CO)₇ (113b). Complex (113b) was also obtained by heating Os₃(CO)₁₂ with 1,2-C₆H₄(AsMe₂)₂ [125]. All these complexes were characterized by spectroscopic and analytical techniques and the structure of (114b) was confirmed by an X-ray diffraction study [126]. Another complex HOs₃(CO)₉(C₆H₄)(PET₂), obtained from the pyrolysis of Os₃(CO)₁₁(PET₂Ph), was also mentioned and presumably it has the structure (114c) [127].

Variable temperature ¹H and ³¹P NMR studies of (113) reveal that the benzyne moiety is fluxional; a rapid rotation and flip of the benzyne ring was suggested to account for the results [124, 125]. Later variable temperature ¹H and ¹³C NMR analysis of (113b) and its C₆H₃iPr analogue indicate that one CO ligand rapidly transfers between two Os atoms and that opposite faces of the µ₃-benzyne ligand interchange during two distinct fast intramolecular processes (Scheme 1-22) [126]. Variable temperature ¹H and ¹³C NMR studies of (114b) and its C₆H₃iPr analogue show that the presence of only two Os-Os bonds does not interfere with the
interchange of the benzyne ligand faces which is accompanied by reversible hydride migration from one Os-Os bond to the other [126].

Scheme 1-22 Two rapid intramolecular processes proposed for Os₃(μ3-C₆H₄)(AsMe₂)₂(CO)₇.

The proposed structure of (115) can be related to (51) by opening the Os(1)-Os(2) bond and attaching an extra CO to Os(2), or can be related to (114) by replacing one CO on Os(3) with PMe₂Ph and coupling the ortho-position of the phenyl group to the benzyne moiety. A crystal structure determination is needed to confirm this new type of structure. The structure of (116) is also a proposed one and the PMe₂Ph ligand is assumed to be on Os(3) (compare with (50), (51), (114) and (115)). If the structure is correct, it is closely related to (114) and (115) by coupling the ortho-position of the phenyl group with the benzyne moiety.

Pyrolysis of Os₃(CO)₁₁[AsMe₂(2-MeC₆H₄)] gives the unexpected isomer HOs₃(μ₃-4-C₆H₃Me)(AsMe₂)(CO)₉ (117). Similarly Os₃(CO)₁₁[AsMe₂(2-MeOC₆H₄)] and Os₃(CO)₁₁[AsMe₂(4-MeOC₆H₄)] both give the 3-methoxy-
benzyne cluster $\text{HoS}_3(\mu_3$-$\text{C}_6\text{H}_3\text{OMe})(\text{AsMe}_2)(\text{CO})_9$ (118) [128]. No other isomers of these complexes were produced in these reactions. A mechanism involving hydrogen atom transfer between metal and $\mu_3$-benzyne that proceeds via $\sigma$-phenyl intermediates was proposed to account for these migration reactions [128].

Another member of the (114) structural series is complex $\text{HoS}_3(\mu_3$-$\text{C}_6\text{H}_4)$($\text{PC}_4\text{H}_2\text{Me}_2$)(CO)$_9$ (119), obtained in very low yield from the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PhPC}_4\text{H}_2\text{Me}_2)$ in heptane. It was characterized by using X-ray crystallography [129]. The hydride is assumed to bridge Os(1)-Os(3) bond. Another complex (120), similar to (114) and (119) containing SMe in place of AsMe$_2$ was isolated in low yield from the reaction of $\text{Os}_3(\text{CO})_{12}$ with
MeSPh. An analogous complex containing SiPr is also known [130]. The structure of (120) was also determined and it is the only known cluster complex where a bonded benzyne moiety is derived from a sulfide rather than a phosphine or arsine [130]. Variable temperature NMR studies of (120) show that, in addition to hydride migration between the Os-Os bonds, there is a higher energy process involving inversion at sulfur [130]. The similarity of the structures of (120), (114), and (119) is apparent.

Another series of complexes Os₃(μ₃-C₆H₄)(PR)(CO)₉ (R=Me, Et, and Ph) (121) which possess a different type of benzyne coordination was obtained by refluxing Os₃(CO)₁₁(PPh₂R) (R=Me, Et, and Ph) in n-nonane [131]. The structure of (121a) was determined by an X-ray diffraction study. The open Os₃ triangle is capped on one face by a phosphinidene group and the other face by a benzyne moiety. These complexes are highly fluxional, probably owing to a rocking motion of the benzyne ring such that the two benzyne carbon atoms become equivalent [131]. These pyrolysis reactions have been re-examined in an attempt to isolate possible intermediates involved [132]. The structures of (121b) and a PEt₃ substituted derivative (122a) have been determined [133]. Reactions of (121b) with PEt₃, PCy₃, and P(OMe)₃ give mono- and di-substituted products Os₃(μ₃-C₆H₄)(PMe).
(CO)₈(PR₃) (R=Et, Cy, OMe) (122) and Os₃(µ₃-C₆H₄)(PMe)(CO)₇(PR₃)₂ (R=Et and OMe) (123) [133]. Both (122) and (123) exist as two isomers as shown in Figure 1.6. A detailed NMR study shows that the C₆H₄ ligand is rapidly mobile in (121b) and in the isomer of (122) with the ligand L at the central Os atom. An exchange mechanism involving a symmetrical intermediate was proposed to complement the rocking motion initially proposed [133]. The fluxionality is substantially suppressed when L is coordinated at a terminal Os atom. The movement of the non-bonded Os···Os edge around the metal triangle also occurs, but slowly [133].

![Figure 1.6 Isomers of complexes (122) and (123).](image)

An analogous complex of (121) but with µ₃-C₆H₃Me and As(4-MeC₆H₄) in place of µ₃-C₆H₄ and PR respectively, is obtained by heating Os₃(CO)₁₁(MeCN) with one equivalent of As(4-MeC₆H₄)₃ in nonane [134, 135]. The structures of (124) and its As(4-MeC₆H₄)₃ derivative (125) were determined and in both structures the methyl group is on the 4 position of the benzyne moiety as in (117). These two structures resemble the benzyne complexes (121) and (122) respectively.
Other phenyl containing ligands including benzene itself can react with Os$_3$(CO)$_{12}$ or Os$_3$(CO)$_{12-n}$(MeCN)$_n$ (n=1, 2) to give benzyne complexes. This is the most attractive route to benzyne complexes, but as yet no high yield synthesis has been developed. The parent compound H$_2$Os$_3$(μ$_3$-C$_6$H$_4$)(CO)$_9$ (126) is obtained in ca. 30% yield by heating benzene with Os$_3$(CO)$_{12}$ at 195°C [136, 137] or with Os$_3$(CO)$_{10}$(MeCN)$_2$ under reflux [138]. The structure of (126) reveals that the benzyne is bound to the Os$_3$ unit in a fashion found in some other cluster benzyne complexes such as (49) and (106). The hydrides are assumed to bridge the longer Os(1)-Os(2) and Os(1)-Os(3) vectors. The hydride ligands in (126) are equivalent on the NMR time scale at room temperature, probably because of rapid rotation and/or flipping of the C$_6$H$_4$ unit and rapid reversible hydride migration between the metal triangle and the benzyne ring [139]. The structure may be related to (50) by replacing the PPh$_3$ group with CO and the PPh$_2$ moiety by a terminal CO and a bridging hydride. The C$_6$H$_3$R (R=Me, nPr, CH-CHPh, Cl) and C$_6$H$_2$Me$_2$ analogues of (126) have also been prepared from the reactions of Os$_3$(CO)$_{10}$(MeCN)$_2$ with appropriate arenes. The complexes derived from toluene and chloro-benzene exist in solution as mixtures of positional isomers (Figure 1.7) [138].
Figure 1.7 Positional isomers of benzyne complexes derived from toluene and chlorobenzene (X=CH$_3$, Cl).

Complex (126) can also be obtained from thermal decarbonylation of HO$_3$($\mu_2$-COPh)(CO)$_{10}$ [140] or HO$_3$(\(\mu\)-OCH$_2$Ph) (CO)$_{10}$ [141, 142] derived respectively from C$_6$H$_5$CHO or C$_6$H$_5$OH. Photo-induced isomerization of the face-capping benzene complex Os$_3$(CO)$_9$(\(\mu_3\)-\(\eta^1\cdot\eta^2\cdot\eta^1\)-C$_6$H$_4$) [143] also leads to (126).

Some important bonding parameters for the determined structures of Os$_3$ benzyne complexes are summarized in Table 1-5. The numbering schemes are shown in Figure 1.8 with the structural types.

The skeleton of the complex (49) is very similar to that of the ruthenium complexes (106) except that in the Ru$_3$ structures, the Ru(2)-Ru(3) bonds are longer than Ru(1)-Ru(3) by 0.02 to 0.06 Å while in (49), Os(2)-Os(3) and Os(1)-Os(3) are the same. The structures of (50) and (51) are very similar to (49) with Os(1)-Os(3) being the longest and Os(2)-Os(3) the shortest; the benzyne ligands donate two electrons via two \(\sigma\) bonds (Os(1)-C(2) and Os(2)-C(1)) and two electrons via a \(\pi\) bond (C(1) and C(2) to Os(3)) to the cluster. Structure (126) has a similar benzyne ligand donating four electrons, but the metal framework is somewhat different in that the
Os(1)-Os(2) bond is much longer than Os(1)-Os(3), in contrast to that found in (50) and (51), while Os(2)-Os(3) remains the shortest. In fact, the Os(1)-Os(2) bond at 3.026(2) Å (3.041(2) Å) is long compared to the Os-Os bond.

Figure 1.8 Numbering and structural types of Os₃ benzyne complexes.
Table 1-5. Important bonding parameters for the determined structures of Os$_3$ benzyne complexes.

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$^a$ Numbers in parentheses indicate standard deviations.

$^b$ Measurements in angstroms.

$^c$ Average values.

$^d$ Values in parentheses indicate standard deviations.
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<tr>
<td>Os3 plane</td>
<td>(65.8)</td>
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<tr>
<td>references</td>
<td>67(116)</td>
<td>68</td>
<td>68</td>
<td>138</td>
<td>126</td>
<td>129</td>
<td>130</td>
<td>131</td>
<td>133</td>
<td>133</td>
<td>134.135</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

a. All bond lengths in Å and angles in °. b. The unbracketed values are from reference 67 and the bracketed values from reference 116. c. Two crystallographically distinct molecules are present and values in brackets are for the second molecule. d. Data not given. e. Only average value 1.42(4) Å for C6 rings is given and no significant variations are found.
distance of 2.877(3) Å in Os₃(CO)₁₂.

Structure type (C) includes (114b), (119), and (120) containing only two Os-Os bonds, and Os(1)-Os(3) bond is about 0.1 Å longer than Os(2)-Os(3). The open edge is symmetrically bridged by AsMe₂ or PCHCMeCMeCH or SMe moieties. The benzyne ligand interacts with Os₃ via two σ bonds and a π bond and thus donates four electrons. It is interesting to note that the benzyne C-Os bonds have similar lengths for the structural types (A), (B), and (C).

The final structure type (D) also contains two Os-Os bonds with Os(1)-Os(2) being longer than Os(2)-Os(3) by ca. 0.1 Å. These complexes contain a triply bridging group X. The central Os(2)-P(1) or Os(2)-As(1) bond is longer than the other two by ca. 0.1 Å. The bonding of the benzyne moiety in (D) is different from that in the other three types, and it is thought to donate two to four electrons, thus bonding contributions from (127a) and (127b) were proposed [131]. Recently Deeming et al. [133], on the basis of the structures of (121b) and (122a), proposed that (127c) is a better bonding representation for benzyne moieties in type (D) structures.

They argue that (127b) would show a long C(1)-C(2) bond and a Os-C(1) bond with double bond character, which is not found in these
structures. Both structures (127a) and (127b) would show a benzyne ring perpendicular to the Os₃ plane which is not the case [133].

Although more structures have been determined for osmium cluster benzyne complexes than for ruthenium, very little data were given on the bonding of the benzyne moieties in these osmium complexes. Data given are often not sufficiently accurate to allow assessment of the bonding in the benzyne moiety. Generally, no significant differences are found in the C-C bond lengths and even C(1)-C(2) bonds are little affected, in contrast to that found in ruthenium complexes (e.g. Figure 1.5).

It seems that osmium systems normally retain their metal triangle framework. While the bonding mode of the benzyne moiety is not very flexible, the Os₃ core and the bridging ligands are very flexible. In ruthenium systems, there is a high tendency for the cluster to fragment and to recombine to form Ru₄, Ru₅, and Ru₆ clusters. In all known Ru cluster benzyne complexes the metal cores are closed, but the bonding

![Diagram](image)

Figure 1.9 Structures of (121b), (107a), and (108a) with CO groups being omitted [133].

56
mode of the benzyne moiety is more flexible.

Deeming et al. [133] made interesting structural comparisons of complex (121b) with related ruthenium compounds (107) and (108) (Figure 1.9). In (121b) and (107a), the extent of direct bonding to the β-carbon atoms is slight, but in (108) both the α- and β-carbon atoms are strongly bonded to the metal atoms. If the above argument is valid, it has an interesting implication that the benzyne complexes on ruthenium and osmium clusters are closely related. For example, the ruthenium analogue of the osmium benzyne complex type (D) is probably somewhat unstable, but if provided with extra electronic and/or steric stabilization it might be isolable. Cullen et al. [121] have isolated a ruthenium cluster complex containing a (benzyne)chromium tricarbonyl moiety Ru₃(CO)₉[PC₆H₅Cr(CO)₃][C₆H₄Cr(CO)₃] (128). The presence of the Cr(CO)₃ moiety and the interaction of the chromium atom with the ruthenium atom, albeit weak (Cr-Ru 3.097(1) Å), may be responsible for the stabilization of the structure. The Ru₃ core is open as found in Os₃ structure type (D). Another example is the isolation of complex Ru₃(CO)₉(AsMe₂)(H)C₆H₄Cr(CO)₃ (129) [144]. This is a novel type of structure and may also be stabilized by an interaction between chromium and one osmium atom (2.9704(6) Å). Another interesting complex Ru₃(CO)₈(PtBu)C₆H₄Cr(CO)₃ (130) shows a symmetrically bonded aryne moiety [145]. This is another new type of aryne structure both for ruthenium and osmium systems. A Cr-Ru bond of 2.920(1) Å is present and again this may be of great importance in stabilizing the novel structure.

A further interesting prediction of the above argument is that a type (B) structure for osmium may also be found for ruthenium, that is, a complex like H₂Ru₃(CO)₉(aryne) may be obtained if provided with some
stabilization. On the other hand, it would be rather difficult if not possible to assemble osmium benzyne complexes analogous to the Ru₄, Ru₅, and Ru₆ ones due to the strength of the Os-Os bonds and the thermodynamic stability of these known benzyne complexes.

1.2.4 Dinuclear μ₂-Benzene (μ-o-Phenylene) Complexes

Small amounts of the dinuclear benzyne complexes HOs₂(CO)₆(AsMe₂)(C₆H₄) (131) and Os₂(CO)₆(AsMe₂)₂(C₆H₄) (132) were obtained in addition to (113b) and (114b) when Os₃(CO)₁₁(AsMe₂Ph) and Os₃(CO)₁₀(AsMe₂Ph)₂ were pyrolyzed [125]. Analogous compounds were not obtained from the corresponding PMe₂Ph complexes.

Complex (133) was formed in low yield via an unstable hydride CpIr(C₆H₅)(H)(CO) by irradiating a benzene solution of CpIr(CO)₂ [146]. Its structure reveals that the benzyne ring is largely unperturbed with average C-C distance being 1.379(3) Å. Ir-Ir and Ir-C bonds are 2.7166(2) and 2.045(3) Å long respectively. Double oxidative additions of 1,2-diiodobenzene to a dipalladium complex Pd₂(Ph₂PCH₂PPh₂)₃ gives benzyne complex (134) [147]. Direct trapping of tetrafluorobenzyne, generated by
the decomposition of C₆F₅MgBr in dioxane, with Fe₃(CO)₁₂ affords (135) [148, 149]. Reaction of C₆F₅Li with Fe(CO)₅ followed by treatment with Me₃SiCl also gives (135). A similar reaction with Co₂(CO)₈ as trapping reagent gives a tetra-nuclear species [Co₄(CO)₁₀(C₆F₄)] [148]. Reaction of [PtCl₄]₄ with Ph₃CCl in benzene at 50°C gives complex (136) the structure of which has been determined [150]. The Pt-C distance is 1.97(2) Å and there is no Pt-Pt bonding (3.258(2) Å) involved. Reduction of trans-(PEt₃)₂Ni(Cl)(2-ClC₆H₄) with lithium generates (137), a dimer of the benzyne complex (PEt₃)₂Ni(C₆H₄) that was the anticipated product of the reaction [110]. Complex (137) is in equilibrium with (138) (Equation 1.10).
Palladation of N,N,N',N'-tetraethyl-1,4-xylene-α,α'-diamine with PdCl$_4^{2-}$ gives μ$_2$-benzyne complex (139) which can be converted to (140) and (141) [151].

The only known μ$_2$-benzyne complex involving a trinuclear cluster is H$_3$(μ-η$^2$-C$_6$H$_4$)(μ-η$^2$-HC-NPh)Os$_3$(CO)$_8$ (142) obtained from the pyrolysis of H$_2$Os$_3$(CO)$_{10}$(CNPh) [152]. The hydrocarbon ligand bridges one edge of the cluster and the bond lengths of Os(1)-C(1) (2.107(10) Å) and Os(3)-C(2) (2.165(9) Å) are similar to those found in μ$_3$-benzyne complexes. The phenylformimidoyl ligand bridges the Os(2)-Os(3) edge and is on the opposite side of the Os$_3$ plane from the benzyne moiety.
In all the known dinuclear benzyne complexes, the benzyne moiety is bonded to two metal atoms via two σ bonds. Relatively little effort has been made to develop a systematic approach to these interesting complexes.

1.2.5 Metal Complexes of Benzdiyne

The more highly unsaturated 1,4-benzdiyne (143) and (144) can also be stabilized by metal complexes. The free molecules have never been observed, and theoretical calculations suggest that their ring opening to give H-C≡C-C≡C≡C≡H is more favorable than the corresponding process for benzyne to give H-C≡C-H and H-C≡C-C≡C-H [33]. However, 1,2,4,5- and 1,2,3,4-tetrabromoarenes do form Diels-Alder bis-adducts upon treatment with equivalents of an organolithium reagent in the presence of a suitable diene [153, 154].

Complex (145) undergoes CH₄ elimination on heating to give a mixture of two pairs of isomeric benzdiyne complexes (146) and (147) (Scheme 1-23) [155]. The isomers in each pair differ in having anti- or syn-arrangements of the PMe₃ ligands. The 1,4-dimethoxy-substituted analogues of (145) give a pair of isomers (148a) and (148b) (Equation 61).
Scheme 1-23 Synthesis of the benzdiyne complexes (146) and (147).

1.11). The structure of (148a) was determined [155]. Complexes (148a) and (148b) undergo insertion with unsaturated organic molecules such as acetone, 2-butyne, and ethylene to give bis(metallacycles) (Scheme 1-24). The compounds derived from ethylene, (149a) and (149b), can be converted to tetrahydrodicyclobutabenzenes (Equation 1.12).
Reaction of the 4-fluorobenzynie nickel complex (150) with a large excess of lithium tetramethylpiperidine (LiTMP) in the presence of Ni(Cy₂PCH₂CH₂PCy₂)(C₂H₄) affords the 1,4-benzdiyne complex (151) (Equation 1.13) [156]. This success was inspired by the observation that chlorobenzene reacts with a base such as LiTMP to generate benzyne which can be trapped by added nucleophiles such as 1,3-diphenylisobenzofuran (Equation 1.14) [157].
The structural analyses of (148a) and (151) show that the coordination geometries are similar to those of the corresponding benzyne complexes (70) and (96). In both complexes the metal atoms are situated slightly away from the plane of the aromatic ring (0.17 and 0.08 Å for (148a) and (151) respectively). The bond lengths and angles are shown in Figure 1.10.

Even more highly unsaturated 1,3,5-benztriyne (C₆) could be stabilized by coordination to transition metal fragments to form a complex such as (152) [158].
Figure 1.10 Comparison of the bond lengths and angles of the 1,4-benzdiyne moieties in (148a) and (151) [27].

1.3 Ferrocene and Its Transition Metal Complexes

1.3.1 Aromaticity of Ferrocene

Ferrocene, $(\eta^5-C_5H_5)_2Fe$ (153), was discovered by Kealy and Pauson [159], and by Miller et al [160]. The description of the isoelectronic cationic Co(III) complex soon followed [161]. These were the first examples of what would become a wide range of sandwich compounds. The correct structure of ferrocene was first proposed [162] and later confirmed by a crystallographic study which also showed that the two cyclopentadienyl rings
adopting a staggered configuration [163]. The most recent crystallographic study, however, shows that the two rings are eclipsed [164].

\[
\text{FeCp}_2
\]

(153)

Ferrocene is unusually stable for an organoiron compound. It does not undergo Diels-Alder reactions, resists catalytic hydrogenation under normal conditions, and resists pyrolysis at \(470{\degree}C\) [162, 165]. In 1952, Woodward et al. reported that ferrocene undergoes Friedel-Crafts acylation [166, 167]. Shortly after this discovery, ferrocene was shown to undergo other aromatic-type substitution reactions including alkylation [168, 169], formylation [170, 171], mercuration [172], and sulfonation [173]. Some of these reactions are summarized in Scheme 1-25. Typical aromatic halogenation and nitration reactions can not be carried out directly because ferrocene is easily oxidized to the ferricenium ion \(\text{FeCp}_2^+\) which is inert to attack by electrophiles. Ferrocene can easily be metalated, especially with n-butyllithium, and the lithiated products are very useful for preparing a wide variety of ferrocene derivatives. Some examples are given in Scheme 1-26.
1.3.2 Ferrocyne

Although the parallel between ferrocene and benzene has long been established, the evidence for the existence of ferrocyne is rather limited. The reactions of haloferrocenes with strong bases could involve ferrocyne intermediates, but such reactions are expected to be more difficult than those of halobenzenes due to the electron rich nature of the metallocene and the higher strain in forming a formal triple bond in a five-membered ring. However, the simple cyclopentadienyl anion seems to be capable of
producing a benzyne analogue. Thus when a solution of potassium 1-diazo-
cyclopentadiene-2-carboxylate (154) is heated in benzene containing
dicyclohexyl-18-crown-6 and tetracyclone, some of the product (155) can
be isolated after protonation [174] and an intermediate such as (156) is
likely to be involved.

Scheme 1-26 Some reactions of mono- and 1,1'-dilithiated ferrocenes
(adapted from reference 308).

Huffman et al [175] found that the reaction of chloroferrocene with
n-butyllithium gives n-butylderrocene and biferrocenyl and proposed a
ferrocyne intermediate. However a different reaction pathway involving metal halogen exchange followed by metathesis can not be excluded, though it is not very likely (Scheme 1-27). Much stronger evidence for a

\[
\begin{align*}
\text{(154)} & \quad \text{(155)} & \quad \text{(156)}
\end{align*}
\]

Scheme 1-27 A possible pathway for the reaction of FcCl with \(\text{nBuLi}\) not involving a ferrocyne intermediate.

ferrocyne intermediate was later provided from the reaction of a substituted haloferrocene with \(\text{nBuLi}\), as shown in Scheme 1-28 [176]. This reaction is remarkably similar to those of substituted halobenzenes or naphthalenes and it clearly indicates the involvement of a ferrocyne
1.3.3 Transition Metal Complexes of Ferrocene

By analogy with benzyne, ferrocene could conceivably be stabilized by coordination to one or more transition metal centers. Some 5-membered ring aryne complexes bonded to Os₃ clusters are known. In particular, complex (158) is formed by oxidative addition of pyrrole or N-methylpyrrole (R-H or Me) to Os₃(CO)₁₂ [177]. A more satisfactory route to such complexes is from the 2-formyl substituted derivatives that add oxidatively to Os₃(CO)₁₀(MeCN)₂ to give acyl clusters. Heating these acyl clusters results in decarbonylation to give products such as (158), (159), and (160) [178-180]. However, the oxidative addition product (161) of ferrocene carboxaldehyde at Os₃(CO)₁₀(MeCN)₂ does not decarbonylate even when one CO is replaced by a labile MeCN ligand [181]. The direct reaction of ferrocene with Os₃(CO)₁₂ is reported to give no tractable materials [181]. The ruthenium analogue of (161) does undergo decarbonylation, but the product is ferrocene with no evidence for ferro-
By analogy with benzdiyne and benztriyne, more highly unsaturated ferrodiyne species such as \((\eta^5-C_5H_5)Fe(\eta^5-C_5H_5)\) and \((\eta^5-C_5H)Fe(\eta^5-C_5H_5)\) could also conceivably be stabilized by coordination to transition metal fragments. Again nothing is known about such species.

Pyrolysis of \(\text{Ru}_3(\text{CO})_{10}(\text{PFcPh}_2)\) affords the benzyne complex (106b) in good yield with no indication of ferrocyne complex formation [119]. Similarly \(\text{Ru}_3(\text{CO})_{10}(\text{bppf})\) affords a number of products including two benzyne complexes (106c) and (107c) [120]. This same reaction affords a rather interesting complex (162) containing an ortho-metalated Cp ring and some iron-ruthenium interaction, certainly encourages further research in preparing cluster complexes containing the ferrocyne moiety.
Chapter 2 Syntheses and Pyrolytic Reactions of Some Triruthenium and Triosmium Phosphine and Arsine Complexes

2.1 Introduction

Together with cyclopentadienes and phosphines, carbon monoxide is one of the most important ligands in transition metal organometallic chemistry. Transition metal carbonyls are common starting materials for the synthesis of other low-valent metal complexes. The carbonyl ligand can not only be substituted by a large number of other ligands such as Lewis bases, olefins and arenes, but the remaining CO groups stabilize the molecules against oxidation or thermal decomposition.

Transition metal carbonyls are among the earliest known classes of organometallic compounds. The first binary metal carbonyl complex, Ni(CO)₄ (163), was prepared a century ago by the reaction of Ni metal with CO [183]. Similar reactions led to the preparation of Fe(CO)₅ (164) [184, 185]. The action of light on Fe(CO)₅ (164) affords the dinuclear Fe₂(CO)₉ (165) [185].

\[
\begin{align*}
\text{Ni} & \quad \text{(163)} \\
\text{Fe} & \quad \text{(164)} \\
\text{Fe} & \quad \text{(165)}
\end{align*}
\]
The first metal cluster carbonyl complex, Fe₃(CO)₁₂ (166), was obtained by heating non-aqueous solutions of Fe₂(CO)₉ [186]. The first ruthenium carbonyl complex obtained by Mond et al. [187] is Ru₃(CO)₁₂ (167), but it was not correctly formulated until an X-ray crystallographic analysis was performed [188]. Improved preparations have been frequently reported, and these usually start from hydrated ruthenium chloride [189]. The first osmium carbonyl complex, Os₃(CO)₁₂ (168), was synthesized by Hieber and Stallman [190]. Better synthetic routes have been developed starting from OsO₄ [191].

![Chemical structures](image)

Most binary metal carbonyl complexes are prepared by the action of carbon monoxide on metal compounds under reductive conditions with sodium, aluminum alkyls, and carbon monoxide itself being the most common reducing agents.

Transition metal carbonyl compounds are not limited to neutral species, and large number of cationic and anionic complexes are known. A

![Chemical structures](image)
few examples are Re(CO)₆⁺ (169), V(CO)₆⁻ (170) and Nb(CO)₅³⁻ (171). The carbonylate anions are very useful for the preparation of mixed dinuclear and polynuclear metal carbonyl complexes.

The strength of metal-metal bonds increase with the atomic number of the metal, and as a result, polynuclear metal carbonyl complexes are more common for second- and third-row transition metals. Carbonyls can bridge two or three metals, but such tendency decreases down a column in the periodic table. The energy difference between a structure with CO bridges and one without them is often small, as illustrated by the fact that Co₂(CO)₈ exists in solution as a mixture of isomers (Equation 2.1) [192]. These carbonyl bridges are very important in the fluxional processes in these complexes.

\[
(\text{CO})_4\text{Co} \rightleftharpoons \text{Co(\text{CO})}_4 \rightleftharpoons (\text{CO})_3\text{Co} \rightleftharpoons \text{Co(\text{CO})}_3 \quad (2.1)
\]

Carbonyls form a great many polynuclear complexes with group 8 metals. Anionic species are especially common in high nuclearity clusters, as are bridging hydride ligands and interstitial atoms [193] such as hydrogen, phosphorus, arsenic, sulfur, and particularly nitrogen and carbon. Four structures (172)-(175) are shown to illustrate the diverse bonding interactions in these clusters.

The structures of Ru₃(CO)₁₂ (167) and Os₃(CO)₁₂ (168) are analogous with M₃ forming a triangle and four terminal carbonyls on each metal center, two being axial and two equatorial [194, 195]. Some structural data
are summarized in Table 2-1. The metal triangles are essentially equilateral, and all CO groups are linear although there is a tendency for the axial ligands to bend due to van der Waals repulsions between axial oxygen atoms.
Table 2-1. Structural data for Ru$_3$(CO)$_{12}$ (167) and Os$_3$(CO)$_{12}$ (168).

<table>
<thead>
<tr>
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<th>Ru$<em>3$(CO)$</em>{12}$</th>
<th>Os$<em>3$(CO)$</em>{12}$</th>
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<tr>
<td>Av. M-M (Å)</td>
<td>2.854(4)</td>
<td>2.877(3)</td>
</tr>
<tr>
<td>M-C (axial) (Å)</td>
<td>1.942(4)</td>
<td>1.946(6)</td>
</tr>
<tr>
<td>M-C (equatorial) (Å)</td>
<td>1.921(5)</td>
<td>1.912(7)</td>
</tr>
<tr>
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<td>1.133(2)</td>
<td>1.134(8)</td>
</tr>
<tr>
<td>C-O (equatorial) (Å)</td>
<td>1.127(2)</td>
<td>1.145(5)</td>
</tr>
<tr>
<td>M-C-O (axial) (°)</td>
<td>173.0(10)</td>
<td>175.3(10)</td>
</tr>
<tr>
<td>M-C-O (equatorial) (°)</td>
<td>178.9(10)</td>
<td>178.4(10)</td>
</tr>
</tbody>
</table>

2.2 Syntheses and Structures of Some Triruthenium and Triosmium Phosphine and Arsine Complexes

2.2.1 Triruthenium Phosphine and Arsine Complexes

The reactions of Ru$_3$(CO)$_{12}$ with phosphines or arsines are commonly effected by thermal or photochemical methods. Both techniques often lead to cluster fragmentation. For example, irradiation of a hexane solution of Ru$_3$(CO)$_{12}$ and PPh$_3$ gives only a low yield of Ru$_3$(CO)$_{11}$(PPh$_3$); mononuclear Ru(CO)$_4$(PPh$_3$) and Ru(CO)$_3$(PPh$_3$)$_2$ are the major products [196]. The thermal reaction generally leads to trisubstituted product except with very bulky phosphines such as PCy$_3$ [115]. If chromatographic separation rather than crystallization is employed to treat the reaction products, mono- and di-substituted products can be obtained from thermal reactions though the tri-substituted complexes often predominate [115]. The first mono- and di-phosphine substituted Ru$_3$(CO)$_{12}$ complexes were prepared by ligand
transfer reactions between low-valent platinum tertiary phosphine complexes and Ru₃(CO)₁₂ [200].

Benzems et al. [201] and Arewgoda et al. [202] first showed that specific CO substitution in metal carbonyl complexes can be electronically induced. Since then a number of mild routes to CO substitution have been developed. Bruce et al. [203] and Arewgoda et al. [204] reported that CO substitution can be catalysed by Na/benzophenone radical anion (BPK). The proposed mechanism for this electron transfer catalysed reaction on Ru₃(CO)₁₂ is outlined in Scheme 2-1 [205]. The investigation of the electrochemical behavior of Ru₃(CO)₁₂ and related species has shed further light on the mechanism [206, 207]. It has been shown that Ru₃(CO)₁₂⁻ radical (t₁/₂=10⁻⁶ s) rapidly isomerizes to an open structure Ru₃(CO)₁₂⁻*(t₁/₂=10⁻⁶ s) which can either dimerize or undergo a redox reaction.

Two requirements have to be met for the catalysis to occur: (1) the cluster carbonyl has to be reduced without fragmentation, and the resulting anion has to have a long enough lifetime for substitution to take place; (2) to facilitate the electron transfer from the substituted radical

\[
\text{Ru₃(CO)₁₂} \xrightarrow{[\text{Ph}_2\text{CO}]} [\text{Ru₃(CO)₁₂}^-] \xrightarrow{L} [\text{Ru₃(CO)₁₁L}^-] \xrightarrow{\text{Ru₃(CO)₁₂}} \]

\[
\left[ \begin{array}{c} \text{Ru} \\ \text{(CO)₄} \\ \text{Ru} \\ \text{(CO)₄} \end{array} \right]^- \xrightarrow{*} \text{Ru₃(CO)₁₁L}
\]

Scheme 2-1 The proposed mechanism for BPK catalyzed mono-substitution of Ru₃(CO)₁₂.
anion to the unsubstituted one, the substituting ligand must be a better Lewis base than the carbonyl ligand. Thus: (1) the efficiency of BPK catalysis decreases with increasing substitution; (2) weak coordinating ligands such as AsPh$_3$ and SbPh$_3$ give moderate or low yields of the products. For most phosphines, either monodentate or bidentate, the mono-, di-, and tri-substitution proceeds readily in high conversion and specificity with no fragmentation being detected [205, 208]. This method has allowed many previously unknown phosphine and arsine complexes to be prepared.

The second method of activating Ru$_3$(CO)$_{12}$ towards substitution was described by Lavigne and Kaesz [209]. A catalytic amount of PPN$^+$OAc$^-$ or PPN$^+$CN$^-$ was found to promote CO substitution of Ru$_3$(CO)$_{12}$ by tertiary phosphines such as PPh$_3$, dppe, but not by AsPh$_3$. Other PPN$^+$ salts show varying degrees of activity and the reaction presumably involves anion attack at a CO group as the first step. Nucleophilic attack of phosphine followed by CO loss and regeneration of the catalytic anion leads to the substituted product. It is also possible that the anion attacks a CO group and decarbonylation leaves the anion attached to a ruthenium center. The anion can then easily be replaced by a phosphine. Detailed study of the reaction mechanism is apparently needed.

CO substitution of Ru$_3$(CO)$_{12}$ by phosphines has also been facilitated by methoxide anion [210, 211], [CpFe(CO)$_2$]$_2$ [212, 213] and [Fe(CO)$_2$L(µ-SMe)]$_2$ (L=CO, PPh$_3$) [214]. A comparative study of the thermal, BPK, and [CpFe(CO)$_2$]$_2$ catalyzed routes suggests that the [CpFe(CO)$_2$]$_2$ route, which may involve iron carbonyl anion, is superior for those reactions reported [215]. Again more research work is needed to establish the generality and scope of these little studied reactions.
One potentially very useful strategy involves the activation of the carbonyl by \( \text{Me}_3\text{NO} \). Since phosphines or arsines are susceptible to oxidation by \( \text{Me}_3\text{NO} \), the carbonyl is usually activated with \( \text{Me}_3\text{NO} \) in the presence of a labile ligand such as \( \text{MeCN} \), this labile ligand can then be readily replaced [216]. Both \( \text{Ru}_3(\text{CO})_{11}(\text{MeCN}) \) and \( \text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2 \) have been prepared by using low temperatures [217]. The complexes are quite unstable so further development is necessary to establish it as a simple and convenient method [218].

With the advent of these mild synthetic methods to \( \text{Ru}_3(\text{CO})_{12} \) derivatives, considerable interest in their chemistry has developed and many complexes are thus known. The most common structural types of monodentate (L) and bidentate (L-L) tertially phosphine and arsine substituted \( \text{Ru}_3(\text{CO})_{12} \) complexes are \( \text{Ru}_3(\text{CO})_{11}L \) (176) (L=\( \text{PPh}_3 \), \( \text{PCy}_3 \), \( \text{AsPh}_3 \), \( \text{PMe}_3 \), \( \text{PMe}_2\text{Ph} \), \( \text{P}(2-\text{MeC}_6\text{H}_4)_3 \), \( \text{P}(4-\text{MeC}_6\text{H}_4)_3 \), \( \text{PET}_3 \), \( \text{PPh}_2\text{Py} \), \( \text{Ph}_2\text{P}=-\text{C}=\text{C}-\text{R} \) where \( \text{R}=\text{tBu}, \text{iPr}, \text{Ph} \)), \( \text{Ru}_3(\text{CO})_{10}L_2 \) (177) (L=\( \text{PPh}_3 \), \( \text{PMePh}_2 \), \( \text{PMe}_2\text{Ph} \), \( \text{PMe}_3 \), \( \text{AsPh}_3 \), \( \text{PCy}_3 \), \( \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 \)), \( \text{Ru}_3(\text{CO})_9L_3 \) (178) (L=\( \text{PMe}_3 \), \( \text{PMe}_2\text{Bz} \), \( \text{PMe}_2\text{Ph} \), \( \text{AsMe}_2\text{Ph} \), \( \text{PMePh}_2 \), \( \text{PET}_3 \), \( \text{P}(3-\text{MeC}_6\text{H}_4)_3 \), \( \text{P}(4-\text{MeC}_6\text{H}_4)_3 \), \( \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 \), \( \text{PPh}_3 \), \( \text{PnBu}_3 \), \( \text{AsMe}_2\text{Bz} \), \( \text{PETPh}_2 \), \( \text{Ph}_2\text{P}=-\text{C}=\text{C}-\text{tBu} \)), \( \text{Ru}_3(\text{CO})_8L_4 \) (179) (L=\( \text{PMe}_3 \), \( \text{PMe}_2\text{Ph} \)), \( \text{Ru}_3(\text{CO})_{10}(\text{L-L}) \) (180) (L-L=\( \text{dppm}, \text{dppe}, \text{dppp}, \text{cis-dppee}, \text{ffars}, \text{CH}_2\text{-C}(\text{PPh}_2)_2, \text{f}_6\text{fos}, \text{dmpm}, \text{dpam}, \text{dpae} \)), \( \text{Ru}_3(\text{CO})_8(\text{L-L})_2 \) (181) (L-L=\( \text{dppm}, \text{dppe}, \text{ffars}, \text{f}_6\text{fos}, \text{dmpm}, \text{dpam} \)), \( \text{Ru}_3(\text{CO})_{11}(\eta^1\text{-L-L}) \) (182) (L=\( \text{dppe} \), \( \text{Ru}_3(\text{CO})_{11}(\text{L-L}) \) (183) (L-L=\( \text{dppm}, \text{dppe}, \text{dppa} \)), \( \text{Ru}_3(\text{CO})_{10}\text{LL}' \) (184) (L=\( \text{AsPh}_3 \), L'=\( \text{P}(4-\text{MeC}_6\text{H}_4)_3 \)), \( \text{Ru}_3(\text{CO})_9(\text{L-L})\text{L}' \) (185) (L-L=\( \text{dppe} \), L'=\( \text{PMe}_3 \)) [115, 196-200, 205, 212, 218-246, 295, 297, 301]. \( \text{PF}_3 \) is the only ligand at present known to displace more than four \( \text{CO} \) ligands [242]. For bidentate ligands, \( \text{Ru}_3(\text{CO})_6(\text{L-L})_3 \) (L-dppm and cis-dppee) have been isolated and characterized spectroscopically [243, 244].
Bruce et al. [219-223, 226, 247] among others [196, 224, 225, 227, 229, 230, 248] have carried out an extensive structural study of some of these complexes. Crystal structures have been determined for \( \text{Ru}_3(\text{CO})_{11}L \) (176) (\( L = \text{PPh}_3 \) [196], \( \text{PCy}_3 \) [219], \( \text{PPh}(\text{OMe})_2, \text{AsPh}_3 \) [220]), \( \text{Ru}_3(\text{CO})_{10}L_2 \) (177) (\( L = \text{PPh}_3 \) and \( \text{PPh}(\text{OMe})_2 \) [221]), \( \text{Ru}_3(\text{CO})_9L_3 \) (178) (\( L = \text{PMe}_3 \) [219], \( \text{PMe}_2\text{Ph}, \text{AsMe}_2\text{Ph}, \text{PMe}_2\text{Bz}, \text{PPh}(\text{OMe})_2 \) [222]), \( \text{Ru}_3(\text{CO})_8L_4 \) (179) (\( L = \text{PMe}_2\text{Ph} \) [223], \( \text{PPh}(\text{OMe})_2 \) [247]), \( \text{Ru}_3(\text{CO})_{10}(L-L) \) (180) (\( L-L = \text{dppm} \) [224], dppe [226], ffars [227b], \( \text{H}_2\text{C}=\text{C}(\text{PPh}_2)_2 \) [229], \( \text{PhP}(\text{CH}_2)(\text{C}_6\text{H}_4)\text{PPh} \) [230]), and \( \text{Ru}_3(\text{CO})_8(L-L)_2 \) (181) (\( L-L = \text{dppm} \) [225] and ffars [227a]). All these complexes have the structures shown above except for \( \text{Ru}_3(\text{CO})_8 \)
[PPh(OMe)2]_4 (186) which adopts a structure with two carbonyls asymmetrically bridging the shorter Ru-Ru bond (2.797(1) Å) [247]. The other two Ru-Ru bonds are identical at 2.879(1) Å and the molecule represents the only known example of a Ru_3(CO)_{12} derivative with the Fe_3(CO)_{12} type structure. Another interesting structure is Ru_3(CO)_9(μ_3-(P^2Bu_2)_3SiMe) (187) in which the tridentate ligand caps one face of the Ru_3 triangle and there are three asymmetrically bridging carbonyls. The Ru-Ru bonds at 2.917(1) Å are longer than those of Ru_3(CO)_{12} (2.854(4) Å). Bent semi-bridging carbonyls are also found in the solid state structures of Ru_3(CO)_{10}(PPh_3)_2 [221, 249] and possibly of Ru_3(CO)_{8}(PMe_2Ph)_4 [223]. The tendency for the formation of bridging CO groups is expected to increase with more electron donating phosphines and with more CO groups being replaced by phosphines [223].

Studies of the structures of monodentate phosphine and arsine complexes of Ru_3(CO)_{12} have resulted in the following generalizations [223]: (1) Phosphine and arsine ligands invariably occupy equatorial coordination sites. In di-, tri-, and tetra-substituted complexes, the bulky ligands occupy positions so that they are as far as possible from each other. (2) As the degree of substitution increases, so does the degree of distortion
from $D_{3h}$ symmetry in Ru$_3$(CO)$_{12}$ to $D_3$ symmetry by a twisting of the Ru(CO)$_n$L$_{4-n}$ groups about the Ru-Ru bonds. (3) Introduction of the group 15 ligands results in a lengthening of the Ru-Ru bonds. For Ru$_3$(CO)$_{11}$L complexes, the Ru-Ru bond cis to the ligand L is affected the most and the lengthening correlates well with the cone angles of the ligands. For Ru$_3$(CO)$_{10}$L$_2$ complexes, no pronounced lengthening of such cis Ru-Ru bonds is observed, though the Ru$_3$ core is expanded. (4) In general, the average Ru-Ru distances increase with increasing degrees of substitution except in (186) where there is a change in structure type.

For bidentate ligands, the Ru-Ru bond distances show two different trends depending on particular ligands as summarized in Table 2-2. In dppm and H$_2$C=C(PPh$_2$)$_2$ complexes, the bridged Ru-Ru bonds are shorter than the unbridged ones. In dppe complex, all the Ru-Ru bonds have similar lengths and they are almost the same as those in Ru$_3$(CO)$_{12}$ (2.854(4) Å). In ffars, PhP(CH$_2$)(C$_6$H$_4$)PPh, and bppf complexes, the bridged Ru-Ru bonds are longer than the unbridged ones. The trend is most apparent in Ru$_3$(CO)$_{10}$(bppf) (188) where the bridged Ru-Ru bond at 2.9284(5) Å is significantly longer than the other two (2.8600(4) Å) [250]. In Ru$_3$(CO)$_8$(ffars)$_2$ (189), while the bridged Ru-Ru bonds are not different from those in Ru$_3$(CO)$_{12}$, the unbridged one is shortened to 2.785(4) Å.
Table 2-2. Ru-Ru bond distances for some Ru₃(CO)₁₀(L-L) and Ru₃(CO)₈
(L-L)₂ complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>L-L bridged</th>
<th>L-L unbridged</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru₃(CO)₁₀(dppm)</td>
<td>2.834(1)</td>
<td>2.841(1), 2.860(1)</td>
<td>224</td>
</tr>
<tr>
<td>Ru₃(CO)₈(dppm)₂</td>
<td>2.833(2), 2.826(2)</td>
<td>2.858(2)</td>
<td>225</td>
</tr>
<tr>
<td>Ru₃(CO)₁₀[CH₂-C(PPh₂)₂]</td>
<td>2.836(1)</td>
<td>2.862(1), 2.840(1)</td>
<td>229</td>
</tr>
<tr>
<td>Ru₃(CO)₁₀(dppe)</td>
<td>2.856(1)</td>
<td>2.855(1), 2.847(1)</td>
<td>236</td>
</tr>
<tr>
<td>Ru₃(CO)₁₀(ffeas)</td>
<td>2.858(6)</td>
<td>2.831(3), 2.831(3)</td>
<td>227b</td>
</tr>
<tr>
<td>Ru₃(CO)₈(ffeas)₂</td>
<td>2.853(3), 2.853(3)</td>
<td>2.785(4)</td>
<td>227a</td>
</tr>
<tr>
<td>Ru₃(CO)₁₀[PhP(CH₂)(C₆H₄)PPh]</td>
<td>2.884(1)</td>
<td>2.851(1), 2.848(1)</td>
<td>230</td>
</tr>
<tr>
<td>Ru₃(CO)₁₀(bppf)</td>
<td>2.9284(5)</td>
<td>2.8600(4), 2.8600(4)</td>
<td>250</td>
</tr>
</tbody>
</table>

Recently, Cullen and coworkers [250] have prepared and characterized a number of ferrocenylphosphine derivatives of Ru₃(CO)₁₂. These include Ru₃(CO)₁₁L (L=PFc₃, PFc₂Ph, PFcPh₂), Ru₃(CO)₁₀L₂ (L=PFc₂Ph, PFcPh₂) in addition to Ru₃(CO)₁₀(bppf). The structure of Ru₃(CO)₁₁(PFcPh₂) was determined and, as expected, the Ru-Ru bond cis to the PFcPh₂ ligand is 2.9000(6) Å being longer than the other two at 2.8641(6) and 2.8560(7) Å [250].

2.2.2 Triosmium Phosphine and Arsine Complexes

Os₃(CO)₁₂ is more robust than Ru₃(CO)₁₂ and a wide variety of reactions can be carried out without any change of nuclearity. Os₃ systems are often quite stable to heat and air, they are easily crystallized, so their
chemistry has been extensively studied. The very inertness of these systems has allowed the isolation of many interesting compounds otherwise unavailable [113].

A large number of reactions leading to triosmium phosphine and arsine derivatives are known, these involve either the parent Os₃(CO)₁₂ or its derivatives that contain labile ligands such as MeCN.

Substitution of CO groups in Os₃(CO)₁₂ by phosphines and arsines has been effected by thermal and chemical methods. Photochemical activation of Os₃(CO)₁₂ towards substitution has been little studied [251].

Conventional thermal reactions involving Os₃(CO)₁₂ and phosphines or arsines are still widely used because, unlike the reactions of Ru₃(CO)₁₂, the rates of the second and third substitutions are not much different from that of the first, so a mixture of mono-, di-, and tri-substituted products is usually obtained. By controlling stoichiometry the desired product can be obtained in good yield although chromatographic separation is often necessary.

Chemical activation of Os₃(CO)₁₂ has been achieved with Me₃NO, which was first introduced by Shvo and Hazum [253] to remove coordinated CO groups through the formation of CO₂. Since phosphine and arsine are also susceptible to oxidation by Me₃NO, the direct reaction of Os₃(CO)₁₂ with phosphine/arsine in the presence of Me₃NO is not often used. Other chemical means of activation include the use of Pt(PPh₃)₄ [252] and [CpFe(CO)₂]₂ [215a]. Na⁺[Ph₂CO]⁻ is found to catalyze the substitution of phosphine or arsine on Os₃(CO)₁₂ but the activity is low [203].

Substitution of Os₃(CO)₁₂ derivatives containing labile ligands is the most useful method for preparing mono- and di-substituted derivatives. Phosphines and arsines react with these derivatives with great specificity.
under mild conditions.

Activation of Os$_3$(CO)$_{12}$ by Me$_3$NO in the presence of a labile ligand such as MeCN has been used to prepare Os$_3$(CO)$_{11}$(MeCN) and Os$_3$(CO)$_{10}$(MeCN)$_2$ [255, 256]. The latter complex was also prepared by the reaction of Os$_3$(CO)$_{10}$(C$_8$H$_{14}$)$_2$ (C$_8$H$_{14}$-cyclo-octene) with MeCN [254]. The cyclo-octene and butadiene derivatives Os$_3$(CO)$_{10}$(s-cis-C$_4$H$_6$) (190) and Os$_3$(CO)$_{10}$(s-trans-C$_4$H$_6$) (191) are also very useful starting materials [257]. The structures of (190) and (191) have been determined [257, 258]. The butadiene is bonded to one osmium atom and occupies one axial site and one equatorial site in (190), while in (191) it occupies one equatorial site on two adjacent osmium metal centers. The s-cis-butadiene complex (190) has been used by Deeming et al. to prepare some unusual isomers such as 1,1-Os$_3$(CO)$_{10}$(PMe$_2$Ph)$_2$ (192) [259] and 1,1-Os$_3$(CO)$_{10}$(dppe) (193) [260, 281]. The structures of Os$_3$(CO)$_{11}$(MeCN) (194) and Os$_3$(CO)$_{10}$(MeCN)$_2$ (195) were also determined, and the MeCN ligands occupy axial positions. The axial CO ligands trans to the MeCN ligand have the shortest Os-C bonds [261].

Some common structure types for phosphine and arsine derivatives of Os$_3$(CO)$_{12}$ are Os$_3$(CO)$_{11}$L (196) (L=PPh$_3$, P(4-MeC$_6$H$_4$)$_3$, P(SiMe$_3$)$_3$, Ph$_2$P-C≡C=tBu, Ph$_2$P-C≡C-Ph, PMe$_3$, PET$_3$, PMe$_2$Ph, AsMe$_2$Ph, PET$_2$Ph, PMePh$_2$, Me$_2$As-CH=CH$_2$, PETPh$_2$, PnBu$_3$, Ph$_2$P(CH$_2$)$_2$Si(OEt)$_3$, Ph$_2$P-CH=CH$_2$, Ph$_2$P(2-
\[ \text{CH}_2=\text{CHC}_6\text{H}_4, \text{AsMe}_2(2-\text{MeC}_6\text{H}_4), \text{AsMe}_2(2-\text{MeOC}_6\text{H}_4), \text{AsMe}_2(4-\text{MeOC}_6\text{H}_4), \text{As}(4-\text{MeC}_6\text{H}_4)_3, \text{Os}_3(\text{CO})_{10} \text{L}_2 \text{ (197) (L-PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PMe}_3, \text{PET}_3, \text{AsMe}_2\text{Ph}, \text{PhPC}_4\text{H}_2\text{Me}_2, \text{AsMe}_2(2-\text{MeC}_6\text{H}_4), \text{AsMe}_2(2-\text{MeOC}_6\text{H}_4), \text{AsMe}_2(4-\text{MeOC}_6\text{H}_4), \text{P}(4-\text{MeOC}_6\text{H}_4)_3, \text{PET}_2\text{Ph}, \text{AsMe}_2(\text{CH-CH}_2), \text{PET}\text{Ph}_2, \text{PET}_{n}\text{Bu}_3, \text{P}(4-\text{MeC}_6\text{H}_4)_3, \text{Ph}_2\text{P}(\text{CH}_2)_2\text{Si(OEt)}_3, \text{Ph}_2\text{P(2-CH}_2-\text{CHC}_6\text{H}_4)), \text{Os}_3(\text{CO})_9 \text{L}_3 \text{ (198) (L-PPh}_3, \text{PMe}_3, \text{PET}_3, \text{PMe}_2\text{Ph}, \text{AsMe}_2\text{Ph}, \text{PET}_2\text{Ph}, \text{AsMe}_2(\text{CH-CH}_2), \text{PET}_{n}\text{Bu}_3, \text{P}(4-\text{MeC}_6\text{H}_4)_3, \text{PMePh}_2, \text{Ph}_2\text{P(2-CH}_2-\text{CHC}_6\text{H}_4)), \text{Os}_3(\text{CO})_{10} \text{(L-L) (199) (L-L-dppm, dmpm, dppe, dppp, dp,b, H}_2\text{C-C(PPh}_2)_2, \text{cis-dppee, f}_4\text{fos}), \text{Os}_3(\text{CO})_8 \text{(L-L) }_2 \text{ (200) (L-L-f}_4\text{fos, H}_2\text{C-C(PPh}_2)_2, \text{Os}_3(\text{CO})_9 \text{(L-L)L'} \text{ (201) (L-L-dppm, L'-PPh}_3, \text{Os}_3(\text{CO})_{11} \text{(L-L) (202) (L-L-dppm, dppe, dppp, dp,b, dmpm, f}_4\text{fos, f}_8\text{fos, dppa), (Os}_3\text{(CO)}_{11} \text{(L-L) }} \]
Crystal structures have been determined for complexes Os₃(CO)₁₁L
(L=PPh₃ [220], PPh(OMe)₂ [220], Ph₂PNHPh [289], tBu₂PNH₂ [294]),
Os₃(CO)₁₀L₂ (L=PPh₃ [221], PPh(OMe)₂ [221], (CF₃)₂PNPPh₃ [290]),
Os₃(CO)₉(PPh₃)₃ [222], (Os₃(CO)₁₁)₂(dppa) [279], 1,2-Os₃(CO)₁₀[H₂C-C(PPh₂)₂]
[244], 1,2-Os₃(CO)₁₀(dppe) [286], 1,1-Os₃(CO)₁₀(dppe) [291], and Os₃(CO)₉
(η²-μ-dppm)(η¹-dppm) (205) [291]. All phosphines occupy equatorial
coordination sites in these structures and no bridging carbonyls are present. The only complex in which two of the axial CO ligands have been described as semi-bridging is Os$_3$(CO)$_9$(μ$_3$-η$^2$-C$_2$Et$_2$)(PPh$_3$) [293]. For monodentate phosphine complexes, the generalizations observed in Ru$_3$ derivatives are also valid for the osmium analogues. In (Os$_3$(CO)$_{11}$)$_2$(dppa) the two Os-Os bonds cis to the phosphine at 2.903(3) 2.907(3) Å are longer than the rest which average to 2.879(3) Å [279]. The complex 1,1-Os$_3$(CO)$_{10}$(dppe) has the structure (199a) and the two Os-Os bonds involving the dppe bound Os atoms (2.913(1) and 2.914(1) Å) are longer than the other (2.889(1) Å) [291]. The complexes 1,2-Os$_3$(CO)$_{10}$(dppe) [286] and 1,2-Os$_3$(CO)$_{10}$(cis-dppee) [244] have the same structures as (199b) and the Os-Os bonds have similar trends as in the Ru$_3$ analogues.

Os$_3$(CO)$_{12}$ derivatives containing ferrocenylphosphine ligands were unknown prior to the present work.

2.3 Pyrolytic Reactions of Some Triruthenium and Triosmium Phosphine and Arsine Complexes

Pyrolysis of phosphine or arsine substituted Ru$_3$ and Os$_3$ carbonyl complexes often leads to intramolecular C-H and/or C-P(As) bond cleavages [299]. Many cluster benzyne complexes described in Chapter 1 are derived from a phenyl group on phosphorus or arsenic through these intramolecular reactions.

2.3.1 Pyrolytic Reactions of Some Triruthenium Phosphine Complexes

Pyrolysis of Ru$_3$(CO)$_9$(PR$_3$)$_3$ (PR$_3$=PPh$_3$, PMePh$_2$, P(3-MeC$_6$H$_4$)$_3$, P(4-
MeC₆H₄)₃ in decalin gives some dinuclear complexes (206a), (206b), (207), and (208), besides the benzyne complexes (106a) and analogues [115]. At lower temperatures in refluxing toluene, Ru₃(CO)₉(PPh₃)₃ also affords the dinuclear complex (209) in addition to (106a) [300]. Pyrolysis of Ru₃(CO)₁₁(AsPh₃) gives dinuclear arsenido complex (206c) and pentanuclear complex (210a) [118]. Pyrolysis of Ru₃(CO)₁₁(PMe₂Ph) gives (210b) in addition to the benzyne complex (109) [118]. The benzyne complexes result from one aryl C-H and two aryl C-P cleavages without cluster breakdown, while the other complexes result from both C-H and/or C-P cleavages and Ru-Ru bond cleavages. Complex (208) results from two aryl C-H cleavages, (207) results from one aryl C-H cleavage and one aryl C-P cleavage, (206) results from two aryl C-P cleavages, and (209) results from one aryl C-P cleavage and a CO insertion into the phenyl group. The crystal structure of (209) shows the two ruthenium atoms and bridging acyl to be coplanar: the Ru-Ru distance is 2.750(1) Å [300]. The formation of (106a), (208) and (207) probably involves ortho-metalation as the first step, but that of (209) indicates that C-P cleavage can take place without C-H cleavage. The structure of (210) contains a Ru₅P or Ru₅As octahedron with three CO groups on each metal center. Its formation involves two sp² C-P
cleavage reactions in addition to complex metal framework rearrangement.

The pyrolysis of Ru$_3$(CO)$_{11}$(PPh$_2$R) (R=Ph, Me, CH$_2$NPh$_2$), studied by Knox et al. [117, 118], affords the benzyne complexes (106a), (107a-c), and (108). The formation of (106a) from Ru$_3$(CO)$_{11}$(PPh$_3$) involves a redistribution of the phosphine ligand together with two aryl C-P and one aryl C-H cleavages. The formation of the other complexes involves two aryl C-P cleavages and one aryl C-H cleavage. Bonnet and coworkers found that the complex Ru$_3$(CO)$_{11}$(PPh$_2$Py) loses CO at ambient temperature to yield an acyl complex (211) [301]. The formation of (211) involves one aryl C-P bond and one Ru-Ru bond cleavages together with a CO insertion, and an intermediate (212) with phosphido and a σ-bonded phenyl group is believed to be involved. The Ru-Ru bond involving oxygen bonded ruthenium in (211) at 2.821(1) Å is shorter than the other one at 2.877(1) Å.

![Chemical structures](image)

Complex (213) readily converts to the hydrido-alkyne cluster (214) at 40°C and to a Ru$_4$C$_2$ cluster (215) at higher temperatures [216, 302]. This chemistry is centered on the more reactive hydrocarbon group. Carty et al. found that pyrolysis of Ru$_3$(CO)$_{11}$(Ph$_2$P−C≡C−R) leads to Ru$_2$(CO)$_6$(PPh$_2$)
(C=C-R) and likewise Ru3(CO)9(Ph2P-C=C-R)3 leads to Ru3(Ph2P-C=C-tBu)
(PPh2)2(μ2-C=C-tBu)(μ2-η2-C=C-tBu) (216) [237, 276]. The structure (216)
has Ru(1)-Ru(2) length of 3.139(1) Å and Ru(1)-Ru(3) length of 3.05(1) Å
[237].

Heating (Ru3(CO)11)2(dppa) results in the formation of the penta-
nuclear cluster (217), and this definitely involves many steps but only one
alkynyl C-P bond cleavage [295]. Ru3(CO)8(dppm)2 converts to the open
Ru3 complex (218) upon heating at 130°C [246]. The structure was
determined and the open Ru3 triangle is capped on one face by the
phosphinidene moiety and the other face by a metalated phosphine
moiety. The dppm bridged Ru-Ru bond at 2.843(1) Å is shorter than the

![Diagrams](images)
other one at 2.884(1) Å. One aryl C-P, one alkyl C-P and one alkyl C-H bond are cleaved in forming (218). An intermediate complex (219) has been isolated in a controlled pyrolysis [303]. The structure consists of a triangular array of metal atoms involving two metal-metal bonds with the dppm bridged Ru-Ru bond at 3.205(1) Å being much longer than the other one at 2.888(1) Å. In fact, the longer Ru-Ru bond in (219) is the longest Ru-Ru bond known. The face-capping moiety derived from dppm acts as a seven electron donor and results from one aryl C-H, one alkyl C-H and one aryl C-P cleavage. It is believed that a species of formula Ru$_3$(CO)$_7$($\mu$-dppm) ($\mu_3$-$\eta^3$-PhPCH$_2$PPh(C$_6$H$_4$)) is the antecedent of (219) [303]. A reaction sequence is proposed as shown in Scheme 2-2. The first step involves the motion of the phosphine from equatorial to axial position; orthometalation of a phenyl group and subsequent reductive elimination of a benzene.

Scheme 2-2 A possible reaction sequence for the formation of (218) from Ru$_3$(CO)$_8$(dppm)$_2$. 

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molecule. C-H activation of the methylene bridge then leads to (219). An alkyl C-P cleavage followed by reductive elimination of the hydride with orthometalated phenyl gives the final complex (218).

Pyrolysis of Ru$_3$(CO)$_{10}$(dppm) affords complex (220), a result of one aryl C-P and one C-H cleavage [230]. Orthometalation is presumably the first step and is followed by reductive elimination of a benzene molecule. The transformed phosphine-phosphido moiety donates six electrons to the cluster. The Ru-Ru bond distances (from 2.818(1) to 2.888(1) Å) are close to the values in the parent Ru$_3$(CO)$_{12}$. Thermolysis of Ru$_3$(CO)$_{10}$(dmpm) and Ru$_3$(CO)$_8$(dmpm)$_2$ leads to HRu$_3$(CO)$_9$(Me$_2$PCHPMe$_2$) (221) and HRu$_3$(CO)$_7$(dmpm)(Me$_2$PCHPMe$_2$), respectively [239]. The methylene C-H bond is cleaved preferentially and the transformed ligand caps one face of the Ru$_3$ triangle. The longest Ru-Ru bond is at 3.097(1) Å and is thought to be bridged by the hydride, the other two Ru-Ru bonds are at 2.812(1) and 2.804(1) Å, respectively.

Two reports concerning the pyrolysis of ferrocenylphosphine substituted Ru$_3$(CO)$_{12}$ derivatives have appeared [119, 120]. The formation of (106b) from Ru$_3$(CO)$_{10}$(FcPPh$_2$)$_2$ involves one phenyl C-H and two phenyl C-P cleavages [119]. Thermolysis of Ru$_3$(CO)$_{10}$(bppf) affords complexes (222) and (223), in addition to (162) and the benzyne
complexes (106c) and (107d) [120]. The formation of (107d) involves at least three C-P bonds and one C-H bond cleavage. Other complexes are included in a proposed reaction sequence shown in Scheme 2-3 [120]. The motion of one phosphorus from an equatorial to an axial position leads to either ferrocenyl orthometalation with subsequent Fe-Ru bond formation to yield (162) or phenyl orthometalation. The latter pathway goes further by a η².

Scheme 2-3 A proposed reaction sequence for the pyrolysis of Ru₃(CO)₁₀(bppf).
bonding interaction to give (222). Complex (222) may then undergo a phenyl C-P cleavage to form (223) or undergo one ferrocenyl C-P and one phenyl C-P cleavages to form (106c). The structure of (162) contains a long Ru-Ru bond bridged by the two phosphorus atoms (3.037(2) Å) and a rather short Ru-Ru bond bridged by the orthometalated ferrocenyl carbon atom (2.692(2) Å). A Fe-Ru distance of 3.098(3) Å indicates bond formation between these metal atoms. Such bonding is necessary for the molecule to be electron precise. Structure (222) contains a Ru$_3$ triangle capped on one face by the metalated phenyl phosphine moiety which acts as a five electron donor. Complex (223) contains a Ru$_3$ triangle capped on one face by the phosphido moiety which acts as a four electron donor.

2.3.2 Pyrolytic Reactions of Some Triosmium Phosphine and Arsine Complexes

Thermal decomposition of Os$_3$(CO)$_{10}$P(PPh$_3$)$_2$ affords complexes (224), (225), and (226) in addition to the three benzyne complexes (49), (50), and (51) [67-69]. Both aryl C-H and C-P cleavages are involved in forming these benzyne complexes, and (51) also contains a new C-C bond. Complexes (224) and (225), resulting from one aryl C-H cleavage, are quite
similar except that in (224) the axial phosphine acts probably as a five
electron donor while in (225) the metalated phenylphosphine remains in
an equatorial position and is a three electron donor. Complex (225) is the
only isolated Os₃ complex showing a simple orthometalated phenyl without
an \( \eta^2 \) interaction of that phenyl with the cluster. In both (224) and (225)
the Os-Os bond cis to PPh₃ is the longest (3.001(2) and 3.047(2) Å),
respectively). Complex (226) is rather unusual in that it has a bridging
phenyl group. One face of the Os₃ triangle is capped by the orthometalated
phosphido moiety acting as a four electron donor, similar to that in (222).
Two aryl C-P bonds and one aryl C-H bond are cleaved in forming (226).
All the three Os-Os bonds are quite long (3.095(2), 3.146(2), and 3.187(2)
Å) and the phenyl bridge is asymmetric (C-Os bonds 2.19(3) and 2.39(3)
Å). The postulated reaction sequence is shown in Equation 2.2 [69].

\[
\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2 \rightarrow (225) \rightarrow (224) \rightarrow (49) + (50) + (51) + (226) \quad (2.2)
\]

The formation of the benzyne complexes (113)-(116) involves one
aryl C-H bond and one or two aryl C-P(As) bond cleavages from PMe₂Ph or
AsMe₂Ph [125]. No alkyl C-H and C-P bond cleavage products were
obtained in the thermolytic reactions of these phosphine or arsine
substituted Os₃ complexes, although dinuclear complexes (130) and (131)
were formed in low yield as a result of aryl C-H and C-As cleavage [125].
Pyrolysis of trialkyl phosphine complexes does result in alkyl C-H bond
cleavage [263]. For example, heating Os₃(\text{CO})_{11}(\text{PMe}_3) affords H₂Os₃
(Me₂PCH)(\text{CO})₉ (227a) in 60% yield. Os₃(\text{CO})_{11}(\text{PET}_3), Os₃(\text{CO})_{10}(\text{PMe}_3)_2, and
Os₃(\text{CO})_{10}(\text{PET}_3)_2 behave similarly to give (227b), (228a), and (228b)
respectively [263]. While (228b) shows only one isomer, (228a) shows two
isomers which are believed to differ in the coordination sites of the PEt3 ligand. The structures of (227) and (228) are believed to be similar to the vinylidene complex Os3(CO)9(H)2(μ3-η-C-CH2) [127]. Only the α C-H bonds are cleaved in PEt3 complexes. Pyrolysis of Os3(CO)11(PEt2Ph) in nonane affords HOs3(Et2PC6H4)(CO)9 (229) and HOs3(EtPCHCH2)(CO)9 (230) in addition to the benzyne complex (114c) [127]. It is interesting that in forming (230) two alkyl C-H bonds and one aryl C-P bond have been cleaved.

Two intermediates, (231) and (232), have been isolated and structurally characterized in the transformation of Os3(CO)11(PMe2Ph) to Os3(CO)9(μ3-PMe)(μ3-C6H4) (121b) [132]. A reaction scheme was proposed as shown in Scheme 2-4 (R=Ph, Me, Et). Complex (231) contains a μ3-η2-metalated phenylphosphine moiety, as in (224) and (229). Complex (232) contains a metalated phosphido capping moiety with a bridging carbonyl, similar to the ruthenium complex (223) or the osmium complex (226) where an equatorial bridging phosphido and bridging phenyl group replace the bridging carbonyl and one terminal carbonyl. This complex is a rare example of an Os3 complex containing a bridging CO group. The transformation of (232) to (121) is very similar to that of the Fe3 cluster.
Scheme 2-4 Proposed mechanism for the pyrolytic reactions of Os₃(CO)₁₁(PRPh₂).

Thermolysis of Os₃(CO)₁₁(PhPCHCHCHCH) gives ring opened products (233) and (234) [305], while Os₃(CO)₁₁(PhPCHCMemCH) gives (235) in good yield in addition to a small amount of (119) [129]. The ring opened phosphido moiety in (233) and (234) is an eight-electron donor. The Os-Os bond involving the η³-allyl bound osmium atom in (234) is of length 2.948(1) Å, while all other Os-Os bonds in (233)-(235) are somewhat

Scheme 2-4

\[ \text{Os}_3(\text{CO})_{11}(\text{PRPh}_2) \rightarrow \text{Os}(\text{CO})_3 \rightarrow \text{Os}(\text{CO})_3 \rightarrow \text{Os}(\text{CO})_3 \]

\[ \text{R=Me} \]

(121) (232)
shorter than those in Os₃(CO)₁₂. Structure (235) is similar to (233) except that the two carbon atoms bearing methyls are not coordinated.

Pyrolysis of Os₃(CO)₁₀(dpPm) in refluxing toluene produces complex (236) in high yield [273]. The crystal structure was determined and one face of the Os₃ triangle is capped by the orthometalated phenyl phosphine moiety. The metalated phenyl carbon bridged Os-Os bond at 2.747(1) Å is significantly shorter than the other two (2.844(1) and 2.834(1) Å). Unlike the common μ-η¹,η² interaction of orthometalated phenyl rings found in (222), (224) and (231), the metalated phenyl in (236) interacts with two osmium atoms through one carbon atom only and the molecule is unsaturated [306]. The reaction can be reversed by bubbling CO at 25°C to give the starting material Os₃(CO)₁₀(dpPm) via a stable intermediate Os₃(CO)₉(H)(Ph₂PCH₂PPhC₆H₄) which contains an orthometalated C₆H₄ moiety.
as in (225) [307]. The carbon bridge in (236) is symmetrical with C-Os lengths of 2.283(13) and 2.297(15) Å. The structure of (236) might be related to the ruthenium complex (162), but in the latter the unsaturation is compensated by a Fe-Ru dative bond. The thermal reaction behavior of Os₃(CO)₁₀(dppm) and Ru₃(CO)₁₀(dppm) or Ru₃(CO)₁₀(dppm)₂ is obviously different. The thermal reaction of Os₃(CO)₁₀(dmpm), however, is completely analogous to that of Ru₃(CO)₁₀(dmpm). Thus, heating Os₃(CO)₁₀(dmpm) yields complex (237), the Os₃ analogue of (221) [282]. Like (221), the Os(1)-Os(2) bond at 3.104(1) is much longer than the other two (2.832(1) and 2.839(1) Å). Pyrolysis of (Os₃(CO)₁₁)₂(dppa) gives complex (238), analogue of (217) [278]. Similarly, heating Os₃(CO)₁₁(Ph₂P-C≡C-R) (R = iPr, tBu, Ph) affords the P-C₃ cleavage products Os₃(CO)₉(C≡C-R)(PPh₂) [231, 276].

2.4 Ferrocenylphosphines and Scope of the Present Work

The aromaticity of ferrocene has led to the preparation and investigation of many derivatives analogous to those of benzene [308]. The use of ferrocenyl phosphines, arsines, and sulfides as ligands for transition metal complexes constitutes an important field of study.

The first ferrocenylphosphine to be reported was triferrocenylphosphine PFc₃ [309]. It was obtained from an unusual Friedel-Crafts reaction between ferrocene and PCl₃ in the presence of AlCl₃ (Equation 2.4). The first transition metal complex of triferrocenylphosphine to be described was trans-bis(triferrocenylphosphine)chlorocarbonylrhodium, obtained from the reaction of PFc₃ with [Rh(CO)₂Cl]₂ [310]. Subsequent IR
studies of M(CO)₅(PR₃) (M=Cr, Mo, W), Fe(CO)₄(PR₃) and Mn₂(CO)₉(PR₃) indicated that PFc₃ is a much better σ-donor ligand than PPh₃ [311]. Similar studies show that the coordinating abilities of the phosphines PFcPh₂, PFc₂Ph, and PFc₃ increase with an increase in the number of ferrocenyl groups [312].

\[
\begin{align*}
\text{Fe}^+ &+ \text{PCl}_3 \xrightarrow{\text{AlCl}_3} \text{PFcCl}_2 + \text{PFc}_2\text{Cl} + \text{PFc}_3 \\
(2.4)
\end{align*}
\]

The unsymmetrical tertiary phosphines PFc₂Ph and PFcPh₂ were first prepared by using Friedel-Crafts reactions involving PhPCl₂ and Ph₂PCl, respectively [313]. The 1,1'-phosphine substituted ferrocenes are readily prepared in high yields since solutions of nBuLi and TMEDA readily dilithiate ferrocene and this product readily reacts with organohalo-phosphines [314]. These bidentate ferrocenylphosphines have been widely used in preparing transition metal complexes, some of these complexes have shown activities as homogeneous catalysts for hydrogenation and hydrosilation. In contrast, complexes of monodentate ferrocenylphosphines have been little investigated.

Studies of the reactions of mono- and bidentate ferrocenyl-phosphines with Ru₃(CO)₁₂ were initiated only a few years ago and the complexes Ru₃(CO)₁₀(bppf), Ru₃(CO)₁₁L (L=PFc₃, PFc₂Ph, PFcPh₂) and Ru₃(CO)₁₀L₂ (L=PFc₂Ph, PFcPh₂) were characterized [119, 120, 250]. Ru₃(CO)₁₀(bppf) and Ru₃(CO)₁₀(PFcPh₂)₂ afford mainly benzyne complexes or intermediates to these benzyne complexes when pyrolyzed [119, 120].
Complexes Ru$_3$(CO)$_{11}$(PPh$_2$) and Ru$_3$(CO)$_{10}$(PPh$_2$)$_2$ have also been studied and evidence for the formation of some unusual compounds was obtained [315]. At the time the present study was initiated, no Os$_3$(CO)$_{12}$ derivatives containing ferrocenylphosphines or arsines were known.

The scope of the present work is:

(1) to study the substitution reactions of ferrocenylphosphines, both monodentate and bidentate, containing alkyl or aryl groups, with Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$;

(2) to establish the relative reactivities of alkyl, aryl, and ferrocenyl C-H and C-P bonds towards oxidative cleavage on pyrolysis of the complexes prepared in (1);

(3) to trap reactive species such as ferrocyne, which might be generated through C-H and C-P cleavage, on the Ru$_3$ and Os$_3$ clusters; and

(4) to investigate other bonding interactions especially Fe (ferrocene)-M (e.g. (162)) dative bonding interaction which might be present in some of the pyrolysis products (Fe (ferrocene)-M bonding interactions, although not common, have been found in a number of metal complexes [316-323]).
PART TWO: EXPERIMENTAL
Chapter 3 Experimental

3.1 General Information

3.1.1 Materials

Solvents used in all the reactions were of reagent grade. Hexanes, cyclohexane, benzene, toluene, p-xylene, heptane, octane, cyclooctane, nonane, and decalin were refluxed over sodium benzophenone ketyl under nitrogen or argon and distilled prior to use. Diethyl ether, dichloromethane, and tetrahydrofuran (THF) were refluxed over LiAlH₄ and freshly distilled under nitrogen before use. Acetonitrile was refluxed over CaH₂ under nitrogen or argon and freshly distilled prior to use. Tetramethylethylene-diamine (TMEDA) was distilled from CaCl₂ under nitrogen.

Nitrogen and argon were Linde (Union Carbide) products and were used without further drying and deoxygenating.

All commercial reagents were of reagent grade and were used as received unless otherwise stated.

Ferrocene, dichlorophenylphosphine, chlorodiphenylphosphine, 2-chloropropane, trimethylamine N-oxide dihydrate, and n-butyllithium (1.6 M solution in hexanes) were obtained from Aldrich Chemical Co.. TMEDA was obtained from BDH Chemicals Ltd.. Bis(triphenylphosphine)iminium chloride (PPN⁺Cl⁻), dichloroethylphosphine, chlorodiethylphosphine, chlorodi(tert-butyl)phosphine, and tris(1-naphthyl)phosphine were obtained from Strem Chemicals. Diphenyl sulfide was obtained from K & K Laboratories, Inc.. Diphenyl disulfide was obtained from Eastman Organic
Chemicals. Diiodophenylarsine was obtained from Eastman Kodak Co. Meso-bis(tert-butylphenylphosphino)ferrocene was provided by T.-J. Kim [333]. Tris(1-naphthyl)arsine was prepared by Prof. W. R. Cullen. RuCl$_3$•xH$_2$O was loaned by Johnson Matthey Ltd.. Os$_3$(CO)$_{12}$ was obtained from commercial sources.

3.1.2 Reaction conditions

Preparation of Gringard reagents, chlorophosphines, ferrocenylphosphines, ferrocenylarsines, and ferrocenyl sulfides were carried under nitrogen or argon by using standard Schlenk vacuum line techniques [334].

Pyrolysis experiments were carried out in a 250 or 100 mL, two-necked, round-bottom flask fitted with a reflux condenser which is connected to a nitrogen or argon line and to a gas bubbler. Magnetic stirring was initiated before heating was turned on. All the reactions were monitored by thin layer chromatography (TLC) and the TLC plates were Merck silica gel 60 F254 on aluminum (0.2 mm thickness) or Whatman silica gel UV254 on aluminum (0.25 mm thickness). After the reaction was stopped, the mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. In most cases, the $^{31}$P and/or $^1$H NMR spectra of this reaction mixture were recorded. Frequently, the solid residue was dissolved in a small amount of CH$_2$Cl$_2$ and appropriate amount of column packing material was added. The solvent was then slowly removed to give a nice powdery sample and this then was loaded through a funnel to a column for separation. This technique is often, but not always, superior to the method of loading a solution sample via a pipette. It is important to prepare the powdery sample right before separation as these clusters tend to absorb onto silica, alumina, or Florisil.
3.1.3 Chromatographic separation

All chromatographic separations were carried out in open air, and the eluting solvents were of reagent grade and used without drying and degassing. The low boiling (35-60°C) fraction of petroleum ether was used. The mixed solvent ratio refers to volume/volume ratio. To obtain pure ligands, repeated chromatography was often necessary especially for those prepared in moderate to low yields such as PFc₂Ph. Ligands were all chromatographed on silica, ruthenium and osmium complexes were chromatographed on silica, alumina, or Florisil. Silica (230-400 mesh) was from Merck, Florisil (60-100 mesh) and alumina (neutral, activity I, 80-200 mesh) were from Fisher Scientific.

3.1.4 Characterization

Elemental analyses were performed by Mr. Peter Borda of the Chemistry Department.

Low resolution Electron Impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer with probe temperature typically at 120, 150, or 180°C. Fast Atom Bombardment (FAB) mass spectra were recorded on an AEI MS-902 or Kratos Concept II HQ spectrometer with 3-nitrobenzyl-alcohol as matrix and argon as exciting gas. These were all run by the Chemistry Department Mass Spectrometry Services. The number given in parentheses for EI mass spectra is the intensity of the designated signal relative to the base peak.

All the ¹H NMR spectra were recorded on a Bruker AC-200E, Varian XL-300, Bruker WH-400, or Bruker AMX-500 spectrometer operating at 200, 300, 400, and 500 MHz, respectively. Unless otherwise stated, all the spectra were recorded at room temperature in CDCl₃. All chemical shifts (δ)
are in ppm with tetramethylsilane (TMS) as external standard and all couplings (J) are in Hz.

All the $^{31}\text{P}$ NMR spectra were recorded on a Bruker AC-200E, Varian XL-300, or Bruker AMX-500 spectrometer operating at 81.0, 121.4, and 202.5 MHz, respectively. Unless otherwise stated, all were recorded at room temperature in CDCl$_3$ with broadband $^1\text{H}$ decoupling. Chemical shifts ($\delta$) are in ppm relative to 85% H$_3$PO$_4$ as external reference and all couplings (J) are in Hz.

All the $^{13}\text{C}$ NMR spectra were recorded on a Bruker AC-200E or Varian XL-300 spectrometer operating at 50.3 and 75.4 MHz respectively. They were recorded at room temperature in CDCl$_3$ with $^1\text{H}$ broadband decoupling. Chemical shifts ($\delta$) are in ppm relative to TMS as external reference and couplings (J) are in Hz.

X-ray single crystal structure analyses were carried out by Dr. Steven J. Rettig of the Chemistry Department Crystallographic Services.

3.2 Preparation of Starting Materials

References following a synthetic procedure to be described in this section means that the synthesis follows a literature procedure.

3.2.1 Preparation of triruthenium dodecacarbonyl Ru$_3$(CO)$_{12}$

Triruthenium dodecacarbonyl Ru$_3$(CO)$_{12}$ was prepared from RuCl$_3$•xH$_2$O by using literature methods [189d, 335]. The apparatus used is located on the roof of the chemistry building dedicated to high pressure syntheses involving CO gas. Typically 4 g of RuCl$_3$•xH$_2$O dissolved in 500
mL methanol was placed in a 2 L high pressure bomb. After installing the reaction container properly, CO was allowed to flush through the system for 5 min and the system was closed. The reaction pressure and temperature were controlled to be around 50-60 atm and 120-130°C. After 20 h the reaction was stopped and the system was allowed to cool to room temperature. The CO gas was carefully vented and the system opened. The solution was filtered and the mother liquor recycled typically for four times. The overall yield is around 75-85%. Pure Ru₃(CO)₁₂ was obtained via extraction with hot hexane from the crude product and subsequent evaporation of the solvent. Anal. calcd. for C₁₂O₁₂Ru₃: C, 22.54; H, 0.00. Found: C, 22.61; H, 0.11.

3.2.2 Preparation of chlorodi(iso-propyl)phosphine ClPr₂ [336, 337]

The Grignard reagent iso-propylmagnesium chloride was prepared as follows.

Magnesium turnings (24.3 g, 1.0 mol) and diethyl ether (400 mL) were placed in a 2 L, round-bottom, three-necked flask equipped with a 500 mL pressure equalizing dropping funnel, a reflux condenser, an inert gas inlet, and a magnetic stirrer. The magnesium turnings were etched with a trace of iodine. The reaction was then started by the addition of iso-propylchloride (78.5 g, 1.0 mol) dissolved in diethyl ether (400 mL). Subsequently, the iPrCl solution was added gradually to keep the solvent at its boiling point (ca. 2 h). After the addition is complete, the mixture was allowed to reflux for an additional hour.

The above Grignard solution was diluted with diethyl ether to 1200 mL and then added dropwise through an addition funnel to a stirred phosphorus trichloride (55 g, 0.4 mol) solution in diethyl ether (100 mL). A
white precipitate formed during the addition and the reaction mixture was refluxed for another two hours. The reaction mixture was then filtered through a medium porosity Schlenk filter into a flask under nitrogen. The solid was washed with diethyl ether (50 mL) twice, and the solvent was then removed by distillation at atmospheric pressure to leave a yellowish oil. This was further purified by vacuum distillation. The product obtained was an air-sensitive, colorless liquid (28 g, 65%). $^{31}$P NMR (121.4 MHz, C$_6$D$_6$): $\delta$ 132.8. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 1.70 (septet of d, 2H), 0.96 (dd, 12H). Anal. calcd. for C$_6$H$_{14}$ClP: C, 47.22; H, 9.25. Found: C, 47.35; H, 9.39. The $^1$H NMR spectroscopic data agree with those in the literature; the $^{31}$P NMR spectrum was not previously recorded.

3.2.3 Preparation of ferrocenyl ligands

3.2.3.1 Preparation of ferrocenyldiphenylphosphine PFcPh$_2$ [313, 315]

n-Butyllithium (32 mL, 0.05 mol) was added to ferrocene (13 g, 0.07 mol) in diethyl ether (75 mL). The solution was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath and Ph$_2$PCl (9 g, 0.04 mol) added dropwise. The solution was allowed to warm to room temperature with stirring and left so for 2 h after which water (50 mL) was added. The organic layer was isolated and the solvent evaporated. The solid residue was applied to a silica chromatographic column. Unreacted ferrocene (15%) was eluted by using petroleum ether. The desired compound PFcPh$_2$ was eluted by using a petroleum ether/diethyl ether (2/1) mixture. Solvent removal in vacuo afforded the product as an orange solid (45%). $^{31}$P NMR (121.4 MHz): $\delta$ -16.9. $^{13}$C NMR (100.6 MHz): $\delta$
139.1 (d, J=9.8), 133.4 (d, J=19.2), 128.3 (d, J=13.8), 128.0 (d, J=6.8), 75.8 (d, J=6.1), 72.8 (d, J=14.8), 70.7 (d, J=3.8), 69.0 (s). $^1$H NMR (200 MHz): $\delta$ 7.48-7.14 (bm, 10H), 4.30 (m, 2H), 4.04 (m, 2H), 4.00 (s, 5H). Mass spectrum (EI, 120°C): m/e 370 (P+, 100.0), 305 (12.8), 293 (36.4), 228 (16.1), 186 (49.4), 121 (20.3), 78 (30.4), 56 (18.5). Anal. calcd. for C$_{22}$H$_{19}$FeP: C, 71.38; H, 5.17. Found: C, 71.42; H, 5.20. The $^1$H NMR data agree with those previously reported; the $^{31}$P and $^{13}$C NMR data were not previously recorded.

3.2.32 Preparation of diferrocenylphenylphosphine PFc$_2$Ph [313, 315]

n-Butyllithium (63 mL, 0.10 mol) was added to ferrocene (25 g, 0.13 mol) in diethyl ether (150 mL). The solution was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath and PhPCl$_2$ (7.0 g, 0.07 mol) added dropwise. The solution was then allowed to warm to room temperature with stirring and left so for 2 h after which water (50 mL) was added. The organic layer was isolated, the solvent removed under reduced pressure, and the residue was applied to a silica chromatographic column. Unreacted ferrocene (25%) was eluted by using a 20/1 petroleum ether/diethyl ether mixture. The desired compound PFc$_2$Ph was eluted as the second band by using a 5/1 petroleum ether/diethyl ether mixture. It was obtained as an orange yellow solid in 35% yield after solvent removal in vacuo. $^{31}$P NMR (81.0 MHz): $\delta$ -30.1. $^1$H NMR (200 MHz): $\delta$ 7.5 (bm, 2H), 7.23 (bm, 3H), 4.26 (m, 2H), 4.22 (m, 2H), 4.14 (m, 2H), 4.05 (s, 10H), 3.91 (m, 2H). Mass spectrum (EI, 150°C): m/e 478 (P+, 100.0), 413 (12.0), 401 (34.4), 335 (12.8), 304 (79.5), 291 (14.2), 248 (16.2), 239 (31.7), 216 (25.6), 186 (14.8), 170 (15.3), 157 (12.9), 121 (26.4), 56 (29.5). Anal. calcd. for C$_{26}$H$_{23}$Fe$_2$P: C, 65.31; H, 4.86. Found: C,
65.42; H, 4.87. The $^1$H NMR data agree with those reported in the literature; the $^{31}$P NMR data were not previously reported.

The third band contained an unusual compound Fc'($\text{PFcPh}$)$_2$. It was obtained as a yellow solid in 5% yield. $^{31}$P NMR (81.0 MHz): $\delta$ -30.7. $^1$H NMR (200 MHz): $\delta$ 7.6-7.36 (bm, 4H), 7.36-7.1 (bm, 6H), 4.4-3.9 (m+s, 15+10H), 3.81 (m, 1H). Mass spectrum (EI, 150°C): m/e 770 (P+, 100.0), 705 (17.2), 507 (14.9), 478 (7.2), 410 (10.8), 399 (7.3), 385 (15.2), 335 (11.9), 304 (49.5), 293 (43.8), 262 (9.4), 248 (9.8), 226 (10.5), 186 (15.3), 170 (10.9), 121 (21.8), 56 (17.3). Anal. calcd. for C$_{42}$H$_{36}$Fe$_3$P$_2$: C, 65.49; H, 4.71. Found: C, 65.74; H, 4.89.

The fourth band contained the diastereoisomer of Fc'($\text{PFcPh}$)$_2$. It was also yellow in colour and was obtained in 3% yield. $^{31}$P NMR (81.0 MHz): $\delta$ -31.4. $^1$H NMR (200 MHz): $\delta$ 7.70-6.96 (m, 10H), 4.72 (m, 2H), 4.50 (m, 2H), 4.43-4.30 (m, 4H), 4.26-3.80 (m, 16H), 3.73 (m, 2H). Mass spectrum (EI, 150°C): same as that of the third band. Anal. calcd. for C$_{42}$H$_{36}$Fe$_3$P$_2$: C, 65.49; H, 4.71. Found: C, 65.79; H, 4.83. This pair of diastereoisomers of Fc'($\text{PFcPh}$)$_2$ was not previously obtained.

3.2.33 Preparation of diethylferrocenylphosphine PEt$_2$Fc
n-Butyllithium (12.8 mL, 0.02 mol) was added to ferrocene (5.2 g, 0.028 mol) in diethyl ether (30 mL). The solution was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath. Et$_2$PCl (1.9 g, 0.016 mol) was then added dropwise and the mixture was allowed to warm to room temperature with stirring and left so for 2 h. Following hydrolysis with water (20 mL), the organic layer was isolated and the solvent removed under reduced pressure. The solid residue was chromatographed on silica. Elution with petroleum ether removed

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unreacted ferrocene (10%), and 20/1 petroleum ether/diethyl ether eluted the desired ligand which was obtained as an orange oil (60%) after solvent removal. $^{31}$P NMR (81.0 MHz): $\delta$ -26.1. $^1$H NMR (200 MHz): $\delta$ 4.28 (m, 2H), 4.21 (m, 2H), 4.17 (s, 5H), 1.60 (q, 4H, $J_{H-H}$=7.1), 1.06 (td, 6H, $J_{H-p}$=14.0, $J_{H-H}$=7.1). Mass spectrum (EI, 180°C): m/e 274 (P+, 40.6), 245 (23.9), 217 (100.0), 186 (19.8), 151 (11.2), 121 (90.0), 56 (18.9). Anal. calcd. for C$_{14}$H$_{19}$FeP: C, 61.34; H, 6.99. Found: C, 61.20; H, 6.86.

3.2.34 Preparation of ferrocenyldi(iso-propyl)phosphine PFciPr$_2$

n-Butyllithium (12.8 mL, 0.02 mol) was added to ferrocene (5.2 g, 0.028 mol) in diethyl ether (30 mL). The solution was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath and iPr$_2$PCl (2.5 g, 0.016 mol) was added dropwise. The mixture was allowed to warm to room temperature with stirring and left so for 2 h after which water (20 mL) was added. The organic layer was isolated, the solvent was removed under reduced pressure, and the solid residue was chromatographed on a silica column. Petroleum ether eluted unreacted ferrocene (10%), and 10/1 petroleum ether/diethyl ether eluted the desired ligand as the second band. Solvent evaporation in vacuo afforded PFciPr$_2$ as a reddish orange oil (60%). $^{31}$P NMR (81.0 MHz): $\delta$ 0.6. $^1$H NMR (300 MHz): $\delta$ 4.51 (m, 2H), 4.36 (m, 2H), 4.06 (s, 5H), 1.62 (m, 2H), 1.26 (dd, 6H), 1.11 (dd, 6H). Mass spectrum (EI, 170°C): m/e 302 (P+, 13.3), 259 (9.5), 217 (72.0), 186 (100.0), 121 (96.6), 56 (14.3). Anal. calcd. for C$_{16}$H$_{23}$FeP: C, 63.59; H, 7.67. Found: C, 63.87; H, 7.90.

3.2.35 Preparation of n-butylferrocenyldiphenylphosphine PnBuFcPh

[250, 315]
n-Butyllithium (12.8 mL, 0.02 mol) was added to ferrocene (2.5 g, 0.013 mol) in diethyl ether (20 mL). The solution was stirred at room temperature for 20 h after which it was cooled in a dry ice-acetone bath and PhPCl₂ (1.5 g, 0.008 mol) was added dropwise. The solution was then allowed to warm to room temperature with stirring and left for 2 h after which water (10 mL) was added. The organic layer was isolated, the solvent was removed under reduced pressure, and the residue dried in vacuo before being chromatographed on a silica column. Elution with 20/1 petroleum ether/diethyl ether removed unreacted ferrocene (20%). A 9/1 petroleum ether/diethyl ether mixture then eluted the desired ligand which was obtained as a yellowish orange solid (25-30%) upon solvent removal. ³¹P NMR (121.4 MHz): δ -27.7. ¹H NMR (200 MHz): δ 7.50-7.30 (m, 2H), 7.30-7.14 (m, 3H), 4.31-4.21 (m, 3H), 4.11-4.04 (s+m, 5+1H), 1.98-1.77 (m, 2H), 1.56-1.23 (m, 4H), 0.92-0.77 (t, 3H, J_H-H=7.0). ¹³C NMR (50.3 MHz): δ 140.3 (d, J=9.8), 132.7 (d, J=19.5), 128.4 (d, J=15.8), 128.1 (d, J=7.0), 73.2 (d, J=5.8), 70.4 (d, J=14.6), 69.9 (d, J=3.8), 69.0 (s), 28.7 (d, J=7.4), 28.5 (s), 24.5 (s), 13.9 (s). Mass spectrum (EI, 150°C): m/e 350 (P+, 37.6), 293 (46.2), 216 (100.0), 186 (21.0), 121 (53.2), 77 (17.9), 56 (23.1). Anal. calcd. for C₂₀H₂₃FeP: C, 68.58; H, 6.63. Found: C, 68.49; H, 6.53. The ¹H NMR data agree with those in the literature; the ³¹P and ¹³C NMR data were not previously recorded.

3.2.36 Preparation of di(tert-butyl)ferrocenylphosphine PtBu₂Fc

n-Butyllithium (34.4 mL, 0.055 mol) was added dropwise to ferrocene (13.3 g, 0.072 mol) in diethyl ether (80 mL). The solution was stirred at room temperature for 60 h, then it was cooled in a dry ice-acetone bath and PtBu₂PCl (8.0 g, 0.044 mol) added dropwise. The solution was then
allowed to warm to room temperature with stirring and left so for 2h. After hydrolysis with water (35 mL), the organic layer was isolated, concentrated under reduced pressure and dried in vacuo. The residue was then subjected to chromatographic column separation on silica. Elution with petroleum ether removed unreacted ferrocene (15%), and 10/1 petroleum ether/diethyl ether then eluted the desired product which was obtained as a darkish orange solid (60%). $^{31}$P NMR (81.0 MHz): $\delta$ 27.8. $^1$H NMR (200 MHz): $\delta$ 4.41 (m, 1H), 4.28 (m, 2H), 4.20 (m, 1H), 4.11 (s, 5H), 1.15 (d, 18H, J$_{p-H}$=11.0). Mass spectrum (EI, 120°C): m/e 330 (P$,^+$, 12.1), 306 (7.7), 273 (30.2), 233 (11.4), 217 (100.0), 186 (47.0), 121 (60.7), 56 (25.8). Anal. calcd. for C$_{18}$H$_{27}$FeP: C, 65.47; H, 8.24. Found: C, 65.11; H, 8.02.

3.2.37 Preparation of ferrocene(1,1'-diyl)phenylphosphine Fe(C$_5$H$_4$)$_2$PPh

n-Butyllithium (6.5 mL, 0.01 mol) and TMEDA (0.6 g, 0.005 mol) were added to ferrocene (0.93 g, 0.005 mol) in diethyl ether (10 mL). The colour of the solution changed from orange yellow to red and then to orange as it was stirred overnight. The solution was then cooled in a dry ice-acetone bath and PhPCl$_2$ (0.8 g, 0.004 mol) was added dropwise. The solution was allowed to warm to room temperature with stirring and water (5 mL) was then added. The organic layer was isolated, the solvent removed under reduced pressure, and the solid residue chromatographed on a silica column. Elution with 5/1 petroleum ether/diethyl ether gave ferrocene as the first band (20%), and the second band contained the desired ferrocenophane ligand. Solvent removal in vacuo afforded Fe(C$_5$H$_4$)$_2$PPh as a dark red crystalline solid (25%). $^{31}$P NMR (121.4 MHz): $\delta$ 11.0. $^1$H NMR (300 MHz): $\delta$ 7.60 (m, 2H), 7.39 (m, 2H), 7.31 (m, 1H), 4.68
(m, 1H), 4.43 (m, 1H), 4.32 (m, 2H), 4.10 (m, 4H). Mass spectrum (EI, 180°C): m/e 292 (P+, 100.0), 233 (7.3), 226 (46.3), 202 (7.6), 186 (38.5), 170 (30.6), 157 (18.1), 133 (10.9), 121 (25.7), 115 (11.1), 81 (8.6), 56 (13.5). Anal. calcd. for C₁₆H₁₃FeP: C, 65.79; H, 4.49. Found: C, 65.60; H, 4.60. The spectroscopic data agree with those in the literature.

3.2.38 Preparation of ethyldiferrocenylphosphine PEtFc₂

n-Butyllithium (34.4 mL, 0.055 mol) was added dropwise to ferrocene (13.3 g, 0.072 mol) in diethyl ether (80 mL). The solution was stirred at room temperature for 60 h, then it was cooled in a dry ice-acetone bath and EtPCl₂ (3.0 g, 0.022 mol) added dropwise. The solution was then allowed to warm to room temperature with stirring and left so for 2 h. After hydrolysis with water (25 mL), the organic layer was isolated, concentrated under reduced pressure and dried in vacuo. The oily residue was then chromatographed on a silica column. Elution with petroleum ether removed unreacted ferrocene (30%), and 15/1 petroleum ether/diethyl ether then eluted the desired ligand in the second band. There were many bands after the PEtFc₂ band, and ³¹P NMR spectroscopy of the fraction revealed the presence of many products. These were not further characterized. PEtFc₂ was obtained as an orange solid (15%) after solvent evaporation. ³¹P NMR (81.0 MHz): δ -34.5. ¹H NMR (200 MHz): δ 4.27-4.15 (bm, 6H), 4.07 (s+m, 10+2H), 1.79 (q, 2H, J₁H₂H=7.7), 1.04 (td, 3H, J₁H₂P=17.5, J₁H₁H=7.7). ¹³C NMR (50.3 MHz): δ 78.8 (d, J=19.6), 72.3 (d, J=15.3), 71.1 (d, J=15.0), 68.9 (s), 21.9 (d, J=5.1), 10.9 (d, J=18.8). Mass spectrum (EI, 120°C): m/e 430 (P⁺, 43.7), 401 (100.0), 333 (13.6), 278 (10.5), 241 (10.2), 215 (29.3), 200 (24.7), 186 (34.9), 157 (16.2), 121 (30.4), 115 (15.9), 103 (10.8), 75 (15.3), 56 (29.0). Anal. calcd. for C₂₂H₂₃
Fe₂P: C, 61.44; H, 5.39. Found: C, 61.52; H, 5.47.

3.2.39 Preparation of diferrocenylphenylarsine AsFc₂Ph

n-Butyllithium (32 mL, 0.10 mol) was added to ferrocene (12.5 g, 0.065 mol) in diethyl ether (70 mL). The solution was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath and PhAsI₂ (8.1 g, 0.02 mol) added dropwise. The solution was allowed to warm to room temperature with stirring and left so for 2 h after which water (50 mL) was added. The diethyl ether fraction was isolated and the solvent was removed under reduced pressure. The residue was chromatographed on a silica column. Unreacted ferrocene (20%) was eluted with petroleum ether. The second band (10%) eluted by using a 3/1 petroleum ether/diethyl ether mixture contained an orange solid. Mass spectrum (EI, 150°C): m/e 648 (1.1), 602 (0.9), 545 (1.6), 522 (100.0), 445 (37.0), 414 (17.7), 370 (12.5), 337 (55.2), 304 (25.6), 260 (29.1), 186 (17.3), 121 (14.0), 56 (8.5).

The third band proved to be the desired compound AsFc₂Ph which was isolated as an orange solid (30%). Mass spectrum (EI, 120°C): m/e 522 (P⁺, 57.3), 445 (43.7), 370 (100.0), 337 (10.6), 304 (59.8), 260 (35.8), 248 (14.5), 186 (22.4), 121 (35.0), 56 (23.2). Anal. calcd. for C₂₆H₂₃AsFe₂: C, 59.81; H, 4.44. Found: C, 60.02; H, 4.45.

The fourth band contained a yellow solid (15%). Mass spectrum (EI, 150°C): m/e 690 (P⁺, 3.7), 582 (8.0), 504 (58.2), 427 (32.6), 413 (8.3), 337 (100.0), 289 (16.9), 270 (36.0), 260 (25.6), 227 (11.3), 214 (44.4), 202 (16.0), 197 (15.9), 186 (54.8), 169 (13.0), 152 (18.8), 141 (43.3), 128 (18.5), 121 (41.7), 115 (35.0), 78 (16.3), 56 (61.0). It is believed to be [(C₅H₄AsFcPh)Fe(C₅H₄AsPh)]₂O.
3.2.310 Preparation of 1,1'-bis(diphenylphosphino)ferrocene

\[ \text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2 \] [314, 333]

n-Butyllithium (27 mL, 0.043 mol) and TMEDA (5.0 g, 0.043 mol) were added to ferrocene (4.0 g, 0.022 mol) in diethyl ether (80 mL). The solution was stirred overnight and \( \text{Ph}_2\text{PCl} \) (9.7 g, 0.044 mol) in diethyl ether (100 mL) was then added through a pressure-equalizing dropping funnel. The reaction mixture was stirred for another 2 h after which water (50 mL) was added. The organic layer was isolated, concentrated under reduced pressure, and dried over anhydrous MgSO\(_4\) overnight. The solution was then filtered, and the solvent removed in vacuo. The solid residue was chromatographed on a silica column. A 20/1 petroleum ether/diethyl ether mixture eluted ferrocene (5%). A 5/1 petroleum ether/diethyl ether mixture then eluted the desired compound \( \text{Fc}'(\text{PPh}_2)_2 \). Solvent evaporation afforded it as an orange crystalline solid (70%). \(^{31}\text{P}\) NMR (121.4 MHz): \( \delta \approx -17.5 \). \(^1\text{H}\) NMR (200 MHz): \( \delta \approx 7.50-7.10 \) (bm, 20H), 4.28 (m, 4H), 4.01 (m, 4H). Anal. calcd. for C\(_{34}\)H\(_{28}\)FeP\(_2\): C, 73.67; H, 5.06. Found: C, 73.40; H, 4.86. The spectroscopic data agree with those in the literature.

3.2.311 Preparation of 1,1'-bis(di-iso-propylphosphino)ferrocene

\[ \text{Fe}(\text{C}_5\text{H}_4\text{iPr}_2)_2 \] [341, 342]

n-Butyllithium (27 mL, 0.043 mol) and TMEDA (5.0 g, 0.043 mol) were added to ferrocene (4.0 g, 0.022 mol) in diethyl ether (80 mL). The solution was stirred overnight and \( \text{iPr}_2\text{PCl} \) (6.8 g, 0.044 mol) in diethyl ether (100 mL) was then added dropwise through a pressure-equalizing dropping funnel. The mixture was stirred for another 2 h after which water (50 mL) was added. The organic layer was isolated, concentrated under reduced pressure, and dried over anhydrous MgSO\(_4\) overnight. The
solution was then filtered, and the solvent was removed in vacuo. The solid residue was applied to a silica chromatographic column. Elution with 20/1 petroleum ether/diethyl ether removed unreacted ferrocene (5%). A 5/1 petroleum ether/diethyl ether mixture then eluted the desired compound Fc'(PiPr2)2. Solvent removal in vacuo afforded it as an orange crystalline solid (80%). 31P NMR (121.4 MHz): δ 0.1. 1H NMR (300 MHz): δ 4.20 (m, 4H), 4.11 (m, 4H), 1.85 (m, 4H), 1.00 (dd, 24H). Mass spectrum (EI, 150°C): m/e 418 (P+, 21.7), 391 (5.0), 375 (100.0), 334 (21.5), 318 (16.2), 289 (20.3), 269 (13.2), 157 (14.0), 246 (28.0), 225 (18.4), 217 (17.8), 186 (20.1), 152 (10.9), 121 (27.0), 56 (24.3). Anal. calcd. for C22H36FeP2: C, 63.17; H, 8.67. Found: C, 63.30; H, 8.75. The spectroscopic data agree with those in the literature.

3.2.312 Preparation of 1,1'-bis(diethylphosphino)ferrocene Fe(C5H4PEt2)2

n-Butyllithium (10.0 mL, 16.0 mmol) and TMEDA (1.2 mL, 8.0 mmol) were added to ferrocene (1.5 g, 8.0 mmol) in diethyl ether (45 mL) and the reaction mixture was stirred overnight. A solution of Et2PCL (2.0 g, 16.0 mmol) in diethyl ether (80 mL) was added dropwise via a pressure-equalizing dropping funnel and the orange solution turned to pale yellow. After another 2 h of stirring, the mixture was hydrolyzed with H2O (10 mL) and the organic layer separated. The solvent was removed under reduced pressure and the residue was chromatographed on silica. Elution with petroleum ether gave ferrocene (10%). The second yellow band (15%) eluted with 10/1 petroleum ether/diethyl ether was identified as PEt2Fc by TLC, 1H, and 31P NMR spectroscopy. The third band proved to be the desired ligand Fc'(PEt2)2 which was obtained as an orange oil (55%). 31P NMR (81.0 MHz): δ -20.9. 1H NMR (200 MHz): δ 4.53 (m, 2H), 4.28 (m, 2H),
4.20 (m, 4H), 2.13 (m, 4H), 1.22 (m, 6H). Anal. calcd. for C_{18}H_{28}FeP_{2}: C, 59.69; H, 7.79. Found: C, 59.07; H, 7.51.

3.2.313 Preparation of (3-diethylphosphinoferrocenodiphenylphosphine (1-PPh_{2}-3-PEt_{2}-C_{5}H_{3})Fe(C_{5}H_{5})

n-Butyllithium (4.6 mL, 7.4 mmol) was added to PFcPh_{2} (2.8 g, 7.5 mmol) in diethyl ether (15 mL) and the solution was stirred at room temperature for 60 h. The yellow solution was cooled in a dry ice-acetone bath and Et_{2}PCl (1.0 g, 8.0 mmol) was added slowly. The reaction mixture was maintained at low temperature for 2 h and then allowed to warm to room temperature. After a further 2 h of stirring, the solution was hydrolyzed with H_{2}O (10 mL), and the organic layer isolated. The solvent was removed under reduced pressure and the residue was chromatographed on silica with 4/1 petroleum ether/CH_{2}Cl_{2} as eluent. The first band gave unreacted ligand PFcPh_{2} (1.8 g, 64%) identified by TLC, ^{1}H, and ^{31}P NMR spectroscopy. The second band proved to be (1-PPh_{2}-3-PEt_{2}-C_{5}H_{3})Fe(C_{5}H_{5}) and it was obtained as a dark orange solid (15%). ^{31}P NMR (81.0 MHz): δ -17.1, -26.5, J<1. ^{1}H NMR (200 MHz): δ 7.35-7.10 (m, 1H), 4.28 (m, 1H), 4.07 (m, 1H), 3.96 (m+s, 1+5H), 1.50 (bm, 4H), 0.95 (bm, 6H). Mass spectrum (EI, 150°C): m/e 458 (P^+, 74.9), 429 (58.6), 401 (76.1), 370 (2.9), 335 (3.4), 323 (2.4), 306 (2.3), 293 (13.8), 244 (13.3), 216 (52.5), 183 (26.5), 170 (27.6), 121 (33.1), 77 (16.0), 69 (18.3), 56 (47.1), 28 (100.0). Anal. calcd. for C_{26}H_{28}FeP_{2}: C, 68.14; H, 6.16. Found: C, 68.32; H, 6.27.

3.2.314 Preparation of ferrocenylphenylsulfide SFcPh [343]

n-Butyllithium (6.4 mL, 0.01 mol) was added to ferrocene (2.6 g, 0.014 mol) in diethyl ether (20 mL). The solution was stirred at room
temperature for 60 h after which it was cooled in a dry ice-acetone bath and Ph$_2$S$_2$ (1.75 g, 0.008 mol) was added dropwise. The solution was allowed to warm to room temperature with stirring and left so for 2 h after which water (10 mL) was added. The organic layer was isolated, the solvent was removed under reduced pressure, and the residue was applied to a silica chromatographic column. Elution with petroleum ether removed unreacted ferrocene (15%). A 3/1 petroleum ether/diethyl ether mixture then eluted the desired ligand SFcPh which was obtained as an orange solid (55%). $^1$H NMR (200 MHz): δ 7.20-6.96 (m, 5H), 4.38 (t, 2H), 4.31 (t, 2H), 4.23 (s, 5H). Mass spectrum (EI, 120°C): m/e 294 (P+, 100.0), 228 (31.9), 217 (7.8), 202 (5.0), 184 (6.6), 173 (12.5), 141 (15.0), 129 (21.9), 121 (17.1), 115 (9.7), 56 (21.0). Anal. calcd. for C$_{16}$H$_{14}$FeS: C, 65.32; H, 4.80. Found: C, 65.39; H, 4.91. The third band contained a bidentate ligand Fc'(SPh)$_2$ (10%) identified by TLC and mass spectrometry. The $^1$H NMR data agree with those in the literature.

3.2.315 Preparation of 1,1'-bis(phenylthio)ferrocene Fe(C$_5$H$_4$SPh)$_2$ [347]

n-Butyllithium (5.4 mL, 8.6 mmol) and TMEDA (1.0 g, 8.6 mmol) were added to ferrocene (0.8 g, 4.4 mmol) in diethyl ether (20 mL). The reaction mixture was stirred overnight and PhSSPh (1.9 g, 8.7 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was stirred for another 2 h and then hydrolyzed with H$_2$O (10 mL). The organic layer was isolated, the solvent was removed by using rotary evaporator, and the residue was chromatographed on silica. Petroleum ether eluted ferrocene (10%), and 5/1 petroleum ether/diethyl ether then eluted the desired compound Fc'(SPh)$_2$ as an orange solid (75%). Mass spectrum (EI, 120°C): m/e 402 (P+, 100.0), 325 (1.4), 306 (5.0), 293 (5.8), 260 (2.2), 229 (8.0),
3.2.316 Preparation of 1,1'-bis(methylthio)ferrocene Fe(C₅H₄SMe)₂ [347]

n-Butyllithium (5.4 mL, 8.6 mmol) and TMEDA (1.0 g, 8.6 mmol) were added to ferrocene (0.80 g, 4.4 mmol) in diethyl ether (20 mL). The mixture was stirred overnight and MeSSMe (0.82 g, 8.7 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was stirred for another 2 h and then hydrolyzed with H₂O (10 mL). The organic layer was isolated and the solvent was removed by using rotary evaporator. The residue was chromatographed on silica. Petroleum ether eluted ferrocene (15%), and 5/1 petroleum ether/diethyl ether then eluted the desired compound Fe'(SMe)₂ as an orange oil (55%). ¹H NMR (200 MHz): δ 4.27 (s, 4H), 4.18 (s, 4H), 2.29 (s, 6H). Mass spectrum (EI, 120°C): m/e 278 (P⁺, 100.0), 263 (18.5), 230 (14.3), 199 (42.4), 185 (18.5), 167 (17.7), 152 (15.3), 121 (21.5), 56 (16.2). Anal. calcd. for C₁₂H₁₄FeS₂: C, 51.81; H, 5.07. Found: C, 51.25; H, 5.01. The ¹H NMR data agree with those in the literature.

3.2.317 Preparation of diferrocenyldisulfide FcSSFc

n-Butyllithium (32 mL, 0.05 mol) was added to ferrocene (13 g, 0.07 mol) in diethyl ether (75 mL) and the solution was left stirring at room temperature for 60 h after which sulfur (1.28 g, 0.04 mol) was then added. The reaction was exothermic and the solution changed from yellow to dark orange. The mixture was refluxed for another 2 h and was allowed to cool to room temperature. After hydrolysis with H₂O (50 mL) the dark red organic layer was separated and solvent removed under reduced pressure. The yellow residue was chromatographed on silica with 5/1 petroleum ether/diethyl ether.
ether/CH$_2$Cl$_2$ as eluent. The first orange band gave ferrocene (15%). The second band proved to be Fc$_2$S$_2$ (25%). The third band proved to be (C$_5$H$_4$SSFc)Fe(C$_5$H$_4$SFc) (10%), and the fourth yellow band proved to be [3]-ferrocenophane Fe(C$_5$H$_4$S)$_2$S (15%).

Fc$_2$S$_2$, yellow solid. $^1$H NMR (200 MHz): $\delta$ 4.35 (m, 4H), 4.20 (m, 4H), 4.03 (s, 10H). $^{13}$C NMR (75.4 MHz): $\delta$ 73.9 (s), 70.4 (s), 69.6 (s, weak), 69.5 (s, C$_5$H$_5$). Mass spectrum (EI, 120°C): m/e 434 (P+, 16.8), 402 (1.1), 338 (9.2), 304 (3.3), 272 (17.3), 217 (100.0), 186 (25.9), 171 (10.9), 152 (41.8), 121 (59.0), 97 (24.5), 56 (82.1). Anal. calcd. for C$_{20}$H$_{18}$Fe$_2$S$_2$: C, 55.33; H, 4.18. Found: C, 55.47; H, 4.30.

(C$_5$H$_4$SSFc)Fe(C$_5$H$_4$SFc), orange solid. Mass spectrum (EI, 120°C): m/e 650 (P+, 2.0), 618 (2.3), 434 (26.4), 402 (8.0), 368 (5.0), 336 (9.0), 304 (22.0), 272 (27.3), 218 (100.0), 186 (35.6), 152 (45.1), 121 (36.8), 97 (23.9), 56 (54.6). Anal. calcd. for C$_{30}$H$_{26}$Fe$_3$S$_3$: C, 55.41; H, 4.03. Found: C, 55.69; H, 4.28.

Fe(C$_5$H$_4$S)$_2$S, orange solid. $^1$H NMR (200 MHz): $\delta$ 4.52 (m, 2H), 4.41 (m, 2H), 4.36 (m, 2H), 3.82 (m, 2H). Mass spectrum (EI, 190°C): m/e 280 (P+, 100.0), 246 (5.8), 216 (20.5), 184 (87.4), 159 (15.5), 152 (14.3), 140 (14.2), 100 (34.9), 96 (52.9), 70 (20.5), 64 (14.6), 56 (11.0). Anal. calcd. for C$_{10}$H$_8$FeS$_3$: C, 42.87; H, 2.88. Found: C, 42.77; H, 2.95. The $^1$H NMR data agree with those in the literature.

3.2.318 Preparation of diferoecnylsulfide SFc$_2$ [343, 348]

n-Butyllithium (1.6 mL, 2.5 mmol) was added to ferrocene (0.65 g, 3.5 mmol) in diethyl ether (10 mL). The solution was stirred at room temperature for 60 h after which a solution of Fc$_2$S$_2$ (0.87 g, 2.0 mmol) in diethyl ether (2 mL) was added dropwise. After an additional hour of
stirring, the reaction mixture was hydrolyzed with water (10 mL). The organic layer was isolated, evaporated, and the solid residue was chromatographed on a silica column. Petroleum ether eluted unreacted ferrocene, and 5/1 petroleum ether/diethyl ether afforded the desired product as an orange solid (60%). $^1$H NMR (200 MHz): δ 4.4 (brm, 2H), 4.29 (s, 10H), 4.25 (brm, 6H). Mass spectrum (EI, 180°C): m/e 402 (P+, 100.0), 336 (9.3), 304 (30.6), 272 (33.1), 217 (11.0), 201 (21.8), 186 (15.3), 144 (17.3), 121 (28.0), 96 (24.4), 70 (14.2), 56 (41.6). Anal. calcd. for C$_{20}$H$_{18}$Fe$_2$S: C, 59.74; H, 4.51. Found: C, 60.01; H, 4.62. The $^1$H NMR data agree with those in the literature.

3.2.319 Preparation of diferrocenylphenylphosphine sulfide S=PFc$_2$P

Diferrocenylphenylphosphine (0.4 g, 0.84 mmol) and S$_8$ (0.026 g, 0.1 mmol) in diethyl ether (15 mL) was stirred for 2 h, and the reaction solvent was removed in vacuo. The residual yellow powder gave satisfactory analytical and spectroscopic results without any further purification. $^{31}$P NMR (81.0 MHz): δ 39.2. $^1$H NMR (200 MHz): δ 8.0-7.8 (brm, 2H), 7.45-7.30 (m, 3H), 4.46 (m, 2H), 4.37 (m, 2H), 4.33 (m, 2H), 4.20 (m, 2H), 4.11 (s, 10H). Mass spectrum (EI, 150°C): m/e 510 (P+, 100.0), 445 (18.7), 433 (32.8), 325 (25.3), 248 (57.2), 186 (20.7), 121 (16.4), 77 (13.2), 56 (12.4). Anal. calcd. for C$_{26}$H$_{23}$Fe$_2$PS: C, 61.21; H, 4.54. Found: C, 60.98; H, 4.60.

3.2.320 Preparation of triferrocenylstibine SbFc$_3$

n-Butyllithium (32 mL, 0.05 mol) was added to ferrocene (13 g, 0.07 mol) in diethyl ether (80 mL). The mixture was stirred at room temperature for 60 h after which it was cooled in a dry ice-acetone bath.
and SbCl₃ (3.0 g, 0.013 mol) was added dropwise via a syringe. The reaction mixture was allowed to warm to room temperature and left stirring for 2 h after which H₂O (20 mL) was added. The organic layer was separated, the solvent removed under reduced pressure, and the residue was chromatographed on a silica column. Elution with petroleum ether removed ferrocene (30%). Elution with 5/1 petroleum ether/diethyl ether gave a complex mixture which was re-chromatographed on silica with 5/1 petroleum ether/CH₂Cl₂ as eluent. The third band afforded SbFc₃ as an orange crystalline solid in 15% yield. ¹H NMR (200 MHz): δ 4.25 (t, 6H), 4.08 (t, 6H), 3.99 (s, 15H). Mass spectrum (DCI, NH₃): m/e 676 (P⁺, 28.7), 491 (100.0), 370 (15.8), 338 (10.2), 304 (59.4), 249 (15.1), 187 (90.6), 138 (15.9), 129 (23.1), 121 (25.0), 60 (65.8). Anal. calcd. for C₃₀H₂₇Fe₃Sb: C, 53.24; H, 4.02. Found: C, 53.28; H, 4.10.

3.3 Preparation of Os₃ Substitution Complexes

3.3.1 Preparation of Os₃(CO)₁₁(PFcPh₂)

Triosmium dodecacarbonyl Os₃(CO)₁₂ (450 mg, 0.50 mmol) in CH₂Cl₂ (80 mL) and MeCN (5 mL) was treated with a solution of Me₃NO (38 mg, 0.50 mmol) in MeOH (5 mL). The reaction mixture was stirred for 2 h after which the volume was reduced to 50 mL and PFcPh₂ (190 mg, 0.50 mmol) was added. After a further 2 h of stirring the solvent was removed in vacuo and the solid residue was chromatographed on silica with 4/1 petroleum ether/CH₂Cl₂ as eluent. The major second band that developed proved to be the desired complex Os₃(CO)₁₁(PFcPh₂) which was isolated as an orange solid in 75% yield. ³¹P NMR (81.0 MHz): δ -10.6. ¹H NMR (200

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MHz): δ 7.5-7.2 (bm, 10H), 4.48 (m, 2H), 4.15 (m, 2H), 3.96 (s, 5H). Mass spectrum (FAB): m/e 1250 (P+), 1222, 1194, 1166, 1138, 1110, 1082, 1054, 1026, 998, 970, 951, 940 (base peak), 890, 874, 862. Anal. calcd. for C_{33}H_{19}FeO_{11}Os_{3}P: C, 31.74; H, 1.53. Found: C, 31.81; H, 1.70.

### 3.3.2 Preparation of Os_{3}(CO)_{10}(PFcPh_{2})_{2}

Triosmium dodecacarbonyl Os_{3}(CO)_{12} (450 mg, 0.50 mmol) in CH_{2}Cl_{2} (80 mL) and MeCN (5 mL) was treated with a solution of Me_{3}NO (75 mg, 1.0 mmol) in MeOH (5 mL). The reaction mixture was stirred for 2 h and PFcPh_{2} (370 mg, 1.0 mmol) was added. After a further 2 h of stirring, the solvent was removed in vacuo and the residue was chromatographed on silica by using 4/1 petroleum ether/CH_{2}Cl_{2} as eluent. The first band contained unreacted Os_{3}(CO)_{12}. The second band was identified as Os_{3}(CO)_{11}(PFcPh_{2}) (10%) by TLC, \textsuperscript{1}H, and \textsuperscript{31}P NMR spectroscopy. The major third band proved to be the desired complex Os_{3}(CO)_{10}(PFcPh_{2})_{2}. Solvent evaporation in vacuo afforded it as a reddish orange solid in 65% yield. \textsuperscript{31}P NMR (81.0 MHz): δ -12.0 (broad, W_{1/2}=150 Hz). \textsuperscript{13}C NMR (50.3 MHz): δ 137.7 (d, J=53.7), 132.8 (d, J=11.0), 130.0 (d, J=2.1), 127.7 (d, J=10.5), 82.0 (d, J=58.8), 73.8 (d, J=11.5), 71.1 (d, J=8.0), 69.9 (s). \textsuperscript{1}H NMR (200 MHz): δ 7.52-7.24 (m, 20H), 4.47 (m, 4H), 4.16 (m, 4H), 3.95 (s, 10H). Mass spectrum (FAB): m/e 1593 (P+, base peak), 1565, 1537, 1509, 1481, 1453, 1424, 1405, 1387, 1372, 1359, 1346, 1334, 1316, 1291, 1231, 1165, 1155, 1087, 1045, 1025, 1012, 997, 968, 940, 892, 862, 835, 805, 778, 749, 683, 672, 645, 617, 590, 559. Anal. calcd. for C_{54}H_{38}Fe_{2}O_{10}Os_{3}P_{2}: C, 40.76; H, 2.41. Found: C, 40.60; H, 2.54.
3.3.3 Preparation of Os$_3$(CO)$_{11}$(PFc$_2$Ph)

Triosmium dodecacarbonyl Os$_3$(CO)$_{12}$ (450 mg, 0.50 mmol) in CH$_2$Cl$_2$ (80 mL) and MeCN (5 mL) was treated with a solution of Me$_3$NO (38 mg, 0.50 mmol) in MeOH (5 mL). The reaction mixture was stirred for 2 h after which the volume was reduced to 50 mL and PFc$_2$Ph (240 mg, 0.50 mmol) was added. After a further 2 h of stirring, the solvent was removed in vacuo and the solid residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The second and only major band proved to be the desired complex Os$_3$(CO)$_{11}$(PFc$_2$Ph) which was obtained as an orange solid in 70% yield. $^{31}$P NMR (81.0 MHz): $\delta$ -22.6. $^1$H NMR (200 MHz): $\delta$ 7.72-7.58 (m, 2H), 7.40-7.24 (m, 3H), 4.53 (m, 4H), 4.34 (m, 2H), 4.20 (s, 5H), 4.08 (m, 2H). Mass spectrum (FAB): m/e 1356 (P$^+$), 1328, 1300 (base peak), 1272, 1244, 1216, 1188, 1160, 1104, 1076, 1055, 1048, 1027, 1020, 999. Anal. calcd. for C$_{37}$H$_{23}$Fe$_2$O$_{11}$Os$_3$P: C, 32.75; H, 1.71. Found: C, 33.04; H, 1.94.

3.3.4 Preparation of Os$_3$(CO)$_{10}$(PFc$_2$Ph)$_2$

A solution of Os$_3$(CO)$_{12}$ (362 mg, 0.40 mmol) in CH$_2$Cl$_2$ (50 mL) and MeCN (5 mL) was treated with Me$_3$NO (60 mg, 0.80 mmol) and the solution was stirred for 5 h after which the ligand PFc$_2$Ph (382 mg, 0.80 mmol) was added. The reaction was continued for 10 h. The solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band contained small amount of Os$_3$(CO)$_{12}$. The second band contained Os$_3$(CO)$_{11}$(PFc$_2$Ph) (5%) identified by TLC, $^{31}$P, and $^1$H NMR spectroscopy. The third band contained trace of an unidentified compound. The fourth band proved to be the desired product Os$_3$(CO)$_{10}$(PFc$_2$Ph)$_2$ which was obtained as an orange crystalline solid.
(75%). $^{31}$P NMR (81.0 MHz): δ -25.4, -29.8 (CDCl$_3$); -25.1, -29.7 (C$_6$D$_6$); -24.8, -29.6 (CD$_3$CN). $^1$H NMR (200 MHz): δ 7.83-7.62 (m, 2H), 7.46-7.14 (m, 8H), 4.55 (m, 4H), 4.47 (m, 4H), 4.42 (m, 2H), 4.35-4.13 (s+s+m, 10+10+4H), 4.05 (m, 2H). Mass spectrum (FAB): m/e 1806 (P+, base peak), 1778, 1750, 1722, 1694, 1666, 1646, 1638, 1618, 1610, 1594, 1582. Anal. calcd. for C$_{62}$H$_{46}$Fe$_4$O$_{10}$Os$_3$P$_2$: C, 41.21; H, 2.57. Found: C, 41.21; H, 2.62. Suitable crystals for X-ray structure analysis were obtained by slow evaporation of a 3/1 hexanes/CH$_2$Cl$_2$ solution.

3.3.5 Preparation of Os$_3$(CO)$_{11}$(PEt$_2$Fc)

A solution of Os$_3$(CO)$_{12}$ (454 mg, 0.50 mmol) in CH$_2$Cl$_2$ (40 mL) and MeCN (10 mL) was treated with Me$_3$NO·2H$_2$O (56 mg, 0.50 mmol) in MeOH (5 mL). After stirring for 2 h, PEt$_2$Fc (137 mg, 0.50 mmol) in CH$_2$Cl$_2$ (5 mL) was added and the reaction was continued for another 2 h. The solvent was then removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band was unreacted Os$_3$(CO)$_{12}$ (5%). The second band contained the desired complex Os$_3$(CO)$_{11}$(PEt$_2$Fc) (70%). The third, fourth, and fifth bands were isolated in 5%, 5%, and 10% yields.

Os$_3$(CO)$_{11}$(PEt$_2$Fc), reddish orange solid. $^{31}$P NMR (81.0 MHz): δ -17.0. $^1$H NMR (200 MHz): δ 4.52 (m, 2H), 4.28 (m+s, 2+5H), 2.50-2.10 (bm, 4H), 1.14 (td, 6H, J$_{H-P}$=19.0, J$_{H-H}$=8.0). Mass spectrum (FAB): m/e 1152 (P+, base peak), 1124, 1096, 1068, 1040, 1012, 984, 956, 928, 900, 884, 872, 855, 841, 826, 814. Anal. calcd. for C$_{25}$H$_{19}$FeO$_{11}$Os$_3$P: C, 26.05; H, 1.66. Found: C, 26.27; H, 1.73.

The third band, orange solid. $^{31}$P NMR (81.0 MHz): δ 4.0. $^1$H NMR (200 MHz):
MHz): δ 4.65 (m, 2H), 4.36 (m, 4H), 4.13 (m, 1H), 4.07 (m, 1H), 2.25 (bm, 4H), 1.37 (m, 6H).

The fourth band, orange solid. $^{31}$P NMR (81.0 MHz): δ -17.1. $^1$H NMR (200 MHz): δ 4.65 (m, 1H), 4.47 (m, 2H), 4.26 (s+m, 5+1H), 2.22 (bm, 4H), 1.08 (td, 6H). Mass spectrum (FAB): m/e 1110 (P$^+$), 1082, 1054, 1026, 970, 942 (base peak), 914, 886, 858, 830.

The orange complex in the fifth band was identified as the unsymmetrical isomer of Os$_3$(CO)$_{10}$(PET$_2$Fc)$_2$. $^{31}$P NMR (81.0 MHz): δ -14.8, -19.1, J=42.9. $^1$H NMR (200 MHz): δ 4.44 (m, 2H), 4.16 (m, 2H), 4.11 (s, 5H), 2.23 (bm, 4H), 1.08 (td, 6H, J$_{H-P}$=18, J$_{H-H}$=9). Mass spectrum (FAB): m/e 1398 (P$^+$), 1378 (base peak), 1342, 1314, 1286, 1258, 1230, 1202, 1174, 1146, 1118, 1090, 1062. Anal. calcd. for C$_{38}$H$_{38}$Fe$_2$O$_{10}$Os$_3$P$_2$: C, 32.63; H, 2.74. Found: C, 32.87; H, 2.88.

3.3.6 Preparation of Os$_3$(CO)$_{11}$(PFciPr$_2$)

A solution of Os$_3$(CO)$_{12}$ (302 mg, 0.33 mmol) in CH$_2$Cl$_2$ (60 mL) and MeCN (5 mL) was treated with Me$_3$NO (25 mg, 0.33 mmol). After 2 h of stirring, PFciPr$_2$ (110 mg, 0.36 mmol) was added and the mixture was left stirring for 3 h. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first greenish yellow band contained Os$_3$(CO)$_{12}$ (2%) identified by TLC. The second band proved to be the desired compound Os$_3$(CO)$_{11}$(PFciPr$_2$) (60%). The third band contained the symmetrical isomer of Os$_3$(CO)$_{10}$(PFciPr$_2$)$_2$ (6%). The fourth band contained the unsymmetrical isomer of Os$_3$(CO)$_{10}$(PFciPr$_2$)$_2$ (10%). The fifth band contained Os$_3$(CO)$_9$(PFciPr$_2$)$_3$ (15%).

Os$_3$(CO)$_{11}$(PFciPr$_2$), orange solid. $^{31}$P NMR (81.0 MHz): δ 18.7. $^1$H NMR
(200 MHz): δ 4.44 (m, 2H), 4.31 (m, 2H), 4.20 (s, 5H), 2.36 (m, 2H), 1.30 (dd, 6H), 1.03 (dd, 6H). 13C NMR (50.3 MHz): δ 77.0 (d, J=44.6), 72.2 (d, J=9.0), 70.2 (s), 70.0 (d, J=7.1), 30.5 (d, J=31.7), 18.8 (d, J=1.8), 18.5 (d, J=1.8). Mass spectrum (FAB): m/e 1182 (P+), 1154, 1126, 1098 (base peak), 1069, 1041, 1013, 997, 985, 968, 957, 940, 929, 912, 901, 884, 873, 856, 837, 828, 800. Anal. calcd. for C27H23FeO11O10s3P: C, 27.46; H, 1.96. Found: C, 27.81; H, 2.03.

The symmetrical isomer of Os3(CO)10(PFciPr2)2, yellow solid. 31P NMR (81.0 MHz): δ 14.3. 1H NMR (200 MHz): δ 4.46 (m, 4H), 4.31 (m, 4H), 4.21 (s, 10H), 2.36 (m, 4H), 1.31 (dd, 12H), 1.03 (dd, 12H). Anal. calcd. for C42H46Fe2O10Os3P2: C, 34.67; H, 3.19. Found: C, 35.03; H, 3.37.

The unsymmetrical isomer of Os3(CO)10(PFciPr2)2, pink solid. 31P NMR (81.0 MHz): δ 8.9 (broad, W1/2=180 Hz). 1H NMR (200 MHz): δ 4.47 (m, 4H), 4.33 (m, 4H), 4.18 (s, 10H), 2.45 (m, 4H), 1.32 (dd, 12H), 1.07 (dd, 12H). 13C NMR (50.3 MHz): δ 78.7 (d, J=41.8), 72.3 (d, J=8.8), 70.1 (s), 69.7 (d, J=7.0), 31.4 (d, J=30.0), 18.9 (d, J=2.2), 18.6 (d, J=2.1). Anal. calcd. for C42H46Fe2O10Os3P2: C, 34.67; H, 3.19. Found: C, 34.88; H, 3.23.

Os3(CO)9(PFciPr2)3, orange solid. 31P NMR (81.0 MHz): δ 4.0. 1H NMR (200 MHz): δ 4.36 (m, 6H), 4.17 (m+s, 6+15H), 2.55 (m, 6H), 1.40-1.05 (complex m, 36H). Anal. calcd. for C57H69Fe3O9Os3P3: C, 39.59; H, 4.02. Found: C, 39.83; H, 3.91.

3.3.7 Preparation of Os3(CO)11(PiBu2Fc)

Trimethylamine N-oxide (19 mg, 0.25 mmol) was added to Os3(CO)12 (230 mg, 0.25 mmol) in CH2Cl2 (30 mL) and MeCN (5 mL). The mixture was stirred for 0.5 h after which PiBu2Fc (100 mg, 0.30 mmol) was added and the solution was left stirring for 2 h. The solvent was removed in vacuo
and the residue turned red overnight. Column chromatography on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent afforded a few minor bands and a major red band which afforded the desired complex Os₃(CO)₁₁(PBU₂Fc) as a red solid in 65% yield after solvent evaporation. ³¹P NMR (121.4 MHz): δ 43.6. ¹H NMR (300 MHz): δ 4.58 (m, 2H), 4.55 (m, 2H), 4.28 (s, 5H), 1.39 (d, 18H, J=13.6). Mass spectrum (FAB): m/e 1208 (P⁺), 1094, 1066, 1038, 1010, 982, 954, 926, 898, 870 (base peak), 842. Anal. calcd. for C₂₉H₂₇FeO₁₁Os₃P: C, 28.81; H, 2.25. Found: C, 28.98; H, 2.42.

3.3.8 Preparation of Os₃(CO)₁₁(PEtFc₂)

A solution of Os₃(CO)₁₂ (272 mg, 0.30 mmol) in CH₂Cl₂ (50 mL) with MeCN (5 mL) was treated with Me₃NO (23 mg, 0.30 mmol). After stirring for 20 min, PEtFc₂ (129 mg, 0.30 mmol) was added and the colour of the solution changed from yellowish orange to pale yellow. The reaction was continued for 2 h after which the solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The first band contained the desired product Os₃(CO)₁₁(PEtFc₂) as an orange solid (50%). ³¹P NMR (81.0 MHz): δ -21.8. ¹H NMR (200 MHz): δ 4.46 (m, 2H), 4.42 (m, 2H), 4.33 (m, 2H), 4.26 (m, 2H), 4.25 (s, 10H), 2.65 (q, 1H, J=7.8), 2.60 (q, 1H, J=7.8), 1.20 (td, 3H, J=19.6, J=7.8). ¹³C NMR (50.3 MHz): δ 82.3 (d, J=57.8), 72.1 (d, J=16.4), 71.1 (d, J=13.6), 69.7 (s), 30.7 (d, J=41.3), 9.8 (d, J=6.4). Mass spectrum (FAB): m/e 1308 (P⁺, base peak), 1252, 1224, 1196, 1168, 1140, 1112, 1084, 1056, 972. Anal. calcd. for C₃₃H₂₃Fe₂O₁₁Os₃P: C, 30.28; H, 1.77. Found: C, 30.41; H, 1.85.

The second band contained orange Os₃(CO)₁₀(PEtFc₂)₂ (15%). Mass spectrum (FAB): m/e 1710 (P⁺, base peak), 1310. Anal. calcd. for C₅₄H₄₆Fe₄O₁₀Os₃P₂: C, 37.91; H, 2.71. Found: C, 38.10; H, 2.86.
3.3.9 Preparation of Os₃(CO)₁₀[Fc'(PiPr₂)₂] and {Os₃(CO)₁₁}₂[Fc'(PiPr₂)₂]

A solution of Os₃(CO)₁₂ (453 mg, 0.50 mmol) and Fc'(PiPr₂)₂ (210 mg, 0.50 mmol) in toluene (100 mL) was refluxed for 4 h. The solvent was then removed under reduced pressure, and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The first band was identified as {Os₃(CO)₁₁}₂[Fc'(PiPr₂)₂] (20%) and the second major band contained complex Os₃(CO)₁₀[Fc'(PiPr₂)₂] (70%).

{Os₃(CO)₁₁}₂[Fc'(PiPr₂)₂], yellow solid. ³¹P NMR (121.4 MHz): δ 14.8. ¹H NMR (200 MHz): δ 4.62 (m, 4H), 4.35 (m, 4H), 2.36 (m, 4H), 1.20 (dd, 12H), 1.02 (dd, 12H). Mass spectrum (FAB): m/e 2174 (P⁺), 2148 (base peak), 1182, 1061, 1003, 975, 947, 919. Anal. calcd. for C₄₄H₃₆FeO₂₂Os₆P₂: C, 24.29; H, 1.67. Found: C, 24.08; H, 1.59.

Os₃(CO)₁₀[Fc'(PiPr₂)₂], orange solid. ³¹P NMR (121.4 MHz): δ 7.3. ¹H NMR (200 MHz): δ 4.3 (m+m, 4+4H), 2.42 (m, 4H), 1.08 (dd, 24H). Mass spectrum (FAB): m/e 1268 (P⁺, base peak), 1242, 1214, 1186, 1172, 1158, 1144, 1130, 1102, 1088, 1074, 1060, 1046, 1032, 1018, 1004, 990, 976, 948, 905. Anal. calcd. for C₃₂H₃₆FeO₁₀Os₃P₂: C, 30.88; H, 2.86. Found: C, 30.49; H, 2.84.

3.4 Preparation of Ru₃ Substitution Complexes

The preparation of the Ru₃ substitution complexes of PFcPh₂ and PFc₂Ph followed the literature procedures with slight modifications [250, 315]. The ¹H NMR spectroscopic data for the mono- and tri-substituted complexes (Ru₃(CO)₁₁L and Ru₃(CO)₉L₃, L=PFcPh₂ or PFc₂Ph) agree reason-
ably well with those in the literature; the $^{31}$P NMR spectra for all these complexes were not previously recorded. The $^1$H NMR data for the disubstituted complexes Ru$_3$(CO)$_{10}$L$_2$ (L=PFcPh$_2$ or PFc$_2$Ph, the symmetrical and the unsymmetrical isomer) did not agree with those in the literature.

3.4.1 Preparation of Ru$_3$(CO)$_{11}$(PFcPh$_2$) \cite{250, 315}

A stirred solution of Ru$_3$(CO)$_{12}$ (260 mg, 0.41 mmol) and PFcPh$_2$ (150 mg, 0.41 mmol) in THF (40 mL) was treated with 10 drops of purple BPK solution. After 20 min the reaction solvent was removed in vacuo, and the residue was chromatographed on silica with petroleum ether as eluent. The first band proved to be the desired compound Ru$_3$(CO)$_{11}$(PFcPh$_2$) which was obtained as an orange solid (80%). $^{31}$P NMR (121.4 MHz): $\delta$ 27.3. $^1$H NMR (300 MHz): $\delta$ 7.60-7.35 (m, 10H), 4.52 (m, 2H), 4.22 (m, 2H), 3.97 (s, 5H). Mass spectrum (FAB): m/e 983 (P$^+$), 898, 871, 843, 814, 786, 732, 706, 685 (base peak), 629, 592. Anal. calcd. for C$_{33}$H$_{11}$FeO$_{11}$PRu$_3$: C, 40.38; H, 1.95. Found: C, 40.68; H, 1.99.

A 10/1 petroleum ether/diethyl ether mixture eluted the second band. Mass spectrum (FAB): m/e 1000, 995, 950, 915, 889, 862, 836, 820, 805, 717, 699.

3.4.2 Preparation of Ru$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ \cite{250, 315}

A stirred solution of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and PFcPh$_2$ (230 mg, 0.62 mmol) in THF (40 mL) was treated with 10 drops of purple BPK solution. After 2 h the reaction solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first orange band contained Ru$_3$(CO)$_{11}$(PFcPh$_2$) (15%) identified by TLC and $^{31}$P NMR spectroscopy.
The second band contained the symmetrical isomer of Ru$_3$(CO)$_{10}$ (PFcPh$_2$)$_2$ (40%) as a pink red solid. $^{31}$P NMR (121.4 MHz): δ 26.9. $^1$H NMR (300 MHz): δ 7.75-7.35 (m, 20H), 4.42 (m, 4H), 4.19 (m, 4H), 3.95 (s, 10H). Mass spectrum (FAB): m/e 1325 (P$^+$), 1269, 1241, 1213, 1185, 1156, 1128 (base peak), 1100, 1072, 994, 938, 859. Anal. calcd. for C$_{54}$H$_{38}$Fe$_2$O$_{10}$P$_2$Ru$_3$: C, 49.00; H, 2.89. Found: C, 49.24; H, 3.00.

The third band contained the unsymmetrical isomer of Ru$_3$(CO)$_{10}$ (PFcPh$_2$)$_2$ (20%) as a purple solid. $^{31}$P NMR (121.4 MHz): δ 24.2, 21.6. $^1$H NMR (300 MHz): δ 7.55-7.15 (m, 20H), 4.56 (m, 2H), 4.34 (m, 2H), 4.13 (m, 4H), 3.91 (s, 5H), 3.88 (s, 5H). Mass spectrum (FAB): m/e 1326 (P$^+$), 1298, 1269 (base peak), 1242, 1213, 1185, 1157, 1129, 1100, 1072, 938, 859, 830. Anal. calcd. for C$_{54}$H$_{38}$Fe$_2$O$_{10}$P$_2$Ru$_3$: C, 49.00; H, 2.89. Found: C, 49.38; H, 3.12.

The fourth band contained dark purple Ru$_3$(CO)$_9$(PFcPh$_2$)$_3$ (10%) identified by TLC and $^{31}$P NMR spectroscopy.

3.4.3 Preparation of Ru$_3$(CO)$_9$(PFcPh$_2$)$_3$ [315]

A solution of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and PFcPh$_2$ (330 mg, 0.89 mmol) in THF (30 mL) was heated for 30 min. The solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The small first and second bands were not identified. The third orange band contained Ru$_3$(CO)$_{11}$(PFcPh$_2$) (5%) identified by TLC, $^{31}$P, and $^1$H NMR spectroscopy. The fourth red band contained the symmetrical isomer of Ru$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ (15%) identified by TLC and $^{31}$P NMR spectroscopy. The fifth band (10%) contained a mixture of the symmetrical and unsymmetrical isomers of Ru$_3$(CO)$_{10}$
(PFcPh₂)₂ identified by ³¹P and ¹H NMR spectroscopy, and micro-analysis. The sixth band contained the desired compound Ru₃(CO)₉(PFcPh₂)₃ (60%).

The symmetrical isomer of Ru₃(CO)₁₀(PFcPh₂)₂, pink red solid. ³¹P NMR (121.4 MHz): δ 26.9.

The fifth band, pink solid. ³¹P NMR (81.0 MHz): δ 26.9; 24.2, 21.6. ¹H NMR (200 MHz): δ 7.75-7.15 (bm), 4.60-4.28 (m), 4.28-4.05 (m), 3.93 (s), 3.91 (s), 3.88 (s), 3.86 (m). Anal calcd. for C₅₄H₃₈Fe₂O₁₀P₂Ru₃: C, 49.00; H, 2.89. Found: C, 48.75; H, 2.98. TLC: 2 spots.

Ru₃(CO)₉(PFcPh₂)₃, dark purple solid. ³¹P NMR (81.0 MHz): δ 28.9. ¹H NMR (200 MHz): δ 7.53-7.20 (m, 30H), 4.34 (m, 6H), 4.11 (m, 6H), 3.77 (s, 15H). Mass spectrum (FAB): m/e 1665 (P⁺), 1637, 1157, 1125, 998 (base peak), 970, 869, 814, 784, 684. Anal. calcd. for C₇₅H₅₇Fe₃O₉P₃Ru₃: C, 54.07; H, 3.45. Found: C, 53.81; H, 3.25.

3.4.4 Preparation of Ru₃(CO)₁₁(PFc₂Ph) [250, 315]

A stirred solution of Ru₃(CO)₁₂ (270 mg, 0.42 mmol) and PFc₂Ph (200 mg, 0.42 mmol) in THF (40 mL) was treated with 10 drops of purple BPK solution. After 20 min the reaction solvent was removed in vacuo, and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The first band afforded the desired product Ru₃(CO)₁₁(PFc₂Ph) as an orange solid in 55% yield. ³¹P NMR (121.4 MHz): δ 16.0. ¹H NMR (300 MHz): δ 7.90-7.60 (m, 2H), 7.45-7.25 (m, 3H), 4.52 (m, 2H), 4.46 (m, 2H), 4.34 (m, 2H), 4.18 (s, 10H), 4.10 (m, 2H). Mass spectrum (FAB): m/e 1091 (P⁺), 1006, 978, 950, 923, 895, 866, 852, 840, 822, 811, 793 (base peak), 781, 766, 737, 714, 680, 608, 580. Anal. calcd. for C₃₇H₂₃Fe₂O₁₁PRu₃: C, 40.79; H, 2.13. Found: C, 41.01; H, 2.23.
The second band contained the unsymmetrical isomer of Ru₃(CO)₁₀(PFc₂Ph)₂ (30%) as a purple red solid. ³¹P NMR (121.4 MHz): δ 13.8, 13.4. ¹H NMR (300 MHz): δ 7.85-7.70 (m, 4H), 7.40-7.30 (m, 6H), 4.51 (m, 4H), 4.44 (m, 4H), 4.36 (m, 4H), 4.19 (s, 20H), 4.11 (m, 4H). Anal. calcd. for C₆₂H₄₆Fe₄O₁₀P₂Ru₃: C, 48.37; H, 3.01. Found: C, 48.03; H, 2.96.

3.4.5 Preparation of Ru₃(CO)₉(PFc₂Ph)₃ [250, 315]

A solution of Ru₃(CO)₁₂ (160 mg, 0.25 mmol) and PFc₂Ph (360 mg, 0.75 mmol) in THF (50 mL) was heated for 20 min. The solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH₂Cl₂ as eluent. The first orange band contained Ru₃(CO)₁₁(PFc₂Ph) (5%) identified by TLC and ³¹P NMR spectroscopy. The second purple red band contained the unsymmetrical isomer of Ru₃(CO)₁₀(PFc₂Ph)₂ (30%) identified by TLC and ³¹P NMR spectroscopy.

The third purple band proved to be the symmetrical isomer of Ru₃(CO)₁₀(PFc₂Ph)₂ (10%). ³¹P NMR (121.4 MHz): δ 11.8. ¹H NMR (300 MHz): δ 7.65-7.50 (m, 4H), 7.45-7.20 (m, 6H), 4.48 (m, 4H), 4.30 (m, 4H), 4.22 (m, 4H), 4.15 (m, 4H), 4.02 (s, 20H). Anal. calcd. for C₆₂H₄₆Fe₄O₁₀P₂Ru₃: C, 48.37; H, 3.01. Found: C, 47.96; H, 3.12.

The fourth dark purple band proved to be Ru₃(CO)₉(PFc₂Ph)₃ (45%). ³¹P NMR (121.4 MHz): δ 9.6. ¹H NMR (300 MHz): δ 7.6-7.2 (m, 15H), 4.59 (m, 6H), 4.42 (m, 6H), 4.24 (m, 6H), 4.07 (s, 30H), 3.99 (m, 6H). Anal. calcd. for C₈₇H₆₉Fe₆O₉P₃Ru₃: C, 52.52; H, 3.50. Found: C, 51.88; H, 3.19.

3.4.6 Preparation of Ru₃(CO)₁₁(PEt₂Fc)

Triruthenium dodecacarbonyl (320 mg, 0.50 mmol) and PEt₂Fc (274 mg, 1.0 mmol) in THF (20 mL) was heated for 35 min. TLC revealed the
formation of five products. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first orange band contained Ru$_3$(CO)$_{11}$(PEt$_2$Fc) (50%). $^{31}$P NMR (81.0 MHz): $\delta$ 19.6. $^1$H NMR (200 MHz): $\delta$ 4.44 (m, 2H), 4.21 (m+s, 2+5H), 2.24-1.94 (m, 4H), 1.17 (td, 6H, $J_{H-P}$=17.8, $J_{H-H}$=8.0). Mass spectrum (FAB): m/e 886 (P$^+$), 804, 773 (base peak), 746, 717, 690, 662, 634, 617, 605, 590, 562. Anal. calcd. for C$_{25}$H$_9$FeO$_{11}$PRu$_3$: C, 33.91; H, 2.16. Found: C, 33.68; H, 2.23.

The second pink band contained a complex mixture (15%). $^{31}$P NMR (121.4 MHz): $\delta$ 27.1, 22.4, $J$=42.8; 26.3, 17.9, $J$=38.7; 44.1. $^1$H NMR (300 MHz): $\delta$ 7.24 (d), 5.29 (d), 4.77 (m), 4.55 (m), 4.50 (m), 4.45-4.20 (bm), 2.9-2.7 (m), 2.35-2.05 (m), 2.00-1.65 (m), 1.50-0.80 (bm). Mass spectrum (FAB): m/e 951 (P$^+$), 866, 839 (base peak), 812, 782, 753.

3.4.7 Preparation of Ru$_3$(CO)$_{11}$(PF$i$Pr$_2$)

A solution of Ru$_3$(CO)$_{12}$ (270 mg, 0.42 mmol) and PF$i$Pr$_2$ (128 mg, 0.42 mmol) in THF (40 mL) was treated with 10 drops of purple BPK solution. After 20 min the reaction solvent was removed in vacuo, and the residue was chromatographed on silica. Elution with petroleum ether afforded the desired product Ru$_3$(CO)$_{11}$(PF$i$Pr$_2$) in the first band. It was obtained as an orange solid (55%). $^{31}$P NMR (121.4 MHz): $\delta$ 46.2. $^1$H NMR (300 MHz): $\delta$ 4.52 (m, 2H), 4.37 (m, 2H), 4.28 (s, 5H), 2.33 (m, 2H), 1.34 (dd, 6H), 1.11 (dd, 6H). Mass spectrum (FAB): m/e 913 (P$^+$), 831, 803 (base peak), 776, 748, 731, 719, 704, 690, 676, 646, 617, 590, 575, 560, 533, 519. Anal. calcd. for C$_{27}$H$_{23}$FeO$_{11}$PRu$_3$: C, 35.50; H, 2.54. Found: C, 35.77; H, 2.64.
The second band contained the symmetrical isomer of Ru$_3$(CO)$_{10}$ (PFciPr$_2$)$_2$ as a purple red solid (30%). $^{31}$P NMR (121.4 MHz): $\delta$ 41.4. $^1$H NMR (300 MHz): $\delta$ 4.44 (m, 4H), 4.38 (m, 4H), 4.12 (s, 10H), 2.40 (bm, 4H), 1.23 (dd, 12H). Mass spectrum (FAB): m/e 1189 (P$^+$), 1133, 1118, 1105, 1099, 1077 (base peak), 1062, 1049, 1032, 1020, 1005, 993, 965, 949, 936, 920, 908. Anal. calcd. for C$_{42}$H$_{46}$Fe$_2$O$_{10}$P$_2$Ru$_3$: C, 42.47; H, 3.90. Found: C, 41.99; H, 3.75.

3.4.8 Preparation of Ru$_3$(CO)$_9$(PFciPr$_2$)$_3$

A solution of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and PFciPr$_2$ (285 mg, 0.94 mmol) in THF (40 mL) was heated for 20 min. The solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first purple band (50%) contained a mixture of the symmetrical and the unsymmetrical isomers of Ru$_3$(CO)$_{10}$(PFciPr$_2$)$_2$ in almost equal amounts. $^{31}$P NMR (121.4 MHz): $\delta$ 41.4; 36.5, 35.2. Anal. calcd. for C$_{42}$H$_{46}$Fe$_2$O$_{10}$P$_2$Ru$_3$: C, 42.47; H, 3.90. Found: C, 42.35; H, 3.69.

The second band proved to be Ru$_3$(CO)$_9$(PFciPr$_2$)$_3$ which was obtained as a pink red solid in 35% yield. $^{31}$P NMR (121.4 MHz): $\delta$ 40.8. $^1$H NMR (300 MHz): $\delta$ 4.48 (m, 6H), 4.36 (m, 6H), 4.27 (s, 15H), 2.33 (m, 6H), 1.34 (dd, 18H), 1.13 (dd, 18H). Anal. calcd. for C$_{57}$H$_{69}$Fe$_3$O$_9$P$_3$Ru$_3$: C, 46.83; H, 4.76. Found: C, 46.17; H, 4.61.

3.4.9 Preparation of Ru$_3$(CO)$_{11}$(P$^1$Bu$_2$Fc)

Triruthenium dodecacarbonyl (256 mg, 0.40 mmol) and P$^1$Bu$_2$Fc (265 mg, 0.80 mmol) in THF (20 mL) was heated for 30 min after which the solvent was removed in vacuo. The residue was separated on a silica
chromatographic column with 3/1 petroleum ether/CH₂Cl₂ as eluent. The only major band that eluted proved to be Ru₃(CO)₁₁(PBu₂Fc) which was obtained as an orange solid in 60% yield. ³¹P NMR (81.0 MHz): δ 76.1. ¹H NMR (200 MHz): δ 4.53 (m, 2H), 4.48 (m, 2H), 4.21 (s, 5H), 1.28 (d, 18H, J=16 Hz). Mass spectrum (FAB): m/e 944 (P⁺), 829, 802, 774, 746, 717, 673, 646, 616, 573, 520, 460 (base peak). Anal. calcd. for C₂₉H₂₇FeO₁₁PRu₃: C, 36.99; H, 2.89. Found: C, 37.27; H, 3.01.

3.4.10 Preparation of Ru₃(CO)₁₁(PnBuFcPh)

A solution of Ru₃(CO)₁₂ (195 mg, 0.30 mmol) and PnBuFcPh (110 mg, 0.31 mmol) in THF (20 mL) was treated with 10 drops of purple BPK solution. After 30 min the reaction solvent was removed in vacuo, and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The second major band contained the desired compound Ru₃(CO)₁₁(PnBuFcPh) which was obtained as an orange solid in 75% yield. ³¹P NMR (121.4 MHz): δ 17.0. ¹H NMR (300 MHz): δ 7.65-7.50 (m, 2H), 7.35-7.20 (m, 3H), 4.38 (m, 2H), 4.32 (m, 2H), 4.15 (s, 5H), 2.12 (m, 2H), 1.73 (m, 2H), 1.46 (m, 2H), 1.03 (m, 3H). Mass spectrum (FAB): m/e 962 (P⁺), 907, 878 (base peak), 850, 823, 795, 767, 739, 710, 693, 666, 638, 610. Anal. calcd. for C₃₁H₂₃FeO₁₁PRu₃: C, 38.72; H, 2.41. Found: C, 39.06; H, 2.57.

3.4.11 Preparation of Ru₃(CO)₁₀[Fc'(PPh₂)₂] [120, 250]

The catalyst PPN⁺Cl⁻ (15 mg) was added to a stirred solution of Ru₃(CO)₁₂ (192 mg, 0.30 mmol) and Fc'(PPh₂)₂ (167 mg, 0.30 mmol) in THF (30 mL). After 30 min the reaction solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The small first yellow and second orange bands were not identified.
The third (15%) and fourth (10%) bands were characterized by $^1$H NMR spectroscopy and mass spectrometry. The fifth band contained the desired compound Ru$_3$(CO)$_{10}$[Fc'(PPh$_2$)$_2$] which was obtained as a red solid in 60% yield. The latter bands (orange and brownish orange) were not eluted.

The third band, pink solid. $^1$H NMR (200 MHz): $\delta$ 7.94 (m), 7.70 (bm), 7.46 (m), 7.31 (m), 6.55 (bm), 6.02 (m), 4.50 (m), 4.40 (m), 4.38 (m), 4.23 (s), 4.19 (s), 4.07 (m), 3.96 (s), 3.87 (m), 3.73 (m), 3.69 (m), 2.82 (m). Mass spectrum (FAB): m/e 1160 (P+), 1105, 1076, 1050, 1021, 994, 966, 885 (base peak), 813. TLC: 2 spots.

The fourth band, orange solid. Mass spectrum (FAB): m/e 1177 (P+), 1149, 1121, 1093, 1065, 1037, 981 (base peak), 937, 911, 859. TLC: 2 spots.

Ru$_3$(CO)$_{10}$[Fc'(PPh$_2$)$_2$], red solid. $^{31}$P NMR (81.0 MHz): $\delta$ 26.7. $^1$H NMR (200 MHz): $\delta$ 7.6-7.3 (bm, 20H), 4.40 (m, 4H), 4.30 (m, 4H). Mass spectrum (FAB): m/e 1139 (P+), 1083 (base peak), 1055, 1026, 998, 970, 944, 915, 886, 859. Anal. calcd. for C$_{44}$H$_{28}$FeO$_{10}$P$_2$Ru$_3$: C, 46.45; H, 2.48. Found: C, 46.19; H, 2.49. The $^1$H NMR data agree with those in the literature; the $^{31}$P NMR data were not previously recorded.

3.4.12 Preparation of Ru$_3$(CO)$_{10}$[Fc'(PFcPh)$_2$]

The catalyst PPN$^+$Cl$^-$ (15 mg) was added to a stirred solution of Ru$_3$(CO)$_{12}$ (192 mg, 0.30 mmol) and Fc'(PFcPh)$_2$ (231 mg, 0.30 mmol) in THF (25 mL). After 2 h the reaction solvent was removed in vacuo, and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The only major band that developed proved to be the desired compound Ru$_3$(CO)$_{10}$[Fc'(PFcPh)$_2$] which was obtained as a red solid in 85% yield. $^{31}$P NMR (81.0 MHz): $\delta$ 20.4. $^{13}$C NMR (50.3 MHz): $\delta$ 139.6 (d, J=42.5),

$^1$H NMR (200 MHz): $\delta$ 7.6-7.3 (bm, 20H), 4.40 (m, 4H), 4.30 (m, 4H). Mass spectrum (FAB): m/e 1139 (P+), 1083 (base peak), 1055, 1026, 998, 970, 944, 915, 886, 859. Anal. calcd. for C$_{44}$H$_{28}$FeO$_{10}$P$_2$Ru$_3$: C, 46.45; H, 2.48. Found: C, 46.19; H, 2.49. The $^1$H NMR data agree with those in the literature; the $^{31}$P NMR data were not previously recorded.
130.3 (d, J=9.2), 129.3 (s), 127.6 (d, J=10.0), 81.0 (d, J=47.7), 74.2 (s), 72.1 (d, J=7.1), 71.7 (d, J=7.6), 69.8 (d, J=1.6), 69.3 (d, J=7.9), 68.0 (s). Mass spectrum (FAB): m/e 1355 (P+), 1299 (base peak), 1271, 1243, 1215, 1187, 1158, 1130. Anal. calcd. for C\textsubscript{52}H\textsubscript{36}Fe\textsubscript{3}O\textsubscript{10}P\textsubscript{2}Ru\textsubscript{3}: C, 46.14; H, 2.68. Found: C, 46.67; H, 2.75.

3.4.13 Preparation of Ru\textsubscript{3}(CO)\textsubscript{10}[Fc'(PtBuPh)\textsubscript{2}]

The catalyst PPN\textsuperscript{+}Cl\textsuperscript{-} (25 mg) was added to a stirred solution of Ru\textsubscript{3}(CO)\textsubscript{12} (200 mg, 0.31 mmol) and Fc'(PtBuPh)\textsubscript{2} (163 mg, 0.32 mmol) in THF (40 mL). The colour of the solution changed immediately to dark red. It was left stirring for 30 min, then the solvent was removed in vacuo, and the residue was chromatographed on silica with 3/1 petroleum ether/CH\textsubscript{2}Cl\textsubscript{2} as eluent. The first band contained Ru\textsubscript{3}(CO)\textsubscript{12} (5%) identified by TLC. The second major band proved to be the desired compound Ru\textsubscript{3}(CO)\textsubscript{10}[Fc'(PtBuPh)\textsubscript{2}] which was obtained as a dark red solid (70%). \textsuperscript{31}P NMR (121.4 MHz): δ 46.9. \textsuperscript{1}H NMR (300 MHz): δ 8.35-8.10 (bm, 4H), 7.60-7.40 (bm, 6H), 4.72 (m, 2H), 4.63 (m, 4H), 4.45 (m, 2H), 0.88 (d, 18H). Mass spectrum (FAB): m/e 1097 (P+), 1039, 1011, 983, 955 (base peak), 901, 874, 801, 773, 745, 717, 659, 644. Anal. calcd. for C\textsubscript{40}H\textsubscript{36}FeO\textsubscript{10}P\textsubscript{2}Ru\textsubscript{3}: C, 43.77; H, 3.31. Found: C, 43.28; H, 3.22.

3.4.14 Preparation of Ru\textsubscript{3}(CO)\textsubscript{10}[Fc'(PiPr\textsubscript{2})\textsubscript{2}]

The catalyst PPN\textsuperscript{+}Cl\textsuperscript{-} (10 mg) was added to a solution of Ru\textsubscript{3}(CO)\textsubscript{12} (260 mg, 0.40 mmol) and Fc'(PiPr\textsubscript{2})\textsubscript{2} (170 mg, 0.40 mmol) in THF (20 mL). The colour of the solution changed instantly from orange to dark red, and the reaction was complete in 30 min as shown by TLC. Solvent removal under reduced pressure afforded a dark red residue which was chromato-
graphed on silica with 3/1 petroleum ether/CH\_2Cl\_2 as eluent. The only major band contained the desired product Ru\_3(CO)\_10[Fe(P\_iPr\_2)\_2] which was obtained as a dark red crystalline solid in 75\% yield. \textsuperscript{31}P NMR (121.4 MHz): \( \delta \) 41.3. \textsuperscript{1}H NMR (300 MHz): \( \delta \) 4.50 (m, 4H), 4.40 (m, 4H), 2.55-2.30 (m, 4H), 1.45-1.10 (m, 24H). Mass spectrum (FAB): \( m/e \) 1001 (P\(^+\)), 973, 945, 917, 889 (base peak), 861, 833, 818, 805, 790, 777, 762, 749, 734, 721, 706, 693, 678, 661, 650, 629, 589, 562, 549. Anal. calcd. for C\(_{32}\)H\(_{36}\)FeO\(_{10}\)P\(_2\)Ru\(_3\): C, 38.37; H, 3.62. Found: C, 38.40; H, 3.77.

3.4.15 Preparation of Ru\(_3\)(CO)\(_9\)Fc'(P\_iPr\_2)\(_2\))(PFc\(_2\)Ph)

A solution of Ru\(_3\)(CO)\(_10\)Fc'(P\_iPr\_2)\(_2\)] (200 mg, 0.20 mmol) and PFc\(_2\)Ph (96 mg, 0.20 mmol) in hexanes (50 mL) was refluxed for 3.5 h. TLC revealed that only one major compound is present. The solvent was removed in vacuo and the dark residue was chromatographed on silica with 1/1 petroleum ether/CH\_2Cl\_2 as eluent. The only major band that developed proved to be the desired product Ru\(_3\)(CO)\(_9\)Fc'(P\_iPr\_2)\(_2\))(PFc\(_2\)Ph) which was obtained as a pinkish red solid in ~90\% yield. \textsuperscript{31}P NMR (81.0 MHz): \( \delta \) 37.6 (d, J=15.0), 36.0 (s), 13.9 (d, J=15.0). \textsuperscript{1}H NMR (200 MHz): \( \delta \) 8.02 (m, 2H), 7.29 (m, 3H), 4.52 (m, 2H), 4.44 (m, 2H), 4.36 (m, 4H), 4.24 (m, 6H), 4.15 (s, 10H), 4.07 (m, 2H), 2.21 (bm, 4H), 1.4-0.8 (very broad, 24H). Anal. calcd. for C\(_{57}\)H\(_{59}\)Fe\(_3\)O\(_9\)P\(_3\)Ru\(_3\): C, 47.16; H, 4.10. Found: C, 47.23; H, 4.17.

3.4.16 Preparation of Ru\(_3\)(CO)\(_9\)Fc'(P\_iPr\_2)\(_2\))(PEtFc\(_2\))

A solution of Ru\(_3\)(CO)\(_10\)Fc'(P\_iPr\_2)\(_2\)] (200 mg, 0.20 mmol) and PEtFc\(_2\) (86 mg, 0.20 mmol) in CH\_2Cl\_2 (15 mL) was stirred at room temperature for 5 days. TLC indicated that a pink product is present. The solvent was removed in vacuo and the residue was chromatographed on silica with 1/1
petroleum ether/CH$_2$Cl$_2$ as eluent. The first band gave unreacted Ru$_3$(CO)$_{10}$[Fc'(P$i$Pr$_2$)$_2$] (40%). The second band proved to be Ru$_3$(CO)$_9$[Fc'(P$i$Pr$_2$)$_2$](PEtFc$_2$) which was obtained as a dark red solid in 45% yield. $^{31}$P NMR (81.0 MHz): $\delta$ 37.0 (d, J=13.5), 35.7 (s), 11.8 (d, J=13.5). $^1$H NMR (200 MHz): $\delta$ 4.56 (m, 2H), 4.48 (m, 2H), 4.36 (m, 2H), 4.32 (m, 2H), 4.26 (m, 6H), 1.6-0.8 (bm, 27H). Anal. calcd. for C$_{53}$H$_{59}$Fe$_3$O$_9$P$_3$Ru$_3$: C, 45.35; H, 4.24. Found: C, 45.48; H, 4.31.

3.4.17 Preparation of Ru$_3$(CO)$_{11}$(PEtFc$_2$)

A solution of Ru$_3$(CO)$_{12}$ (130 mg, 0.20 mmol) and PEtFc$_2$ (130 mg, 0.30 mmol) in cyclohexane (20 mL) was heated for 5 h. TLC revealed the formation of one product which did not undergo further reaction. The solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The only major orange band that developed proved to be Ru$_3$(CO)$_{11}$(PEtFc$_2$) (65%). $^{31}$P NMR (121.4 MHz): $\delta$ 15.2. $^1$H NMR (300 MHz): $\delta$ 4.48 (m, 2H), 4.43 (m, 2H), 4.33 (m, 2H), 4.18 (s, 10H), 4.12 (m, 2H), 2.51 (m, 2H), 1.34 (m, 3H). Mass spectrum (FAB): m/e 1043 (P$^+$, base peak), 1015, 987, 959, 931, 902, 874, 846, 819, 790, 761, 733. Anal. calcd. for C$_{33}$H$_{23}$Fe$_2$O$_{11}$PRu$_3$: C, 38.06; H, 2.23. Found: C, 38.25; H, 2.08.

3.5 Pyrolysis of Os$_3$ Complexes

3.5.1 Pyrolysis of Os$_3$(CO)$_{11}$(PFcPh$_2$)

(a) in octane for 3 h
A solution of Os$_3$(CO)$_{11}$(PFcPh$_2$) (60 mg, 0.048 mmol) in octane (25 mL) was refluxed for 3 h. $^{31}$P NMR spectroscopy revealed one major resonance at 207.3 and three small ones at 195.9, 65.4, and -6.0 ppm. The solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first greenish yellow band contained Os$_3$(CO)$_{12}$ (2%). The second band contained complex (239) (80%). The third band contained complex (240) (3%). The fourth band (1%) contained trace of a complex identified only by mass spectrometry. The fifth band (2%) contained a complex mixture including complex (245) (Section 3.5.3) as judged by TLC and hydride resonances in the $^1$H NMR spectrum. Crystals of (239) suitable for X-ray structure analysis were obtained by slow evaporation of the eluted band.

(239), red solid. $^{31}$P NMR (81.0 MHz): $\delta$ 207.3. $^1$H NMR (300 MHz): $\delta$ 7.63 (m, 2H), 7.12 (m, 2H), 4.63 (m, 2H), 4.54 (m, 2H), 4.26 (s, 5H). Mass spectrum (FAB): m/e 1116 (P+, base peak), 1088, 1060, 1032, 1004, 976, 948, 920, 892, 875, 864. Anal. calcd. for C$_{25}$H$_{13}$FeO$_9$Os$_3$P: C, 26.94; H, 1.18. Found: C, 27.16; H, 1.33.

(240), dark red solid. $^{31}$P NMR (81.0 MHz): $\delta$ 65.4. $^1$H NMR (400 MHz): $\delta$ 7.77 (m, 2H), 7.51 (m, 2H), 4.51 (m, 1H), 4.13 (s, 5H), 4.11 (m, 2H), 3.60 (m, 1H). Mass spectrum (FAB): m/e 1142 (P+, base peak), 1114, 1086, 1058, 1030, 1002, 974, 946, 918, 890, 862.

The fourth band, orange solid. Mass spectrum (FAB): m/e 1114 (P+, base peak), 1086, 1058, 1030, 1002, 974, 946, 918, 890, 862.

The fifth band, orange solid. $^1$H NMR (400 MHz): $\delta$ 9.29 (m), 8.22 (m), 7.90 (m), 7.65-7.51 (m), 7.47-7.32 (bm), 7.25-7.10 (m), 6.18 (m), 5.18 (m), 4.87 (m), 4.80 (m), 4.72 (m), 4.70 (m), 4.63 (m), 4.50 (m), 4.46 (m), 4.33 (m), 4.28 (m), 4.22 (m), 4.12 (m), 4.08 (m), 4.04 (m), 4.00 (m), 3.97 (s),
3.75 (m), 3.62 (m), 3.22 (m), 3.03 (m), -11.69 (d, J=6.2), -12.16 (d, J=4.3),
(245), -12.51 (s), -12.54 (d, J=11.4), -16.29 (d, J=8.7), -16.86 (d, J=13.4),
(245), -17.78 (d, J=17.1), -18.14 (d, J=19.0), -18.43 (d, J=15.0).

(b) in octane for 21 h

A solution of Os$_3$(CO)$_{11}$(PFcPh$_2$) (100 mg, 0.080 mmol) in octane (50
mL) was refluxed for 21 h. $^{31}$P NMR spectroscopy revealed a major
resonance at 207.3 and four minor ones at 290.2, 235.0, 166.8, and 125.7
ppm. The resonances at 195.9, 65.4, and -6.0 ppm were not observed. The
reaction solvent was removed in vacuo and the residue was
chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The
first red band contained (239) (65%) identified by TLC, $^{31}$P, and $^1$H NMR
spectroscopy. The second orange band (2%) contained a mixture of (239)
and three other complexes by TLC. The third band (2%) contained a
mixture of two complexes. The fourth pink band (4%) contained a mixture
of two complexes by TLC. The fifth band (5%) contained a complex mixture
of at least four compounds. The sixth band contained complex (241) (8%).
The seventh band (2%) contained a mixture of two complexes. The eighth
yellow band contained traces of a mixture of two complexes by TLC.

The third band, orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 306.6. TLC: 2
spots.

The fifth band, dark brown solid. $^{31}$P NMR (81.0 MHz): $\delta$ 360.2, 357.2,
290.2 (major), 264.9, 235.0, 142.1, 125.7 (major). The $^1$H NMR (300 MHz)
spectrum is very complex with many interesting resonances. TLC: 5 spots.

(241), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 166.8. $^1$H NMR (400
MHz): $\delta$ 8.97 (m, 2H), 8.01 (m, 1H), 7.43 (m, 1H), 7.32 (m, 2H), 7.03 (m, 2H),
5.00 (m, 2H), 4.52 (m, 2H), 4.41 (m, 4H), 3.90 (s, 10H). Mass spectrum
(FAB): m/e 2201 (P⁺), 2145, 2117 (base peak), 2089, 2061, 1720, 1652.

The seventh band, dark orange solid. ³¹P NMR (81.0 MHz): δ 229.3, 43.8. ¹H NMR (200 MHz): δ 7.72 (m), 7.52 (m), 7.40 (m), 5.28 (m), 5.06 (m), 4.58-5.35 (m), 4.25 (s), 4.22 (s), 4.12 (s), 3.96 (m), 3.88 (m), 3.82 (s), 3.70 (m). TLC: 2 spots.

(c) in cyclohexane

A solution of Os₃(CO)₁₁(PFcPh₂) (110 mg, 0.090 mmol) in cyclohexane (30 mL) was refluxed for 25 h after which the solvent was removed in vacuo. TLC revealed the presence of the starting material (80%), complex (239) (10%), and three other complexes. ³¹P NMR spectroscopy revealed a major resonance at -10.6 ppm due to the starting material, two moderately strong resonances at 207.3 and -6.1 ppm due to complexes (239) and (242) respectively, and three very small resonances at 65.4, 13.6, and -17.1 ppm.

(d) in heptane

The reaction mixture from (c) was dried in vacuo and heptane (20 mL) was added. This mixture was then refluxed for 5 h after which the solvent was removed in vacuo. ³¹P NMR spectroscopy revealed three major resonances at -10.6, -6.1, and 207.3 ppm due to the starting material, compounds (242), and (239), respectively. The resonances at 65.4 and -17.1 ppm were also more significant. The solid residue was chromatographed on silica with 4/1 petroleum ether/CH₂Cl₂ as eluent. The first red band contained (239) (25%). The second red band (5%) contained a mixture of (240) identified by ¹H and ³¹P NMR spectroscopy and a complex with a ³¹P NMR resonance at -17.1 ppm. The third band contained complex (242) (20%). The fourth orange band contained unreacted starting
material (30%) identified by TLC and $^{31}$P NMR spectroscopy. The fifth band (8%) contained a mixture of complexes (243) and (245). The last brown band contained traces of a mixture of two complexes by TLC. Crystals of (242) suitable for X-ray structure determination were obtained from a 3/1 hexane/CH$_2$Cl$_2$ solution.

(242), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -6.1. $^1$H NMR (300 MHz): $\delta$ 7.55-7.35 (m, 2H), 7.35-7.20 (m, 3H), 6.75-6.60 (m, 2H), 6.60-6.45 (m, 2H), 5.16 (m, 1H), 4.78 (m, 1H), 4.48 (m, 1H), 4.37 (s, 5H), 3.26 (m, 1H), -17.82 (d, 1H, J=17.5). Mass spectrum (FAB): m/e 1194 (P+, base peak), 1166, 1138, 1110, 1082, 1060, 1054, 1032, 1026, 998, 970, 942, 920, 892. Anal. calcd. for C$_{31}$H$_{19}$FeO$_9$P: C, 31.21; H, 1.61. Found: C, 31.35; H, 1.58.

(243) and (245), dark orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 13.8, (243); -5.9, (245). $^1$H NMR (300 MHz): $\delta$ 7.35-7.20 (bm, 10H), 5.15 (m, 2H), 4.67 (m, 1H), 4.32 (m, 1H), 4.02 (m, 1H), 3.20 (m, 1H), 3.01 (m, 1H), -12.19 (d, 1H, J=4.2), -16.88 (d, 1H, J=13.5), (245); 7.69-7.60 (m, 2H), 7.57-7.52 (m, 3H), 7.43 (m, 1H), 7.28 (m, 1H), 7.19-7.11 (m, 2H), 4.71 (m, 1H), 4.60 (m, 2H), 4.16 (m, 1H), 3.97 (s, 5H), -12.56 (d, 1H, J=7.8) (243).

3.5.2 Pyrolysis of Os$_3$(CO)$_9$(PFc)(C$_6$H$_4$) (239)

A solution of Os$_3$(CO)$_9$(PFc)(C$_6$H$_4$) (239) (60 mg, 0.050 mmol) in decalin (20 mL) was refluxed for 10 h after which the solvent was removed in vacuo. TLC revealed the presence of more than ten complexes in the mixture, and $^{31}$P NMR spectroscopy revealed many resonances between 250 and 400 ppm. A detailed analysis gives the following major resonances: 377.7, 295.7, J=51.8; 357.6, 328.7, J=47.5; 351.5, 312.3, J=119.8; 306.4, 270.6, J=43.1; 281.9, 270.1, J=55.5; 289.6, 266.4, J=60.5; 340.3, 316.9, J=37.5. No chromatographic separation was carried out.
3.5.3 Pyrolysis of Os₃(CO)₁₀(PF₂Ph₂)

A solution of Os₃(CO)₁₀(PF₂Ph₂)₂ (240 mg, 0.15 mmol) in octane (50 mL) was refluxed for 5 h. The solvent was removed in vacuo and the residue was applied to a silica chromatographic column. Elution with 3/1 petroleum ether/CH₂Cl₂ gave more than fifteen bands. The bands after the twelfth were not eluted. The fifth and eleventh bands contained traces of mixtures. The ninth band (4%) contained complexes (248) and (249). The other bands in the order of elution contained complexes (239) (5%), (240) (2%), (242) (3%), (244) (5%), (245) (4%), (246) (15%), (247) (20%), (250) (8%), and (251) (25%), respectively. Crystals of (245) and (251) suitable for X-ray structure determinations were obtained from 2/1 and 1/1 hexane/CH₂Cl₂ solutions respectively.

(239), red solid. ³¹P NMR (81.0 MHz): δ 207.3. ¹H NMR (200 MHz): δ 7.58 (m, 2H), 7.07 (m, 2H), 4.59 (m, 2H), 4.50 (m, 2H), 4.22 (s, 5H).

(240), dark red solid. ³¹P NMR (81.0 MHz): δ 65.4. ¹H NMR (200 MHz): δ 7.76 (m, 2H), 7.50 (m, 2H), 4.61 (m, 1H), 4.13 (s, 5H), 4.08 (m, 2H), 3.58 (m, 1H).

(242), orange solid. ³¹P NMR (81.0 MHz): δ -6.0. ¹H NMR (200 MHz): δ 7.55-7.35 (m, 2H), 7.35-7.20 (m, 3H), 6.75-6.60 (m, 2H), 6.60-6.45 (m, 2H), 5.16 (m, 1H), 4.78 (m, 1H), 4.48 (m, 1H), 4.37 (s, 5H), 3.26 (m, 1H), -17.82 (d, 1H, J=17.7).

(244), yellow solid. ³¹P NMR (121.4 MHz): δ 21.2. ¹H NMR (300 MHz): δ 8.16 (m, 2H), 7.68 (m, 2H), 7.58-7.25 (m, 6H), 5.19 (m, 2H), 4.80 (m, 2H), 4.32 (m, 2H), 3.31 (m, 2H), -5.43 (d, 1H, J=21.8). Mass spectrum (FAB): m/e 1220 (P⁺), 1192 (base peak), 1164, 1136, 1107, 1079, 1050, 1022, 994, 966, 938, 860. Anal. calcd. for C₃₂H₁₉FeO₁₀Os₃P: C, 31.48; H, 1.57. Found: C, 31.81; H, 1.69.
The fifth band, orange solid. $^{31}$P NMR (81.0 MHz): $\delta$ -10.6, -17.1. $^1$H NMR (400 MHz): $\delta$ 9.3, 8.6, 8.2, 7.9-6.9, 4.95, 4.88, 4.70, 4.62, 4.46-4.30, 3.92, 3.76, 3.24, -11.69 (d, J=5.98), -12.53 (d, J=18.12), -15.00 (d, J=11.63), -15.10 (d, J=8.24). TLC: 3 spots.

(245), orange solid. $^{31}$P NMR (81.0 MHz): $\delta$ -6.0. $^1$H NMR (200 MHz): $\delta$ 7.30-7.15 (bm, 10H), 5.12 (m, 2H), 4.62 (m, 1H), 4.27 (m, 1H), 3.98 (m, 1H), 3.16 (m, 1H), 2.97 (m, 1H), -12.23 (d, 1H, J=4.2), -16.94 (d, 1H, J=13.4). Mass spectrum (FAB): m/e 1164 (P+, base peak), 1136, 1108, 1080, 1050, 1024, 993, 966, 936, 861. Anal. calcd. for C$_{30}$H$_{19}$Fe$_8$O$_{8}$S$_3$P: C, 30.93; H, 1.64. Found: C, 31.20; H, 1.71.

(246), pink solid. $^{31}$P NMR (81.0 MHz): $\delta$ 157.7. $^1$H NMR (200 MHz): $\delta$ 7.73 (bm, 4H), 7.36 (bm, 6H), 6.60 (bm, 2H), 6.04 (m, 2H), 4.53 (m, 2H), 4.46 (m, 2H), 4.34 (m, 2H), 4.27 (s, 10H), 3.99 (m, 2H). Mass spectrum (FAB): m/e 1430 (P+, base peak), 1402, 1374, 1346, 1318, 1290, 1262, 1232, 1153, 1087-1078, 1046. Anal. calcd. for C$_{45}$H$_{32}$Fe$_2$O$_7$Os$_3$P$_2$: C, 37.82; H, 2.26. Found: C, 38.04; H, 2.35.

(247), pink solid. $^{31}$P NMR (202.5 MHz): $\delta$ 187.4, 143.8, J=166.1. $^1$H NMR (500 MHz): $\delta$ 8.03 (q, 2H), 7.81 (q, 2H), 7.60-7.50 (bm, 6H), 7.01 (d, 1H, J=8.0), 6.51 (d, 1H, J=8.0), 6.40 (t, 1H, J=8.0), 6.31 (t, 1H, J=8.0), 4.51 (m, 1H), 4.42 (m, 1H), 4.30 (s, 5H), 4.24 (m, 1H), 4.13 (m, 1H), 3.99 (s, 5H), 3.80 (m, 1H), 3.78 (m, 1H), 2.76 (m, 1H), 2.30 (m, 1H). Mass spectrum (FAB): m/e 1430 (P+, base peak), 1400, 1371, 1344, 1315, 1289, 1259, 1231, 1153, 1087, 1044, 968. Anal. calcd. for C$_{45}$H$_{32}$Fe$_2$O$_7$Os$_3$P$_2$: C, 37.82; H, 2.26. Found: C, 37.96; H, 2.47.

(248) and (249), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 42.3, -13.6 (248); 40.8, -12.7 (249). $^1$H NMR (500 MHz): $\delta$ 7.94 (q, 2H), 7.54 (m, 2H), 7.47 (m, 3H), 7.41 (m, 2H), 7.32 (m, 3H), 7.17 (m, 3H), 6.72 (d, 1H), 6.53 (d, 1H),
6.44 (t, 1H), 6.21 (t, 1H), 4.47 (m, 2H), 4.28 (m, 2H), 4.24 (s, 5H), 4.16 (m, 2H), 4.05 (s, 5H), 3.98 (m, 1H), 3.94 (m, 1H), -14.17 (dd, 1H, J1=J2=12.1) (248); 7.88 (q, 2H), 7.70 (m, 2H), 7.49 (m, 3H), 7.30 (m, 3H), 7.22 (m, 2H), 6.92 (m, 3H), 6.82 (tm, 1H), 6.10 (t, 1H), 6.07 (d, 1H), 6.02 (bm, 1H), 4.44 (m, 1H), 4.32 (m, 1H), 4.18 (s, 5H), 4.03 (m, 2H), 3.98 (m, 2H), 3.93 (m, 2H), 3.88 (s, 5H), -14.20 (dd, 1H, J1=12.4, J2=11.0) (249).

(250), orange solid. 31P NMR (81.0 MHz): δ 195.8, 0.0. 1H NMR (200 MHz): δ 7.97-7.78 (m, 2H), 7.65-7.48(m, 4H), 7.45-7.30 (m, 4H), 7.12 (bm, 2H), 6.18 (bm, 2H), 4.55-4.45 (bm, 4H), 4.35-4.26 (bm, 2H), 4.24-4.19 (bm, 1H), 3.98 (s, 5H), 3.94 (s, 5H). Mass spectrum (FAB): m/e 1458 (P+, base peak), 1430, 1402, 1374, 1345, 1317, 1289, 1261, 1233, 1155.

The eleventh band, pink solid. 31P NMR (81.0 MHz): δ 154.1; 109.0, -24.0; -6.8, -12.4. 1H NMR (200 MHz): δ 8.2-5.8 (complex), 4.7-2.2 (complex), -7.85 (d, J=9.6), -9.25 (d, J=11.9), -13.91 (d, J=12.5). TLC: 3 spots.

(251), orange solid. 31P NMR (81.0 MHz): δ 0.1, -2.5, J=15.1. 1H NMR (400 MHz): δ 7.43-7.37 (m, 1H), 7.37-7.25 (bm, 4H), 7.19-7.07 (bm, 3H), 7.05-6.98 (tm, 1H), 6.94-6.81 (bm, 3H), 6.78-6.71 (tm, 1H), 6.57-6.47 (bm, 4H), 6.44-6.38 (tm, 1H), 6.16-6.09 (tm, 1H), 5.14 (m, 1H), 4.68 (m, 1H), 4.51 (m, 1H), 4.42 (m, 2H), 4.39 (m, 1H), 4.17 (s, 5H), 3.88 (m, 1H), 3.87 (s, 5H), 3.28 (m, 1H), -17.42 (dd, 1H, J1=17.8, J2=8.8). Mass spectrum (FAB): m/e 1536 (P+, base peak), 1508, 1480, 1452, 1424, 1396, 1368, 1196, 1144, 1138, 1070, 1033, 957, 924. Anal. calcd. for C$_{52}$H$_{38}$Fe$_2$O$_8$Os$_3$P$_2$: C, 40.69; H, 2.50. Found: C, 40.81; H, 2.54.

3.5.4 Pyrolysis of Os$_3$(CO)$_{11}$(PFc$_2$Ph)

A solution of Os$_3$(CO)$_{11}$(PFc$_2$Ph) (200 mg, 0.15 mmol) in octane (80 mL) was refluxed for 3 h. TLC showed the presence of more than ten
products. The reaction solvent was removed in vacuo and the residue was chromatographed on a silica column by using 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band contained Os$_3$(CO)$_9$(PFc)C$_6$H$_4$ (239) (8%). The second band (20%) proved to be a novel ferrocene complex (252). The third and fourth bands contained complexes (253) (3%) and (254) (2%) respectively. The fifth band contained small amount of an unidentified mixture. The sixth band contained complex (255) (2%). The seventh dark red band contained (240) (4%) identified by $^{31}$P and $^1$H NMR spectroscopy. The eighth to fifteenth bands contained complexes (256) (3%), (257) (6%), (258) (5%), (259) (3%), (260) (4%), (261) (10%), (262) (6%), and (263) (5%), respectively. A few very small bands after the fifteenth band were not eluted. Crystals of (252) and (263) suitable for X-ray structure determinations were obtained from 3/1 hexane/CH$_2$Cl$_2$ solutions. Crystals of (261) were obtained by slow evaporation of the eluted band. Crystals of (254), obtained from a 2/1 hexane/CH$_2$Cl$_2$ solution, await analysis.

(239), red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 207.2. $^1$H NMR (400 MHz): $\delta$ 7.62 (m, 2H), 7.11 (m, 2H), 4.62 (m, 2H), 4.55 (m, 2H), 4.26 (s, 5H). Mass spectrum (FAB): m/e 1116 (P$^+$, base peak), 1088, 1060, 1032, 1004, 976, 948, 920, 892, 875, 864. Anal. calcd. for C$_{25}$H$_{13}$FeO$_9$Os$_3$P: C, 26.94; H, 1.18. Found: C, 27.01; H, 1.20.

(252), green solid. $^{31}$P NMR (121.4 MHz): $\delta$ 189.8. $^1$H NMR (400 MHz): $\delta$ 5.04 (dm, 2H), 4.52 (m, 4H), 4.36 (s, 5H), 4.20 (s, 5H), 3.98 (m, 1H). Mass spectrum (FAB): m/e 1224 (P$^+$, base peak), 1196, 1168, 1140, 1112, 1084, 1056, 1028, 1015, 1000, 984, 970, 922, 905, 881, 864, 851. Anal. calcd. for C$_{29}$H$_{17}$Fe$_2$O$_9$Os$_3$P: C, 28.48; H, 1.39. Found: C, 28.21; H, 1.27.

(253), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -24.2. $^1$H NMR (400
MHz): δ 8.09 (m, 2H), 7.68 (m, 3H), 5.22 (m, 1H), 4.53 (m, 1H), 4.48 (m, 1H),
4.44 (m, 1H), 4.33 (m, 1H), 4.30 (m, 2H), 4.27 (m, 1H), 4.02 (m, 1H), 3.92
(m, 1H), 3.90 (m, 1H), 3.76 (s, 5H), -16.86 (d, 1H, J=29.6), -18.60 (d, 1H,
J=13.8). Mass spectrum (FAB): m/e 1332 (P+), 1276 (base peak), 1248,
1220, 1192, 1164, 1135, 1106, 1078, 1045.

(254), reddish orange solid. 31P NMR (121.4 MHz): δ -33.3. 1H NMR
(400 MHz): δ 7.89 (m, 2H), 7.52 (m, 3H), 5.31 (m, 1H), 4.87 (m, 2H), 4.63
(m, 1H), 4.55 (m, 1H), 4.42 (m, 1H), 4.34 (m, 1H), 4.24 (m, 1H), 4.21 (m,
1H), 4.10 (s, 5H), 3.96 (m, 1H), 3.84 (m, 1H), -17.25 (d, 1H, J=30.5), -18.76
(d, 1H, J=14.6).

(255), reddish orange solid. 31P NMR (121.4 MHz): δ 43.5. 1H NMR
(300 MHz): δ 5.12 (m, 1H), 4.48 (m, 2H), 4.31 (s, 5H), 4.24 (m, 2H), 4.10 (s,
5H), 3.96 (m, 1H), 3.72 (m, 1H). Mass spectrum (FAB): m/e 1252 (P+, base
peak), 1224, 1196, 1168, 1139, 1110, 1082, 1054, 1026, 988, 960.

(256), orange solid. 31P NMR (121.4 MHz): δ -26.7. 1H NMR (300
MHz): δ 7.81 (m, 1H), 7.54 (m, 1H), 7.32 (m, 1H), 7.06 (m, 1H), 5.04 (m, 2H),
4.62 (m, 2H), 4.53 (m, 2H), 4.30 (s, 10H), 4.18 (m, 2H), -18.53 (d, 1H,
J=13.0). Mass spectrum (FAB): m/e 1300 (P+), 1272 (base peak), 1244,
1216, 1187, 1159, 1130, 1102, 1074, 1046.

(257), reddish orange solid. 31P NMR (121.4 MHz): δ 146.9. 1H NMR
(300 MHz): δ 8.15 (m, 2H), 7.55 (m, 2H), 7.46 (m, 1H), 5.88 (m, 1H), 5.60
(m, 1H), 4.74 (s, 5H), 4.47 (m, 1H), 4.40 (m, 1H), 4.29 (s, 5H), 4.12 (m, 1H),
3.90 (m, 1H), 3.78 (m, 1H), -18.71 (bs, 1H). Mass spectrum (FAB): m/e
1274 (P+), 1244 (base peak), 1216, 1188, 1160, 1132, 1104, 1076, 1048.
Anal. calcd. for C34H23Fe2O8Os3P: C, 32.08; H, 1.82. Found: C, 31.72; H, 1.59.

(258), reddish orange solid. 31P NMR (121.4 MHz): δ 150.2. 1H NMR
(300 MHz): δ 8.07 (m, 2H), 7.60-7.45 (m, 3H), 5.61 (m, 1H), 5.37 (m, 1H),
4.68 (m, 1H), 4.47 (s, 5H), 4.33 (m, 1H), 4.18 (s, 5H), 4.11 (m, 1H), 3.98 (m, 1H),
3.67 (m, 1H), -18.79 (bs, 1H). Mass spectrum (FAB): m/e 1274 (P+, base peak), 1244, 1216, 1188, 1160, 1132, 1104, 1076, 1048.

(259), brownish orange solid. 31P NMR (121.4 MHz): δ -13.9. 1H NMR (300 MHz): δ 8.12 (m, 1H), 7.62 (m, 1H), 7.48 (m, 1H), 7.15 (m, 1H), 4.89 (m, 2H), 4.67 (m, 2H), 4.48 (m, 2H), 4.21 (s, 10H), 3.97 (m, 2H), -12.01 (d, 1H, J=6.8). Mass spectrum (FAB): m/e 1330 (P+), 1302 (base peak), 1274, 1246, 1218, 1190, 1161, 1133, 1104, 1076, 1048, 970.

(260), pink solid. 31P NMR (121.4 MHz): δ -15.8. 1H NMR (300 MHz): δ 7.83 (m, 2H), 7.45-7.38 (m, 3H), 5.23 (m, 2H), 4.86 (m, 2H), 4.57 (m, 2H),
4.25 (m, 2H), 4.18 (s, 5H), 4.01 (m, 2H), 3.74 (m, 2H), -12.51 (d, 1H, J=19.3).
Mass spectrum (FAB): m/e 1300 (P+, base peak), 1272, 1244, 1216, 1188, 1160, 1132, 1104, 1076, 1048, 970.

(261), orange solid. 31P NMR (121.4 MHz): δ -20.4. 1H NMR (500 MHz): δ 7.76-7.60 (bm, 2H), 7.50-7.34 (bm, 3H), 5.10-5.00 (m, 2H), 4.64 (m, 1H), 4.55 (m, 1H), 4.45-4.30 (m, 3H), 4.08 (m, 1H),
4.02 (s, 5H), 3.42 (m, 1H), 3.36 (m, 1H), 3.08 (m, 1H), -12.13 (d, 1H, J=4.5), -16.91 (d, 1H, J=12.5).
Mass spectrum (FAB): m/e 1274 (P+, base peak), 1246, 1218, 1190, 1162, 1134, 1106, 1078, 1050. Anal. calcd. for C34.5H24C1Fe2O8O8s3P ,
(261)-0.5CH2Cl2: C, 31.50; H, 1.84. Found: C, 32.60; H, 1.85.

(262), orange solid. 31P NMR (121.4 MHz): δ -22.0. 1H NMR (500 MHz): δ 7.85-7.70 (m, 2H), 7.45-7.25 (bm, 3H), 5.13 (m, 1H), 5.04 (m, 1H),
4.72 (m, 1H), 4.59 (m, 1H), 4.52 (m, 2H), 4.33 (m, 1H), 4.13 (s, 5H), 3.99 (m, 1H),
3.43 (m, 1H), 3.28 (m, 1H), 3.04 (m, 1H), -12.16 (d, 1H, J=3.87), -17.05 (d, 1H, J=12.97).
Mass spectrum (FAB): m/e 1274 (P+, base peak), 1246, 1218, 1190, 1162, 1134, 1106, 1078, 1050.
(263), reddish brown solid. $^{31}$P NMR (121.4 MHz): $\delta$ 39.3. $^1$H NMR (400 MHz): $\delta$ 4.91 (t, 2H), 4.79 (t, 2H), 4.67 (t, 2H), 4.22 (m, 2H), 4.07 (s, 5H), 3.78 (q, 2H), 3.12 (q, 2H). Mass spectrum (FAB): m/e 1222 ($P^+$, base peak), 1194, 1166, 1138, 1110, 1082, 1054, 1026, 998, 970. Anal. calcd. for C$_{29}$H$_{17}$Fe$_2$O$_9$Os$_3$P: C, 28.49; H, 1.40. Found: C, 28.66; H, 1.53.

3.5.5 Pyrolysis of Os$_3$(CO)$_{10}$(PF$_2$C$_2$Ph)$_2$

(a) in octane for 18 h

A solution of Os$_3$(CO)$_{10}$(PF$_2$C$_2$Ph)$_2$ (50 mg, 0.028 mmol) in octane (20 mL) was refluxed for 18 h after which the solvent was removed in vacuo. TLC revealed the presence of six major products and many minor ones as was also shown by $^{31}$P NMR spectroscopy. Hydride resonances in the $^1$H NMR spectrum showed mainly those associated with Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_3$PF$_2$C$_2$Ph)Fe(C$_5$H$_4$)] (261).

(b) in octane for 19.5 h

A solution of Os$_3$(CO)$_{10}$(PF$_2$C$_2$Ph)$_2$ (200 mg, 0.11 mmol) in octane (50 mL) was refluxed for 19.5 h. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band contained (252) (8%) by TLC, $^1$H, and $^{31}$P NMR spectroscopy. The second band (5%) contained complexes (253) and traces of (254) identified by $^{31}$P and $^1$H NMR spectroscopy. The third band (3%) contained a mixture of three complexes. The fourth band (6%) contained new complexes (264) and (265). The fifth band contained complex (261) (20%). The sixth, seventh, and eighth bands (2%, 4%, and 6%) contained
mixtures. The ninth band contained complex (266) (5%). The tenth yellow band (4%) contained a complex unidentified mixture.

The third band, yellow oily solid. $^{31}$P NMR (121.4 MHz): $\delta$ 43.5, (255); 41.1. $^1$H NMR (400 MHz): $\delta$ 7.81, 7.53, 7.26, 5.12, 4.96, 4.54, 4.49, 4.38 (s), 4.30 (s), 4.27, 4.24, 4.10 (s), 4.03, 3.95, 3.88 (s), 3.82, 3.72, 3.54. TLC: 3 spots.

(264) and (265), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 14.3; 12.8 (very small). $^1$H NMR (400 MHz): $\delta$ 7.88, 7.71, 7.56, 7.50, 7.13, 7.00, 6.90, 6.75, 5.00, 4.72, 4.64, 4.53, 4.41, 4.38, 4.35 (s), 4.28, 4.23, 4.15 (s), 4.09, 4.02, 3.76, 3.68, -5.54 (d, J=25.9) (very small), -5.57 (d, J=23.4).

(261), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -20.2. $^1$H NMR (300 MHz): $\delta$ 7.74-7.62 (bm, 2H), 7.48-7.38 (bm, 3H), 5.09 (m, 1H), 5.06 (m, 1H), 4.67 (m, 1H), 4.57 (m, 1H), 4.44 (m, 1H), 4.39 (m, 2H), 4.07 (m, 1H), 4.03 (s, 5H), 3.43 (m, 1H), 3.38 (m, 1H), 3.10 (m, 1H), -12.12 (d, 1H, J=4.5), -16.91 (d, 1H, J=12.6). Anal. calcd. for C$_{34}$H$_{23}$Fe$_2$O$_8$Os$_3$P: C, 32.08; H, 1.82. Found: C, 32.60; H, 1.85.

The sixth band, orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 22.7, 21.5, -25.7. TLC: 2 spots.

The seventh band, pink solid. $^{31}$P NMR (121.4 MHz): $\delta$ 145.0-134.0 (broad), 22.8, 21.6. The $^1$H NMR spectrum is very complex (hydrides): $\delta$ -15.84 (dd, J$_1=14.2$, J$_2=12.5$).

The eighth band, orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 145.0-134.0 (broad) (small), 43.6, 22.8, 21.6, -3.8, -22.6, -25.2, -28.3, -29.6, -30.5. TLC: 5 spots including one the same as (262).

(266), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ -22.6, -30.0. Mass spectrum (FAB): m/e 1785 (P+, base peak), 1757, 1729, 1712, 1695, 1668, 1600, 1572, 1544, 1275, 1193, 1130, 1075, 1030.
3.5.6 Pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PEt}_2\text{Fc})$

A solution of $\text{Os}_3(\text{CO})_{11}(\text{PEt}_2\text{Fc})$ (100 mg, 0.087 mmol) in octane (30 mL) was refluxed for 8 h. The colour of the solution changed from bright reddish orange to dark orange. The solvent was removed in vacuo and the greenish yellow residue was chromatographed on a silica column by using 3/1 petroleum ether/CH$_2$C$l_2$ as eluent. The first greenish yellow band contained $\text{Os}_3(\text{CO})_{12}$ (1%) identified by TLC and mass spectrometry (unusually, as its CH$_2$C$l_2$ solvate shown by the mass spectrum (FAB): m/e 990 ($P^+$, base peak), 962, 934, 906, 878, 865, 850). The second band contained complex (267) (15%). The third orange band contained unreacted starting material (10%) identified by $^{31}\text{P}$ and $^1\text{H}$ NMR spectroscopy. The fourth, fifth, and sixth bands contained complexes (268) (2%), (269) (65%), and (270) (2%), respectively.

(267), yellow solid. $^{31}\text{P}$ NMR (81.0 MHz): $\delta$ -50.8. $^1\text{H}$ NMR (200 MHz): $\delta$ 4.50 (m, 1H), 4.38 (m, 2H), 4.20 (m, 1H), 4.16 (s, 5H), 2.88 (m, 1H), 2.52 (m, 1H), 2.24 (d, 3H, $J_{\text{P-H}}$=24.2), 1.50 (td, 3H, $J_{\text{P-H}}$=24.0), -15.13 (d, 1H, $J$=9.6), -19.62 (d, 1H, $J$=10.0). Mass spectrum (FAB): m/e 1096 ($P^+$, base peak), 1068, 1040, 1012, 984, 956, 928, 913, 900, 883, 872, 854, 844, 827, 816. Anal. calcd. for C$_{23}$H$_{19}$FeO$_9$Os$_3$P: C, 25.19; H, 1.75. Found: C, 25.40; H, 1.72.

(268), orange solid. $^{31}\text{P}$ NMR (81.0 MHz): $\delta$ 22.3. $^1\text{H}$ NMR (200 MHz): $\delta$ 4.80 (m, 1H), 3.36 (m, 1H), 3.00 (m, 1H), 2.15-1.90 (m, 2H), 1.3-0.9 (m, 3H), -19.50 (d, 1H, $J$=12.5).

(269), orange solid. $^{31}\text{P}$ NMR (81.0 MHz): $\delta$ -22.7. $^1\text{H}$ NMR (200 MHz): $\delta$ 5.16 (m, 1H), 5.02 (m, 1H), 4.71 (m, 1H), 4.18 (m, 2H), 4.06 (m, 1H), 3.08 (m, 1H), 2.18 (m, 1H), 1.86 (m, 2H), 1.28 (m, 1H), 1.04-0.90 (bm, 6H), -12.22 (d, 1H, $J_{\text{P-H}}$=4.5, satellite, $J_{\text{Os-H}}$=36.0), -17.39 (d, 1H, $J_{\text{P-H}}$=11.4,
satellite, $J_{O_{5-H}}=45.6$). Mass spectrum (FAB): m/e 1068 (P$^+$), 1040, 1012 (base peak), 984, 956, 928, 900, 872, 844, 827, 816, 788. Anal. calcd. for C$_{22}$H$_{19}$FeO$_8$ Os$_3$P: C, 24.72; H, 1.79. Found: C, 24.99; H, 1.92.

(270), greenish orange solid. $^{31}$P NMR (81.0 MHz): $\delta$ -20.7. $^1$H NMR (200 MHz): $\delta$ 4.85 (m, 1H), 4.62 (m, 1H), 4.21 (s, 5H), 4.07 (m, 1H), 2.07 (m, 2H), 1.87 (m, 2H), 1.03 (m, 6H), -14.39 (d, 1H, J=4.3).

3.5.7 Pyrolysis of Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_3$PET$_2$)Fe(C$_5$H$_4$)] (269)

A solution of (269) (50 mg, 0.047 mmol) in decalin (15 mL) was refluxed for 30 min after which the solvent was removed in vacuo. $^{31}$P NMR spectroscopy revealed the presence of mainly complex (269) and a resonance at 164.0 ppm (10%) and some small signals at 250.8, 145.9, 52.0, -25.9, -65.5 ppm including those of (267) and (270) which were also confirmed by their respective hydride resonances in the $^1$H NMR spectrum.

3.5.8 Pyrolysis of Os$_3$(CO)$_{12}$ with PET$_2$Fc in 1:2 molar ratio

A solution of Os$_3$(CO)$_{12}$ (272 mg, 0.30 mmol) and PET$_2$Fc (160 mg, 0.60 mmol) in p-xylene (40 mL) was refluxed for 10 h. $^{31}$P NMR spectroscopy revealed the following resonances in significant intensities: 4.6, 0.9, -8.7, -9.6, -17.0, -17.7, -18.6, -19.4, -19.6, -20.0, -22.3, -24.6, -25.8, -30.6, -62.1, -62.7. Interesting hydride resonances in the $^1$H NMR spectrum include those at -12.56 (d), -13.13 (d), -13.33 (dd), -14.68 (d), -14.86 (t), -15.11 (d), -15.39 (d), -16.26 (d), -17.32 (d), -19.30 (dd), -19.45 (d), -20.48 (m), -21.05 (d). The solvent was removed in vacuo and the residue was applied to a silica chromatographic column by using 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first greenish yellow band contained
unreacted Os$_3$(CO)$_{12}$ (5%). The second band contained mainly complex (271) and some of its isomer (272) ((271)/(272)>20/1), and the third band contained almost equal amounts of (271) and (272). These were separated by careful repeated chromatography: (271) (20%); (272) (14%). The fourth orange band contained (269) (10%) identified by TLC, $^1$H, and $^{31}$P NMR spectroscopy. The fifth band contained complex (273) (8%). The sixth brown band (2%) contained a mixture of three complexes by TLC. A number of bands after the sixth band were not eluted.

(271), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -24.6, -62.7. $^1$H NMR (300 MHz): $\delta$ 4.49 (m, 3H), 4.34 (m, 1H), 4.28 (m, 4H), 4.23 (s, 5H), 4.17 (s, 5H), 2.97 (m, 1H), 2.72 (m, 1H), 2.42 (dd, 3H, J$_1$=18, J$_2$=5), 2.20 (bm, 4H), 1.57 (m, 3H), 1.25 (bm, 6H), -14.82 (pt, 1H, J$_1$=J$_2$=9.9), -20.42 (pt, 1H, J$_1$=J$_2$=11.0). Mass spectrum (FAB): m/e 1342 (P$^+$), 1314, 1286 (base peak), 1258, 1230, 1200, 1172, 1142. Anal. calcd. for C$_{36}$H$_{38}$Fe$_2$O$_8$Os$_3$P$_2$: C, 32.20; H, 2.85. Found: C, 31.85; H, 2.70.

(272), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -25.8, -62.1. $^1$H NMR (300 MHz): $\delta$ 4.5-4.3 (m, 8H), 4.28 (s, 5H), 4.22 (s, 5H), 2.83 (m, 1H), 2.72 (m, 1H), 2.55 (dd, 3H, J$_1$=18, J$_2$=5), 2.20 (bm, 4H), 1.57 (m, 3H), 1.25 (bm, 6H), -15.13 (pt, 1H, J$_1$=J$_2$=10.0), -20.60 (dd, 1H, J$_1$=11.0, J$_2$=8.8). Anal. calcd. for C$_{36}$H$_{38}$Fe$_2$O$_8$Os$_3$P$_2$: C, 32.20; H, 2.85. Found: C, 32.02; H, 2.74.

(273), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 48.3, -8.0, J=20.2. $^1$H NMR (300 MHz): $\delta$ 4.59 (m, 1H), 4.47 (m, 1H), 4.41 (m, 2H), 4.32 (m, 1H), 4.28 (s, 5H), 4.21 (m, 1H), 4.13 (m, 3H), 3.98 (m, 1H), 3.77 (m, 1H), 2.72 (m, 2H), 2.58-2.40 (m, 4H), 2.20-2.05 (m, 2H), 1.53 (m, 3H), 1.38 (m, 3H), 1.35-1.15 (m, 6H), -16.09 (dd, 1H, J$_1$=14.5, J$_2$=5.8), -16.66 (dd,1H, J$_1$=22.0, J$_2$=8.5).
3.5.9 Pyrolysis of Os$_3$(CO)$_{11}$(PF$i$Pr$_2$)

A solution of Os$_3$(CO)$_{11}$(PF$i$Pr$_2$) (120 mg, 0.10 mmol) in octane (30 mL) was refluxed for 5 h. The colour of the solution changed from golden yellow to brownish red in 1 h. $^{31}$P NMR spectroscopy revealed the presence of four major products and a number of minor ones. The solvent was removed in vacuo and the dark residue was chromatographed on a silica column with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first to seventh bands contained complexes (274) (6%), (275) (20%), (276) (22%), (277) (12%), (278) (20%), (279) (5%), and (280) (2%), respectively. The last band (2%) contained a mixture of three complexes. Crystals of (278), obtained by slow evaporation of 3/1 petroleum ether/CH$_2$Cl$_2$ solution, were suitable for a successful X-ray diffraction study. Crystals of (274), (275), and (279), all obtained by slow evaporation of 1/1 hexanes/CH$_2$Cl$_2$ solutions, await structure determinations.

(274), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 203.9. $^1$H NMR (300 MHz): $\delta$ 5.77 (t, 1H), 5.08 (d, 1H), 4.68 (s, 5H), 3.74 (d, 1H), 3.03 (m, 1H, CHMe$_2$), 2.44 (m, 1H), 1.78 (dd, 3H), 1.75-1.62 (overlapping dd, 9H), -18.78 (bs, 1H). Mass spectrum (FAB): m/e 1096 (P$^+$, base peak), 1082, 1068, 1040, 1026, 1012, 998, 984, 956, 940, 928, 914, 900, 886, 872, 844, 828, 788. Anal. calcd. for C$_{24}$H$_{23}$FeO$_8$Os$_3$P: C, 26.28; H, 2.11. Found: 26.02; H, 2.28.

(275), brownish red solid. $^{31}$P NMR (81.0 MHz): $\delta$ 0.0. $^1$H NMR (300 MHz): $\delta$ 5.28 (d, 1H, J=2.2), 5.26 (m, 1H), 5.00 (d, 1H, J=2.2), 4.65 (m, 1H), 4.62 (m, 1H), 3.96 (t, 1H, J=2.2), 3.93 (m, 1H), 2.81 (m, 1H), 2.54 (m, 1H), 1.71 (dd, 3H, J$_1$=16.8, J$_2$=7.4), 1.41 (dd, 3H, J$_1$=13.6, J$_2$=7.0), 1.37 (dd, 3H, J$_1$=J$_2$=7.6), 1.32 (dd, 3H, J$_1$=10.2, J$_2$=7.4), -17.21 (dd, 1H, J$_1$=28.0, J$_2$=1.5), -18.99 (dd, 1H, J$_1$=12.2, J$_2$=1.5). Mass spectrum (FAB): m/e 1152 (P$^+$, base
peak), 1124, 1096, 1078, 1068, 1048, 1034, 1020, 1006, 992, 978, 964, 948, 934, 920, 906, 894, 878, 838. Anal. calcd. for C_{26}H_{23}FeO_{10}O_s_{3}P: C, 27.09; H, 2.01. Found: C, 27.23; H, 2.11.

(276), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 73.2 (broad). $^1$H NMR (300 MHz): $\delta$ 4.33 (m, 1H), 4.26 (m, 2H), 4.04 (s, 5H), 2.12 (m, 1H), 1.63 (dd, 3H, $J_1=18.5$, $J_2=7.3$), 1.53 (dd, 3H, $J_1=17.7$, $J_2=6.9$), -17.35--17.65 (very broad, 1H), -17.85--18.40 (very broad, 1H). Mass spectrum (FAB): m/e 1082 (P+, base peak), 1054, 1026, 998, 970, 942, 914, 870, 844, 788. Anal. calcd. for C_{22}H_{17}FeO_{9}O_s_{3}P: C, 24.40; H, 1.58. Found: C, 24.28; H, 1.62.

(277), yellow solid. $^{31}$P NMR (81.0 MHz): $\delta$ 14.3. $^1$H NMR (400 MHz): $\delta$ 4.52 (m, 1H), 4.35 (m, 2+1H), 4.25 (s, 5H), 2.42 (m, 1H), 1.33 (dd, 3H), 1.09 (dd, 3H). Mass spectrum (FAB): m/e 1108 (P+, base peak), 1080, 1052, 1024, 996, 982, 968, 954, 940, 926, 912, 898, 884, 870, 856, 842, 828, 814, 786. Anal. calcd. for C_{23}H_{15}FeO_{10}O_s_{3}P: C, 24.91; H, 1.36. Found: C, 25.30; H, 1.58.

(278), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 2.5. $^1$H NMR (400 MHz): $\delta$ 5.41 (m, 1H), 5.12 (m, 1H), 4.77 (m, 1H), 4.31 (m, 1H), 4.24 (m, 1H), 4.12 (m, 1H), 3.08 (m, 1H), 2.55 (m, 1H), 1.86 (m, 1H), 1.43 (dd, 3H), 1.36 (dd, 3H), 1.25 (dd, 3H), -12.07 (d, 1H, $J=4.1$), -17.13 (d, 1H, $J=12.0$). Mass spectrum (FAB): m/e 1096 (P+), 1068, 1040 (base peak), 1012, 984, 956, 942, 928, 914, 900, 886, 872, 858, 844, 826, 788. Anal. calcd. for C_{24}H_{23}FeO_{8}O_s_{3}P: C, 26.28; H, 2.11. Found: C, 26.40; H, 2.17.

(279), greenish yellow solid. $^{31}$P NMR (81.0 MHz): $\delta$ 11.2. $^1$H NMR (400 MHz): $\delta$ 4.98 (m, 1H), 4.88 (m, 1H), 4.67 (m, 1H), 4.47 (s, 5H), 2.47 (m, 1H), 2.29 (m, 1H), 1.67 (dd, 3H), 1.56 (dd, 3H), 1.22 (dd, 3H), 0.85 (dd, 3H), -15.23 (d, 1H, $J=14.6$). Mass spectrum (FAB): m/e 1124 (P+), 1096, 1068, 1040 (base peak), 1012, 988, 974, 960, 932, 918, 870, 856, 846, 826, 800, 159.
Anal. calcd. for C_{25}H_{23}FeO_{9}Os_{3}P: C, 26.69; H, 2.06. Found: C, 26.53; H, 1.98.

(280), yellow solid. \(^1^H\) NMR (300 MHz): \(\delta 5.11\ (m, 1H), 5.03\ (m, 1H), 4.44\ (m, 2H), 4.30\ (m, 2H), 4.21\ (m, 1H), 4.06\ (m, 1H), 2.54\ (m, 2H), 1.50\ (dd, 3H), 1.33\ (dd, 3H), 1.06\ (dd, 3H), 0.86\ (m, 3H), -13.2\ (d, 1H, J=8.4). Mass spectrum (FAB): m/e 1152 (P\(^+\), base peak), 1124, 1096, 1068, 1040, 1012, 988, 974, 960, 946, 932, 918, 904, 890, 876, 862, 848, 834, 790.

The last band, brownish orange solid. \(^{31} P\) NMR (121.4 MHz): \(\delta 287.0, 5.2\) (small). TLC: 3 spots.

3.5.10 Pyrolysis of Os\(_3\)(CO)\(_{12}\) with P\(_n\)BuFcPh

A solution of Os\(_3\)(CO)\(_{12}\) (272 mg, 0.30 mmol) and P\(_n\)BuFcPh (100 mg, 0.29 mmol) in octane (30 mL) was refluxed for 4 h. \(^{31} P\) NMR spectroscopy revealed the following major resonances: 209.9, 164.6, 151.3, 133.5, 56.7, 34.0, -5.9, -6.0, -10.1, -10.5, -10.6, -20.1, -58.4, -59.2, -59.3, -91.8, and -95.7 ppm. Many other minor signals were also present. The solvent was removed in vacuo and the solid residue was subjected to chromatographic separation on silica by using 4/1 petroleum ether/CH\(_2\)Cl\(_2\) as eluent. Careful analyses of the collected bands gave the following compounds in the order of elution (Os\(_3\)(CO)\(_{12}\) (2%) eluted as the first band): (281) (3%), (282) (3%), (283) (4%), (284) (1%), (285) (11%), (286) (8%), (287) (6%), (288) (4%), (289) (2%), (290) (2%), (291) (6%), (292) (8%), (293) (6%), (294) (6%). Crystals of (281) and (282), obtained from 3/1 hexane/CH\(_2\)Cl\(_2\) solutions, await analysis.

(281), greenish orange solid. \(^{31} P\) NMR (121.4 MHz): \(\delta 209.8. \(^1^H\) NMR (300 MHz): \(\delta 4.95\ (d, 2H, J=2.7), 4.12\ (s, 5H), 3.91\ (t, 1H, J=2.7), 3.03\ (m, 2H), 1.92\ (m, 2H), 1.62\ (m, 2H), 1.04\ (t, 3H). Mass spectrum (FAB): m/e
1094· (P+), 1066 (base peak), 1038, 1010, 982, 954, 926, 898, 870, 842, 814, 786. Anal. calcd. for C\textsubscript{23}H\textsubscript{17}Fe\textsubscript{9}O\textsubscript{9}Os\textsubscript{3}P: C, 25.23; H, 1.57. Found: C, 25.49; H, 1.70.

(282), orange solid. \textsuperscript{31}P NMR (121.4 MHz): \textgreek{d} -91.8. \textsuperscript{1}H NMR (300 MHz): \textgreek{d} 8.90-8.50 (m, 2H), 7.10-6.70 (m, 3H), 4.42 (m, 2H), 4.23 (s, 5H), 3.80 (m, 1H), 2.62 (m, 2H), 2.10 (m, 2H), 1.62 (m, 2H), 0.88 (m, 3H), -16.87 (d, 1H, J=9.6). Mass spectrum (FAB): m/e 1172 (P+, base peak), 1144, 1116, 1088, 1060, 1032, 1010, 1004, 982, 976, 948, 926, 898, 870, 842, 814. Anal. calcd. for C\textsubscript{19}H\textsubscript{23}Fe\textsubscript{9}O\textsubscript{9}Os\textsubscript{3}P: C, 29.70; H, 1.98. Found: C, 30.02; H, 2.07.

(283), orange solid. \textsuperscript{31}P NMR (121.4 MHz): \textgreek{d} -95.7. \textsuperscript{1}H NMR (300 MHz): \textgreek{d} 8.90-8.50 (m, 2H), 7.10-6.70 (m, 3H), 4.25 (m, 1H), 4.17 (m, 1H), 4.13 (s, 5H), 4.11 (m, 1H), 2.65 (m, 2H), 1.87 (m, 2H), 1.30 (m, 2H), 0.92 (m, 3H), -16.66 (d, 1H, J=8.1). Mass spectrum (FAB): m/e 1172 (P+, base peak), 1144, 1116, 1088, 1060, 1032, 1010, 1004, 982, 976, 948, 926, 898, 870, 842, 814. Anal. calcd. for C\textsubscript{19}H\textsubscript{23}Fe\textsubscript{9}O\textsubscript{9}Os\textsubscript{3}P: C, 29.70; H, 1.98. Found: C, 29.96; H, 2.14.

(284), orange solid. \textsuperscript{31}P NMR (121.4 MHz): \textgreek{d} 59.4. \textsuperscript{1}H NMR (300 MHz): \textgreek{d} 4.81 (m, 2H), 4.63 (m, 2H), 4.14 (m, 2H), 3.76 (m, 2H), 2.88 (m, 2H), 1.94 (m, 2H), 1.64 (m, 2H), 1.13 (t, 3H). Mass spectrum (FAB): m/e 1094 (P\textsuperscript{+}), 1066, 1038 (base peak), 1010, 982, 954, 926, 870, 842, 814, 786, 758. Anal. calcd. for C\textsubscript{23}H\textsubscript{17}Fe\textsubscript{9}O\textsubscript{9}Os\textsubscript{3}P: C, 25.23; H, 1.57. Found: C, 25.51; H, 1.72.

(285), orange solid. \textsuperscript{31}P NMR (121.4 MHz): \textgreek{d} 56.7. \textsuperscript{1}H NMR (300 MHz): \textgreek{d} 4.23 (complex m, 3H), 4.11 (s, 5H), 2.60 (bm, 1H), 2.13 (bm, 1H), 1.95 (bm, 1H), 1.77 (bm, 1H), 1.58 (bm, 2H), 1.03 (bt, 3H). Mass spectrum (FAB): m/e 1122 (P\textsuperscript{+}, base peak), 1094, 1066, 1038, 1010, 982, 954, 926, 898, 870, 842, 814, 786. Anal. calcd. for C\textsubscript{24}H\textsubscript{17}Fe\textsubscript{10}O\textsubscript{10}Os\textsubscript{3}P: C, 25.67; H, 1.53. Found: C, 25.84; H, 1.67.
(286), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -20.1. $^1$H NMR (300 MHz): $\delta$ 7.60-7.40 (m, 2H), 7.30-7.15 (m, 3H), 4.54 (m, 1H), 4.42 (m, 2H), 4.28 (m, 1H), 4.10 (s, 5H), 2.87 (bm, 2H), 2.04 (bm, 2H), 1.52 (m, 2H), 1.12 (t, 3H). Mass spectrum (FAB): m/e 1228 ($P^+$), 1200, 1172 (base peak), 1144, 1116, 1094, 1088, 1060, 1032, 1010, 1004, 976, 948, 920, 892, 864, 842. Anal. calcd. for $C_{31}H_{23}FeO_{11}Os_{3}P$: C, 30.30; H, 1.89. Found: C, 30.58; H, 1.97.

(287), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -10.1. $^1$H NMR (300 MHz): $\delta$ 7.50-7.30 (m, 2H), 6.79-6.64 (m, 2H), 4.23 (m, 1H), 4.16 (m, 1H), 4.11 (m, 1H), 4.06 (s, 5H), 3.97 (m, 1H), 2.53 (bm, 2H), 1.96 (m, 2H), 1.64 (m, 2H), 1.18 (t, 3H), -17.89 (d, 1H, $J$=15.6). Mass spectrum (FAB): m/e 1172 ($P^+$), 1144, 1116, 1088 (base peak), 1060, 1032, 1010, 1004, 982, 976, 948, 926, 898, 870, 842, 814. Anal. calcd. for $C_{29}H_{23}FeO_9Os_{3}P$: C, 29.70; H, 1.98. Found: C, 29.91; H, 2.12.

(288), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -10.6. $^1$H NMR (300 MHz): $\delta$ 7.03 (m, 2H), 6.75 (m, 1H), 6.58 (m, 1H), 4.32 (m, 1H), 4.27 (m, 1H), 4.14 (s, 5H), 4.09 (m, 1H), 3.02 (m, 1H), 2.60 (m, 2H), 2.08 (m, 2H), 1.62 (m, 2H), 1.06 (t, 3H), -17.80 (d, 1H, $J$=15.9). Mass spectrum (FAB): m/e 1172 ($P^+$), 1144, 1116, 1088 (base peak), 1060, 1032, 1010, 1004, 982, 976, 948, 926, 898, 870, 842, 814. Anal. calcd. for $C_{29}H_{23}FeO_9Os_{3}P$: C, 29.70; H, 1.98. Found: C, 29.81; H, 2.05.

(289), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -16.1. $^1$H NMR (300 MHz): $\delta$ 7.7-7.3 (bm, 5H), 5.31 (m, 1H), 5.15 (m, 1H), 4.82 (m, 1H), 4.63 (m, 1H), 4.42 (m, 1H), 3.98 (m, 1H), 3.51 (m, 1H), 2.55(m, 2H), 2.20 (m, 2H), 1.62 (m, 2H), 0.93 (m, 3H), -12.14 (d, 1H, $J$=4.8), -16.99 (d, 1H, $J$=12.9). Mass spectrum (FAB): m/e 1144 ($P^+$, base peak), 1116, 1088, 1060, 1032, 1010, 1004, 982, 976, 948, 926, 898, 870, 842, 814.
(290), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -17.7. $^1$H NMR (300 MHz): $\delta$ 7.7-7.3 (bm, 5H), 5.45 (m, 1H), 5.21 (m, 1H), 4.77 (m, 1H), 4.72 (m, 1H), 4.26 (m, 1H), 4.18 (m, 1H), 3.90 (m, 1H), 2.64 (m, 2H), 2.23 (m, 2H), 1.58 (m, 2H), 0.76 (m, 3H), -12.30 (d, 1H, J=4.5), -17.06 (d, 1H, J=12.0). Mass spectrum (FAB): m/e 1144 (P+, base peak), 1116, 1088, 1060, 1032, 1010, 1004, 982, 976, 942, 926, 898, 870, 842, 814. Anal. calcd. for C$_{28}$H$_{23}$FeO$_8$Os$_3$P: C, 29.37; H, 2.02. Found: C, 29.80; H, 2.21.

(291), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 151.3. $^1$H NMR (300 MHz): $\delta$ 7.89 (m, 2H), 7.35 (m, 2H), 4.46 (m, 2H), 4.41 (m, 2H), 4.33 (m, 2H), 4.29 (s, 10H), 3.96 (m, 2H), 2.92 (m, 2H), 2.63 (m, 2H), 2.42 (m, 2H), 1.95 (m, 2H), 1.43 (bm, 4H), 0.95 (t, 6H). Mass spectrum (FAB): m/e 1388 (P+), 1360, 1332 (base peak), 1304, 1276, 1248, 1220, 1192, 1136, 1080. Anal. calcd. for C$_{41}$H$_{40}$Fe$_2$O$_7$Os$_3$P$_2$: C, 35.45; H, 2.90. Found: C, 35.80; H, 3.12.

(292), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 164.6, 133.5, J=148.8. $^1$H NMR (300 MHz): $\delta$ 7.6-7.4 (m, 2H), 6.7-6.6 (m, 2H), 4.50 (m, 1H), 4.42 (m, 2H), 4.31 (s, 5H), 4.27 (m, 2H), 4.08 (s, 5H), 3.96 (m, 1H), 3.88 (m, 2H), 2.92 (m, 2H), 2.68 (m, 2H), 2.43 (m, 2H), 2.38 (m, 2H), 1.35 (m, 4H), 1.0-0.8 (m, 6H). Mass spectrum (FAB): m/e 1388 (P+), 1360, 1332 (base peak), 1304, 1276, 1248, 1220, 1192, 1136, 1080.

(293), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -25.8, -58.2. $^1$H NMR (300 MHz): $\delta$ 7.7-7.3 (bm, 10H), 4.50 (m, 2H), 4.42 (m, 3H), 4.36 (s, 5H), 4.30 (m, 1H), 4.21 (s, 5H), 4.04 (m, 2H), 2.43 (m, 2H), 2.00 (m, 2H), 1.92 (m, 2H), 1.50 (m, 4H), 1.02 (m, 3H), 0.90 (m, 3H), -14.72 (dd, 1H, J$_1$=10.6, J$_2$=8.0), -19.62 (t, 1H, J$_1$=J$_2$=10.7). Anal. calcd. for C$_{48}$H$_{46}$Fe$_2$O$_8$Os$_3$P$_2$: C, 38.56; H, 3.10. Found: C, 38.98; H, 3.36.

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The last band, orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 115.1, 112.7, 111.5. TLC: 3 spots.

A major component (~15%) of the initial reaction mixture had a $^{31}$P NMR resonance at 34.0 ppm, but it was not found in any band. Likewise, a few minor complexes initially showing $^{31}$P NMR resonances at 211.2, 147.8, 122.7, 121.6, 24.8, -5.6, and -55.0 ppm were not found.

3.5.11 Pyrolysis of Os$_3$(CO)$_{12}$ with PtBu$_2$Fc

A solution of Os$_3$(CO)$_{12}$ (200 mg, 0.22 mmol) and PtBu$_2$Fc (80 mg, 0.24 mmol) in toluene (50 mL) was refluxed for 6 h. The initial bright orange colour turned to dark red. TLC showed the formation of three major products. $^{31}$P NMR spectroscopy revealed major resonances at 58.6, 52.5, and 37.1 ppm. Two major hydride resonances at $-17.53$ (d, $J=30.3$) and $-18.49$ ppm (d, $J=9.0$), and two minor ones at $-12.87$ (d, $J=7.2$) and $-14.54$ ppm (d, $J=4.8$) were observed. The solvent was removed in vacuo and the residue was chromatographed on silica by using 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first greenish yellow band contained unreacted Os$_3$(CO)$_{12}$ (3%). The second band contained complex (295) (20%). The third band (3%) contained a mixture. The fourth band contained complex (296) (4%). The fifth band contained complex (297) (3%). The sixth band contained complex (298) (3%). The seventh band (1%) contained a mixture. The eighth band contained complex (299) (8%). A major product (~35%)
with $^{31}$P NMR resonance at 58.6 ppm was not found and presumably adsorbed on column. Crystals of (295), (298), and (299), obtained from 2/1 hexane/CH$_2$Cl$_2$ solutions, await structure determinations.

(295), purple solid. $^{31}$P NMR (121.4 MHz): $\delta$ 37.1. $^1$H NMR (300 MHz): $\delta$ 5.25 (m, 1H), 5.18 (m, 1H), 4.92 (m, 2H), 4.53 (m, 2H), 3.95 (m, 1H), 3.78 (m, 1H), 2.30 (d, 2H, $J$=14.3), 1.74 (d, 3H, $J$=13.3), 1.69 (d, 3H, $J$=9.1), 1.40 (d, 9H, $J$=13.2), -17.53 (d, 1H, $J$=30.3), -18.48 (d, 1H, $J$=9.3). Anal. calcd. for C$_{27}$H$_{27}$FeO$_9$Os$_3$P: C, 28.13; H, 2.36. Found: C, 28.42; H, 2.56. Mass spectrum (FAB): m/e 1154 (P$^+$), 1098 (base peak), 1070, 1042, 1014, 985, 957, 929, 901, 873, 844, 816, 788.

The third band, yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 50.2, 47.2, 40.3 (very small). $^1$H NMR (300 MHz): $\delta$ 4.70 (m), 4.65-4.50 (m), 4.31 (s), 4.26 (s), 1.93 (d, $J$=19.6), 1.43 (d, $J$=14.2), 1.40 (d, $J$=14.7), 1.35 (d, $J$=14.4), -12.83 (d, $J$=5.1). TLC: 3 spots.

(296), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 310.5. $^1$H NMR (300 MHz): $\delta$ 5.40 (m, 1H), 5.22 (m, 1H), 4.94 (s, 5H), 3.41 (m, 1H), 1.45 (d, 9H, $J$=14.1), -12.82 (d, 1H, $J$=6.8), -19.10 (d, 1H, $J$=9.0). Mass spectrum (FAB): m/e 1068 (P$^+$, base peak), 1040, 1012, 984, 956, 927, 900, 871, 843, 815, 787, 758.

(297), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 62.8. $^1$H NMR (300 MHz): $\delta$ 5.32 (m, 1H), 4.95 (m, 1H), 4.66 (m, 1H), 4.51 (m, 1H), 4.48 (m, 1H), 4.18 (m, 2H), 3.93 (m, 1H), 1.58 (d, 18H, $J$=12.9), -12.87 (d, 1H, $J$=7.2). Anal. calcd. for C$_{27}$H$_{27}$FeO$_9$Os$_3$P: C, 28.13; H, 2.36. Found: C, 28.37; H, 2.49.

(298), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 67.6. $^1$H NMR (300 MHz): $\delta$ 5.03 (m, 1H), 4.43 (s, 5H), 4.40 (m, 1H), 4.29 (m, 1H), 1.78 (d, 18H, $J$=13.6), -14.53 (d, 1H, $J$=4.8).

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The seventh band, orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 66.8, 54.5 (medium), 52.6, 16.0 (major). TLC: 3 spots.

(299), green solid. $^{31}$P NMR (121.4 MHz): $\delta$ 52.3. $^1$H NMR (300 MHz): $\delta$ 4.43 (m, 1H), 4.37 (m, 1H), 4.31 (s, 5H), 4.27 (m, 1H), 0.98 (d, 9H, J=14.9).
Anal. calcd. for C$_{24}$H$_{17}$FeO$_{10}$Os$_3$P: C, 25.67; H, 1.53. Found: C, 26.12; H, 1.62.

3.5.12 Pyrolysis of Os$_3$(CO)$_{12}$ with Fe(C$_5$H$_4$)$_2$PPh

A solution of Os$_3$(CO)$_{12}$ (190 mg, 0.21 mmol) and Fe(C$_5$H$_4$)$_2$PPh (65 mg, 0.22 mmol) in octane (100 mL) was refluxed for 7 h. The solvent was removed in vacuo and the residue was chromatographed on a silica column by using 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first greenish yellow band contained unreacted Os$_3$(CO)$_{12}$ (10%). The small second (2%) and fourth (3%) orange bands were not characterized. The third band proved to be complex (300) (70%). Crystals of (300) suitable for X-ray structure determination were obtained from a 2/1 pentane/CH$_2$Cl$_2$ solution.

(300), red orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 59.9. $^1$H NMR (300 MHz): $\delta$ 7.55-7.15 (bm, 5H), 4.77 (m, 2H), 4.70 (m, 2H), 4.62 (m, 2H), 3.00 (m, 2H). Mass spectrum (FAB): m/e 1114 (P+, base peak), 1086, 1058, 1030, 1002, 974, 946, 918, 890, 862. Anal. calcd. for C$_{25.5}$H$_{14}$ClFeO$_9$Os$_3$P, (300)-0.5CH$_2$Cl$_2$: C, 26.47; H, 1.22. Found: C, 26.53; H, 1.30.

3.5.13 Pyrolysis of Os$_3$(CO)$_{12}$ with PEtFc$_2$

A solution of Os$_3$(CO)$_{12}$ (110 mg, 0.12 mmol) and PEtFc$_2$ (52 mg, 0.12 mmol) in octane (70 mL) was refluxed for 19 h. The colour of the solution changed from bright orange to dark brown and TLC revealed the formation of more than fifteen products. $^{31}$P NMR spectroscopy revealed major resonances at 335.8, 213.5, 151.0, 148.4, 56.4, 31.0, -21.8, -23.2, -24.8, -
26.5, -27.4, -32.9, -34.5, and -80.5 ppm. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH₂Cl₂ as eluent. The first greenish yellow band contained unreacted Os₃(CO)₁₂ (2%). The second band (2%) contained an unidentified mixture of a yellow and a green complex by TLC. The third band (2%) contained an unidentified yellow complex. The fourth band (6%) contained complexes (301) and (302). The fifth band (2%) contained a mixture. The sixth, seventh, and eighth bands contained complexes (303) (12%), (304) (4%), and (305) (3%), respectively. The ninth band (7%) contained complexes (306) and (307). The tenth band (3%) contained a mixture. The eleventh, thirteenth, and fourteenth bands contained complexes (308) (20%), (309) (4%), and (310) (1%), respectively. The twelfth green band (1%) contained an unidentified compound. The fifteenth, sixteenth, and eighteenth bands all contained mixtures. The seventeenth band contained complex (311) (1%), the diastereoisomer of (308). Crystals of (308) were obtained by slow evaporation of the eluted band. Crystals of (301), (303), and (305), obtained from 2/1 hexane/CH₂Cl₂ solutions, await analysis.

(301), greenish orange solid. ³¹P NMR (121.4 MHz): δ -78.9. ¹H NMR (300 MHz): δ 5.14 (m, 1H), 4.88 (m, 2H), 4.69 (m, 1H), 4.41 (s, 5H), 4.27 (m, 1H), 4.15 (s, 5H), 3.84 (m, 1H), 3.65 (m, 1H), 3.03 (m, 1H, Et), 2.82 (m, 1H, Et), 1.81 (m, 3H), -17.80 (d, 1H, J=12.3). Mass spectrum (FAB): m/e 1252 (P⁺, base peak), 1224, 1195, 1167, 1140, 1113, 1084, 1056, 1027, 1000, 983. Anal. calcd. for C₃₁H₂₃Fe₂O₉Os₃P: C, 29.72; H, 1.85. Found: C, 29.33; H, 1.67.

(302), greenish orange solid. ³¹P NMR (121.4 MHz): δ -85.7. ¹H NMR (300 MHz): δ 5.17 (m, 1H), 4.92 (m, 1H), 4.78 (m, 1H), 4.72 (m, 1H), 4.46 (s, 5H), 4.22 (m, 1H), 4.10 (s, 5H), 3.98 (m, 1H), 3.74 (m, 1H), 2.96 (m, 1H, Et),
2.77 (m, 1H, Et), 1.74 (m, 3H), -18.20 (d, 1H, J=11.4). Anal. calcd. for C$_{31}$H$_{23}$Fe$_2$O$_9$Os$_3$P: C, 29.72; H, 1.85. Found: C, 29.49; H, 1.70.

The fifth band, yellow solid. $^{31}$P NMR (121.4 MHz): δ 52.2, 1.6. TLC: 3 spots.

(303), orange solid. $^{31}$P NMR (121.4 MHz): δ 148.5. $^1$H NMR (300 MHz): δ 5.79 (m, 1H), 5.08 (m, 1H), 4.68 (s, 5H), 4.55 (m, 2H), 4.46 (m, 1H), 4.37 (m, 1H), 4.35 (s, 5H), 3.82 (m, 1H), 3.29 (m, 1H, Et), 3.11 (m, 1H, Et), 1.73 (m, 3H), -18.65 (bs, 1H). Mass spectrum (FAB): m/e 1226 (P+, base peak), 1198, 1170, 1141, 1113, 1085, 1057, 1029, 999. Anal. calcd. for C$_{30}$H$_{23}$Fe$_2$O$_8$Os$_3$P: C, 29.42; H, 1.89. Found: C, 29.56; H, 2.03.

(304), orange solid. $^{31}$P NMR (121.4 MHz): δ 151.0. $^1$H NMR (300 MHz): δ 5.65 (m, 1H), 5.27 (m, 1H), 4.77 (m, 2H), 4.64 (m, 1H), 4.32 (m, 1H), 4.23 (s, 5H), 4.08 (s, 5H), 3.94 (m, 1H), 2.90 (m, 1H, Et), 2.78 (m, 1H, Et), 1.72 (m, 3H), -18.59 (bs, 1H). Mass spectrum (FAB): m/e 1226 (P+, base peak), 1197, 1170, 1142, 1113, 1085, 1057, 1029, 1000.

(305), orange solid. $^{31}$P NMR (121.4 MHz): δ 32.6. $^1$H NMR (300 MHz): δ 4.36 (m, 1H), 4.31 (m, 1H), 4.25 (m, 2H), 4.05 (s, 5H), 2.64 (m, 2H, Et), 1.27 (m, 3H), -16.50 to -17.30 (very broad, 1H), -17.50 to -18.80 (very broad, 1H). Mass spectrum (FAB): m/e 1068 (P+, base peak), 1040, 1013, 985, 957, 928, 899, 871, 844, 814. Anal. calcd. for C$_{21}$H$_{13}$FeO$_9$Os$_3$P: C, 23.64; H, 1.23. Found: C, 23.97; H, 1.31.

(306), yellow solid. $^{31}$P NMR (121.4 MHz): δ -31.3. $^1$H NMR (300 MHz): δ 5.17 (m, 1H), 4.69 (m, 1H), 4.52 (m, 1H), 4.41 (m, 1H), 4.25 (m, 1H), 4.11 (m, 2H), 4.07 (m, 1H), 4.01 (m, 1H), 3.92 (m, 1H), 3.83 (s, 5H), 3.64 (m, 1H), 1.72 (m, 1H), 1.65 (m, 1H), 1.28 (m, 3H), -17.15 (dd, 1H, J$_1$=27.3, J$_2$=2.1), -18.96 (dd, 1H, J$_1$=13.1, J$_2$=2.1). Mass spectrum (FAB): m/e 1282 (P+), 1254,
(307), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -32.9. $^1$H NMR (300 MHz): $\delta$ 5.20 (m, 1H), 4.84 (m, 1H), 4.80 (m, 1H), 4.58 (m, 2H), 4.43 (m, 1H), 4.37 (m, 1H), 4.21 (s, 5H), 4.14 (m, 1H), 4.05 (m, 1H), 3.87 (m, 1H), 3.66 (m, 1H), 1.73 (m, 1H), 1.68 (m, 1H), 1.25 (m, 3H), -17.10 (dd, 1H, $J_1=27.6$, $J_2=2.0$), -18.39 (dd, 1H, $J_1=11.2$, $J_2=2.0$). Anal. calcd. for $C_{32}H_{23}Fe_2O_{10}Os_3P$: C, 30.01; H, 1.82. Found: C, 29.74; H, 1.83.

The tenth band, dark orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 274.9, 163.4, -21.6. TLC: 4 spots with one being Os$_3$(CO)$_{11}$(PETFc$_2$).

(308), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -27.4. $^1$H NMR (300 MHz): $\delta$ 4.99 (m, 2H), 4.62 (m, 1H), 4.54 (m, 1H), 4.41 (m, 2H), 4.32 (m, 1H), 4.28 (m, 1H), 4.24 (s, 5H), 4.01 (m, 1H), 3.26 (m, 1H), 3.00 (m, 1H), 2.68 (m, 2H, Et), 1.22 (td, 3H, $J_{P-H}=15.2$, $J_{H-H}=7.8$), -12.13 (d, 1H, $J=4.3$), -17.04 (d, 1H, $J=12.3$). Mass spectrum (FAB): m/e 1224 (P+, base peak), 1196, 1168, 1140, 1112, 1085, 1057, 1029, 1000. Anal. calcd. for $C_{30}H_{23}Fe_2O_8Os_3P$: C, 29.42; H, 1.89. Found: C, 29.48; H, 1.95.

(309), red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 58.0. $^1$H NMR (300 MHz): $\delta$ 4.74 (m, 2H), 4.61 (m, 2H), 4.55 (m, 2H), 3.13 (m, 2H), 2.74 (m, 2H, Et), 1.30 (m, 3H). Mass spectrum (FAB): m/e 1067 (P+, base peak), 1040, 1012, 983, 955, 927, 899, 871, 843, 815.

(310), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 116.6, -38.0, $J=99.3$. $^1$H NMR (300 MHz): $\delta$ 5.22 (m, 1H), 5.03 (m, 1H), 4.64 (m, 2H), 4.57 (m, 2H), 4.46 (m, 3H), 4.38 (s, 5H), 4.32 (m, 1H), 4.23 (m, 2H), 4.18 (s, 5H), 4.01 (m, 1H), 3.87 (m, 1H), 3.42 (m, 1H), 2.85 (m, 1H, Et), 2.76 (m, 1H, Et), 2.72-2.65 (m, 2H, Et), 1.34 (m, 3H), 1.21 (m, 3H), -20.68 (dd, 1H, $J_1=11.4$, $J_2=9.0$).
The fifteenth band, greenish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 172.1, 61.4, 18.0, -19.4. TLC: 4 spots.

The sixteenth band, red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 212.7, 211.8. TLC: 2 spots.

(311), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ -26.5. $^1$H NMR (300 MHz): $\delta$ 4.92 (m, 1H), 4.85 (m, 1H), 4.54 (m, 1H), 4.42 (m, 2H), 4.36 (m, 1H), 4.29 (s, 5H), 4.24 (m, 1H), 4.10 (m, 1H), 3.96 (m, 1H), 3.32 (m, 1H), 3.14 (m, 1H), 2.51 (m, 2H, Et), 1.30 (td, 3H, $J_{P-H}$=14.7, $J_{H-H}$=7.6), -12.17 (d, 1H, $J$=3.9), -17.45 (d, 1H, $J$=11.7).

The eighteenth band, brownish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 226.6, 221.3, 216.2, 215.2. $^1$H NMR (hydrides only) (300 MHz): $\delta$ -17.88 (d, $J$=19.2), -17.90 (d, $J$=19.2). TLC: 4 spots.

Those complexes showing $^{31}$P NMR resonances at 335.8 and -80.5 ppm were not found.

3.5.14 Pyrolysis of Os$_3$(CO)$_{11}$(PETFc$_2$)

A solution of Os$_3$(CO)$_{11}$(PETFc$_2$) (100 mg, 0.076 mmol) in octane (50 mL) was refluxed for 11 h. $^{31}$P NMR spectroscopy revealed major resonances at 150.8, 148.2, -21.8, -26.5, -27.4, -92.8, and -111.0 ppm. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first orange band contained (303) (20%). The second orange band contained (304) (6%). The third band proved to be the starting material (10%). The fourth orange band contained (308) (30%). The fifth reddish orange band (5%) contained an unidentified mixture. The sixth orange band contained (311) (2%). All the previously characterized complexes were identified by TLC, $^{31}$P, and $^1$H NMR spectroscopy.
3.5.15 Pyrolysis of Os$_3$(CO)$_{12}$ with AsFc$_2$Ph

A solution of Os$_3$(CO)$_{12}$ (272 mg, 0.30 mmol) and AsFc$_2$Ph (150 mg, 0.29 mmol) in octane (20 mL) was refluxed for 3.5 h. TLC revealed the formation of more than ten products, while $^1$H NMR spectroscopy revealed the presence of one major and many minor hydride resonances. The solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first yellow band (5%) was identified as a mixture of unreacted Os$_3$(CO)$_{12}$ and ferrocene. The sixth yellow and fourteenth pink bands contained traces of unidentified mixtures. The other bands in the order of elution contained complexes (312) (4%), (313) (4%), (314) (2%), (315) (20%), (316) (5%), (317) (8%), (318) (10%), (319) (6%), (320) (2%), and (321) (12%), respectively. Crystals of (312), (313), (317), and (318), obtained from 3/1 hexane/CH$_2$Cl$_2$ solutions, await analysis. Crystals of (315) suitable for X-ray structure determination were obtained from a 2/1 petroleum ether/CH$_2$Cl$_2$ solution.

(312), green solid. $^1$H NMR (300 MHz): $\delta$ 7.53-7.47 (m, 2H), 7.43-7.33 (m, 3H), 5.06 (d, 2H, J=2.4), 4.14 (s, 5H), 4.05 (t, 1H, J=2.4). Mass spectrum (FAB): m/e 1158 (P$,^+$, base peak), 1130, 1101, 1073, 1045, 1016, 990, 961, 935, 905. Anal. calcd. for C$_{25}$H$_{13}$AsFeOs$_9$O$_3$: C, 25.91; H, 1.13. Found: C, 26.34; H, 1.28.

(313), orange solid. $^1$H NMR (300 MHz): $\delta$ 7.63 (m, 2H), 7.10 (m, 2H), 4.53-4.48 (m, 4H), 4.23 (s, 5H). Mass spectrum (FAB): m/e 1158 (P$,^+$, base peak), 1131, 1101, 1074, 1045, 1016, 991, 960, 934, 906. Anal. calcd. for C$_{25}$H$_{13}$AsFeOs$_9$O$_3$: C, 25.91; H, 1.13. Found: C, 26.07; H, 1.16.

(314), greenish orange solid. $^1$H NMR (300 MHz): $\delta$ 4.47 (m, 4H), 4.32 (m, 4H). Anal. found: C, 20.68; H, 0.95.
(315), orange solid. $^1$H NMR (300 MHz): $\delta$ 9.2-8.5 (broad, 2H), 6.9-6.4 (broad, 2H), 4.4-3.7 (broad overlapping multiplets with two C$_5$H$_5$ singlets superimposed, 18H), -16.42 (s, 1H). Mass spectrum (FAB): m/e 1344 (P+, base peak), 1316, 1288, 1260, 1232, 1204, 1176, 1148, 1120, 1092. Anal. calcd. for C$_{35}$H$_{23}$AsFe$_2$O$_9$Os$_3$: C, 31.26; H, 1.72. Found: C, 31.35; H, 1.76.

(316), yellow solid. $^1$H NMR (300 MHz): $\delta$ 7.52 (m, 2H), 7.31 (m, 3H), 4.46 (bm, 4H), 4.23 (bm, 2H), 4.17 (s, 10H), 4.03 (bm, 2H). Mass spectrum (FAB): m/e 1402 (P+), 1374, 1346 (base peak), 1319, 1290, 1262, 1233, 1205, 1177, 1149, 1122, 1092. Anal. calcd. for C$_{37}$H$_{23}$AsFe$_2$O$_{11}$Os$_3$: C, 31.72; H, 1.65. Found: C, 31.47; H, 1.58.

(317), orange solid. $^1$H NMR (300 MHz): $\delta$ 6.94 (q, 2H), 6.69 (q, 2H), 4.64 (m, 2H), 4.45 (m, 2H), 4.21 (s, 5H), 4.11 (s, 5H), 4.08 (m, 2H), 3.57 (m, 2H), -15.31 (s, 1H). Mass spectrum (FAB): m/e 1072 (P+, base peak), 1044, 1016, 987, 959, 931, 903. Anal. calcd. for C$_{32}$H$_{23}$AsFe$_2$O$_6$Os$_2$: C, 35.90; H, 2.17. Found: C, 35.76; H, 2.08.

(318), orange solid. $^1$H NMR (300 MHz): $\delta$ 7.78 (m, 1H), 7.66 (m, 1H), 7.61 (m, 1H), 7.45 (m, 2H), 5.17 (m, 1H), 5.08 (m, 1H), 4.77 (m, 1H), 4.75 (m, 1H), 4.63 (m, 1H), 4.61 (m, 1H), 4.52 (m, 1H), 4.42 (m, 2H), 4.31 (m, 1H), 4.02 (s, 5H), 3.59 (m, 1H), 3.28 (m, 1H), -12.24 (s, 1H), -16.79 (s, 1H). Mass spectrum (FAB): m/e 1318 (P+, base peak), 1290, 1262, 1234, 1205, 1177, 1149, 1121, 1093. Anal. calcd. for C$_{34}$H$_{23}$AsFe$_2$O$_8$Os$_3$: C, 31.01; H, 1.76. Found: C, 30.68; H, 1.88.

(319), pink solid. $^1$H NMR (300 MHz): $\delta$ 6.36 (m, 1H), 5.77 (m, 1H), 5.60 (m, 1H), 5.20 (m, 1H), 4.57 (m, 1H), 4.53 (m, 1H), 4.35 (s, 5H), 4.14 (m, 1H), 3.61 (m, 1H). Anal. found: C, 24.17; H, 1.26.

(320), orange solid. $^1$H NMR (300 MHz): $\delta$ 7.38 (m, 2H), 7.22-7.11 (m, 3H), 6.72 (m, 1H), 6.39 (m, 2H), 6.26 (m, 1H), 4.88 (m, 1H), 4.79 (m, 1H),
4.53-4.46 (m, 3H), 4.45-4.39 (m, 2H), 4.35-4.29 (m, 2H+2H), 4.27 (s, 5H), 4.23 (s, 5H), 4.16 (s, 10H), 4.06 (m, 2H), 3.88 (m, 1H), 3.75 (m, 1H), 3.52 (m, 1H), -14.23 (s, 1H). Mass spectrum (FAB): m/e 1838 (P+, base peak), 1810, 1782, 1754, 1726, 1697, 1669, 1641.

(321), orange solid. $^1H$ NMR (300 MHz): δ 7.82 (m, 1H), 7.48-7.28 (m, 3H), 4.88 (m, 1H), 4.82 (m, 1H), 4.47 (m, 1H), 4.43 (m, 1H), 4.32 (m, 2H), 4.23 (m, 1H), 4.18 (s, 5H), 4.08 (m, 1H), 4.04 (m, 1H), 3.96 (m, 1H), 3.94 (m, 1H), 3.91 (m, 1H), 3.87 (s, 5H), 3.82 (m, 1H), 3.79 (m, 1H), 3.73 (m, 1H), 3.60 (m, 1H). Mass spectrum (FAB): m/e 1546 (P+, base peak), 1490, 1462, 1434, 1406, 1377.

3.5.16 Pyrolysis of Os$_3$(CO)$_{10}$[Fc'(PPr$_2$)$_2$]

A solution of Os$_3$(CO)$_{10}$[Fc'(PPr$_2$)$_2$] (150 mg, 0.12 mmol) in octane (80 mL) was refluxed for 7.5 h. The solvent was removed in vacuo, and the $^{31}$P and $^1$H NMR spectra, and $^{31}$P-$^{31}$P COSY spectrum of the reaction mixture were recorded. The solid residue was chromatographed on silica by using 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first to eleventh bands contained complexes (322) (20%), (323) (10%), (324) (10%), (325) (6%), (326) (10%), (327) (1%), (328) (1%), (329) (8%), (330) (15%), (331) (3%), and (332) (1%), respectively, in the order of elution. Crystals of (323), (325), (326), (329), and (330) for X-ray structure analyses were obtained by slow evaporation of the collected bands. Crystals of (322), obtained by slow evaporation of its solution in 1/1 hexane/CH$_2$Cl$_2$, await analysis.

(322), yellow solid. $^{31}$P NMR (121.4 MHz): δ 76.3, 40.4, J=2.8. $^1$H NMR (300 MHz): δ 4.72 (m, 1H), 4.43 (m, 2H), 4.34 (m, 2H), 4.06 (m, 1H), 3.84 (m, 1H), 2.75 (bm, 2H), 2.20 (bm, 1H), 1.88 (d, 3H, J=20.8), 1.76 (d, 3H, J=21.0), 1.66 (dd, 3H), 1.49 (dd, 3H), 1.35 (dd, 3H), 1.22 (dd, 3H), -17.66
(ddd, 1H, J1=17.7, J2=11.4, J3=1.2), -19.16 (ddd, 1H, J1=27.6, J2=5.4, J3=1.2).
Mass spectrum (FAB): m/e 1170 (P+, base peak), 1142, 1114, 1086, 1058, 1030, 974, 874, 856, 842, 832, 818. Anal. calcd. for C27H30FeO8Os3P2: C, 27.70; H, 2.58. Found: C, 28.03; H, 2.71.

(323), yellow solid. 31P NMR (121.4 MHz): δ 18.0, 16.2, J=19.3. 1H NMR (200 MHz): δ 4.41 (m, 1H), 4.28 (m, 3H), 4.21 (m, 1H), 4.13 (m, 2H), 4.00 (m, 1H), 2.87 (m, 1H), 2.64 (m, 1H), 2.49 (m, 1H), 1.65 (dd, 3H, J1=17.6, J2=7.1), 1.32 (dd, 3H, J1=16.7, J2=6.2 ), 1.30 (dd, 3H, J1=15.7, J2=7.6), 1.25 (dd, 3H, J1=16.2, J2=7.1), 0.97 (dd, 3H, J1=17.1, J2=7.1), 0.74 (dd, 3H, J1=11.9, J2=6.7), -17.98 (dd, 1H, J1=18.0, J2=8.4). Mass spectrum (FAB): m/e 1198 (P+, base peak), 1170, 1142, 1126, 1114, 1099, 1086, 1070, 1058, 1042, 1030, 1002, 974, 960, 946, 930, 903, 887, 860, 818. Anal. calcd. for C28H30FeO9Os3P2: C, 28.05; H, 2.52. Found: C, 28.27; H, 2.66.

(324), yellow solid. 31P NMR (121.4 MHz): δ 28.2, 6.0, J=12.7. 1H NMR (200 MHz): δ 4.46 (m, 2H), 4.28 (m, 3H), 4.17 (m, 1H), 3.98 (m, 1H), 2.50 (m, 1H), 2.34 (m, 1H), 2.20 (m, 1H), 1.57(dd, 3H), 1.47 (dd, 3H), 1.39 (dd, 3H), 1.35 (dd, 3H), 1.18 (dd, 3H), 1.11 (dd, 3H), -17.84 (dd, 1H, J1=J2=11.3), -18.92 (dd, 1H, J1=22.2, J2=6.1). Mass spectrum (FAB): m/e 1170 (P+, base peak), 1142, 1128, 1114, 1086, 1072, 1058, 1044, 1030, 1016, 1002, 988, 960, 932, 918, 890, 876, 844, 832, 818. Anal. calcd. for C27H30FeO9Os3P2: C, 27.70; H, 2.58. Found: C, 27.81; H, 2.82.

(325), orange solid. 31P NMR (121.4 MHz): δ -5.3. 1H NMR (300 MHz): δ 6.26 (s, 2H), 5.50 (s, 2H), 2.90 (m, 2H), 2.35 (m, 2H), 1.40 (m, 12H), 1.26 (m, 12H), -17.36 (d, 2H, J=27.9), -19.54 (d, 2H, J=12.6). Anal. calcd. for C38H36FeO16Os6P2: C, 22.73; H, 1.81. Found: C, 22.87; H, 1.89.

(326), yellow solid. 31P NMR (121.4 MHz): δ 70.1, 22.6, J=18.7. 1H NMR (500 MHz): δ 4.68 (m, 1H), 4.52 (m, 1H), 4.40 (m, 1H), 4.35 (m, 1H),
4.30 (m, 1H), 3.97 (m, 1H), 3.74 (m, 1H), 2.71 (m, 1H), 2.59 (m, 1H), 2.50 (m, 1H), 1.59 (dd, 3H), 1.43 (dd, 3H), 1.38 (dd, 3H), 1.18 (dd, 3H), 1.05 (dd, 3H), 0.83 (dd, 3H), -15.94 (dd, 1H, J1=18.2, J2=6.3), -17.27 (dd, 1H, J1=27.0, J2=10.8). Mass spectrum (FAB): m/e 1170 (P+, base peak), 1142, 1128, 1114, 1086, 1072, 1058, 1044, 1030, 1016, 1002, 988, 974, 960, 946, 932, 918, 890, 876, 858, 844, 832, 818. Anal. calcd. for C27H30FeO8Os3P2: C, 27.70; H, 2.58. Found: C, 27.94; H, 2.65.

(327), orange solid. 31P NMR (121.4 MHz): δ 0.0. 1H NMR (200 MHz) (hydrides only): δ -16.91 (d, J=25.8), -19.05 (d, J=12.8).

(328), orange solid. 31P NMR (121.4 MHz): δ 2.7. 1H NMR (200 MHz) (hydrides only): δ -16.78 (d, J=25.0), -18.91 (d, J=11.9).

(329), orange solid. 31P NMR (81.0 MHz): δ 268.3, 16.5, J<1. 1H NMR (400 MHz): δ 5.26 (m, 1H), 5.21 (m, 1H), 4.93 (m, 1H), 4.89 (m, 1H), 3.88 (m, 1H), 3.69 (m, 1H, CHMe2), 3.56 (m, 1H), 3.28 (m, 1H), 2.92 (m, 1H), 2.61 (m, 1H, CHMe2), 2.12 (m, 1H, CHMe2), 1.89 (dd, 3H, J1=15.9, J2=6.9), 1.83 (dd, 3H, J1=16.2, J2=7.0), 1.57 (dd, 3H, J1=7.4, J2=2.5), 1.51 (dd, 3H, J1=12.9, J2=7.6), 1.49 (dd, 3H, J1=13.0, J2=7.2), 1.40 (dd, 3H, J1=18.5, J2=7.4), -21.92 (dd, 1H, J1=13.9, J2=7.6). Mass spectrum (FAB): m/e 1142 (P+, base peak), 1114, 1086, 1072, 1058, 1044, 1030, 1016, 1002, 988, 974, 960, 946, 918, 886, 872, 858, 844, 830, 816. Anal. calcd. for C26H30FeO7Os3P2: C, 27.32; H, 2.65. Found: C, 27.49; H, 2.71.

(330), pink solid. 31P NMR (121.4 MHz): δ 59.2, 19.2, J=3.8. 1H NMR (300 MHz): δ 4.62 (m, 1H), 4.43 (m, 2H), 4.37 (m, 1H), 4.28 (m, 2H), 4.16 (m, 1H), 3.97 (m, 1H), 3.08 (m, 1H), 2.58 (m, 3H), 2.33 (m, 1H), 2.23 (m, 1H), 1.56 (dd, 3H), 1.45 (dd, 3H), 1.28 (dd, 3H), 1.25 (dd, 3H), 1.15 (dd, 3H), 0.88 (dd, 3H), 0.67 (dd, 3H), -13.60 (dd, 1H, J1=7.5, J2=6.0). Mass spectrum (FAB): m/e 1240 (P+, base peak), 1212, 1184, 1156, 1128, 1100, 1082,
3.5.17 Pyrolysis of \([\text{Os}_3(\text{CO})_{11}]_2[\text{Fc'P}^{\text{iPr}}\text{Pr}_2]_2\)

A solution of \([\text{Os}_3(\text{CO})_{11}]_2[\text{Fc'P}^{\text{iPr}}\text{Pr}_2]_2\) (50 mg, 0.023 mmol) in octane (20 mL) was refluxed for 2.5 h. TLC, \(^{31}\text{P}\) NMR, and \(^1\text{H}\) NMR spectroscopy revealed the formation of many complexes including (325), (327), and (328). The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH\(_2\)Cl\(_2\) as eluent. Only the third band (15%) was identified to be complex (325). \(^{31}\text{P}\) NMR (121.4 MHz): \(\delta -5.3\). \(^1\text{H}\) NMR (300 MHz): \(\delta 6.26 (s, 2\text{H}), 5.50 (s, 2\text{H}), 2.89 (\text{bm, } 2\text{H})\),
2.34 (bm, 2H), 1.40 (bm, 12H), 1.26 (bm, 12H), -17.34 (d, 2H, J=27.9), -19.52 (d, 2H, J=12.6). Anal. calcd. for C_{38}H_{36}FeO_{16}Os_{6}P_{2}: C, 22.73; H, 1.81. Found: C, 23.05; H, 1.92.

3.5.18 Pyrolysis of Os_{3}(CO)_{12} with P(1-C_{10}H_{7})_{3}

A solution of Os_{3}(CO)_{12} (180 mg, 0.19 mmol) and P(1-C_{10}H_{7})_{3} (80 mg, 0.19 mmol) in octane (30 mL) was refluxed for 24 h. TLC revealed the presence of more than eight products. $^{31}$P NMR spectroscopy revealed three major resonances at 51.1, 42.4, and 30.9 ppm, and a number of minor ones. The reaction solvent was removed in vacuo and the residue was chromatographed on florisil with 3/1 petroleum ether/CH_{2}Cl_{2} as eluent. The first band contained unreacted Os_{3}(CO)_{12} (3%) identified by TLC and micro-analysis. The second band contained traces of an unidentified mixture. The third (2%) and last (5%) bands were characterized only by $^{1}$H and $^{31}$P NMR spectroscopy. The fourth, fifth, and sixth bands contained complexes (333) (35%), (334) (30%), and (335) (10%), respectively.

The third band, yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 79.2. $^{1}$H NMR (200 MHz): $\delta$ 8.16 (m), 8.10-7.90 (m), 7.85-7.00 (m), -20.53 (s, 1H).

(333), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 30.9. $^{1}$H NMR (200 MHz): $\delta$ 8.86 (m, 2H), 8.1-6.8 (m, 17H), -17.59 (d, 1H, J=5.6), -21.47 (d, 1H, J=30.8). Mass spectrum (FAB): m/e 1208 (P+, base peak), 1180, 1152, 1124, 1096, 1068, 1039, 1011, 983, 856, 730. Anal. calcd. for C_{38}H_{21}O_{8}Os_{3}P: C, 37.81; H, 1.75. Found: C, 37.89; H, 1.79.

(334), brown solid. $^{31}$P NMR (121.4 MHz): $\delta$ 51.1. $^{1}$H NMR (200 MHz): $\delta$ 8.3-6.8 (m), -18.53 (d, J=37.7, satellite, J_{H-Os1}=44.0, J_{H-Os2}=31.2). Mass spectrum (FAB): m/e 1236 (P+, base peak), 1208, 1181, 1151, 1124, 1095, 1067, 1039, 1011, 984, 855, 731. Anal. calcd. for C_{39}H_{21}O_{9}Os_{3}P: C, 37.92; H, 1.79.
1.71. Found: C, 37.99; H, 1.84.

(335), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 42.3. $^1$H NMR (200 MHz): $\delta$ 8.6 (m), 8.2-7.7 (m), 7.6-6.8 (m). Mass spectrum (FAB): m/e 1292 (P$^+$), 1264, 1236, 1208 (base peak), 1181, 1153, 1125, 1096, 1067, 1039, 1011, 984, 856. Anal. calcd. for C$_{41}$H$_{21}$O$_{11}$Os$_3$P: C, 38.14; H, 1.64. Found: C, 38.00; H, 1.87.

The last band, yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 41.9. $^1$H NMR (200 MHz): $\delta$ 8.63 (d, 1H), 8.02 (m, 1H), 7.90 (d, 1H), 7.44 (t, 1H), 7.30 (m, 4H). Anal. found: C, 41.37; H, 2.32.

3.5.19 Pyrolysis of Os$_3$(CO)$_{12}$ with As(1-C$_{10}$H$_7$)$_3$

A solution of Os$_3$(CO)$_{12}$ (200 mg, 0.22 mmol) and As(1-C$_{10}$H$_7$)$_3$ (90 mg, 0.20 mmol) in octane (40 mL) was refluxed for 25 h. TLC revealed the presence of at least ten products, while $^1$H NMR spectroscopy showed only two major hydride resonances at -17.69 and -21.65 ppm. The reaction solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band (5%) contained a mixture of four complexes including (336), being yellow, pink, pink, and orange in colour as revealed by TLC. Naphthalene was also present in the solution. The major second band (65%) contained complex (336). The third band (8%) contained a mixture of (336) and a pink complex. The fourth band (5%) contained a yellow complex. The fifth band (3%) contained a yellow complex. The other bands were not eluted. Crystals of (336) suitable for X-ray structure analysis were obtained from a 2/1 hexane/CH$_2$Cl$_2$ solution.

(336), yellow solid. $^1$H NMR (400 MHz): $\delta$ 8.51 (m,1H), 8.45 (m,1H), 8.20 (m,1H), 8.03 (m, 2H), 7.93-7.82 (m, 3H), 7.79 (m,1H), 7.70 (m,1H),
7.50-7.38 (m, 5H), 7.38-7.31 (m, 3H), 7.27 (m, 1H), -17.69 (s, 1H, Os satellite, J_{Os1}=27.6, J_{Os2}=43.8), -21.65 (s, 1H, Os satellite, J_{Os1}=28.0, J_{Os2}=45.6). Mass spectrum (FAB): m/e 1252 (P+, base peak), 1224, 1196, 1167, 1138, 1110, 1094, 1080, 1066, 1052, 1037, 1024, 982, 969, 954, 940, 928, 912, 898, 884, 870, 856, 843, 829, 703. Anal. calcd. for C_{38}H_{21}AsO_{8}Os_{3}: C, 36.48; H, 1.69. Found: C, 36.55; H, 1.74.

The fourth band, mass spectrum (FAB): m/e 1452 (P+), 1424, 1396, 1368, 1312, 1284, 1256, 1240, 1224, 1182, 1154, 1126, 1096 (base peak), 970, 880, 850.

The fifth band, mass spectrum (FAB): m/e 1554 (P+, base peak), 1524, 1478, 1370, 1334, 1312, 1223, 1092, 981, 908, 880, 852.

3.6 Pyrolysis of Ru3 Complexes

The pyrolyses of Ru3(CO)$_{11}$L (L=PFcPh$_2$ or PFC$_2$Ph) and Ru$_3$(CO)$_{10}$ (PFcPh$_2$)$_2$ were studied previously [315]. In the first two reactions no complexes were firmly characterized [315], and in the last reaction only one complex (344) was characterized [119].

3.6.1 Pyrolysis of Ru3(CO)$_{11}$(PFcPh$_2$) [315]

(a) in cyclohexane for 1 h

A solution of Ru$_3$(CO)$_{11}$(PFcPh$_2$) (150 mg, 0.15 mmol) in cyclohexane (50 mL) was refluxed for 1 h. $^{31}$P NMR spectroscopy revealed four major resonances at 408.1, 387.8, 149.6, 1nd 112.7 ppm. The solvent was removed
in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first yellow band contained Ru$_3$(CO)$_{12}$ (2%) identified by TLC and mass spectrometry. The second orange band contained unreacted starting material (5%) identified by TLC, $^1$H, and $^{31}$P NMR spectroscopy. The third band contained complex (337) (20%). The fourth pink band contained complex (338) (to be described in the next section) (2%) identified by TLC, $^{31}$P, and $^1$H NMR spectroscopy. The fifth band contained complex (339) (20%). The sixth band contained complex (340) (5%). One major compound (~20%) showing a $^{31}$P NMR resonance at 112.7 ppm was not found in any collected bands. Crystals of (339), obtained from a 2/1 hexane/CH$_2$Cl$_2$ solution, await analysis.

(337), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 387.8. $^1$H NMR (300 MHz): $\delta$ 7.62 (m, 2H), 7.12 (m, 2H), 4.62-4.56 (m, 4H), 4.28 (s, 5H). Mass spectrum (FAB): m/e 847 (P$^+$), 819, 791, 764, 735, 709 (base peak). Anal. calcd. for C$_{25}$H$_{13}$FeO$_9$PRu$_3$: C, 35.41; H, 1.54. Found: C, 35.73; H, 1.64.

(339), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 408.1. $^1$H NMR (300 MHz): $\delta$ 6.99 (m, 2H), 6.52 (m, 2H), 4.53 (m, 2H), 4.36 (m, 2H), 4.21 (s, 5H). Mass spectrum (FAB): m/e 1004 (P$^+$), 977, 950, 921 (base peak), 895, 866, 839, 809, 781, 753, 725, 694. Anal. calcd. for C$_{27}$H$_{11}$FeO$_{11}$PRu$_4$: C, 32.26; H, 1.30. Found: C, 32.48; H, 1.51.

(340), yellow solid. $^{31}$P NMR (121.4 MHz): $\delta$ 149.5. $^1$H NMR (300 MHz): $\delta$ 8.15 (t, 1H), 7.58-7.47 (m, 2H), 7.37 (m, 1H), 4.81 (m, 1H), 4.68 (m, 1H), 4.52 (m, 1H), 4.47 (m, 1H), 4.08 (s, 5H). Mass spectrum (FAB): m/e 720 (P$^+$), 692, 664 (base peak), 636, 608, 580, 552, 523, 509, 495. Anal. calcd. for C$_{24}$H$_{13}$FeO$_8$PRu$_2$: C, 40.10; H, 1.82. Found: C, 40.23; H, 1.89.
A solution of \( \text{Ru}_3(\text{CO})_{11}(\text{PFcPh}_2) \) (200 mg, 0.20 mmol) in cyclohexane (100 mL) was refluxed for 3 h. \(^{31}\text{P}\) NMR spectroscopy revealed \(339\) and \(340\) as major products and some new compounds. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/\(\text{CH}_2\text{Cl}_2\) as eluent. The first yellow band contained \(\text{Ru}_3(\text{CO})_{12}\) (1%). The second band contained \(337\) (20%) identified by \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectroscopy. The third band contained complex \(341\) (8%). The fourth band contained \(338\) (3%) identified by TLC, \(^{31}\text{P}\), and \(^1\text{H}\) NMR spectroscopy. The fifth band contained \(339\) (25%) identified by \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectroscopy. The sixth band contained complex \(342\) (12%). The seventh and eighth bands contained small amount of mixtures. The ninth band (2%) contained a complex mixture including complex \(340\). The tenth band contained complex \(343\) (4%). Crystals of \(342\) were obtained from a 1/1 hexane/\(\text{CH}_2\text{Cl}_2\) solution.

\(341\), orange solid. \(^{31}\text{P}\) NMR (121.4 MHz): \(\delta 415.3\). \(^1\text{H}\) NMR (300 MHz): \(\delta 5.63 \text{ (m, 1H), 5.42 \text{ (m, 1H), 4.78-4.72 \text{ (m, 2H), 4.68-4.60 \text{ (m, 4H), 4.29 \text{ (s, 5H). Mass spectrum (FAB): m/e 1163 (P+, base peak), 1135, 1107, 1080, 1051, 1022, 994, 967, 938, 909, 881, 854.}}\)

\(342\), red solid. \(^{31}\text{P}\) NMR (121.4 MHz): \(\delta 390 \text{ (broad), 162.2 \text{ (d, J=17.5).}}\). \(^1\text{H}\) NMR (300 MHz): \(\delta 8.22 \text{ (m, 1H), 7.82 \text{ (m, 1H), 7.60 \text{ (m, 1H), 7.52 \text{ (m, 1H), 6.95 \text{ (m, 1H), 6.88 \text{ (m, 1H), 5.90 \text{ (m, 1H), 5.85 \text{ (m, 1H), 4.72 \text{ (m, 2H), 4.65 \text{ (m, 1H), 4.60 \text{ (m, 1H), 4.55 \text{ (m, 1H), 4.41 \text{ (m+s, 1+5H), 4.34 \text{ (m, 1H), 4.18 \text{ (s, 5H), 3.98 \text{ (m, 1H). Mass spectrum (FAB): m/e 1398 (P+), 1369, 1341, 1313, 1285, 1257, 1228, 1201, 1086 (base peak). Anal. calcd. for C}_{44}\text{H}_{28}\text{Cl}_2\text{Fe}_2\text{O}_{11}\text{P}_2\text{Ru}_5, (342)\cdot\text{CH}_2\text{Cl}_2: C, 35.65; H, 1.90. Found: C, 35.26; H, 1.81.}\)
The seventh band, red solid. $^3\text{P}$ NMR (121.4 MHz): $\delta$ 450.6; 420.6 (small); 389.8, 162.2 (342). TLC: 3 spots.

The eighth band, orange solid. $^3\text{P}$ NMR (121.4 MHz): $\delta$ 387.2, 192.8, J=73.4; 40.7 TLC: 3 spots.

The ninth band, red solid. $^3\text{P}$ NMR (121.4 MHz): $\delta$ 423.5; 415.3; 239.9; 149.5 (340). TLC: 4 spots.

(343), red solid. $^3\text{P}$ NMR (121.4 MHz): $\delta$ 410.5, 275.0, J=30.1. $^1\text{H}$ NMR (300 MHz): $\delta$ 8.12 (m, 1H), 7.72 (m, 1H), 7.55 (m, 2H), 7.41 (m, 1H), 6.71 (m, 1H), 6.64 (m, 2H), 4.55 (m, 2H), 4.36 (m, 1H), 4.23 (m, 1H), 4.13 (m, 1H), 4.07 (s, 5H), 4.00 (m, 1H), 3.97 (s, 5H), 3.88 (m, 1H), 3.42 (m, 1H). Mass spectrum (FAB): m/e 1268 (P+, base peak), 1240, 1212, 1185, 1157, 1118, 1090, 1062, 1034, 1016, 984.

(c) in hexanes

A solution of Ru$_3$(CO)$_{11}$(PFcPh$_2$) (50 mg, 0.05 mmol) in hexanes (50 mL) was refluxed for 14 h. $^3\text{P}$ NMR spectroscopy revealed complexes (339) and (342) as the major products. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first pink band contained an unidentified compound (2%). The second orange band was identified to be (339) (20%) by $^3\text{P}$ and $^1\text{H}$ NMR spectroscopy. The third red band contained (342) (8%) identified by TLC and $^3\text{P}$ NMR spectroscopy. A number of small bands were not collected. Complexes (337), (341), and (343) were probably present in the mixture. A $^3\text{P}$ NMR resonance at 434.5 ppm corresponds to a complex previously unobserved.
3.6.2 Pyrolysis of Ru$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ [119, 315]

(a) in cyclohexane

A solution of Ru$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ (30 mg, 0.020 mmol) in cyclohexane (30 mL) was refluxed for 70 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica with 3/1 petroleum ether/diethyl ether as eluent. Three bands were collected but the second dark yellow and third yellow ones were not characterized. The first pink band appeared pure by TLC in various combinations of petroleum ether/diethyl ether solvent, but TLC in 4/1 petroleum ether/CH$_2$Cl$_2$ revealed that indeed it contained two pink compounds. $^{31}$P NMR spectroscopy revealed the presence of (338) and (344). The $^1$H NMR spectrum also shows extra signals besides those for (344) which has been previously described [119].

(b) in hexanes

A solution of Ru$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ (40 mg, 0.030 mmol) in hexanes (100 mL) was refluxed for 20 h. TLC indicated the formation of (338) and (344) at 1.5 h. $^{31}$P NMR spectroscopy revealed complexes (338) and (344) as the major products formed. Their spectroscopic and analytical data appear in the next section.

3.6.3 Pyrolysis of Ru$_3$(CO)$_{9}$(PFcPh$_2$)$_3$

(a) in hexanes

A solution of Ru$_3$(CO)$_{9}$(PFcPh$_2$)$_3$ (50 mg, 0.030 mmol) in hexanes (50
mL) was refluxed for 15 h after which the solvent was removed in vacuo. Both $^{31}$P and $^1$H NMR spectroscopy, and TLC showed little reaction.

(b) in cyclohexane

A solution of Ru$_3$(CO)$_9$(PFcPh)$_3$ (150 mg, 0.090 mmol) in cyclohexane (70 mL) was refluxed for 13 h. TLC and $^{31}$P NMR spectroscopy revealed the presence of five major products. The solvent was removed in vacuo and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first purple band contained complex (338) (25%). The second band contained complex (344) (18%). The third band (5%) contained a mixture of an unidentified complex and the starting material. The fourth band contained complex (345) (8%). The fifth band (3%) contained a mixture of four complexes. The last band (15%) contained complexes (346) and (347). Crystals of (344) were obtained from a 3/1 hexane/CH$_2$Cl$_2$ solution.

(338), purple solid. $^{31}$P NMR (121.4 MHz): $\delta$ 236.8. $^1$H NMR (300 MHz): $\delta$ 7.82 (m, 2H), 7.60-7.46 (m, 6H), 7.34 (m, 2H), 6.53 (m, 2H), 6.10 (m, 2H), 4.54 (m, 2H), 4.39 (m, 2H), 4.27 (s, 10H), 4.23 (m, 2H), 3.94 (m, 2H). Mass spectrum (FAB): m/e 1162 (P+, base peak), 1108, 1078, 1051, 1022, 995, 966, 887, 864, 810. Anal. calcd. for C$_{45}$H$_{32}$Fe$_2$O$_7$P$_2$Ru$_3$: C, 46.53; H, 2.78. Found: C, 46.74; H, 2.94.

(344), purple solid. $^{31}$P NMR (121.4 MHz): $\delta$ 272.5, 208.5, J=199.6. $^1$H NMR (300 MHz): $\delta$ 7.98 (m, 2H), 7.81 (m, 2H), 7.74 (m, 1H), 7.58-7.46 (m, 4H), 7.23 (m, 1H), 7.00 (m, 1H), 6.61 (m, 1H), 6.51 (m, 1H), 6.40 (m, 1H), 4.58 (m, 1H), 4.45 (m, 2H), 4.32 (s, 5H), 4.13 (m, 1H), 4.03 (m+s, 1+5H), 3.77 (m, 1H), 3.71 (m, 1H), 2.86 (m, 1H). Mass spectrum (FAB): m/e 1163 (P+), 1106 (base peak), 1079, 1050, 1023, 994, 967, 888, 821, 810. Anal. calcd. for C$_{45}$H$_{32}$Fe$_2$O$_7$P$_2$Ru$_3$: C, 46.53; H, 2.78. Found: C, 46.81; H, 2.89. The spectro-
scopic data agree with those in the literature.

The third band, dark red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 250.9; 29.0. TLC: 2 spots with one being the starting material Ru$_3$(CO)$_9$(PFcPh$_2$)$_3$.

(345), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 265.1, 208.3, J=201.6. $^1$H NMR (300 MHz): $\delta$ 8.11 (m, 2H), 7.68 (m, 2H), 7.55 (m, 1H), 7.42 (m, 3H), 7.30 (m, 3H), 7.22 (m, 1H), 7.04 (m, 1H), 6.85 (m, 1H), 4.68 (m, 1H), 4.48 (m, 2H), 4.34 (s, 5H), 4.20 (m, 1H), 4.11 (m, 1H), 4.05 (s, 5H), 3.88 (m, 1H), 3.82 (m, 1H), 3.57 (m, 1H). Mass spectrum (FAB): m/e 1191 (P$^+$), 1163, 1135, 1107, 1079 (base peak), 1051, 1022, 994, 966, 887.

The fifth band, dark red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 268.0, 30.8, J=166.7; 265.0, 28.8, J=153.2. $^1$H NMR (300 MHz): $\delta$ 8.40, 8.15-7.95, 7.75-7.05, 6.62, 6.45, 4.55-3.72 (many peaks). Mass spectrum (EI, 200°C): m/e 1025 (P$^+$), 997, 970 (base peak), 942, 862, 788, 760, 680, 651. TLC: 2 major and 2 minor spots.

(346), pink solid. $^{31}$P NMR (202.5 MHz): $\delta$ 245.1, 240.0, 24.3, J$_{AB}$=191.0, J$_{BX}$=18.0, J$_{AX}$<2.0. (347), pink solid. $^{31}$P NMR (202.5 MHz): $\delta$ 235.3, 237.8, 26.5, J$_{AB}$=205.8, J$_{BX}$=12.6, J$_{AX}$<2.0. The $^1$H NMR (300 MHz) spectrum of the mixture of (346) and (347) is shown in Figure 5.12. Mass spectrum of the mixture (FAB): m/e 1503 (P$^+$, base peak), 1475, 1447, 1418, 1390, 1361, 1333, 962, 890. Anal. calcd. for C$_{66}$H$_{51}$Fe$_3$O$_6$P$_3$Ru$_3$: C, 52.71; H, 3.42. Found: C, 52.48; H, 3.39.

3.6.4 Pyrolysis of Ru$_3$(CO)$_{11}$(PFc$_2$Ph) [315]

(a) in hexanes

A solution of Ru$_3$(CO)$_{11}$(PFc$_2$Ph) (200 mg, 0.18 mmol) in hexanes (100
mL) was refluxed for 15 h. $^{31}$P NMR spectroscopy revealed the presence of four major resonances at 408.2, 377.8, 364.4, and 24.6 ppm, and three minor ones at 373.4, 328.9, and 15.8 ppm. The solvent was removed in vacuo, and the residue was chromatographed on silica with 2/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first, third, fourth, and sixth bands contained complexes (348) (15%), (339) (10%), (349) (25%), and (350) (20%), respectively. The second band (6%) contained a mixture of two unidentified complexes and the starting material. The fifth band contained traces of a green and an orange compound which were not identified.

(348), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 364.4. $^1$H NMR (300 MHz): $\delta$ 5.68 (m, 1H), 4.80 (s, 5H), 4.39 (m, 2H), 4.17 (m, 2H), 4.08 (s, 5H), 3.87 (m, 2H). Mass spectrum (FAB): m/e 1086 (P$^+$), 1003, 977, 951, 896, 869 (base peak), 845, 816, 788, 762, 732, 704, 661, 606, 593.

The second band, red solid. $^{31}$P NMR (121.4 MHz): $\delta$ 129.1, 125.1, 15.9. TLC: 3 spots.

(339), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 408.0. $^1$H NMR (300 MHz): $\delta$ 7.00 (t, 2H), 6.52 (t, 2H), 4.51 (m, 2H), 4.35 (m, 2H), 4.22 (s, 5H). Mass spectrum (FAB): m/e 1006 (P$^+$), 922 (base peak), 878, 793, 764, 737. Anal. calcd. for C$_{27}$H$_{13}$FeO$_{11}$PRu$_4$: C, 32.28; H, 1.30. Found: C, 32.54; H, 1.41.

(349), pink solid. $^{31}$P NMR (121.4 MHz): $\delta$ 377.8. $^1$H NMR (300 MHz): $\delta$ 8.12 (m, 2H), 7.70 (m, 2H), 4.69 (m, 1H), 4.50 (m, 2H), 4.32 (s, 5H), 4.29 (m, 1H), 4.07 (m, 1H), 4.00 (m, 1H), 3.73 (s, 5H), 3.21 (m, 1H), 2.33 (m, 1H). Mass spectrum (FAB): m/e 1008 (P$^+$), 951, 926, 896, 782 (base peak).

(350), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 24.6. $^1$H NMR (300 MHz): $\delta$ 8.0 (m, 2H), 7.5 (m, 3H), 5.5 (m, 2H), 4.5 (s, 5H), 4.4-4.2 (m, 3H), 4.0 (s, 5H), 3.6 (m, 1H), 3.0 (m, 1H), -15.0 (d, 1H, J=28.1). Mass spectrum (FAB): m/e 1035 (P$^+$), 1007, 979, 950, 922, 893, 864, 838 (base
peak), 809, 776. Anal. calcd. for C\textsubscript{35}H\textsubscript{23}Fe\textsubscript{2}O\textsubscript{9}PRu\textsubscript{3}: C, 40.68; H, 2.24. Found: C, 40.78; H, 2.30.

(b) in cyclohexane

A solution of Ru\textsubscript{3}(CO)\textsubscript{11}(PF\textsubscript{c}\textsubscript{2}Ph) (100 mg, 0.090 mmol) in cyclohexane (50 mL) was refluxed for 6 h. \textsuperscript{31}P NMR spectroscopy revealed similar resonances as in (a). The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH\textsubscript{2}Cl\textsubscript{2} as eluent. The first band gave Ru\textsubscript{3}(CO)\textsubscript{12} (2%). The second to fifth bands contained complexes (348) (15%), (339) (25%), (349) (15%), and (350) (20%), respectively, identified by TLC and \textsuperscript{31}P NMR spectroscopy. The sixth band contained a mixture of three complexes as shown by TLC and \textsuperscript{31}P NMR spectroscopy.

(c) in toluene

A solution of Ru\textsubscript{3}(CO)\textsubscript{11}(PF\textsubscript{c}\textsubscript{2}Ph) (220 mg, 0.20 mmol) in toluene (40 mL) was refluxed for 5 h. The solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH\textsubscript{2}Cl\textsubscript{2} as eluent. The first, second, fourth, and sixth bands contained complexes (339) (15%), (348) (25%), (349) (5%), and (350) (20%), respectively, identified by TLC and \textsuperscript{31}P NMR spectroscopy. The third and fifth bands contained new complexes (351) (10%) and (352) (5%), which will be described in the next section, identified by TLC, \textsuperscript{1}H, and \textsuperscript{31}P NMR spectroscopy. The seventh band contained a mixture of three complexes as shown by TLC and \textsuperscript{31}P NMR spectroscopy (424.5, 414.3, and 110.1 ppm).
3.6.5 Pyrolysis of \( \text{Ru}_3(\text{CO})_{12} \) with \( \text{PF}_2\text{Ph} \)

A solution of \( \text{Ru}_3(\text{CO})_{12} \) (256 mg, 0.40 mmol) and \( \text{PF}_2\text{Ph} \) (190 mg, 0.40 mmol) in octane (50 mL) was refluxed for 3.5 h. \( ^{31}\text{P} \) NMR spectroscopy revealed three major resonances at 408.0, 364.2, and 328.5 ppm, two medium resonances at 418.1 and 371.6 ppm, and very minor ones at 424.2, 414.3, 221.7, 141.2, 138.7, 132.6, and 110.1 ppm. \( ^1\text{H} \) NMR spectroscopy showed the absence of any hydrides. The reaction solvent was removed in vacuo, and the residue was chromatographed on alumina with 4/1 petroleum ether/\( \text{CH}_2\text{Cl}_2 \) as eluent. The first band (2%) contained a complex characterized only by \( ^1\text{H} \) NMR spectroscopy. The second band contained complex (351) (12%). The third orange band contained (339) (20%) identified by TLC, \( ^1\text{H} \), and \( ^{31}\text{P} \) NMR spectroscopy. The fourth band contained small amount of a mixture of two complexes. The fifth band contained complex (352) (16%). The other bands were small and not eluted. The major complex (348) showing the \( ^{31}\text{P} \) NMR resonance at 364.4 ppm and a new minor complex showing a \( ^{31}\text{P} \) NMR resonance at 371.6 ppm were not found. Crystals of (351) suitable for an X-ray diffraction study were obtained from a 5/1 hexane/\( \text{CH}_2\text{Cl}_2 \) solution.

The first band, orange solid. \( ^1\text{H} \) NMR (300 MHz): \( \delta \) 4.65 (m, 2H), 4.59 (m, 2H), 4.52 (s, 5H), 4.36 (m, 2H), 4.13 (s, 5H), 4.05 (m, 2H).

(351), red solid. \( ^{31}\text{P} \) NMR (121.4 MHz): \( \delta \) 418.0. \( ^1\text{H} \) NMR (300 MHz): \( \delta \) 5.28 (m, 1H), 5.18 (m, 1H), 4.80 (m, 1H), 4.54 (m, 2H), 4.50 (m, 1H), 4.44 (m, 1H), 4.35 (m, 1H), 4.31 (s, 5H). Mass spectrum (FAB): m/e 993 (P\(^+\)), 966, 935, 909 (base peak), 880, 853, 826, 797, 768, 741, 683. Anal. calcd. for \( \text{C}_{26}\text{H}_{13}\text{FeO}_{11}\text{PRu}_4 \): C, 31.47; H, 1.32. Found: C, 31.61; H, 1.38.

(352), green solid. \( ^{31}\text{P} \) NMR (121.4 MHz): \( \delta \) 328.5. \( ^1\text{H} \) NMR (300 MHz): \( \delta \) 6.12 (tm, 1H), 4.97 (s, 5H), 4.35 (m, 2H), 4.22 (dm, 2H), 4.16 (s, 5H), 4.12
(m, 2H). Mass spectrum (FAB): m/e 956 (P+, base peak), 928, 900, 873, 844, 816, 787, 759, 731, 702.

3.6.6 Pyrolysis of Ru₃(CO)₁₂ with PEt₂Fc

Triruthenium dodecacarbonyl (200 mg, 0.31 mmol) and PEt₂Fc (75 mg, 0.27 mmol) in octane was refluxed for 18 h. TLC revealed the formation of more than ten products. The solvent was removed in vacuo, and the residue was chromatographed on Florisil with 4/1 petroleum ether/CH₂Cl₂ as eluent. The first yellow band contained ferrocene (2%) identified by TLC and ¹H NMR spectroscopy. The second band (5%) contained a mixture of four compounds. The third band contained complex (353) (15%). The fourth band contained complex (354) (25%). The fifth reddish orange band (10%) contained a mixture of three complexes by TLC. The sixth band contained a pure complex (10%) by TLC but was not characterized. Crystals of (353) and (354), obtained by slow evaporation of the collected bands, await analysis.

The second band, yellow solid. ³¹P NMR (121.4 MHz): δ 448.6, 293.4, 282.5, 94.5. TLC: 4 spots.

(353), orange solid. ³¹P NMR (81.0 MHz): δ 370.4. ¹H NMR (200 MHz): δ 2.34 (m), 2.12 (m), 1.33 (m), 1.26 (m). Mass spectrum (FAB): m/e 1189 (P+, base peak), 1159, 1133, 1025, 1077, 1046, 1017, 991, 963, 935, 906.

(354), brownish red solid. ³¹P NMR (81.0 MHz): δ 366.8. ¹H NMR (200 MHz): δ 4.62 (s, 5H), 4.30 (s, 1H), 2.23 (m, 2H), 2.04 (m, 2H), 1.40-1.15 (m, 6H). Mass spectrum (FAB): m/e 1137 (P+, base peak), 1109, 1080, 1052, 1024, 995, 964, 935, 907, 879.
3.6.7 Pyrolysis of Ru$_3$(CO)$_{12}$ with PEtFc$_2$

A solution of Ru$_3$(CO)$_{12}$ (150 mg, 0.23 mmol) and PEtFc$_2$ (110 mg, 0.26 mmol) in toluene (40 mL) was refluxed for 10 h. TLC revealed the presence of more than ten products. The solvent was removed in vacuo, and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The second band contained complex (355) which was obtained as a dark green solid. $^{31}$P NMR (81.0 MHz): $\delta$ 425.1. Mass spectrum (FAB): m/e 995 (P$^+$, base peak), 967, 938, 910, 882, 854, 826, 798, 770, 742. Anal. calcd. for C$_{21}$H$_{11}$O$_{12}$PRu$_5$: C, 25.38; H, 1.32. Found: C, 25.57; H, 1.41.

3.6.8 Pyrolysis of Ru$_3$(CO)$_{10}$[Fc'(PPh$_2$)$_2$]

(a) in cyclohexane for 4 h [120]

A solution of Ru$_3$(CO)$_{10}$ (60 mg, 0.053 mmol) in cyclohexane (50 mL) was refluxed for 4 h. The solvent was removed in vacuo and the residue was chromatographed on a silica column by using 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first small yellow and second purple bands were not identified. The third band contained complex (356). The fourth band contained complex (357). The fifth band contained trace of an unidentified compound and the sixth band contained complex (358). The $^1$H NMR data for those complexes ((356), (357), (359), and (361)) agree with those in the literature [120] except for the hydride resonances for the complex (356). The $^{31}$P NMR data were not previously recorded. Complexes (358), (360), and (362) were not previously reported.
(356), greenish orange solid. $^3\text{P}$ NMR (81.0 MHz): $\delta$ 35.0, 3.5, J=4.5.
$^1\text{H}$ NMR (200 MHz): $\delta$ 7.73 (m, 2H), 7.54 (m, 2H), 7.46-7.20 (m, 15H), 7.09 (m, 1H), 4.48 (m, 1H), 4.42 (m, 1H), 4.36 (m, 1H), 4.20 (m, 1H), 4.12 (m, 1H), 4.00 (m, 1H), 3.92 (m, 1H), -16.47 (dd, 1H, J$_1$=16.4, J$_2$=12.2).

(357), reddish orange solid. $^3\text{P}$ NMR (81.0 MHz): $\delta$ 40.6, 36.0, J=20.5.
$^1\text{H}$ NMR (200 MHz): $\delta$ 7.99 (m, 1H), 7.73 (m, 3H), 7.62 (m, 3H), 7.58-7.35 (m, 10H), 7.18 (m, 1H), 6.70 (m, 1H), 4.85 (m, 1H), 4.72 (m, 1H), 4.28 (m, 2H), 4.12 (m, 1H), 3.87 (m, 1H), 3.48 (m, 1H), 3.27 (m, 1H), -16.80 (dd, 1H, J$_1$=26.4, J$_2$=10.6).

(358), red solid. $^3\text{P}$ NMR (81.0 MHz): $\delta$ 0.0. $^1\text{H}$ NMR (200 MHz): $\delta$ 7.52 (m, 2H), 7.45-7.15 (m, 16H), 6.98 (m, 2H), 4.48 (m, 2H), 4.26 (m, 4H), 4.01 (m, 2H).

(b) in cyclohexane for 40 h

A solution of Ru$_3$(CO)$_{10}$(bppyf) (120 mg, 0.11 mmol) in cyclohexane (60 mL) was refluxed for 40 h. The solvent was removed in vacuo and the residue was chromatographed on a silica column by using 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first and second yellow bands contained small amounts of unidentified compounds. The third band contained complex (359) (12%). The fourth band, separated from the third by repeated chromatography, contained complex (360) (10%). The fifth band contained complex (361) (8%). The sixth band contained traces of an unidentified compound. The seventh band contained complex (362) (4%). The subsequent bands contained, in the order of elution, complexes (357) (4%), (356) (55%), and (358) (2%).

(359), purple solid. $^3\text{P}$ NMR (81.0 MHz): $\delta$ 263.9, 215.9, J=190.7. $^1\text{H}$ NMR (200 MHz): $\delta$ 7.92-7.80 (m, 2H), 7.50-7.20 (m, 13H), 6.45 (m, 2H), 6.26
(m, 2H), 4.51 (m, 1H), 4.44 (m, 1H), 4.37 (m, 1H), 4.19 (s, 5H), 3.75 (m, 1H). Mass spectrum (FAB): m/e 1055 (P+, base peak), 1027, 999, 970, 943, 915, 887, 859, 780, 702, 624. Anal. calcd. for C$_{41}$H$_{28}$FeO$_7$P$_2$Ru$_3$: C, 46.74; H, 2.68. Found: C, 46.95; H, 2.73.

(360), purple solid. $^{31}$P NMR (81.0 MHz): $\delta$ 274.9, 204.1, J=195.7. $^1$H NMR (200 MHz): $\delta$ 7.78-7.50 (m, 6H), 7.40-7.20 (m, 5H), 7.08-6.86 (m, 6H), 6.70 (m, 2H), 4.08 (m, 1H), 4.01 (m, 1H), 3.92 (s, 5H), 3.65 (m, 1H), 2.78 (m, 1H). Mass spectrum (FAB): m/e 1055 (P+, base peak), 1027, 999, 970, 943, 915, 887, 859, 780, 702, 624. Anal. calcd. for C$_{41}$H$_{28}$FeO$_7$P$_2$Ru$_3$: C, 46.74; H, 2.68. Found: C, 47.03; H, 2.69.

(361), orange solid. $^{31}$P NMR (81.0 MHz): $\delta$ 166.9, 111.9, J=12.8.

(362), dark purple solid. $^{31}$P NMR (81.0 MHz): $\delta$ 184.0, 128.4, J=15.0. $^1$H NMR (200 MHz): $\delta$ 7.62-7.50 (m, 2H), 7.45-7.15 (m, 13H), 4.52 (m, 1H), 4.40 (m, 1H), 4.28 (m, 2H), 4.14 (m, 1H), 3.88 (m, 1H), 3.24 (m, 1H). Mass spectrum (FAB): m/e 1031 (P+), 1003, 975, 947 (base peak), 920, 892, 864, 786, 708.

3.6.9 Pyrolysis of Ru$_3$(CO)$_{10}$[Fc'(P'BuPh)$_2$]

A solution of Ru$_3$(CO)$_{10}$[Fc'(P'BuPh)$_2$] (80 mg, 0.070 mmol) in hexanes (50 mL) was refluxed for 15 h. The solvent was removed in vacuo and the residue was chromatographed on a silica column by using 3.5/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band (4%) contained a mixture of two complexes. The second band contained a yellow compound (2%). The third to seventh bands contained complexes (363) (15%), (364) (12%), (365) (15%), (366) (10%), and (367) (18%), respectively. Suitable crystals of (365) for an X-ray diffraction study were obtained from a toluene solution.
The first band, greenish orange solid. $^{31}$P NMR (121.4 MHz): δ 432.7, 298.5, 162.9. $^1$H NMR (300 MHz): δ 8.0-7.3, 5.0-4.0, 1.7-1.1. Mass spectrum (FAB): m/e 910 (P+), 881 (base peak), 851, 825, 792, 768, 741, 706, 628.

The second band, yellow solid. $^1$H NMR (300 MHz): δ 7.90 (m, 1H), 7.55 (m, 1H), 7.46 (m, 1H), 7.25 (m, 4H), 7.10 (m, 2H), 4.73 (m, 1H), 4.70 (m, 1H), 4.40 (m, 1H), 4.32 (m, 2H), 4.25 (m, 1H), 4.21 (m, 1H), 4.13 (m, 1H), 1.52 (d, 9H), 1.40 (d, 9H).

(363), reddish orange solid. $^{31}$P NMR (121.4 MHz): δ 62.3, 56.8. $^1$H NMR (300 MHz): δ 8.20 (m, 2H), 7.50 (m, 3H), 7.35 (m, 3H), 6.65 (m, 1H), 5.98 (m, 1H), 4.75 (m, 1H), 4.38 (m, 4H), 4.30 (m, 1H), 2.30 (m, 1H), 1.33 (d, 9H), 1.14 (d, 9H), -16.94 (dd, 1H, $J_1$=20.1, $J_2$=6.2). Mass spectrum (FAB): m/e 1042 (P+), 1014, 987, 960, 930, 902, 873, 844, 818, 790, 762, 703 (base peak), 638, 629. Anal. calcd. for C$_{38}$H$_{36}$FeO$_8$P$_2$Ru$_3$: C, 43.81; H, 3.48. Found: C, 43.99; H, 3.64.

(364), reddish orange solid. $^{31}$P NMR (121.4 MHz): δ 60.6, 51.7. $^1$H NMR (300 MHz): δ 8.52 (m, 1H), 8.19 (m, 1H), 7.78 (m, 3H), 7.40 (m, 2H), 6.90 (m, 1H), 6.76 (m, 1H), 6.56 (m, 1H), 4.53 (m, 2H), 4.47 (m, 1H), 4.40 (m, 2H), 4.20 (m, 1H), 3.25 (m, 1H), 1.28 (d, 9H), 1.09 (d, 9H), -16.58 (dd, 1H, $J_1$=21.3, $J_2$=10.8). Mass spectrum (FAB): m/e 1042 (P+), 1014, 987, 960, 930, 902, 873, 844, 818, 790, 762, 703 (base peak), 638, 629.

(365), orange solid. $^{31}$P NMR (121.4 MHz): δ 90.1, 40.4. $^1$H NMR (300 MHz): δ 8.21 (m, 1H), 8.10 (m, 2H), 7.72 (m, 2H), 7.41 (m, 3H), 4.86 (m, 1H), 4.70 (m, 1H), 4.57 (m, 1H), 4.45 (m, 1H), 4.40 (m, 1H), 4.28 (m, 1H), 3.75 (m, 1H), 2.65 (m, 1H), 1.23 (d, 9H), 0.88 (d, 9H), -16.07 (dd, 1H, $J_1$=$J_2$=10.5). Mass spectrum (FAB): m/e 1042 (P+), 1014, 987 (base peak), 960, 930, 902, 874, 846, 818, 790, 762, 704, 630. Anal. calcd. for C$_{38}$H$_{36}$FeO$_8$P$_2$Ru$_3$: C, 43.81; H, 3.48. Found: C, 44.13; H, 3.59.

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(366), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 80.6, 41.1. $^1$H NMR (300 MHz): $\delta$ 8.18 (m, 2H), 8.02 (m, 1H), 7.42 (m, 3H), 7.23 (m, 2H), 6.92 (m, 1H), 4.51 (m, 1H), 4.40 (m, 1H), 4.24 (m, 1H), 4.20 (m, 1H), 4.12 (m, 1H), 3.93 (m, 1H), 3.52 (m, 1H), 3.02 (m, 1H), 1.42 (d, 9H), 1.16 (d, 9H), -12.76 (dd, 1H, $J_1$=9.0, $J_2$=5.4). Mass spectrum (FAB): m/e 1070 (P$^+$), 1042 (base peak), 1014, 986, 960, 930, 902, 874, 846, 818, 790, 762, 704, 630.

(367), reddish orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 35.0, 22.8. $^1$H NMR (300 MHz): $\delta$ 8.13 (m, 3H), 7.64 (m, 1H), 7.50 (m, 2H), 7.11 (m, 1H), 6.88 (m, 1H), 6.50 (m, 1H), 5.48 (m, 2H), 5.11 (m, 1H), 4.75 (m, 1H), 4.66 (m, 1H), 3.38 (m, 2H), 1.15 (d, 9H), 1.03 (d, 9H). Mass spectrum (FAB): m/e 1095 (P$^+$), 1072, 1042, 1013, 986, 956 (base peak), 928, 900, 872, 644.

3.6.10 Pyrolysis of Ru$\textsubscript{3}$(CO)$\textsubscript{10}$[Fc'(PiPr$_\textsubscript{2}$)$_\textsubscript{2}$]

Complex Ru$\textsubscript{3}$(CO)$\textsubscript{10}$[Fc'(PiPr$_\textsubscript{2}$)$_\textsubscript{2}$] (200 mg, 0.20 mmol) in cyclohexane (100 mL) was refluxed for 15 h. Decomposition was detected after 2 h by TLC and the starting material had completely disappeared after 15 h. The solvent was removed in vacuo and the residue was chromatographed on a silica column with 3/1 petroleum ether/CH$_\textsubscript{2}$Cl$_\textsubscript{2}$ as eluent. Two major bands were eluted, and subsequently a minor one was eluted with CH$_\textsubscript{2}$Cl$_\textsubscript{2}$. The first major band was subsequently resolved into two bands containing complexes (368) and (369) on a silica column by using 3/1 petroleum ether/ diethyl ether as eluent. The second major band contained complex (370), and the minor band contained complex (371). The approximate yields were as follows: (368), 25%; (369), 15%; (370), 20%; (371), 1%. Crystals of (368) and (371) were obtained from 1/1 hexane/CH$_\textsubscript{2}$Cl$_\textsubscript{2}$ solutions.
(368), red orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 269.4, 67.5. $^1$H NMR (300 MHz): $\delta$ 5.22-5.14 (m, 1H), 5.00-4.88 (m, 1+2H), 4.60-4.52 (m, 1H), 4.45-4.22 (m, 2+1H), 2.35-2.20 (m, 1H), 2.20-2.05 (m, 1H), 1.5-1.2 (m, 12H), -18.50 (ddd, 1H, $J_1=33.3$, $J_2=15.6$, $J_3=2.0$), -19.23 (ddd, 1H, $J_1=21.3$, $J_2=9.0$, $J_3=2.0$). Mass spectrum (FAB): m/e 861 (P+), 835, 807, 779, 749 (base peak), 721, 706, 693, 678, 665, 650, 622, 604, 591, 565, 550. Anal. calcd. for C$_{24}$H$_{24}$FeO$_8$P$_2$Ru$_3$: C, 33.46; H, 2.81. Found: C, 33.20; H, 2.75.

(369), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 177.4, 73.7. $^1$H NMR (300 MHz): $\delta$ 4.80 (m, 1H), 4.58 (m, 2H), 4.32 (m, 1H), 4.01 (m, 2H), 3.94 (m, 1H), 3.85 (m, 1H), 2.85 (m, 1H), 2.58 (m, 2H), 1.8-1.2 (very complex m, 17H), -14.95 (ddd, 1H, $J_1=32.4$, $J_2=19.2$, $J_3=1.8$), -15.45 (ddd, 1H, $J_1=16.4$, $J_2=9.5$, $J_3=1.8$). Mass spectrum (FAB): m/e 903 (P+), 849 (base peak), 821, 793, 765, 749, 737, 721, 709, 693, 663, 650, 619, 590, 550. Anal. calcd. for C$_{27}$H$_{30}$FeO$_8$P$_2$Ru$_3$: C, 35.89; H, 3.35. Found: C, 36.04; H, 3.45.

(370), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 429.3, 53.7. $^1$H NMR (300 MHz): $\delta$ 5.25 (m, 1H), 5.20 (m, 1H), 4.90 (m, 2H), 3.83 (m, 1H), 3.50 (m, 1H), 3.37 (m, 1H), 3.22 (m, 1H), 2.95 (m, 1H), 2.6-2.4 (m, 2H), 1.7-1.6 (m, 6H), 1.10-0.85 (m, 12H), -21.02 (dd, 1H, $J_1=22.8$, $J_2=9.0$). Mass spectrum (FAB): m/e 849 (P+-CO), 821 (base peak), 793, 765, 737. Anal. calcd. for C$_{26}$H$_{30}$FeO$_7$P$_2$Ru$_3$: C, 35.67; H, 3.45. Found: C, 35.78; H, 3.54.

(371), orange solid. $^{31}$P NMR (121.4 MHz): $\delta$ 20.9. $^1$H NMR (300 MHz): $\delta$ 5.00-4.95 (m, 2H), 4.5-4.4 (m, 6H), 2.4-2.1 (m, 4H), 1.4-1.0 (m, 24H). Mass spectrum (FAB): m/e 997 (P+), 943, 915, 887, 859 (base peak), 815. Anal. calcd. for C$_{30}$H$_{37}$ClFeO$_9$P$_2$Ru$_3$: C, 36.10; H, 3.74; Cl, 3.55. Found: C, 35.89; H, 3.62; H, 3.20.

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3.6.11 Pyrolysis of Ru$_3$(CO)$_{12}$ with P(1-C$_{10}$H$_7$)$_3$

A solution of Ru$_3$(CO)$_{12}$ (130 mg, 0.20 mmol) and P(1-C$_{10}$H$_7$)$_3$ (80 mg, 0.20 mmol) in cyclohexane (30 mL) was refluxed for 24 h. TLC and $^{31}$P NMR spectroscopy revealed the presence of two major products and three minor ones. The solvent was removed in vacuo and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band contained unreacted Ru$_3$(CO)$_{12}$ (5%). The second band contained complex (372) (50%). The third band contained complex (373) (15%). The fourth band contained a small amount of a mixture of (373) and another compound. The fifth band contained traces of a complex identified only by mass spectrometry. A complex showing a $^{31}$P NMR resonance at 40.6 and a hydride at -17.89 ppm (s) was not found.

(372), yellow solid. $^{31}$P NMR (81.0 MHz): $\delta$ 68.7. $^1$H NMR (400 MHz): $\delta$ 9.05 (m, 1H), 8.27-8.15 (m, 2H), 8.10 (d, 2H), 8.04 (m, 1H), 7.92-7.78 (m, 4H), 7.73 (m, 1H), 7.46-7.34 (m, 4H), 7.30 (m, 1H), 7.22 (m, 1H), 7.16 (m, 1H), 7.07 (m, 1H), -15.78 (d, 1H, J=5.2), -19.88 (d, 1H, J=37.4). Mass spectrum (FAB): m/e 941 (P$^+$), 913, 885, 857, 829, 800, 771, 743, 728, 714 (base peak), 585. Anal. calcd. for C$_{38}$H$_{21}$O$_8$PRu$_3$: C, 48.57; H, 2.25. Found: C, 48.66; H, 2.32.

(373), pink brown solid. $^{31}$P NMR (81.0 MHz): $\delta$ 71.9. $^1$H NMR (200 MHz): $\delta$ 8.30-6.85 (complex m). Mass spectrum (FAB): m/e 1067 (P$^+$, base peak), 1038, 1012, 984, 956, 928, 914, 900, 883, 872, 855, 844, 827, 814, 800, 771, 744, 714, 645, 615, 596, 568, 540, 527, 512.

The fourth band, brown solid. $^{31}$P NMR (81.0 MHz): $\delta$ 92.8; 71.9 (373). $^1$H NMR (200 MHz): $\delta$ 9.0-8.6 (m), 8.3-6.8 (complex m). TLC: 2 spots.

The fifth band, brown solid. Mass spectrum (FAB): m/e 1456 (P$^+$),
1427, 1399, 1371 (base peak), 1343, 1310, 1290, 1264, 1240, 1213, 1183, 1155, 1013.

3.6.12 Pyrolysis of Ru$_3$(CO)$_{12}$ with As(1-C$_{10}$H$_7$)$_3$

Triruthenium dodecacarbonyl (128 mg, 0.20 mmol) and As(1-C$_{10}$H$_7$)$_3$ (95 mg, 0.21 mmol) in cyclohexane (30 mL) was refluxed for 10 h. $^1$H NMR spectroscopy revealed the presence of two hydrides with equal intensity. The solvent was removed in vacuo, and the residue was chromatographed on silica with 4/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band gave Ru$_3$(CO)$_{12}$ (5%). The second orange, fourth reddish orange, and fifth brown bands have not been characterized. The third major band contained complex (374) (70%).

(374), yellow solid. $^1$H NMR (200 MHz): $\delta$ 8.46 (m, 2H), 8.08 (d, 1H), 8.02 (d, 1H), 7.91 (m, 2H), 7.86-7.72 (m, 4H), 7.58 (m, 1H), 7.44-7.14 (m, 8H), -15.93 (s, 1H), -20.35 (s, 1H). Mass spectrum (FAB): m/e 984 (P$^+$, base peak), 956, 928, 900, 871, 843, 815, 787, 759, 630. Anal. calcd. for C$_{38}$H$_{21}$AsO$_8$Ru$_3$: C, 46.40; H, 2.15. Found: C, 46.57; H, 2.09.

3.6.13 Pyrolysis of Ru$_3$(CO)$_{12}$ with SFcPh

A solution of Ru$_3$(CO)$_{12}$ (250 mg, 0.39 mmol) and SFcPh (100 mg, 0.34 mmol) in toluene (50 mL) was refluxed for 11 h. The solution changed colour from orange to dark red in 15 min and to dark brown in 50 min. TLC revealed the presence of three major products. The solvent was removed in vacuo and the residue was chromatographed on silica with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first band (25%) contained a mixture of two complexes. The second yellow band contained (375) (55%).

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The third band (10%) contained a complex characterized only by $^1$H NMR spectroscopy.

The first band, yellow solid. $^1$H NMR (400 MHz): $\delta$ 7.48 (bm), 7.25 (m), 7.16 (m), 7.04 (m), 4.77 (bm), 4.41 (bm), 4.32 (m), 4.27 (s), 4.17 (bm). TLC: 2 spots.

(375), yellow solid. $^1$H NMR (200 MHz): $\delta$ 6.57 (m, 1H, Ph), 6.05 (m, 2H, Ph), 5.28 (m, 1H, Ph), 4.65 (m, 1H, Ph), 4.41 (m, 1H), 4.24 (m, 1H), 4.21 (s, 5H), 4.14 (m, 1H), 4.07 (m, 1H). Mass spectrum (FAB): m/e 823 (P$^+$), 794, 767, 739, 710, 683, 654, 626, 597 (broad, base peak), 532, 521. Anal. calcd. for C$_{24}$H$_{11}$Fe$_3$O$_8$Ru$_3$S: C, 35.09; H, 1.72. Found: C, 35.18; H, 1.88.

The third band, orange solid. $^1$H NMR (200 MHz): $\delta$ 7.25-7.10 (m), 7.08-7.00 (m), 6.88-6.78 (m), 4.38 (m), 4.33 (m), 4.25 (s), 4.17-4.07 (m), 3.90-3.80 (m), 3.80-3.50 (very broad m), 3.12 (m), 2.93 (m).

3.6.14 Pyrolysis of Ru$_3$(CO)$_{12}$ with SP$_2$

A solution of Ru$_3$(CO)$_{12}$ (192 mg, 0.30 mmol) and SP$_2$ (1 mL, excess) in toluene (25 mL) was refluxed for 15 h. TLC revealed the formation of one major and two minor products. The solvent was removed in vacuo, and the residue was chromatographed on alumina with 3/1 petroleum ether/CH$_2$Cl$_2$ as eluent. The first orange band (15%) has not been characterized. The second major band contained complex (376) which was obtained as a yellow solid in 70% yield. $^1$H NMR (300 MHz): $\delta$ 7.41 (m, 2H), 7.23-7.08 (m, 3H), 6.58 (tm, 1H), 6.00 (m, 2H), 5.34 (tm, 1H), 4.70 (dm, 1H). Mass spectrum (FAB): m/e 715 (P$^+$), 687, 659, 630 (base peak), 601, 574, 548, 519, 490. Anal. calcd. for C$_{20}$H$_{10}$O$_8$Ru$_3$S: C, 33.66; H, 1.41. Found: C, 33.33; H, 1.52.
PART THREE: RESULTS AND DISCUSSION
Chapter 4 Pyrolysis of Triosmium Complexes
Containing Ferrocenyl Ligands

4.1 Pyrolysis of Os$_3$(CO)$_{11}$(PFcPh$_2$)

The pyrolysis of Os$_3$(CO)$_{11}$(PFcPh$_2$) has been examined under several reaction conditions. In all, five complexes, (339) to (343), have been characterized, and their characterization is described below.

Pyrolysis of Os$_3$(CO)$_{11}$(PFcPh$_2$) in octane for 3 h affords one major and at least three minor products as judged by TLC, $^1$H, and $^{31}$P NMR spectroscopy. The hydride resonances in the $^1$H NMR spectrum are due to minor products including complex Os$_3$(CO)$_8$(H)$_2$(C$_5$H$_3$PPh$_2$)Fe(C$_5$H$_4$)] (245)

![Figure 4.1 300 MHz $^1$H NMR spectrum of complex (239).](image)
which will be described in the next section.

Complex (239), the only major product obtained from the reaction, shows a $^{31}$P NMR resonance at 207.3 ppm suggesting the presence of a phosphinidene moiety. The mass spectrum gives the parent ion at 1114 corresponding to the loss of one phenyl and two CO groups from the starting material. The $^1$H NMR spectrum, Figure 4.1, shows the presence of a $\text{C}_6\text{H}_4$ moiety and a ferrocenyl group corresponding to a formula such as $\text{Os}_3(\text{CO})_9(\text{PFC})(\text{C}_6\text{H}_4)$. The pyrolysis of $\text{Os}_3(\text{CO})_1(\text{PPh}_2\text{R})$ (R-Ph, Et, Me) is known to afford asymmetrically bound benzyne derivatives (121) [131-133], and (239) is probably closely related. This was confirmed by using X-ray crystallography. An ORTEP diagram of (239) with 50.0% probability thermal ellipsoids is shown in Figure 4.2.

Figure 4.2 ORTEP diagram of complex (239).
Crystal data: $fw=1114.79$, red, irregular, triclinic system, space group P1 (2), $a=10.858(3)$, $b=13.960(3)$, $c=10.383(3)$ Å, $\alpha=95.54(3)$, $\beta=110.98(2)$, $\gamma=106.34(2)^\circ$, $V=1375.5(7)$ Å$^3$, $Z=2$, $D_{\text{calc}}=2.691$ g/cm$^3$, $R=0.035$, $R_w=0.040$.

As expected, the structure of (239) is very similar to Os$_3$(CO)$_9$(PMe)(C$_6$H$_4$) (121b) [133] and Os$_3$(CO)$_9$(PET)(C$_6$H$_4$) (121a) [131]. It consists of an open Os$_3$ metal framework capped on one face by a benzyne moiety and on the other by a phosphinidene moiety. An alternative description would have the aryne moiety bonded to the Os$_3$P butterfly assembly (the angle between the Os(1)Os(2)P(1) and Os(2)Os(3)P(1) planes is 53.77$^\circ$). The C$_6$H$_4$ ligand is asymmetrically bonded as described previously for (121) with C(11) bonded only to Os(1) while C(12) bridges Os(2) and Os(3). The C(11)-Os(1) bond at 2.118(7) and C(12)-Os(2) at 2.160(8) Å are consistent with two $\sigma$ bonds, but the longer C(12)-Os(3) bond at 2.318(7) Å indicates a weaker interaction. The C(12) bridged Os(2)-Os(3) bond at 2.780(1) Å is shorter than the Os(1)-Os(2) bond at 2.9156(9) Å, and the Os(1)-Os(2)-Os(3) angle is 88.54(3)$^\circ$. The phosphinidene moiety PFc is also bonded to the Os$_3$ framework asymmetrically with the P(1)-Os(2) bond being the longest at 2.423(2) Å, P(1)-Os(1) and P(1)-Os(3) bonds are shorter at 2.310(2) and 2.333(2) Å respectively.

The structure of (239) is better than that of (121a) and (121b) in a crystallographic sense and comparison of some bond lengths in (239) can be made that are not possible for the other compounds. Those carbonyls trans to the P-Os or $\sigma$ C(C$_6$H$_4$)-Os bonds have appreciably longer Os-C bonds (Os(1)-C(18) 1.948(8), Os(1)-C(19) 1.951(8), Os(3)-C(24) 1.959(8) Å), Os(1)-C(17) at 1.876(8) and Os(3)-C(25) at 1.885(9) Å are somewhat shorter than the rest which average to 1.915 Å. In the ferrocenyl moiety, the two Cp rings shows an eclipsed configuration and have a small ring tilt.
angle of 2.74°. The benzyne moiety is tilted 65.10° from the Os₃ plane, and this value is greater than 60.7 and 58.9° reported for (121b) and (121a) respectively, but it is smaller than 72.3° of (122a) which has a PE₃ ligand bonded to Os(3) [133]. Os(1) and Os(2) are out of the C₆H₄ plane by 0.4246 and 0.4370 Å respectively. The C(11)-C(12), C(11)-C(16), and C(12)-C(13) bonds (1.43(1), 1.43(1), and 1.40(1) Å) are probably slightly lengthened.

The AA'BB'X (X=3¹P) pattern for the benzyne moiety observed in the ¹H NMR spectrum indicates a fluxionality of the moiety as was noted for (121a) and (121b) [131, 133]. The processes leading to these exchanges have been discussed previously in Section 1.2.3.2 and one process involves a symmetrical intermediate in which there are two equivalent σ bonds to the terminal Os atoms [133]. A ferrocyne complex (252) with such symmetrical structure has been characterized and is discussed later in Section 4.3.

Complex (240) shows a 3¹P NMR resonance at 65.4 ppm suggesting the presence of a phosphido moiety. The mass spectrum gives the parent ion at 1142 corresponding to the loss of one CO and one phenyl group from the parent. The ¹H NMR spectrum shows the presence of a C₆H₄ moiety and a ferrocenyl group. By analogy with Os₃(CO)₉(µ-CO)(PMeC₆H₄) (232) obtained from Os₃(CO)₁₁(PMePh₂) [132], a formula such as Os₃(CO)₉(µ-CO)(PFcC₆H₄) is very likely, and a structure similar to (232) is proposed and shown in Figure 4.3.

The complex in the fourth band was not obtained in sufficient quantity to be fully characterized. Its mass spectrum gives the parent ion at 1114, the same as that of (239), and possibly it is a ferrocyne complex such as Os₃(CO)₉(PPh)([(C₅H₃)Fe(C₅H₅)]), analogous to Os₃(CO)₉(PFc)([(C₅H₃)Fe(C₅H₅)]) (252) which will be described in Section 4.3.
Figure 4.3 A proposed structure for complex (240).

The fifth band contains a complex mixture, and its NMR spectrum shows many interesting hydride resonances including those of (242) described below and (245) which will be described in the next section.

Pyrolysis of the same starting material (Os₃(CO)₁₁(PFcPh₂)) in octane for 21 h affords a greater number of products, and 3¹P NMR spectroscopy revealed the presence of many complexes containing phosphido/phosphinidene moieties. The third, fifth, and seventh bands all contain such phosphido/phosphinidene complexes in small quantities. Clearly more extensive cleavage reactions have occurred. The characterization of complex (241), obtained from the above reaction, is described below.

Complex (241) shows a 3¹P NMR resonance at 166.8 ppm suggesting the presence of a phosphido/phosphinidene moiety. The ¹H NMR spectrum shows the presence of two C₆H₄ moieties and two equivalent ferrocenyl groups. The mass spectrum gives the parent ion at 2201 corresponding to a formula such as Os₆(CO)₁₇(PFcC₆H₄)₂. The Os₃ metal framework is likely to be intact, so the complex presumably contains two Os₃ units linked by PFcC₆H₄ moieties. Several plausible structures could be conceived and it is difficult to distinguish among these without a structure determination.
Pyrolysis of the same starting material Os$_3$(CO)$_{11}$(PFcPh$_2$) in cyclohexane for 25 h does not proceed far giving mainly complex (239), complex (242) in low yield, and traces of complexes (240) and (243) and a new complex showing a $^{31}$P NMR resonance at -17.1 ppm. To obtain more of complex (242), the reaction solvent was changed to heptane and the pyrolysis was continued for another 5 h. TLC and $^{31}$P NMR spectroscopy now revealed the presence of the starting material (30%), complexes (239) (25%), (240) (5%), (242) (20%), and traces of the complex with the $^{31}$P NMR resonance at -17.1 ppm. The newly isolated products, complexes, (242) and (243), are described below.

Complex (242) shows a $^{31}$P NMR resonance at -6.0 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of a phenyl group, a ferrocenyl group, four protons between 6.75 and 6.45 ppm assignable to a C$_6$H$_4$ moiety, and a hydride. The mass spectrum gives the parent ion at 1192 corresponding to the loss of two CO groups from the parent. A formula such as Os$_3$(CO)$_9$(H)(PFcPhC$_6$H$_4$) is likely and its structure is probably analogous to that of Os$_3$(CO)$_9$(H)(PMePhC$_6$H$_4$) (231) [132] and Os$_3$(CO)$_8$(PPh$_3$)(H)(PPh$_2$C$_6$H$_4$) (224) [67-69]. The structure was established conclusively by an X-ray crystallographic study. An ORTEP diagram with 33.0% probability thermal ellipsoids is shown in Figure 4.4.

Crystal data: fw=1192.91, orange, prism, triclinic system, space group P1 (#2), a=11.380(2), b=15.930(3), c=9.467(1) Å, $\alpha=92.82(1)$, $\beta=100.32(1)$, $\gamma=71.55(1)^\circ$, $V=1601.8(5)$ Å$^3$, $Z=2$, $D_{calc}=2.473$ g/cm$^3$, R=0.028, $R_w=0.030$.

The structure of (242) is very similar to Os$_3$(CO)$_9$(H)(PMePhC$_6$H$_4$) (231) [132] and Os$_3$(CO)$_8$(PPh$_3$)(H)(PPh$_2$C$_6$H$_4$) (224) [67-69]. It consists of a closed Os$_3$ triangle capped on one face by an axially bonded phosphine and an orthometalated C$_6$H$_4$ moiety showing also a $\eta^2$ interaction. Each osmium
atom is bonded to three carbonyls, two equatorial and one axial. The longest Os(1)-Os(2) bond at 3.0259(6) Å is bridged by a hydride which was located in the refinement. The Os(2)-Os(3) bond, bridged by the metalated carbon atom C(12), is the shortest at 2.7576(5) Å and the Os(1)-Os(3) bond is 2.8659(5) Å long. The C₆H₄ moiety is σ bonded to Os(2) (Os(2)-C(12) 2.135(5) Å) and π bonded to Os(3) (Os(3)-C(11) 2.386(5), Os(3)-C(12) 2.371(5) Å), and overall the PFcPhC₆H₄ moiety acts as a five electron donor. The planarity of the C(11)-C(16) ring is slightly distorted with the mean deviation being 0.0276 Å, the mean deviation for the C(17)-C(22) plane is only 0.0032 Å. Also P(1) is displaced 0.7348 Å away from the C(11)-C(16) plane, but only 0.0617 Å from the C(17)-C(22) plane and 0.2454 Å from the Cp(1) plane. In the ferrocenyl moiety, the two Cp rings

Figure 4.4 ORTEP diagram of complex (242).
show an eclipsed configuration and they have a small ring tilt angle of 2.99°. The C(11)-C(16) ring makes an angle of 44.75° to the Os3 plane, and Os(1), Os(2), Os(3) are 0.4653, 0.3111, and 2.0461 Å away respectively from the C6H4 plane. The C(11)-C(12), C(11)-C(16), and C(12)-C(13) bonds (av. 1.442 Å) are slightly lengthened due to the σ and π interaction, the other three C-C bonds average to 1.376 Å. These may be compared to the average C-C length of 1.382 Å for the other phenyl ring. The axial carbonyl C(25)-Os(1) bond at 1.936(5) and C(28)-Os(2) at 1.935(5) Å are the longest and C(31)-Os(3) at 1.873(6) Å is the shortest, the rest average to 1.905 Å.

Complex (243) shows a 31P NMR resonance at 13.8 ppm suggesting the presence of a phosphine. The 1H NMR spectrum shows the presence of a phenyl group, a ferrocenyl group, a C6H4 moiety, and a hydride. Although no mass spectrum was obtained, a formula such as Os3(CO)10(H)(PPh2C6H4) is likely and a proposed structure is shown in Figure 4.5. One example of a complex containing such an orthometalated C6H4 moiety without η2 interaction is complex Os3(CO)9(PPh3)(H)(PPh2C6H4) (225)

Figure 4.5 Proposed structures for complexes (243) and (244).
described previously in Section 2.3.2 [67-69].

Pyrolysis of the benzyne complex $\text{Os}_3(\text{CO})_9(\text{PFc})(\text{C}_6\text{H}_4)$ (239) in decalin for 10 h affords many products judged by TLC and $^{31}\text{P}$ NMR spectroscopy. Although no chromatographic separation was performed, it is clear that many complexes formed contain two phosphinidene moieties.

The formation of complex (241) from $\text{Os}_3(\text{CO})_{11}(\text{PFcPh}_2)$ certainly involves many steps, but the formation of other complexes, (239), (240), (242), and (243), can be rationalized by a reaction sequence entirely analogous to Scheme 2-4 for the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PMcPh}_2)$ discussed earlier in Section 2.3.2 [132]. Although some ferrocenyl activated products such as (245) to be discussed in the following section are also formed, the reactions are mainly associated with phenyl groups. The pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PFcPh}_2)$ in octane for 21 h and the pyrolysis of (239) in decalin showed that under more vigorous reaction conditions, many other potentially interesting phosphido/phosphinidene complexes are formed. It should be of interest, therefore, to investigate these reactions further in future work.

4.2 Pyrolysis of $\text{Os}_3(\text{CO})_{10}(\text{PFcPh}_2)_2$

Pyrolysis of $\text{Os}_3(\text{CO})_{10}(\text{PFcPh}_2)_2$ in octane for 5 h affords more than ten products as judged by TLC, $^1\text{H}$, and $^{31}\text{P}$ NMR spectroscopy. In all, eleven complexes have been characterized. The previously characterized complexes $\text{Os}_3(\text{CO})_9(\text{PFc})(\text{C}_6\text{H}_4)$ (239), $\text{Os}_3(\text{CO})_9(\mu-\text{CO})(\text{PFcC}_6\text{H}_4)$ (240), and $\text{Os}_3(\text{CO})_9(\text{H})(\text{PFcPhC}_6\text{H}_4)$ (242), identified by TLC, $^{31}\text{P}$, and $^1\text{H}$ NMR spectro-
scopy, have been described in the previous section. The characterization of
the other eight complexes, (244) to (251), is described here.

Complex (244) shows a $^{31}$P NMR resonance at 21.2 ppm suggesting
the presence of a phosphine. The $^1$H NMR spectrum shows the presence of
two phenyl groups, eight ferrocenyl protons with no C$_5$H$_5$ ring, and,
presumably, a terminal hydride. The mass spectrum gives the parent ion
at 1220 indicating that only one PFcPh$_2$ ligand is lost from the parent. A
formula such as Os$_3$(CO)$_{10}$H[(C$_5$H$_4$PPh$_2$)Fe(C$_5$H$_4$)] is thus likely and a
possible structure is shown in Figure 4.5.

The fifth band contained a mixture. The $^{31}$P NMR resonances at -10.6
and -17.1 ppm suggest the presence of phosphines. The $^1$H NMR spectrum
is very complex, yet the interesting hydride resonances are all doublets
indicating that only one phosphine is present in each complex.

Complex (245) shows a $^{31}$P NMR resonance at -6.0 ppm suggesting
the presence of a phosphine. The $^1$H NMR spectrum shows the presence of
two phenyl groups, seven ferrocenyl protons with no C$_5$H$_5$ ring, and two
hydrides. The mass spectrum gives the parent ion at 1164 corresponding
to the loss of one PFcPh$_2$ and two CO groups from the parent. The structure
of this complex was solved by an X-ray diffraction study. An ORTEP
diagram with 50.0% probability thermal ellipsoids is shown in Figure 4.6.

Crystal data: fw=1164.90, orange, prism, monoclinic system, space
group P2$_1$/c (#14), a=9.484(3), b=18.144(4), c=17.421(3) Å, $\beta=90.10(2)^\circ$,
V=2998(2) Å$^3$, Z=4, D$_{calc}=2.581$ g/cm$^3$, R=0.038, $R_w=0.042$.

The molecular structure of (245) consists of a closed Os$_3$ triangle
capped on one face by a phosphine and a doubly-metalated ferrocenyl
moiety. Os(2) and Os(3) are each bonded to three carbonyls, while Os(1) is
bonded to two carbonyls and to the iron atom of the ferrocenyl moiety.
Figure 4.6 ORTEP diagram of complex (245).

The Fe(1)-Os(1) length of 2.826(1) Å is one of the shortest of such bonds [316-323]. The longest Os(1)-Os(2) bond at 3.067(9) Å and shortest Os(1)-Os(3) bond at 2.8445(8) Å are each bridged by a hydride which was located crystallographically. The Os(2)-Os(3) bond has an intermediate length of 2.878(1) Å. The Os(1)-C(14) bond at 2.07(1) Å is slightly shorter than Os(3)-C(9) at 2.16(1) Å, but both are normal σ bonds. The two Cp rings show only a small ring tilt angle of 1.87°, yet they are slightly staggered with the torsion angle C(9)Os(3)Os(1)C(14) being 10.6(5)°. Due to the bonding of the C(9) and C(14) atoms with the Os(3) and Os(1) centers respectively, the Fe(1)-C(9) bond at 2.09(1) Å is longer than the other Fe(1)-C (Cp(1)) bonds (av. 2.035 Å), and Fe(1)-C(14) at 1.97(1) Å is shorter than the other Fe(1)-C (Cp(2)) (av. 2.043 Å). P(1) is 0.0903 and 0.1719 Å away respectively from the C6(1) and C6(2) planes, and it is displaced 0.0706 Å from the Cp(1) plane towards Fe(1). Os(1) is similarly out of the
The Cp(1) and Cp(2) planes make angles of 79.17 and 80.75° respectively with the Os₃ plane. The Os-C distances for Os(1) bound carbonyls (av. 1.85 Å) are significantly shorter than the others which average to 1.91 Å.

This complex (245) shows a strong Fe-Os interaction as indicated by the very short Fe-Os bond. Such Fe (ferrocene)-M bonding is well known for group 10 and 11 metals [316-323], but there is only one example describing such an interaction of Fe with group 8 metals [120]. The complex (162) contains a weak Fe-Ru bond (3.098(3) Å), in addition, the ferrocenyl moiety is orthometalated. In fact, the structures of (245) and (162) are broadly similar with P(2) in (162) being replaced by a direct C(14)-Os(1) bond and the second hydride in (245). In (162), C(9) has a secondary interaction with Ru(2) (Ru(2)-C(9) 2.45(2) Å) and this brings the Fe atom within the bonding distance of Ru(2). Eight carbonyls and one hydride make the whole complex electron precise. In complex (245), the secondary interaction of C(9) with Os(1) is weaker (2.58(1) Å), and this is compensated by a much stronger Fe-Os interaction. P(1) in both complexes occupy axial coordination sites, while P(2) in (162) is bonded to Ru(2) equatorially. However in (245), C(14) can not occupy such an equatorial site. Also in (162), the two Cp rings in dppf ligand are significantly opened up to a ring tilt angle of 19.7° while in (245) they are almost parallel.

Complex (246) gives the parent ion at 1430 in the mass spectrum corresponding to the loss of one phenyl and three CO groups from the parent. A single ³¹P NMR resonance at 157.8 ppm suggests the equivalence of two, most likely, phosphido moieties. The ¹H NMR spectrum also shows the presence of two phenyl groups and two equivalent ferrocenyl moieties, and a symmetrical benzyne moiety. These data establish the molecular
formula as $\text{Os}_3(\text{CO})_7(\text{PFcPh})_2(\text{C}_6\text{H}_4)$ and the structure must have both ferrocenyl groups (or phenyl groups) pointing towards the same side of the Os$_3$ plane. Apparently, this is a new type of isomer which has not been described previously. By comparing its ferrocenyl $^1$H NMR pattern with that of the two isomers of Ru$_3$(CO)$_7$(PPh$_2$)(PFcPh)(C$_6$H$_4$) ((359) and (360)) obtained from Ru$_3$(CO)$_{10}$(bppy) which will be described in Section 5.7, and with those of the two isomers of Ru$_3$(CO)$_7$(PFcPh)$_2$(C$_6$H$_4$) ((338) and (344)) obtained from Ru$_3$(CO)$_{12-x}$(PFcPh)$_x$ ($x=2$ or 3) which will be described in Section 5.3, a structure with both ferrocenyl groups pointing towards the benzyne side of the Os$_3$ plane is proposed, however still two solid state structures are possible and these are shown in Figure 4.7. In solution these two structures probably exchange readily. The fluxionality of benzyne moiety in such cluster complexes is well established, therefore both structures account for the observed $^{31}$P and $^1$H NMR spectra.

Complex (247) is an unsymmetrical isomer of the benzyne complex of the same formula $\text{Os}_3(\text{CO})_7(\text{PFcPh})_2(\text{C}_6\text{H}_4)$. The mass spectrum is identical to that of (246), and the $^{31}$P NMR spectrum shows two resonances.

![Figure 4.7 Proposed structures for complexes (246) and (247).](image)

Figure 4.7 Proposed structures for complexes (246) and (247).
at 187.3 and 143.8 ppm indicative of two phosphido moieties and a coupling of 166 Hz typical of a trans arrangement of these two moieties. The $^1$H NMR spectrum shows the presence of two different phenyl groups, two different ferrocenyl groups, and an asymmetrically bound benzyne moiety unlike that found in (246). The structure belongs, undoubtedly, to the series (106), (49), (113) and is shown in Figure 4.7.

Complexes (248) and (249) show similar $^{31}$P and $^1$H NMR (especially hydride) spectra, and they are believed to be isomeric complexes. Complex (248) shows two $^{31}$P NMR resonances at 42.3 and -13.6 ppm suggesting the presence of a phosphido moiety and a phosphine. The $^1$H NMR spectrum shows the presence of three phenyl groups, a C$_6$H$_4$ presumably benzyne moiety, two ferrocenyl groups, and a hydride. By analogy with the products of the pyrolysis of Os$_3$(CO)$_{10}$ (PPh$_3$)$_2$ [67-69], the most likely formula for these two complexes is Os$_3$(CO)$_8$(PFCPh$_2$) (H) (C$_6$H$_4$)(PFcPh) and plausible structures are shown in Figure 4.8.

Complex (250) shows two $^{31}$P NMR resonances at 195.8 and 0.0 ppm suggesting the presence of a phosphinidene moiety and a phosphine. The mass spectrum gives the parent ion at 1458 corresponding to the loss of one phenyl and two CO groups from the parent, and fragment peaks are

![Figure 4.8 Proposed structures for complexes (248) and (249).](image-url)
clearly associated with the loss of eight CO and two phenyl groups. The $^1$H NMR spectrum shows the presence of two phenyl groups, two ferrocenyl groups, and a $C_6H_4$ moiety. Thus a structure, shown in Figure 4.9, is proposed for the complex $\text{Os}_3(\text{CO})_8(\text{PFc})(\text{C}_6\text{H}_4)(\text{PFcPh}_2)$ (250). A few similar complexes (122) and (123) are known, but these were obtained by substituting a CO group with a phosphine in a pre-formed benzyne complex [133].

The eleventh band contained three complexes in small quantities. The $^{31}$P NMR spectrum shows resonances at 154.1 ppm for one complex, -6.8 and -12.4 ppm for another, and 109.0 and -24.0 ppm for the third one. The first complex might be the last of the possible isomers of complexes (246) and (247). The second complex contains two phosphines and it may be $\text{Os}_3(\text{CO})_9(\text{PFcPh}_2)(\text{H})(\text{PFcPhC}_6\text{H}_4)$. The third complex contains a phosphido moiety and a phosphine, and it is probably similar to complex (51) obtained from $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [67-69].

Complex (251) shows two $^{31}$P NMR resonances at 0.1 and -2.5 ppm suggesting the presence of two phosphines. The mass spectrum gives the

Figure 4.9 Proposed structures for complex (250).
parent ion at 1536 corresponding to the loss of two CO groups from the parent. The $^1$H NMR spectrum, Figure 4.10, shows the presence of two ferrocenyl groups, a hydride, and resonances associated with complex phenyl protons. Its formula Os$_3$(CO)$_8$(PFcPh$_2$)(H)(PFcPhC$_6$H$_4$) and structure were established by an X-ray crystallographic study. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.11.

Figure 4.10 400 MHz $^1$H NMR spectrum of complex (251).
Crystal data: (251)CH₂Cl₂, fw=1620.04, orange, prism, triclinic system, space group P1 (#2), a=13.151(3), b=17.177(4), c=12.619(3) Å, \(\alpha=91.98(2)\), \(\beta=104.18(2)\), \(\gamma=67.72(2)^\circ\), \(V=2552(1)\) Å³, \(Z=2\), \(D_{calc}=2.108\) g/cm³, \(R=0.026\), \(R_w=0.027\).

The structure of (251) is analogous to that of complex (242) described earlier in Section 4.1, and of complexes (224), and (230) which have been discussed in Section 2.3.2 [67-69, 127, 132]. The important bond

Figure 4.11 ORTEP diagram of complex (251).
lengths are: Os(1)-Os(3) 3.0344(8), Os(1)-Os(2) 2.7746(8), Os(2)-Os(3) 2.8661(9), Os(1)-C(9) 2.141(5), Os(2)-C(9) 2.359(5), Os(2)-C(10) 2.369(4), Os(1)-P(1) 2.342(1), Os(3)-P(2) 2.363(1) Å, Os-C (carbonyls) ranging from 1.876(5) to 1.930(6) Å with an average of 1.900 Å, P-C (ferrocenyl) av. 1.808 Å, P-C (phenyl) av. 1.831 Å, C(9)-C(10), C(9)-C(14), and C(10)-C(11) av. 1.448 Å, the other three C-C bonds in C₆H₄ ring av. 1.376 Å.

P(1) is bonded equatorially to Os(1) while P(2) is bonded to Os(3) axially. Os(1), Os(2), Os(3), and P(2) are 0.2603, 2.0365, 0.4927, and -0.6572 Å away, respectively, from the C(9)-C(14) plane. This plane makes an angle of 44.87° with the Os₃ plane. P(2) is displaced 0.1333 and 0.0873 Å away respectively from the C(25)-C(29) and C(47)-C(52) planes, and P(1) is displaced 0.2356, 0.1962, and 0.1230 Å away respectively from the C(15)-C(19), C(35)-C(40), and C(41)-C(46) planes. Both ferrocenyl moieties show the usual eclipsed configurations. The Cp(1) and Cp(2) rings have a small ring tilt angle of 3.13°, and the Cp(3) and Cp(4) rings have one of 4.08°.

The formation of complexes (244) and (245) from Os₃(CO)₁₀(PFcPh₂)₂ involves the loss of one PFcPh₂ ligand and ferrocenyl hetero-annular or orthometalation. A Fe-Os bond is also involved in forming (245). The formation of the other products, (246) to (251), involve only reactions on phenyl groups. Clearly the reactions are, as discussed in the above section, centered on phenyl groups. All these complexes, (246) to (251), contain two phosphorus moieties indicating that CO groups are preferentially lost over PFcPh₂ ligands during the pyrolysis. Three types of benzyne complexes, (246) and (247), (248) and (249), and (250) are formed, and they all involve orthometalation and P-C bond cleavage reactions. A reaction sequence analogous to that proposed for Os₃(CO)₁₀(PPh₃)₂ in
Section 2.3.2 can be conceived to account for the formation of (246) to (249), and (251). A reaction sequence analogous to that in Scheme 2-4 for the pyrolysis of Os$_3$(CO)$_{11}$(PMePh$_2$) discussed earlier in Section 2.3.2 can be conceived to account for the formation of (250).

4.3 Pyrolysis of Os$_3$(CO)$_{11}$(PFc$_2$Ph)

Pyrolysis of Os$_3$(CO)$_{11}$(PFc$_2$Ph) in octane for 3 h affords five major products and some minor ones as judged by TLC, $^{31}$P, and $^1$H NMR spectroscopy. In all, fourteen complexes, (239), (240), and (242) to (263), have been characterized. Complexes (239) and (240), identified by spectroscopic and analytical techniques, have been described in Section 4.1. The characterization of the other complexes, (252) to (263), is described below.

Complex (252) was characterized to be a novel ferrocene derivative. A $^{31}$P NMR resonance at 189.8 ppm suggests the presence of a phosphinidene moiety, while the $^1$H NMR spectrum, Figure 4.12, shows the presence of only ferrocenyl protons with two C$_5$H$_5$ rings. The mass spectrum gives the parent ion at 1224 corresponding to the loss of one Ph and two CO groups from the parent. On this evidence a formula such as Os$_3$(CO)$_9$(PFc)[(C$_5$H$_3$)Fe(C$_5$H$_5$)] seems very likely. The unprecedented formulation was unambiguously established by a single crystal X-ray structure determination. An ORTEP view of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.13.

Crystal data: (252)-0.5CH$_2$Cl$_2$, fw=1265.18, green, prism, triclinic system, space group P1 (#2), a=12.638(4), b=15.244(5), c=9.867(3) Å,
α=100.85(2), β=105.56(2), γ=69.80(2)°, V=1708.9(9) Å³, Z=2, D_{calc}=2.458 g/cm³, R=0.028, R_w=0.030.

The structure consists of an open Os₃ triangle capped on one face by a symmetrically bonded ferrocene and on the other by a phosphinidene moiety. The molecule is rather symmetrical: Os(1)-Os(3) (2.827(1) Å) and Os(2)-Os(3) (2.828(1) Å) are equal, Os(1)-C(1) (2.110(6) Å) and Os(2)-C(2) (1.132(6) Å) are equal, Os(3)-C(1) (2.445(6) Å) and Os(3)-C(2) (2.421(6) Å) are equal, and finally Os(1)-P(1) (2.336(2) Å) and Os(2)-P(1) (2.328(2) Å)

Figure 4.12 400 MHz $^1$H NMR spectrum of complex (252).
are also equal. The Os(3)-P(1) bond at 2.454(2) Å is significantly longer. The ferrocyn moiety is σ bonded to Os(1) and Os(2), and π bonded to Os(3). This interaction lengthens the C-C bonds in C₅H₃ ring especially the C(1)-C(2) bond considerably. This C(1)-C(2) bond at 1.519(9) Å is almost as long as a C-C single bond (1.54 Å). C(1)-C(5) (1.449(9) Å) and C(2)-C(3) bonds (1.468(9) Å) are longer than the other two in the aryne ring (av. 1.410 Å) which are slightly longer than the C-C bonds in the Cp(2) ring (av. 1.39 Å). The Cp(1) plane makes angles of 49.10° with the Os(1)Os(3)P(1) plane and 49.63° with the Os(2)Os(3)P(1) plane. The Cp(2) ring points away from the Os(3) center, thus eliminating the possibility of any Fe-Os interaction. As will be seen from the reaction Scheme 4-3, only the
orientation of the Cp(2) ring found in F leads to the formation of this ferrocyn complex. Os(1) and Os(2) are displaced 0.2167 and 0.1754 Å away from the Cp(1) plane, while Os(3) is 2.0540 Å away from the same plane but on the opposite side. Both the ferrocyn and ferrocenyl moieties show small ring tilt angles (4.44° and 4.65° respectively), but the two Cp rings in the ferrocyn moiety show a staggered configuration while those in the ferrocenyl group show the more usual eclipsed configuration.

The interaction of C(1) and C(2) with the Os3 triangle makes the Fe(1)-C(1) (2.096(6) Å) and Fe(1)-C(2) (2.085(6) Å) bonds ca. 0.05 Å longer than the other Fe-C (Cp(1)) bonds (av. 2.034 Å), the Fe-C (Cp(2)) distances average to 2.037 Å. Although the iron atom Fe(1) in the ferrocyn fragment seems to shift away from the bound arene ring Cp(1) (Fe(1)-Cp(1) 1.645(3) Å) relative to the Fe(1)-Cp(2) distance (1.571(4) Å), the former value seems to be normal when compared with Fe(2)-Cp(3) (1.644(4) Å) and Fe(2)-Cp(4) (1.654(6) Å), while the latter is apparently shortened. In contrast, in the (benzyne)chromium tricarbonyl complex (128) described in Section 1.2.3.2 [121], Cr(1) is 1.694(2) Å from the centroid of the arene ring, while Cr(2) is 1.751(3) Å from the arene ring centroid clearly indicating a shift of the Cr(2) atom away from the arene moiety. Each osmium atom in (252) is bonded to three carbonyls, and Os-C (carbonyl) distances range from 1.947(8) Å for Os(1)-C(23) to 1.875(7) Å for Os(3)-C(29).

This ferrocyn complex is the first example of a new type of arene structure. It is an analogue of the symmetrical benzyne intermediate proposed to account for the fluxionality of Os3(CO)9(PR)(C6H4) (R=Me, Et, Ph) (121) [131-133]. The energy difference between a symmetrical and an unsymmetrical structure is probably rather small, and it is intriguing that...
ferrocycyne is bound symmetrically yet benzyne is not. In the symmetrical (benzyne)chromium tricarbonyl complex (130) described in Section 1.2.3.2, which is based on a closed Ru$_3$ triangle, the Cr(CO)$_3$ fragment of the benzyne moiety lies above Ru(3) and, in fact, a Cr(1)-Ru(3) bond of length 2.920(1) Å is present [145]. The aryne ring is almost perpendicular to the Ru$_3$ plane in that molecule, and it almost bisects the Ru(1)-Ru(3) and Ru(2)-Ru(3) bonds (e.g. Ru(1)-C(1) 2.228(4), Ru(3)-C(1) 2.331(4) Å). Apparently, a two σ bonds and one π bond description of the interaction of C(1) and C(2) with Ru$_3$ is not very appropriate, it may better be described as two two electron-three center (2e-3c) bonds.

Complex (253) shows a $^{31}$P NMR resonance at -24.2 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of one phenyl group, sixteen ferrocenyl protons with one C$_5$H$_5$ ring, and two hydrides. The hydride chemical shifts and couplings are very similar to those of Os$_3$(CO)$_{10}$H$_2$[(C$_5$H$_4$P$_3$Pr$_2$)Fe(C$_5$H$_3$)] (275) which will be described in Section 4.7. The mass spectrum gives the parent ion at 1328 corresponding to the loss of one CO group from the parent. Thus the formula is established to be Os$_3$(CO)$_{10}$ (H)$_2$[(C$_5$H$_4$P$_3$FcPh)Fe(C$_5$H$_3$)], and a structure similar to that of (275), is proposed and shown in Figure 4.14.

Complex (254) shows a $^{31}$P NMR resonance at -33.3 ppm again suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of one phenyl group, sixteen ferrocenyl protons with only one C$_5$H$_5$ ring, and two hydrides. The hydrides are very similar to those of (275) and (253), so it seems that (254) is an isomer of (253). Possible diastereoisomeric structures are shown in Figure 4.14.

Complex (255) shows a $^{31}$P NMR resonance at 43.5 ppm suggesting the presence of a phosphido moiety. The $^1$H NMR spectrum shows the
presence of only seventeen ferrocenyl protons with two different C₅H₅ rings. The mass spectrum gives the parent ion at 1250 corresponding to the loss of one CO and one C₆H₆ molecule from the parent. In analogy with Os₃(CO)₉(μ-CO)(PRC₆H₄) (232) described in Section 2.3.2 [132], a proposed structure is shown in Figure 4.14.

![Figure 4.14 Proposed structures for complexes (253), (254), and (255).](image)

Complex (256) shows a ³¹P NMR resonance at -26.7 ppm suggesting the presence of a phosphine. The ¹H NMR spectrum shows the presence of a C₆H₄ moiety, two equivalent ferrocenyl groups, and a hydride. The mass spectrum gives the parent ion at 1300 corresponding to the loss of two CO groups from the starting material. Thus the complex likely has the formula Os₃(CO)₉(H)(PFc₂C₆H₄) and a likely structure is shown in Figure 4.15.

Complex (257) shows a ³¹P NMR resonance at 146.9 ppm suggesting the presence of a phosphido moiety and the ¹H NMR spectrum, Figure 4.16, shows the presence of a phenyl group, two ferrocenyl moieties with two different C₅H₅ rings, and a hydride. The mass spectrum gives the parent
ion at 1274 corresponding to the loss of three carbonyls from the parent. All these data are consistent with a formula such as Os$_3$(CO)$_8$(H)(PFcPh) [(C$_5$H$_3$)Fe(C$_5$H$_5$)] and a proposed structure is shown in Figure 4.15. The stereochemistry at the P atom is unknown, but a comparison of its ferrocenyl proton resonances with those of the two isomers of Ru$_3$(CO)$_7$(PFcPh)(PPh$_2$) (C$_6$H$_4$) ((359) and (360)) which will be described in Section 5.7 favors the one with the Fc group pointing towards the ferrocycne side of the Os$_3$ plane. Also, a ferrocycne with the FeCp moiety pointing towards the third osmium atom is unlikely.

Complex (258) is characterized to be an isomer of (257). The $^{31}$P NMR resonance at 150.2 ppm and the $^1$H NMR spectrum showing the presence of one phenyl group, two ferrocenyl moieties with two different C$_5$H$_5$ rings, and a hydride, are very similar to those of (257). The mass spectrum is virtually identical to that of (257). A comparison of its ferrocenyl proton resonances with those of (360) suggests (258) to be an isomer of (257) with the phenyl group pointing towards the ferrocycne side of the Os$_3$ plane, as shown in Figure 4.15.

Complex (259) shows a $^{31}$P NMR resonance at -13.9 ppm indicating

Figure 4.15 Possible structures for complexes (256), (257), and (258).
that all the original P-C bonds are intact. The $^1$H NMR spectrum which shows the presence of a C$_6$H$_4$ moiety, two equivalent ferrocenyl groups, and a hydride, is consistent with a formula such as Os$_3$(CO)$_2$(H)(PFc$_2$C$_6$H$_4$). The mass spectrum gives the parent ion at 1330 suggesting the presence of ten CO groups. A structure similar to (243), which has been described in Section 4.1, is proposed and shown in Figure 4.17.

Complex (260) shows a $^{31}$P NMR resonance at -15.8 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of a phenyl group, seventeen ferrocenyl protons with only one C$_5$H$_5$ ring, and a hydride. The mass spectrum gives the parent ion at 1300 corresponding to the loss of two CO groups from the parent. This is consistent with the structure proposed in Figure 4.17.

![Figure 4.16 300 MHz $^1$H NMR spectrum of complex (257).](image)
Figure 4.17 Possible structures for complexes (259) and (260).

Complex (261) shows a $^{31}$P NMR resonance at -20.4 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum, Figure 4.18, shows the presence of one phenyl group, sixteen ferrocenyl protons with only one C$_5$H$_5$ ring, and two hydrides. The hydride chemical shifts and couplings are very similar to those of (245) described in Section 4.2. The mass spectrum gives the parent ion at 1274 corresponding to the loss of three CO groups from the parent. These data suggest a formula such as Os$_3$(CO)$_8$(H)$_2$[[C$_5$H$_3$PFcPh]Fe(C$_5$H$_4$)] and it was confirmed by an X-ray diffraction study. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.19.

Crystal data: (261)·0.5CH$_2$Cl$_2$, fw=1315.29, orange, prism, triclinic system, space group P1 (#2), a=13.878(2), b=14.145(3), c=10.698(2) Å, $\alpha$=104.28(1), $\beta$=101.88(1), $\gamma$=63.91(1)*, V=1816.4(5) Å$^3$, Z=2, D$_{calc}$=2.405 g/cm$^3$, R=0.027, R$_w$=0.028.

The molecular structure of (261) is very similar to that of (245) described earlier in Section 4.2 except that here a ferrocenyl group
replaces one of the two phenyl groups in (245). It consists of a closed Os$_3$ triangle with one face capped by a phosphine and a doubly metalated ferrocenyl moiety; there is also an iron-osmium bond. Two Os-Os bonds are each bridged by a hydride which was located in the structure refinement. As in (245), the Os(1)-Os(2) bond at 3.0675(7) Å is the longest and Os(1)-

Figure 4.18 500 MHz $^1$H NMR spectrum of complex (261).
Figure 4.19 ORTEP diagram of complex (261).

Os(3) at 2.8488(6) Å is the shortest, and these are bridged by the hydrides. The Os(2)-Os(3) bond has an intermediate length of 2.8876(7) Å. The Os(1)-C(14) (2.065(6) Å) and Os(3)-C(9) (2.148(6) Å) lengths are typical of Os-alkyl σ bonds. This Fe(1)-Os(1) bond at 2.830(1) Å is also one of the shortest Fe (ferrocene)-M bonds known [316-323]. This interaction makes the Fe(1)-C(9) bond at 2.134(5) Å significantly longer than the other Fe(1)-C (Cp(1)) bonds (av. 2.037 Å), and the Fe(1)-C(14) bond at 1.964(6) Å significantly shorter than the other Fe(1)-C (Cp(2)) bonds (av. 2.061 Å). The Cp(1) and Cp(2) rings make angles of 78.10 and 80.32° respectively with the Os₃ plane. P(1) is almost coplanar with the C(29)-C(34) plane (0.0067 Å away) and the Cp(1) plane (0.0350 Å towards Fe(1)), but is
0.3455 Å away from the Cp(3) plane. Os(3) is displaced 0.6043 Å away from the Cp(1) plane. The Fe(1)-Os(1) bond is almost perpendicular to the Os₃ plane and as a result Os(1) is displaced 1.2374 Å away from the Cp(2) plane. The interaction of the doubly metalated ferrocenyl moiety with the Os₃ metal framework makes the Cp(1) and Cp(2) rings slightly staggered as shown by the torsion angle Os(1)C(14)Os(3)C(9) of 10.3(3)°, while the Cp(3) and Cp(4) shows the more usual eclipsed configuration. However the Cp(1) and Cp(2) rings have an even smaller ring tilt angle (2.24°) than the Cp(3) and Cp(4) rings (5.93°). As noted for (245), the two carbonyls bonded to Os(1) have significantly shorter Os-C bonds (av. 1.844 Å) than the other carbonyls (av. 1.902 Å).

Complex (262) shows a ³¹P NMR resonance at -22.0 ppm also suggesting the presence of a phosphine. The ¹H NMR spectrum shows the presence of a phenyl group, sixteen ferrocenyl protons with only one C₅H₅ ring, and two hydrides at -12.16 (Jₜₚ = 3.87 Hz) and -17.05 ppm (Jₜₚ = 12.97 Hz), very similar to that of (261). The mass spectrum is virtually identical with that of (261). Since in (261) both the P(1) center and the ferrocenyl moiety are chiral, two diastereoisomers are possible, and clearly (262) is a diastereoisomer of (261).

The last compound to be isolated, complex (263), shows a ³¹P NMR resonance at 39.3 ppm suggesting the presence of a phosphine/phosphido moiety. The ¹H NMR spectrum, Figure 4.20, shows the presence of seventeen ferrocenyl protons with only one C₅H₅ ring. The mass spectrum gives the parent ion at 1222 corresponding to the loss of one Ph and two CO groups from the parent. A formula such as Os₃(CO)₉[(C₅H₄PFc)Fe(C₅H₄)] seems likely. The presence of only nine carbonyls rather than ten indicates that there is probably some Os-C (Cp ring) π or Fe-Os interaction. An X-ray
Figure 4.20 400 MHz $^1$H NMR spectrum of complex (263).

crystallographic study was undertaken to unambiguously establish the structure. An ORTEP view of the molecule with 32.0% probability thermal ellipsoids is shown in Figure 4.21.

Crystal data: $\text{fw}=1222.71$, red brown, prism, triclinic system, space group P1 (#2), $a=12.304(1)$, $b=12.336(2)$, $c=10.886(2)$ Å, $\alpha=115.38(2)$, $\beta=92.34(1)$, $\gamma=91.76(1)^\circ$, $V=1489.5(5)$ Å$^3$, Z=2, $D_{\text{calc}}=2.726$ g/cm$^3$, $R=0.036$, $R_w=0.038$.

The structure consists of a closed Os$_3$ triangle capped on one face by a phosphido moiety and a hetero-annular metalated ferrocenyl fragment. The phosphido bridged Os(2)-Os(3) bond at 2.8041(5) Å is shorter than both Os(1)-Os(2) at 2.8984(9) Å and Os(1)-Os(3) at 2.8845(8) Å which are almost equal. The phosphido bridge is close to symmetrical (P(1)-Os(2) 2.337(2) Å, P(1)-Os(3) 2.356(2) Å). Os(1) is $\sigma$ bonded to the metalated
carbon C(6) (2.051(9) Å) and is also bonded to Fe(1) (2.994(2) Å) in an almost axial position. This Fe(1)-Os(1) bond is much longer than those found in complexes (245), (261), (269), (278), (308), and (329) (Sections 4.2, 4.5, 4.7, 4.11, and 4.13, respectively), but it is considerably shorter than the Fe-Ru bond in complex (162) [120]. Each osmium is bonded to three CO groups, one axial and two equatorial. The carbonyls C(21) and C(23) are semi-bridging between Os(1)-Os(3) and Os(1)-Os(2) respectively as judged by the following bonding parameters [325]: Os(1)-C(21)-O(1) 162.2(8)°, Os(3)-Os(1)-C(21) 63.1(3)°, Os(3)•••C(21) 2.65(1) Å; Os(1)-C(23)-O(3) 167.1(9)°, Os(2)-Os(1)-C(23) 66.0(3)°, Os(2)•••C(23) 2.75(1) Å. These
two semi-bridging carbonyls (Os(1)-C(21) 1.963(9), Os(1)-C(23) 1.93(1) Å) and two axial carbonyls (Os(2)-C(26) 1.95(1), Os(3)-C(29) 1.94(1) Å) have the longest Os-C (carbonyls) lengths, while Os(1)-C(22) is much shorter at 1.85(1) Å, and the rest average to 1.90 Å. P(1) is displaced 0.3831 and 0.1116 Å away respectively from the Cp(1) and Cp(3) planes. Os(1) is also out of the Cp(2) plane by 0.9978 Å. The Cp(1) and Cp(2) rings are slightly opened up (ring tilt angle 8.83°) compared to the Cp(3) and Cp(4) rings (ring tilt angle 3.20°), this is also indicated by the Cp(1)-Fe(1)-Cp(2) angle (168.4(3)°). This slight opening up of the Cp(1) and Cp(2) rings makes the Fe(1)-C(1) bond (2.105(9) Å) longer than the other Fe-C (Cp(1)) bonds (av. 2.05 Å), and the Fe(1)-C(6) bond (1.97(1) Å) shorter than the other Fe-C (Cp(2)) bonds (av. 2.07 Å). The Cp(2) and Cp(1) rings make angles of 58.12 and 49.42° respectively with the Os₃ plane. The Os(2)Os(3)P(1) plane is perpendicular to the Os₃ plane (90.14°).

The possible reaction pathways for the formation of complexes (239), (240), and (252) to (263) from Os₃(CO)₁₁(PFc₂Ph) are outlined in Schemes 4-1 to 4-4. In all the schemes, those complexes labelled by letters have not been isolated or characterized.

Movement of the phosphine to an axial position gives A, Scheme 4-1, which can oxidatively add a phenyl C-H bond to give (259). (259) loses a CO to afford (256) or loses a ferrocene molecule to afford (240). In analogy with the reaction scheme proposed to account for the pyrolysis of Os₃(CO)₁₁(PPh₂R) (R=Me, Et, Ph) (Scheme 2-4 in Section 2.3.2) [132, 133], (256) may lead to (240) via CO addition and ferrocene elimination. (240) loses a CO to give the benzyne complex (239). Interestingly, no complex B is isolated, in contrast with the pyrolysis of Os₃(CO)₁₂ and AsFc₂Ph to be described in Section 4.12. Complexes (239), (240), (256), and (259) were
produced only in low yields indicating that phenyl C-H activation in A is only a minor reaction pathway.

Intermediate A can also undergo hetero-annular ferrocenyl C-H activation to give C, Scheme 4-2, which can then undergo a number of different reactions. It can reductively eliminate a benzene molecule to afford E which expels a further CO with the concomitant formation of a Fe-Os bond to give (263). C can lose a CO to give D via ferrocenyl C-H activation and (260) via Fe-Os bond formation. A further CO loss from D
Scheme 4-2 A possible reaction sequence for the pyrolysis of 
\[ \text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph}) \].

accompanied by Fe-Os bond formation gives (261) and (262). A ferrocenyl C-H activation in (260) also results in the formation of (261) and (262). (260) can reductively eliminate a benzene molecule to give (263). Finally, C can lead to (253) and (254) by opening the cluster and further activating a hetero-annular C-H bond.
In other pathways, A can undergo ferrocenyl orthometalation to give F (Scheme 4-3), or H (Scheme 4-4) depending on the orientation of the FeCp moiety attached to the metalated Cp ring. In F the FeCp moiety points away from the Os(CO)$_4$ center, thus rendering its further reactions (Scheme 4-3) entirely analogous to those of the orthometalated phenyl complex (259) (Scheme 4-1). F loses a CO to give G and loses a benzene molecule to afford (255). G may also lead to (255) by a reaction analogous to that of

![Scheme 4-3](image)

Scheme 4-3 A proposed reaction sequence for the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph})$. 

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the phenyl derivative (256) (Scheme 4-1). A further CO loss from G results in the formation of (257) and (258), while CO loss from (255) leads to the ferrocene complex (252). It should be noted that complexes (257) and (258) have a closed structure as the mass spectra suggest, while complex B (Scheme 4-1) most likely has an open structure in accord with other similar complexes such as (318) to be described in Section 3.12.

Intermediate H which has the FeCp moiety pointing towards the Os(CO)₄ center behaves rather differently, Scheme 4-4. Reductive elimination of a benzene molecule may occur in H to give (255). H can lose

Scheme 4-4 A proposed reaction sequence for the pyrolysis of Os₃(CO)₁₁(PFc₂Ph).
a CO to give I and/or J depending on whether Fe-Os bond formation or hetero-annular metalation takes place first. Both I and J are probably unstable intermediates and they lose a CO to give (261) and (262).

Overall, Schemes 4-1 to 4-4 give a satisfactory explanation for the pyrolysis of \( \text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph}) \). Unlike that of \( \text{Os}_3(\text{CO})_{11}(\text{PFcPh}_2) \) discussed in Section 4.1, pyrolysis of \( \text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph}) \) is dominated by ferrocenyl C-H activation with both hetero-annular and orthometalation occurring. From these results, it seems that ferrocenyl C-H activation is more or less as facile as phenyl C-H activation. It should be noted, however, that P-C (phenyl) cleavage is more facile than P-C (ferrocenyl) cleavage. For example, C, F, G, H and (260) all undergo P-C (phenyl) cleavage not P-C (ferrocenyl) cleavage when there is a choice. Complexes (259) and (256) do undergo P-C (ferrocenyl) cleavage to give (240). The isolation of (257) and (258) but not B, which was somewhat unexpected, can be attributed to the more facile C-H activation of the ferrocenyl groups compared to that of the phenyl group.

### 4.4 Pyrolysis of \( \text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \)

Pyrolysis of \( \text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \) in octane for 19.5 h affords many products as shown by TLC, but unfortunately all were in low yields. Purification proved to be difficult and therefore only a limited number of complexes were characterized. The complexes (252), (253), (254), (261), and presumably (255) were produced as in the pyrolysis of \( \text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph}) \) described in the above section, however only traces of (254) was found, and (262) was not detected. These complexes were identified by
TLC, $^{31}$P, and $^1$H NMR spectroscopy. Their characterization has been described in the above section. The characterization of three new complexes, (264) to (266), is described below.

Complexes (264) and (265) are likely to be isomers since they have similar $^{31}$P and hydride NMR resonances. The $^{31}$P NMR chemical shifts and the splitting pattern of the hydride suggest the presence of a phosphine in each complex. Although the $^1$H NMR spectrum cannot be readily interpreted, only one C$_5$H$_5$ singlet is present for each complex. The hydride chemical shifts and couplings are very similar to those of complex (244) obtained from Os$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ which was described in Section 4.2, thus a structure such as is shown in Figure 4.22 is proposed. The chirality of one of the osmium atoms presumably gives rise to the isomerism.

Complex (266) shows two $^{31}$P NMR resonances at -22.6 and -30.0 ppm suggesting the presence of two phosphines. The mass spectrum gives the parent ion at 1785 corresponding to the loss of one CO from the parent compound. A plausible structure is shown in Figure 4.22.

Most of the pyrolysis products contain only one phosphine indicating that one PFc$_2$Ph ligand is easily lost from the parent compound. This behaviour is different from the pyrolysis of Os$_3$(CO)$_{10}$(PFcPh$_2$)$_2$ described in Section 4.2 which tends to retain both phosphines. Since PFc$_2$Ph is more electron donating than PFcPh$_2$, this difference must be attributed to the fact that PFc$_2$Ph ligand (cone angle 167°) is more bulky than PFcPh$_2$ (cone angle 156°) thus encouraging its dissociation [250]. It would be of great interest to study the pyrolysis of similar complexes such as Os$_3$(CO)$_{10}$(PFc$_2$Ph)(PMe$_2$Ph), Os$_3$(CO)$_{10}$(PFcPh$_2$)(PFciPr$_2$), and Os$_3$(CO)$_{10}$(PMe$_3$)(PPh$_3$) in which the two ligands are different in C-H and C-P bond metatation reactivities, and in cone angles.
Figure 4.22 Possible structures for complexes (264), (265), and (266).

4.5 Pyrolysis of Os₃(CO)₁₁(PEt₂Fc)

Pyrolysis of Os₃(CO)₁₁(PEt₂Fc) in octane for 8 h affords two major and two minor products as revealed by TLC, ³¹P, and ¹H NMR spectroscopy. The characterization of these four complexes, (267) to (270), is described below. For convenience, the characterization of (269) is described first.

The molecular formula Os₃(CO)₈(H)₂[(C₅H₃PEt₂)Fe(C₅H₄)] is established for complex (269) on the basis of the spectroscopic and analytical data and by comparing them with those of (245), (261), (278), and (308) (Sections 4.2, 4.3, 4.7, and 4.11, respectively). A ³¹P NMR resonance at -22.7 ppm suggests that all P-C bonds are intact. The ¹H NMR spectrum, Figure 4.23, shows the presence of two ethyl groups, seven ferrocenyl protons with no C₅H₅ ring, and two characteristic hydrides derived from the ferrocenyl moiety. The mass spectrum gives the parent ion at 1068 corresponding to the loss of three CO groups from the parent. The structure
Figure 4.23 200 MHz $^1$H NMR spectrum of complex (269).

Figure 4.24 ORTEP diagram of complex (269a).
of (269) was confirmed by an X-ray diffraction study. Interestingly, two different forms of crystals of (269) were found and they were obtained from the same solvent. A stereoview of (269a) with 33.0% probability thermal ellipsoids from the triclinic system and an ORTEP diagram of (269b) with 32.0% probability thermal ellipsoids from the monoclinic system are shown in Figures 4.24 and 4.25, respectively.

Crystal data: (269a), fw=1068.81, red orange, prism, triclinic system, space group P1 (#2), a=15.653(1), b=15.799(1), c=11.257(1) Å, α=90.388(7), β=109.740(6), γ=82.445(6)°, V=2595.4(4) Å³, Z=4, D_calc=2.735 g/cm³, R=0.033, R_w=0.031. (269b), fw=1068.81, red orange, prism, monoclinic system, space group P2₁/n (#14), a=9.889(2) b=13.642(3),
c=18.927(4) Å, β=97.36(9)°, V=2532.3(9) Å³, Z=4, D_{calc}=2.803 g/cm³, R=0.037, R_w=0.036.

Since the structure and bonding parameters of the two molecules are very close, metrical remarks will be confined to the structure (269b) from the monoclinic system. The structure is very similar to those of (245), (261), (278), and (308) (Sections 4.2, 4.3, 4.7, and 4.11, respectively). It consists of a closed Os₃ triangle capped on one face by an axially bound phosphine and a doubly metalated ferrocenyl moiety. Both Os(2) and Os(3) atoms are bonded to three terminal carbonyls and Os(1) to two. The Os-Os bonds show large variations with Os(1)-Os(2) bond at 3.0765(9) Å being the longest and Os(1)-Os(3) at 2.8274(7) Å being the shortest; the remaining Os(2)-Os(3) bond is of intermediate length at 2.8754(8) Å. The longest and shortest Os-Os bonds are each bridged by a hydride which was located crystallographically. Two ferrocenyl C-H bonds, an ortho- and a hetero-annular, are cleaved and a Fe-Os bond is established in forming (269) from the starting material. The Fe-Os bond length of 2.826(2) Å is similar to that found for the other compounds (245), (261), (278), (308).

The C(1)-Os(3) bond at 2.168(8) Å and C(6)-Os(1) bond at 2.08(1) Å are typical of C-Os σ bonds, but there is probably also some interaction between C(1) and Os(1) since this distance of 2.584(9) Å is not extreme. The Cp(1) plane makes an angle of 78.62° with the Os₃ plane. The two Cp rings have a very small ring tilt angle of 1.44° despite the C-Os and Fe-Os bonding interactions, and the two rings are slightly staggered with the torsion angle C(1)Os(3)Os(1)C(6) being 12.1(4)°. P(1) is almost coplanar with the Cp(1) ring (0.0118 Å away), and as for the other structures (245), (261), (278), and (308), the Fe(1)-C(1) bond at 2.120(8) Å is slightly longer than the other Fe(1)-C (Cp(1)) bonds (av. 2.044 Å), while the Fe(1)-C(6)
bond at 1.95(1) Å is slightly longer than the other Fe(1)-C (Cp(2)) bonds (av. 2.063 Å). Carbonyl C-Os and C-O bond distances are not unusual and all Os-C-O vectors are close to linear.

Complex (268) shows a $^{31}\text{P}$ NMR resonance at 22.3 ppm suggesting the presence of a phosphine or phosphido moiety. The $^1\text{H}$ NMR spectrum shows the presence of one ethyl group, a CH-CH$_2$ moiety, and a hydride. A comparison of these data with those of (230) obtained from Os$_3$(CO)$_{11}$ (PEt$_2$Ph) [127] suggests that they are identical, and the previously proposed structure is shown in Figure 4.26.

Complex (270) shows a $^{31}\text{P}$ NMR resonance at -20.7 ppm suggesting the presence of a phosphine, and the $^1\text{H}$ NMR spectrum shows the presence of two ethyl groups, eight ferrocenyl protons with one C$_5$H$_5$ ring, and a hydride. No mass spectrum was obtained, but a formula such as Os$_3$(CO)$_9$ (H)[(C$_5$H$_3$PEt$_2$)Fe(C$_5$H$_5$)] is more likely than one with ten carbonyls. A possible structure is shown in Figure 4.26.

Complex (267) shows a $^{31}\text{P}$ NMR resonance at -50.8 ppm, a highfield shift of 33.8 ppm from the parent compound, suggesting the presence of a phosphine. The mass spectrum gives the parent ion at 1096 corresponding

![Figure 4.26](image)

Figure 4.26 Possible structures for complexes (268) and (270).

243
Figure 4.27 200 MHz $^1$H NMR spectrum of complex (267).

to the loss of two carbonyls from the parent, and the analytical data are consistent with such a formulation. The $^1$H NMR spectrum, Figure 4.27, shows the presence of one ferrocenyl moiety, one ethyl group, one methyl group, and two hydrides presumably derived from the $\alpha$-position of one ethyl group. Pyrolysis of Os$_3$(CO)$_{11}$(PEt$_3$) affords H$_2$Os$_3$(CO)$_9$(Et$_2$PCMe) (227b) with the structure proposed as for H$_2$Os$_3$(CO)$_9$(Me$_2$PCH) (227a) described in Section 2.3.2 [263], and (267) is closely related. The $^1$H NMR spectrum of (267) is very similar to that of (227b), however the two hydride signals in (267) are sharp and well separated at room temperature indicating that the hydride exchange found in (227) is largely suppressed.
in (267). The resonances of the two α hydrogen atoms of the PEt group of (267) are non-equivalent since the P atom is chiral and are shifted downfield from those in Os₃(CO)₁₁(PEt₂Fc). The methyl group attached to the methylene carbon has a chemical shift of 2.24 ppm, a downfield shift of 1.14 ppm from that of the parent complex.

The structure of (267) is not obvious. Table 4-1 lists the chemical shifts and coupling constants of the hydride resonances for complexes (267), (227a), (227b), (228a), (228b), (271), (272), and also (269). From these data, it seems reasonable to assume that all these complexes, except (269), have a similar hydride arrangement.

For complex (227a), four types of hydride arrangements may be considered, Figure 4.28. Type (III) is symmetrical for (227a) and is not consistent with the inequivalency of the two hydrides. Type (IV) is not consistent with the almost equal \( j_{P-H} \) couplings since one hydride is three bonds and the other two bonds away from the P atom. Support for this statement is provided by complex (269) for which hydrides were located in the crystal structure. This complex shows a coupling of 4.4 Hz for the hydride that is three bonds away from the P atom and a coupling of 11.4

![Figure 4.28 Four types of hydride arrangement in complex (227a).](image-url)
Table 4-1 Hydride NMR resonances for complexes (227), (228), (267), (269), (271), and (272).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydride chemical shifts (ppm) and hydride-phosphorus couplings (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os$_3$(CO)$_9$(H)$_2$(Me$_2$PCH) (227a)$^a$</td>
<td>-15.75, $J$=10.8 \hspace{2cm} -20.08, $J$=6.2</td>
</tr>
<tr>
<td>Os$_3$(CO)$_9$(H)$_2$(Et$_2$PCMe) (227b)$^a$</td>
<td>-15.19, $J$=9.4 \hspace{2cm} -20.05, $J$=8.0</td>
</tr>
<tr>
<td>Os$_3$(CO)$_8$(PMe$_3$)(H)$_2$ (Me$_2$PCH) (228a)$^a$ isomer A</td>
<td>-15.68, $J$=11.2, 11.2 \hspace{2cm} -20.44, $J$=12.0, 8.0</td>
</tr>
<tr>
<td>Os$_3$(CO)$_8$(PMe$_3$)(H)$_2$ (Me$_2$PCH) (228a)$^a$ isomer B</td>
<td>-16.06, $J$=11.2, 11.2 \hspace{2cm} -19.25, $J$=24.7, 8.9</td>
</tr>
<tr>
<td>Os$_3$(CO)$_8$(PEt$_3$)(H)$_2$ (Et$_2$PCMe) (228b)$^a$</td>
<td>-15.30, $J$=10.0, 10.0 \hspace{2cm} -20.75, $J$=11.0, 9.0</td>
</tr>
<tr>
<td>(267)</td>
<td>-15.13, $J$=9.6 \hspace{2cm} -19.72, $J$=10.0</td>
</tr>
<tr>
<td>(271)</td>
<td>-14.82, $J$=9.9, 9.9 \hspace{2cm} -20.42, $J$=11.0, 11.0</td>
</tr>
<tr>
<td>(272)</td>
<td>-15.13, $J$=10.0, 10.0 \hspace{2cm} -20.60, $J$=11.0, 8.8</td>
</tr>
<tr>
<td>(269)</td>
<td>-12.22, $J$=4.4 \hspace{2cm} -17.39, $J$=11.4</td>
</tr>
</tbody>
</table>

$a$. Data taken from reference 263.
Hz for the one that is two bonds away. Type (II) is inconsistent with the fact that the two methyl groups in (227a) are found to be inequivalent, two methyl resonances are seen in the $^1$H NMR spectrum [263]. Moreover the hydride-phosphorus couplings observed for (227a), Table 4-1, are much larger than the ca. 4 Hz expected for a three bond coupling. Therefore, although Deeming [263] favours a type (IV) structure for (227a) and (227b), we prefer a type (I) hydride arrangement as this structure seems to be more consistent with the NMR data. Such double hydride bridge is known and the magnitude of the difference of hydride chemical shifts is not unreasonable [324].

If complex (267) has the same hydride arrangement as (227a) and (227b), two isomers are possible depending on whether the hydrides are syn to the Fc group or to the Et group and these are shown as A and B in Figure 4.29. It is possible that (267) is a rapidly interconverting mixture of these two isomers, but we prefer to believe that it has a structure with two hydrides syn either to the Fc or to the Et group with the latter being more likely since the hydride chemical shifts and couplings are very close to those of (227b). However, there is no rational explanation to account for the absence of the other isomer.

The relative yields of (267) and (269) from Os$_3$(CO)$_{11}$(PEt$_2$Fc) suggest

![Figure 4.29 Possible structures for complex (267).](image-url)
that C-H activation of ferrocenyl moiety is more facile than that of ethyl groups; both ferrocenyl and ethyl C-P cleavage reactions are not as facile as phenyl C-P cleavage. The good yield of (269) will allow its chemistry to be explored in future work. However, because of the ready formation of this complex, as yet unknown, but plausible, ferrocyne complexes such as HOs₃(CO)₉(µ-PEt₂)µ₃-(C₅H₃)Fe(C₅H₅) might have to be prepared by routes other than the pyrolysis of Os₃(CO)₁₁(PEt₂Fc).

Pyrolysis of Os₃(CO)₈(H)₂[(C₅H₃)PEt₂]Fe(C₅H₄)] (269) in decalin for 30 min gives a complex with a ³¹P NMR resonance at 164.0 ppm in ~10% yield and some very minor unidentified products, for example, those showing ³¹P resonances at 269.7, 250.8, 145.9, 52.0, -25.9, and -65.6 ppm. The complexes (267) and (270) were also present in trace quantities and these were identified on the basis of their known ¹H and ³¹P NMR spectra. Hydride resonances very similar to those of complexes (274) and (275) to be described in Section 4.7 are also observed. Clearly, pyrolysis of Os₃(CO)₁₁(PEt₂Fc) at higher temperatures should afford complexes containing phosphido, phosphinidene, and/or ferrocyne moieties.

The formation of complexes (267), (268), (269), and (270) from Os₃(CO)₁₁(PEt₂Fc) is illustrated in the reaction Schemes 4-5 to 4-8. Also shown are some other possible interesting complexes which might be obtained through pyrolysis at higher temperatures. In all the reaction schemes those complexes designated by letters have not been observed or isolated, but some end products such as H, K, and L are believed to be obtainable under appropriate conditions such as higher temperatures.

Movement of the phosphine from an equatorial to an axial position gives A, Scheme 4-5, which can undergo a number of different reactions.
Intermediate A can undergo alkyl C-H cleavage, but unlike i-propyl groups in which only β C-H cleavage occurs, an α C-H bond in the ethyl group is cleaved preferentially to give B, Scheme 4-5. As mentioned above, pyrolysis of Os₃(CO)₁₂ₓ(P_hex)ₓ (x=1, 2) affords only α C-H metalated products [263], supporting the proposed reaction sequence. B can undergo a further α C-H activation to give the isolated product (267). C-H activation of the Fc or Et group in B is unlikely, but reductive elimination of ethane or ferrocene to give C or D could occur with the latter being more likely.

Ferrocenyl hetero-annular C-H activation in A leads to E, Scheme 4-6. E can undergo an orthometalation in the C₅H₄P_hex ring to give F or form an iron-osmium bond to give G. A further CO loss from F leads to (269) by forming the iron-osmium bond. (269) can also be formed from G by ortho-

Scheme 4-5 A possible reaction sequence for the pyrolysis of Os₃(CO)₁₁(P_hexFc).
Scheme 4-6 A possible reaction sequence for the pyrolysis of Os₃(CO)₁₁(PEt₂Fc).

metalating the C₅H₄PEt₂ ring. E may undergo a further metalation on the metalated Cp ring to afford H. Reductive elimination of ethane from E is very unlikely.

Ferrocenyl orthometalation in A leads to I and I' differing in the orientation of the FeCp moiety relative to Os(CO)₄ metal center, Scheme 4-7. Intermediate I' (not shown in the Scheme) undergoes hetero-annular metalation/iron-osmium bond formation and/or iron-osmium bond formation/hetero-annular metalation to give (269), a sequence similar to that proposed for the pyrolysis of Os₃(CO)₁₁(PFc₂Ph) described in Section
Scheme 4-7 A possible reaction sequence for the pyrolysis of Os$_3$(CO)$_{11}$(PEt$_2$Fc).

4.3 (Scheme 4-4). Intermediate I can lose a CO to afford (270) which can lead to J by taking up one CO molecule and eliminating one ethane molecule, a reaction similar to that proposed for the pyrolysis of the phenyl analogue Os$_3$(CO)$_{11}$(PPh$_2$R) (R=Me, Et, Ph) [132, 133]. Under the present reaction conditions, ethane elimination does not seem to occur to give J, neither does the sp$^2$ C-P cleavage necessary to produce the ferrocyan complexes K and L.
Finally, Scheme 4-8 shows the possible pathways to form complex (268). A β C-H activation of the metalated ethyl group in D gives (268). Alternatively, (267) can reductively eliminate a ferrocene molecule to afford M which can then isomerize to (268). Reductive elimination of ethane from (267) is unlikely.

Scheme 4-8 A possible reaction sequence for the pyrolysis of Os₃(CO)₁₁(PEt₂Fc).

In summary, Schemes 4-5 to 4-8 accounts for the results of the pyrolysis of Os₃(CO)₁₁(PEt₂Fc). They are somewhat similar to those schemes proposed for the pyrolysis of Os₃(CO)₁₁(PFCiPr₂) to be discussed in Section 4.7 except that i-propyl groups undergo β C-H cleavage, while ethyl groups prefer α C-H cleavage.
4.6 Pyrolysis of Os₃(CO)₁₂ with PEt₂Fc in 1:2 molar ratio

When Os₃(CO)₁₂ is refluxed in p-xylene with PEt₂Fc in 1:2 molar ratio, major products (271) and (272) are formed. Both complexes show two ³¹P NMR resonances at similar chemical shifts. Their ¹H NMR spectra show the presence of two ferrocenyl groups, three ethyl groups, one methyl group, and two hydrides. The mass spectrum of (271) gives the parent ion at 1342 corresponding to the loss of two CO groups from the parent. These data are similar to those for H₂Os₃(CO)₈(PMe₃)(Me₂PCH) (228a) and H₂Os₃(CO)₈(PEt₃)(Et₂PCMe) (228b) [263] thus establishing the formulation as H₂Os₃(CO)₈(PEt₂Fc)(EtFcPCMe).

From Table 4-1 in the above section, it is clear that both complexes (271) and (272), which contain two phosphines, are very similar to isomer A of (228a) and to (228b). The two isomers of (228a) interconvert in solution. Deeming et al. [263] have considered three possible coordination sites for the PMe₃ ligand indicated as a, b, and c below, and suggest that the two isomers differ in the sites occupied by the phosphine PMe₃.

In solution, (271) and (272) do not equilibrate over several weeks at room temperature indicating that they do not differ in the sites of PEt₂Fc substitution. Since the hydrides couple to two phosphorus atoms approximately equally, the PEt₂Fc ligand must be bonded to the osmium
atom that is bridged by the two hydrides. One of the possible structures is shown in Figure 4.30. It should be noted that both the P and C atoms in (271) and (272) are chiral, and there are two diastereoisomers accounting nicely for the two isomers obtained.

Complex (273) shows two $^{31}$P NMR resonances at 48.3 and -8.0 ppm. The $^{1}$H NMR spectrum shows the presence of sixteen ferrocenyl protons with only one C$_5$H$_5$ ring, four ethyl groups, and two hydrides. Since the two hydride resonances are similar to those of Os$_3$(CO)$_{10}$(H)$_2$[(C$_5$H$_4$PR$_2$)Fe(C$_5$H$_3$)] (R$_2$=FcPh) ((253) and (254)) described earlier in Section 4.3 and (R$_2$=iPr$_2$) (275) which will be described in the next section, a plausible formula for (273) is Os$_3$(CO)$_9$(PEt$_2$Fc)(H)$_2$[(C$_5$H$_4$PEt$_2$)Fe(C$_5$H$_3$)] and a plausible structure is shown in Figure 4.30.

![Figure 4.30 Possible structures for complexes (271), (272), and (273).](image)

4.7 Pyrolysis of Os$_3$(CO)$_{11}$(PFc$i$Pr$_2$)

Pyrolysis of Os$_3$(CO)$_{11}$(PFc$i$Pr$_2$) in octane for 5 h affords four major products and five minor ones as judged by TLC, $^{1}$H, and $^{31}$P NMR
spectroscopy. One minor product showing a $^{31}$P NMR resonance at 36.7 ppm was not found in any of the fractions after column separation. The characterization of seven complexes, (274) to (280), is described below.

Complex (274) shows a $^{31}$P NMR resonance at 203.9 ppm suggesting the presence of a phosphinidene/phosphido moiety. The $^1$H NMR spectrum, Figure 4.31, shows the presence of eight ferrocenyl protons with one C$_5$H$_5$ ring, two intact i-propyl groups, and a hydride. The mass spectrum gives the parent ion at 1096 corresponding to the loss of three CO groups from the parent complex. On this basis a structure with a closed Os$_3$ framework
is proposed and is shown in Figure 4.33. This complex is analogous to complexes (257) and (258) previously described in Section 4.3, and to (303) and (304) which will be described in Section 4.11.

Complex (275) shows a $^{31}$P NMR resonance at 0.0 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum, Figure 4.32, clearly shows

Figure 4.32 300 MHz $^1$H NMR spectrum of complex (275).
the presence of seven ferrocenyl protons from \( \text{C}_5\text{H}_4 \) and \( \text{C}_5\text{H}_3 \) rings, two intact i-propyl groups, and two hydrides. The NMR pattern of the ferrocenyl protons and hydrides of this complex is rather different from those of the series of complexes \( \text{Os}_3(\text{CO})_8(\text{H})_2[(\text{C}_5\text{H}_3\text{PRR}_1)\text{Fe}(\text{C}_5\text{H}_4)] \) (\( \text{RR}_1=\text{Ph}_2 \)) (245), \( \text{FcPh} \) (261), \( \text{Et}_2 \) (269), and \( \text{iPr}_2 \) (278)) (Sections 4.2, 4.3, 4.5, and 4.7, respectively). The mass spectrum gives the parent ion at 1154 corresponding to a formula such as \( \text{Os}_3(\text{CO})_{10}(\text{H})_2[(\text{C}_5\text{H}_4\text{PiPr}_2)\text{Fe}(\text{C}_5\text{H}_3)] \). A possible structure is shown in Figure 4.33. This complex is similar to (253) and (254) described earlier in Section 4.3. One CO group might also be bridging the open Os...Os edge.

Complex (276) shows a relatively broad \( ^3\text{P} \) NMR resonance at 73.2 ppm suggesting the presence of a phosphido moiety. The \( ^1\text{H} \) NMR spectrum shows the presence of one i-propyl group, eight ferrocenyl protons with a \( \text{C}_5\text{H}_5 \) ring, and two broad hydride resonances. The mass spectrum gives the parent ion at 1082 corresponding to the loss of one i-propyl and two CO

\[
\begin{align*}
\text{Os} & \quad \text{Fe} \\
\text{(CO)}_3 & \quad \text{H} \\
\text{(CO)}_3 & \quad \text{P}\text{Pr}_2 \\
\text{(CO)}_2 & \quad \text{Os} \\
\text{Os} & \quad \text{Os} \\
\text{(CO)}_3 & \quad \text{H} \\
\text{(CO)}_3 & \quad \text{H} \\
\text{P}\text{Pr}_2 & \quad \text{Os} \\
\text{Os} & \quad \text{Os} \\
\text{(CO)}_3 & \quad \text{H} \\
\text{(CO)}_3 & \quad \text{H} \\
\text{P}\text{Pr}_2 & \quad \text{Os} \\
\end{align*}
\]

(274)  (275)  (276)

Figure 4.33 Proposed structures for complexes (274), (275), and (276).
groups from the parent. A formula such as $\text{Os}_3(\text{CO})_9(\text{H})_2[(\text{C}_5\text{H}_3\text{P}^i\text{Pr})\text{Fe}(\text{C}_5\text{H}_5)]$ is very likely and a probable structure is shown in Figure 4.33.

Complex (277) shows a $^{31}$P NMR resonance at 14.3 ppm. The $^1$H NMR spectrum shows the presence of one i-propyl group and eight ferrocenyl protons with one $\text{C}_5\text{H}_5$ ring. The mass spectrum gives the parent ion at 1108 indicating the loss of one CO and one propane molecule from the parent and corresponding to a formula such as $\text{Os}_3(\text{CO})_{10}[(\text{C}_5\text{H}_3\text{P}^i\text{Pr}_2)\text{Fe}(\text{C}_5\text{H}_5)]$. Thus complex (277) presumably has the structure shown in Figure 4.36.

Complex (278) shows a $^{31}$P resonance at 2.5 ppm suggesting the
presence of a phosphine. The $^1$H NMR spectrum, Figure 4.34, shows the presence of two intact i-propyl groups, seven ferrocenyl protons with no C$_5$H$_5$ ring, and two hydrides. The mass spectrum gives the parent ion at 1096 corresponding to the loss of three CO groups from the parent. The structure was established by X-ray crystallography. An ORTEP view of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.35.

Crystal data: fw=1096.86, red orange, irregular, triclinic system, space group P1 (#2), a=10.26(2), b=15.53(2), c=9.84(2) Å, $\alpha$=98.21(2), $\beta$=117.85(2), $\gamma$=98.59(2)$^\circ$, $V$=1330.2(6) Å$^3$, Z=2, D$_{calc}$=2.738 g/cm$^3$, R=0.025, R$_w$=0.025.

The structure is another example of the series Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_3$PRR$_1$)Fe(C$_5$H$_4$)] (RR$_1$=Ph$_2$ (245), FcPh (261), Et$_2$ (269), EtFc (308)) (Sections 4.2, 4.3, 4.5, and 4.11, respectively) and it contains a strong Fe-Os

Figure 4.35 ORTEP diagram of complex (278).
bond (2.858(1) Å). The important bonding parameters are listed below:

Os(1)-Os(2) 3.075(1), Os(1)-Os(3) 2.8398(7), Os(2)-Os(3) 2.861(1), Os(1)-
C(6) 2.067(5), Os(3)-C(1) 2.173(5), Os(2)-P(1) 2.419(1), Os(1)-C(17)
1.869(6), Os(1)-C(18) 1.851(6), the other Os-C (carbonyl) av. 1.916 Å, P(1)-
C(2) 1.817(5), P(1)-C(11) and P(1)-C(14) av. 1.869 Å, Fe(1)-C(1) 2.123(5),
the other Fe(1)-C (Cp(1)) av. 2.052 Å, Fe(1)-C(6) 1.977(5), the other Fe(1)-C
(Cp(2)) av. 2.070 Å, Cp(1)-Cp(2) ring tilt angle 1.26°, Cp(1)-Os3 planes
80.14°, Cp(2)-Os3 planes 78.92°, Os(1), Os(2), Os(3), and P(1) are -2.0299, -
0.5358, 0.7647, and 0.0680 Å away respectively from the Cp(1) plane,
Os(1) is 1.2242 Å away from the Cp(2) plane, C(1)Os(3)Os(1)C(6) torsion
angle 5.1(3)°. The longest Os(1)-Os(2) and shortest Os(1)-Os(3) bonds are
each bridged by a hydride which was located crystallographically.

Complex (279) shows a 31P resonance at 11.2 ppm suggesting the
presence of a phosphine. The 1H NMR spectrum, Figure 4.37, shows the
presence of eight ferrocenyl protons with one C5H5 ring, two intact i-propyl
groups, and a hydride. The mass spectrum gives the parent ion at 1124
corresponding to the loss of two carbonyls from the parent. Thus a formula
such as Os3(CO)9(H)[(C5H3Pr2) Fe(C5H5)] is very likely and a probable
structure is shown in Figure 4.36. The alternative FeCp orientation relative
to the C5H3 ring is believed to lead to complex (278) since the FeCp moiety
is in close proximity with the third osmium atom thus allowing a hetero-
annular ferrocenyl C-H activation and iron-osmium interaction to occur
readily.

Complex (280) was not obtained in sufficient quantity to allow its 31P
NMR spectrum to be recorded. The 1H NMR spectrum clearly shows the
presence of two intact i-propyl groups, eight ferrocenyl protons with no
C5H5 ring, and a hydride. The mass spectrum gives the parent ion at 1152
Figure 4.36 Possible structures for complexes (277), (279), and (280).

Figure 4.37 400 MHz $^1$H NMR spectrum of complex (279).
indicating that only one CO is lost in forming (280) from the starting material. A plausible structure is shown in Figure 4.34.

The last band contained a mixture, and a $^{31}$P NMR resonance at 287.0 ppm was observed, this chemical shift suggests the presence of a PFc or PPr moiety. Possible formulae include $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{PFc})$, $\text{Os}_3(\text{CO})_9(\text{PPr})[\text{(C}_5\text{H}_3)\text{Fe(C}_5\text{H}_5)]$ or $\text{Os}_3(\text{CO})_8(\text{H})_2(\text{PPr})[(\text{C}_5\text{H}_3)\text{Fe(C}_5\text{H}_5)]$. The absence of any hydride resonances favors the second alternative.

Schemes 4-9 to 4-11 are proposed to account for the formation of these isolated products from $\text{Os}_3(\text{CO})_{11}(\text{PFcPr}_2)$. Those complexes designated by letters have not been isolated or characterized. Complexes L, E, and G are interesting end products that may be formed in undetected quantity or under different reaction conditions.

Movement of the equatorial PFcPr$_2$ ligand to an axial position gives A, Scheme 4-9. Ferrocenyl hetero-annular C-H activation in A affords (280) which leads to (275) by a further hetero-annular C-H activation. It can lead to (278) by orthometalation and formation of a Fe-Os bond, a process similar to that proposed for the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph})$ (Scheme 4-3). (278) may also be formed from intermediate B' via intermediates K and/or J.

Orthometalation of the ferrocenyl moiety in A gives B, Scheme 4-10, and B', Scheme 4-9, depending on whether the FeCp fragment points away or towards the Os(CO)$_4$ moiety. Scheme 4-10 shows possible transformations of B. It can lose one CO to give (279), a process well known for orthometalated phenyl analogues, or it might reductively eliminate a propane molecule to give (277). Complex (277) may also be formed from (279). This suggestion is based on studies of complexes of the type
Os₃(CO)₁₁(PPh₂R) [132, 133]. (277) may lose a CO to afford L, and (279) loses a CO to give (274).

Intermediate A could also undergo i-propyl β C–H activation, a process observed in the pyrolysis of Ru₃(CO)₁₀Fc'(PiPr₂)₂ to be discussed in Section 5.9 and Os₃(CO)₁₀Fc'(PiPr₂)₂ to be discussed in Section 4.13, to give

Scheme 4-9 A possible reaction sequence for the pyrolysis of Os₃(CO)₁₁(PFc'iPr₂).
Scheme 4-10 A possible reaction sequence for the pyrolysis of Os₃(CO)₁₁(PFciPr₂).

C which easily loses a propene molecule to give D and D', Scheme 4-11. It seems that D and D' interconvert readily since no D' and/or its successor complexes H or I are isolated. D can undergo ferrocenyl orthometalation to give (276) which is a major product isolated. E is not obtained, but it might be derived from (276) at higher temperatures. D might also undergo ferrocenyl hetero-annular metatation to give F and Fe-Os bond formation then leads to G.

Unlike the pyrolysis of Ru₃(CO)₁₀Fc'(PiPr₂)₂ to be discussed in Section
Scheme 4-11 A possible reaction sequence for the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PFc} \text{Pr}_2)_2$.

5.9 and $\text{Os}_3(\text{CO})_{10}\text{Fe'(PiPr}_2)_2$ to be discussed in Section 4.13 where $\text{sp}^3$ C-H and C-P cleavages are clearly dominating although $\text{sp}^2$ C-H and C-P cleavages do occur when such processes are not facile for analogous $\text{sp}^3$
bonds for steric considerations (e.g. inaccessibility), the pyrolysis of Os$_3$(CO)$_{11}$(PFc$^1$Pr$_2$) follows a different path. PFc$^1$Pr$_2$ is a monodentate ligand and the Fc moiety is as accessible to the metal center as the i-Pr groups. In this case sp$^2$ C-H activation becomes favored over sp$^3$ C-H activation. The formation of (275), (278), (279), and (280) all involves only sp$^2$ C-H cleavage, while that of (274) also involves sp$^2$ C-P cleavage in addition to sp$^2$ C-H cleavage. The formation of (277) does involve sp$^3$ C-P cleavage. The formation of (276) involves i-propyl β C-H activation as the first step and subsequent sp$^3$ C-P cleavage and sp$^2$ C-H cleavage. Activation of an i-propyl β C-H bond in B followed by elimination of propene to give (276) is not very likely. Such a process does not seem to occur for (280), nor does the reductive elimination of propane from (280). sp$^2$ C-H cleavage to form (275) and (278) from is likely to be a facile process. Ferrocenyl heteroannular C-H activation of D to give complexes such as Os$_3$(CO)$_9$(H)$_2$[(C$_5$H$_4$P$^i$Pr)Fe(C$_5$H$_4$)] (F) or Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$P$^i$Pr)Fe(C$_5$H$_4$)] (G) with an iron-osmium bond is possible but not observed. Pyrolysis of Os$_3$(CO)$_{11}$(PFc$^1$Pr$_2$) at higher temperatures might give the ferrocyne complexes (274), L, and E in good yields together with (275), (278), and some new complexes such as F and G.

4.8 Pyrolysis of Os$_3$(CO)$_{12}$ with PnBuFcPh

Pyrolysis of Os$_3$(CO)$_{12}$ with PnBuFcPh in 1:1 molar ratio in octane for 4 h affords numerous complexes as revealed by TLC, $^{31}$P, and $^1$H NMR spectroscopy. A number of these products were isolated by using chromatography and characterized by spectroscopic techniques. The
characterization of fourteen complexes, (281) to (294), is described in this section.

Complex (281) shows a $^{31}$P NMR resonance at 209.8 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum shows the presence of eight ferrocenyl protons with one $C_5H_5$ ring and one n-butyl group. The mass spectrum giving the parent ion at 1094 is consistent with a ferrocynne complex such as $\text{Os}_3(\text{CO})_9(P\text{nBu})[(\text{C}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_5)]$. By analogy with $\text{Os}_3(\text{CO})_9(\text{PFc})[(\text{C}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_5)]$ (252) described in Section 4.3, a likely structure is shown in Figure 4.38.

Complex (282) gives the parent ion at 1172 in the mass spectrum corresponding to the loss of two CO groups from the presumed precursor $\text{Os}_3(\text{CO})_{11}(\text{PnBuFcPh})$. A $^{31}$P NMR resonance at -91.8 ppm suggests the presence of a phosphine, and the $^1$H NMR spectrum shows the presence of one phenyl group, one n-butyl group, eight ferrocenyl protons with one $C_5H_5$ ring, and one hydride. Since only nine CO groups are present in the molecule, a $\eta^2$ bond between the orthometalated $C_5H_3$ ring with one

![Possible structures for complexes (281), (282), and (283).](image)

Figure 4.38 Possible structures for complexes (281), (282), and (283).
osmium atom is likely to be involved. Possible structures are shown in Figure 4.38.

Complex (283) shows a mass spectrum identical to that of (282), and its $^{31}\text{P}$ and $^1\text{H}$ NMR spectra are very similar to those of (282). Thus it is the diastereoisomer of (282) as shown in Figure 4.38. Without a structure determination, the absolute configurations of these two diastereoisomers cannot be established.

Complex (284) shows a $^{31}\text{P}$ NMR resonance at 59.4 ppm suggesting the presence of a phosphido moiety. The mass spectrum gives the parent ion at 1094 indicating the presence of nine CO groups and a phosphido moiety with n-butyl and ferrocenyl groups attached. The $^1\text{H}$ NMR spectrum shows the presence of one n-butyl group and eight ferrocenyl protons with no $C_5H_5$ ring. A formula such as Os$_3$(CO)$_9$[(C$_5H_4$PnBu)Fe(C$_5H_4$)] seems very likely. By analogy with complexes Os$_3$(CO)$_9$[(C$_5H_4$PFc)Fe(C$_5H_4$)] (263) described in Section 4.3 and Os$_3$(CO)$_9$[(C$_5H_4$PPh)Fe(C$_5H_4$)] (300) to be described in Section 4.10, an iron-osmium bond is likely to be present and a structure similar to that of (263) and (300) is shown in Figure 4.39.

![Figure 4.39 Possible structures for complexes (284) and (285).](image-url)
Complex (285) shows a $^{31}$P NMR resonance at 56.7 ppm suggesting the presence of a phosphido moiety. The $^1$H NMR spectrum shows the presence of one n-butyl group and eight ferrocenyl protons with one C$_5$H$_5$ ring. The mass spectrum and micro-analysis are consistent with a formula such as Os$_3$(CO)$_{10}$[(C$_5$H$_3$PnBu)Fe(C$_5$H$_5$)], and a structure similar to complex (277) described in the previous section is shown in Figure 4.39.

Complex (286) shows a $^{31}$P NMR resonance at -20.1 ppm suggesting the presence of a phosphine, and its $^1$H NMR spectrum suggests that the phosphine is intact. The mass spectrum establishes the complex as the simple monosubstituted product Os$_3$(CO)$_{11}$(PnBuFcPh). The phosphine is expected to occupy an equatorial coordination site.

Complex (287) shows a $^{31}$P NMR resonance at -10.1 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of one n-butyl group, one ferrocenyl group, a C$_6$H$_4$ moiety, and a hydride. The mass spectrum gives the parent ion at 1172 corresponding to a formula such as Os$_3$(CO)$_9$(H)(PnBuFcC$_6$H$_4$), and therefore a structure similar to that of (242) described in Section 4.1, Figure 4.40, is proposed.

Complex (288) shows $^1$H and $^{31}$P NMR spectra very similar to those of (287), and the mass spectrum is consistent with the formulation Os$_3$(CO)$_9$(PnBuFcPh). It is tempting to assign complex (288) as an isomer of (287), however that would require the Os-C σ bond and Os-C$_2$ η$^2$ bond to be non-fluxional which is unlikely. It is rather difficult to propose an alternative structure.

Complex (289) shows a $^{31}$P NMR resonance at -16.1 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of one phenyl group, one n-butyl group, seven ferrocenyl protons with no C$_5$H$_5$ ring, and two hydrides. The NMR pattern for the ferrocenyl protons
and hydrides is very similar to that of the series $\text{Os}_3(\text{CO})_8(\text{H})_2[(\text{C}_5\text{H}_3\text{PRR}_1)\text{Fe}(\text{C}_5\text{H}_4)]$ ($\text{RR}_1=\text{Ph}_2$ (245), $\text{FcPh}$ (261), $\text{iPr}_2$ (278), and $\text{Et}_2$ (269) (Sections 4.2, 4.3, 4.7, and 4.5, respectively). The mass spectrum gives the parent ion at 1144 consistent with such a formulation ($\text{RR}_1=\text{nBuPh}$). The two possible diastereoisomeric structures are shown in Figure 4.40.

Complex (290) shows $^{31}\text{P}$, $^1\text{H}$ NMR, and mass spectra very similar to those of (289), and its micro-analysis also supports the formulation $\text{Os}_3(\text{CO})_8(\text{H})_2[(\text{C}_5\text{H}_3\text{PnBuPh})\text{Fe}(\text{C}_5\text{H}_4)]$. This complex is thus the diastereoisomer of (289) due to chiralities of the phosphorus atom and the $\text{C}_5\text{H}_3$ plane. It should have one of the two structures shown in Figure 4.40. The absolute stereochemistry of these two complexes remains unknown in the absence of a structure determination.

Complex (291) shows a $^{31}\text{P}$ NMR resonance at 151.3 ppm suggesting the presence of a phosphido moiety. The mass spectrum gives the parent ion at 1388 suggesting a formula such as $\text{Os}_3(\text{CO})_7(\text{C}_6\text{H}_4)(\text{PnBuFc})_2$. The $^1\text{H}$ NMR spectrum shows the presence of a $\text{C}_6\text{H}_4$ moiety, two ferrocenyl groups, two $\text{n}$-butyl groups, further supporting the assignment. By analogy
with complex (246) described earlier in Section 4.2, two possible structures are shown in Figure 4.41.

Complex (292) shows two $^{31}$P NMR resonances at 164.6 and 133.5 ppm with a typical trans $^{31}$P-$^{31}$P coupling of 149 Hz, similar to those (247) described in Section 4.2, suggesting the presence of two phosphido moieties. The mass spectrum is identical to that of (291), while its $^1$H NMR spectrum shows the presence of a $C_6H_4$ moiety, two inequivalent ferrocenyl moieties, and two inequivalent n-butyl groups. A structure similar to (247) is shown in Figure 4.41.

![Figure 4.41 Possible structures for complexes (291) and (292).](image)

Complex (293) shows two $^{31}$P NMR resonances at -25.8 and -58.2 ppm suggesting the presence of two phosphines. A satisfactory mass spectrum was not obtained, but the analysis is consistent with the presence of two phosphines. The $^1$H NMR spectrum shows the presence of two phenyl groups, two ferrocenyl groups, one intact n-butyl group, one α doubly metalated n-butyl group, and two hydrides. The NMR pattern, especially that of the hydrides in terms of chemical shifts and coupling...
constants, is very similar to that of Os₃(CO)₈(H)₂(P₂Et₂Fc)(EtFcPCMe) ((271) and (272)) described earlier in Section 4.6, and therefore an analogous structure, Figure 4.42, is shown. The absolute configurations of the chiral carbon and phosphorus centers are unknown. Also the coordination site of the PnBuFcPh ligand is unknown, only one type is shown.

Complex (294) shows ¹H and ³¹P NMR spectra very similar to those of (293). As discussed previously in Section 4.6 for the P₂Et₂Fc complexes (271) and (272), this complex is believed to be the diastereoisomer of (293) due to the phosphorus and carbon center chiralities. The PnBuFcPh coordination site is unknown, and two structures showing one type of PnBuFcPh coordination site are shown in Figure 4.42.

\[
\text{Ph} \quad \overset{\text{P}}{\text{Fc}} \quad \overset{\text{C}}{\text{Pr}} \quad \overset{\text{Ph}}{\text{Os}} \quad \overset{\text{(CO)₃}}{\text{Os}} \quad \overset{\text{H}}{\text{Os}} \quad \overset{\text{CO}}{\text{C}} \quad \overset{\text{Os}}{\text{P}} \quad \overset{\text{H}}{\text{Os}} \quad \overset{\text{CO}}{\text{C}} \quad \overset{\text{Os}}{\text{P}} \quad \overset{\text{Ph}}{\text{Fc}} \quad \overset{\text{Pr}}{\text{nBuF}}
\]

(293) & (294)

Figure 4.42 Possible structures for complexes (293) and (294) showing one type of PnBuFcPh coordination site.

The formation of complexes (281)-(285) and (287)-(290) presumably involves the formation of the monosubstituted product Os₃(CO)₁₁(PₙBuFcPh) (286) as the first step; (291)-(294) are clearly derived from Os₃(CO)₁₀(PₙBuFcPh)₂ which could be formed during the reaction. Reaction schemes similar to those proposed for the pyrolysis of
Os₃(CO)₁₁(PFc₂Ph) discussed in Section 4.3 can be envisaged to account for the formation of (281)-(285) and (287)-(290) from (286), and similar reaction schemes can be envisaged to account for the formation of (291) and (292) from a disubstituted precursor. The formation of (293) and (294) presumably involves successive α C-H metalation of one n-butyl group in Os₃(CO)₁₀(PnBuFcPh)₂ each accompanied by a CO loss, similar to Scheme 4-5 proposed for the pyrolysis of Os₃(CO)₁₁(PEt₂Fc) discussed in Sections 4.5. It is fascinating that in the presence of competing phenyl groups which readily undergo orthometalation, the alkyl metation still takes place to give (293) and (294). Further work with this ligand and similar ones should be very interesting. In view of the formation of several pairs of diastereoisomers, it would be interesting in future work to study the pyrolysis of each enantiomer of PnBuFcPh with Os₃(CO)₁₂.

4.9 Pyrolysis of Os₃(CO)₁₂ with PtBu₂Fc

Pyrolysis of Os₃(CO)₁₂ with PtBu₂Fc in toluene for 6 h affords more than ten products with three in good yields. The most abundant one with a ³¹P NMR resonance at 58.6 ppm was not found in any fractions after column purification and presumably is a very polar compound. The characterization of five complexes, (295) to (299), is described below.

Complex (295) shows a ³¹P NMR resonance at 37.1 ppm suggesting the presence of a phosphido moiety or a phosphine. The ¹H NMR spectrum, Figure 4.43, shows the presence of eight ferrocenyl protons with no C₅H₅ ring, an intact t-butyl group, a β C-H metalated t-butyl group, and two hydrides. The mass spectrum gives the parent ion at 1154 corresponding
to a formula such as \( \text{Os}_3(\text{CO})_9(\text{H})_2[(\text{C}_5\text{H}_4\text{P}^\text{tBu})_2\text{Me}_2\text{CH}_2]\text{Fe(}\text{C}_5\text{H}_4)\)]. A proposed structure is shown in Figure 4.44.

Complex (296) shows a \(^{31}\text{P}\) NMR resonance at 310.5 ppm suggesting the presence of a phosphinidene moiety. The \(^1\text{H}\) NMR spectrum shows the presence of eight ferrocenyl protons with one \(\text{C}_5\text{H}_5\) ring, an intact \(\text{t-Bu}\) group, and two hydrides. A ferrocyne complex such as \(\text{Os}_3(\text{CO})_8(\text{H})_2(\text{P}^\text{tBu})[(\text{C}_5\text{H}_3)\text{Fe(}\text{C}_5\text{H}_5)\)] is most likely and such a formula is supported by the mass spectrum which gives the parent ion at 1068. A likely structure is shown in Figure 4.44.

Complex (297) shows a \(^{31}\text{P}\) NMR resonance at 62.8 ppm suggesting the presence of a phosphido moiety or a phosphine. The \(^1\text{H}\) NMR spectrum

Figure 4.43 300 MHz \(^1\text{H}\) NMR spectrum of complex (295).
Figure 4.44 Possible structures for complexes (295) and (296).

shows the presence of eight ferrocenyl protons with no C₅H₅ ring, two intact t-butyl groups, and a hydride. A formula such as Os₃(CO)₉(H) [(C₅H₄P₅Bu₂)Fe(C₅H₅)] is most likely since the hydride chemical shift is very similar to that in Os₃(CO)₉(H) [(C₅H₄PFCPh)Fe(C₅H₅)] (260) described in Section 4.3, but not Os₃(CO)₁₀(H) [(C₅H₄P₂Ph)Fe(C₅H₅)] (244) described in Section 4.2 or Os₃(CO)₁₀(H) [(C₅H₄PFCPh)Fe(C₅H₅)] (264) and (265) described in Section 4.4. A likely structure is shown in Figure 4.45.

Complex (298) shows a ³¹P NMR resonance at 67.6 ppm suggesting the presence of a phosphido moiety or a phosphine. The ¹H NMR spectrum shows the presence of eight ferrocenyl protons with one C₅H₅ ring, two t-butyl groups, and a hydride. A formula such as Os₃(CO)₉(H) [(C₅H₃P₅Bu₂)Fe (C₅H₅)] is most likely since the hydride chemical shift and coupling are very similar to those of Os₃(CO)₉(H) [(C₅H₃PET₂)Fe(C₅H₅)] (270) described in Section 4.5, and therefore a similar structure is shown in Figure 4.45.

Complex (299) shows a ³¹P NMR resonance at 52.3 ppm suggesting the presence of a phosphido moiety or a phosphine. The ¹H NMR spectrum shows the presence of eight ferrocenyl protons with one C₅H₅ ring, and an
intact t-butyl group. A consistent formula is Os$_3$(CO)$_{10}$[(C$_5$H$_3$PtBu)Fe(C$_5$H$_5$)] and a proposed structure is shown in Figure 4.45.

Scheme 4-12 outlines a possible reaction sequence to form the isolated products (295) to (299) from Os$_3$(CO)$_{12}$ and PtBu$_2$Fc. Movement of the phosphine in a presumed precursor Os$_3$(CO)$_{11}$(PtBu$_2$Fc) to an axial position gives A which then undergoes ferrocenyl orthometalation or hetero-annular metalation to give E. Further CO loss from B leads to C by activating a $\beta$ C-H bond of a tBu group, or to (299). Further reactions of C by both sp$^3$ and sp$^2$ P-C cleavages give (296). Turning to the other route, E could lose a CO to give (297) by forming a Fe-Os bond and to (295) by activating a tBu group. (296) may be formed by a pathway similar to that proposed for (276) (Scheme 4-11), that is, via tBu C-H metalation as the first step followed by ferrocenyl orthometalation. (295), however, is unlikely to be formed via tBu C-H activation followed by ferrocenyl hetero-annular metalation since reductive elimination of 2-methylpropene is expected to be a facile process by analogy with propene elimination.
Scheme 4-12 A possible sequence for the pyrolysis of Os₃(CO)₁₂ and PtBu₂Fc.

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bulkiness of the tBu groups may restrict the orientation of the FeCp moiety, and it may prevent ferrocenyl metalation in E as well.

Overall, the pyrolytic reaction of Os₃(CO)₁₂ with PtBu₂Fc is significantly different from that of Os₃(CO)₁₁(PFclPr₂) discussed in Section 4.7. For example, the ferrocenyl moiety in E does not undergo further C-H activation to give analogues of (275) and/or (278). The reason for this difference is unclear.

By analogy with the pyrolysis of Os₃(CO)₁₁(PFclPr₂) as shown in Scheme 4-10, more extensive pyrolytic reactions on Os₃(CO)₁₂ and PtBu₂Fc may lead to ferrocyne complexes such as Os₃(CO)₈(PtBu₂)(H)₁[(C₅H₃)Fe(C₅H₅)] (from (298)) and Os₃(CO)₉(PtBu)(C₅H₃)Fe(C₅H₅)] (from (299)). (295) and (297) under such conditions may also give new products such as Os₃(CO)₉[(C₅H₄PtBu)Fe(C₅H₄)] (x=8 or 9) and Os₃(CO)₉[(C₅H₄PtBu)Fe(C₅H₄)].

4.10 Pyrolysis of Os₃(CO)₁₂ with Fe(C₅H₄)₂PPh

Pyrolysis of Os₃(CO)₁₂ with the [1]-ferrocenophane Fe(C₅H₄)PPh in octane for 7 h affords one major product and two minor ones as judged by TLC and ³¹P NMR spectroscopy. The minor compound showing a ³¹P NMR resonance at -31.5 ppm was not obtained after separation, but it is presumably the simple monosubstituted product Os₃(CO)₁₁[Fe(C₅H₄)₂PPh]. The characterization of the major product, complex (300), is described below.

Complex (300) shows a ³¹P NMR resonance at 59.9 ppm suggesting the presence of a phosphido moiety. The ¹H NMR spectrum shows that both phenyl and ferrocenyl moieties are present. The ferrocenyl protons show a
chemical shift pattern similar to that of $\text{Os}_3(\text{CO})_9[(\text{C}_5\text{H}_4\text{PFc})\text{Fe}(\text{C}_5\text{H}_4)]$ (263) described in Section 4.3. The mass spectrum gives the parent ion at 1114 consistent with the expected formula $\text{Os}_3(\text{CO})_9[(\text{C}_5\text{H}_4\text{PPh})\text{Fe}(\text{C}_5\text{H}_4)]$. The complex is stable towards further change in refluxing octane. Its structure was unequivocally established by an X-ray diffraction study. An ORTEP view of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.46.

Crystal data: (300)·0.5CH$_2$Cl$_2$, $\text{fw} = 1157.26$, red orange, plate, triclinic system, space group P1 ($\simeq$2), $a = 12.427(2)$, $b = 13.061(1)$, $c = 9.209(1)$ Å, $\alpha = 96.562(8)$, $\beta = 91.25(1)$, $\gamma = 76.956(9)^\circ$, $V = 1446.5(3)$ Å$^3$, $Z = 2$, $\text{D}_{\text{calc}} = 2.657$ g/cm$^3$, $R = 0.031$, $R_w = 0.027$.

![Figure 4.46 ORTEP diagram of complex (300).](image)

The structure is broadly similar to that of complex (263) discussed earlier in Section 4.3. It consists of a closed Os$_3$ triangle with one face
capped by the phosphido and ferrocenyl moieties. Each osmium atom is bonded to three CO groups, two equatorial and one axial. Os(1)-Os(3) at 2.8838(6) Å and Os(2)-Os(3) at 2.8832(5) Å are identical and longer than Os(1)-Os(2) at 2.7997(6) Å which is bridged symmetrically by the phosphido moiety (Os(1)-P(1) 2.340(2), Os(2)-P(1) 2.347(2) Å). The Os(1)Os(2)Os(3) plane and Os(1)Os(2)P(1) plane are perpendicular (89.16°). Os(3) is bonded to C(6) of the ferrocenyl moiety (Os(3)-C(6) 2.050(8) Å) and to the central Fe atom (Os(3)-Fe(1) 2.974(1) Å). This Fe-Os bond is significantly longer than those found in complexes (245), (261), (269), (278) (Sections 4.2, 4.3, 4.5, and 4.7, respectively), but considerably shorter than that found in (162) (3.098 Å) described in Section 2.3.1 [120]. Fe(1) occupies an axial coordination site of Os(3), while C(6) takes an almost equatorial position (0.9292 Å away from the Os₃ plane). The two Cp rings are almost eclipsed, but have a ring tilt angle of 9.04°. P(1) and Os(3) are displaced 0.4262 and 1.0850 Å away respectively from the Cp(1) and Cp(2) planes. These Cp(1) and Cp(2) planes make angles of 49.29° and 58.24° respectively with the Os₃ plane. The lengthening of Fe(1)-C(1) (2.080(6) Å) compared to the other Fe-C (Cp(1)) distances (av. 2.048 Å) and the shortening of Fe(1)-C(6) (2.011(8) Å) compared to the other Fe-C (Cp(2)) distances (av. 2.065 Å) are not very significant. As noted for complex (263), the Os-C (carbonyl) distances show large variation. Two axial carbonyls C(19)-Os(1) (1.96(1) Å) and C(22)-Os(2) (1.94(1) Å), two equatorial carbonyls C(23)-Os(3) (1.98(1) Å) and C(24)-Os(3) (1.997(8) Å) distances are very long, while the other axial carbonyl C(25)-Os(3) bond trans to Os(3)-Fe(1) bond is rather short at 1.83(1) Å, the rest average to 1.89 Å. The carbonyls C(23)-O(7) and C(24)-O(8) are clearly semi-bridging between Os(2)-Os(3) and Os(1)-Os(3), respectively, as judged by the
following parameters [325]: Os(3)-C(23)-O(7) 164.3(7)°, Os(2)-C(23) 2.667(8) Å, Os(2)-Os(3)-C(23) 63.4(2)°; Os(3)-C(24)-O(8) 162.8(8)°, Os(1)-C(24) 2.703(8) Å, Os(1)-Os(3)-C(24) 64.3(2)°. Overall, the molecule is rather symmetrical and it is electronically saturated.

The formation of complex (300) from Os₃(CO)₁₂ and Fe(C₅H₄)₂PPh probably involves a simple substitution reaction to form Os₃(CO)₁₁[Fe(C₅H₄)₂PPh] (A) as the first step. A proposed reaction sequence is shown in Scheme 4-13. Movement of the phosphine in A to an axial position gives B. Ferrocenyl P-C cleavage across an Os-Os bond in B takes place to afford C. Exclusion of another CO accompanied by iron-osmium bond formation then gives the product (300). The reaction from B to C is presumably a result of the ferrocenophane ring strain, and it may be a general route to complexes of this type from Os₃(CO)₁₂ and other strained ferrocenophanes such as Fe(C₅H₄)₂P(S)Ph and Fe(C₅H₄)₂AsPh. A particularly interesting aspect of future work will be to establish the scope of this reaction with Ru₃(CO)₁₂, Fe₃(CO)₁₂, and other metal complexes including mononuclear, dinuclear compounds, and high nuclearity clusters.

It is well known that orthometalation of a phenyl group is a facile and common process, and it is clear through the present study that ferrocenyl metalation is also facile at least on Os₃ clusters. Pyrolysis of such phenyl and/or ferrocenyl phosphine cluster complexes normally involves C-H cleavage as the first step. However, in some cases P-C cleavage occurs preferentially. For example, complexes of the type M₃(CO)₁₂-x(Ph₂P-C≡C-R)ₓ (M=Ru, Os; R=tBu, iPr, Ph; x=1, 2, 3) [231, 237, 276] and (M₃(CO)₁₁)₂(μ-Ph₂P-C≡C-PPh₂) (M=Ru, Os) [278, 295] generally undergo P-C (sp) cleavage upon pyrolysis. Phosphole complexes Os₃(CO)₁₁(PhPC₄H₄) [305] and Os₃(CO)₁₁(PhPCHCMeCMeCH) [129] undergo
ring opening (P-C cleavage) readily when pyrolyzed to form (233), (234), and (235) described in Section 2.3.2. The reaction step from B to C in the above sequence is another example of such preferred C-P cleavage.

Scheme 4-13 A possible sequence for the pyrolytic reaction of Os$_3$(CO)$_{12}$ with Fe(C$_5$H$_4$)$_2$PPh.

4.11 Pyrolysis of Os$_3$(CO)$_{12}$ with PEtFc$_2$

Pyrolysis of Os$_3$(CO)$_{12}$ with PEtFc$_2$ in octane for 19 h affords many products, and only some major ones were characterized. The characterization of eleven complexes, (301) to (311), is described here.
Complex (301) shows a $^{31}$P NMR resonance at -78.9 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of seventeen ferrocenyl protons with two C$_5$H$_5$ rings, an intact ethyl group, and a hydride. The mass spectrum gives the parent ion at 1252 corresponding to a formula such as Os$_3$(CO)$_9$(H)[(C$_5$H$_3$PFcEt)Fe(C$_5$H$_5$)], and structures similar to that of (270), (279), (282), and (283) (Sections 4.5, 4.7, and 4.8, respectively) are shown in Figure 4.47.

Complex (302) shows a $^{31}$P NMR resonance at -85.7 ppm, also suggesting the presence of a phosphine. Its $^1$H NMR spectrum is very similar to that of (301), and is likely an isomer of (301). Presumably it has one of the two structures shown in Figure 4.47.

Complex (303) shows a $^{31}$P NMR resonance at 148.5 ppm suggesting the presence of a phosphido moiety. The $^1$H NMR spectrum shows the presence of seventeen ferrocenyl protons with two C$_5$H$_5$ rings, an intact ethyl group, and a hydride. The mass spectrum gives the parent ion at 1226 corresponding to a formula such as Os$_3$(CO)$_8$(H)(PETFc)[(C$_5$H$_3$)Fe(C$_5$H$_5$)]. Thus (303) is similar to complexes (257) and (258) obtained from Os$_3$(CO)$_{11}$(PFc$_2$Ph) described earlier in Section 4.3, and plausible structures

![Figure 4.47 Possible structures for complexes (301) and (302).](image-url)
are shown in Figure 4.48.

Complex (304) shows $^{31}$P and $^1$H NMR spectra, and mass spectrum very similar to those of (303), thus it is an isomer of (303) differing presumably in the arrangement of PEtFc moiety as in (257) and (258), and it should have one of the two structures shown in Figure 4.48.

Complex (305) shows a $^{31}$P NMR resonance at 32.6 ppm suggesting the presence of a phosphido moiety or a phosphine. The $^1$H NMR spectrum shows the presence of eight ferrocenyl protons with one C$_5$H$_5$ ring, an ethyl group, and two broad hydrides. Such broad hydride resonances are only seen in complex (276) obtained from Os$_3$(CO)$_{11}$(PFcIPr)$_2$ described earlier in Section 4.7, and indeed their entire $^1$H NMR spectra are very similar. The mass spectrum gives the parent ion at 1068 corresponding to a formula such as Os$_3$(CO)$_9$(H)$_2$[(C$_5$H$_3$PEt)Fe(C$_5$H$_5$)], however a structure similar to that of (276) is not possible because the ferrocenyl group cannot be lost as ferrocylene. No obvious structures can be conceived.

Complex (306) shows a $^{31}$P NMR resonance at -31.3 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of sixteen ferrocenyl protons with only one C$_5$H$_5$ ring, an intact ethyl group,

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{complexes_303_304.png}
\caption{Possible structures for complexes (303) and (304).}
\end{figure}
and two hydrides. The hydride resonances are very similar to those in (253) and (254) obtained from Os$_3$(CO)$_{11}$(PFC$_2$Ph) described in Section 4.3 or (275) obtained from Os$_3$(CO)$_{11}$(PF$i$Pr$_2$) described in Section 4.7, and are clearly different from Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_3$PETFc)Fe(C$_5$H$_4$)] (308). The mass spectrum gives the parent ion at 1282 corresponding to a formula such as Os$_3$(CO)$_{10}$(H)$_2$[(C$_5$H$_4$PETFc)Fe(C$_5$H$_3$)], and likely structures are shown in Figure 4.49.

Complex (307) shows $^{31}$P and $^1$H NMR spectra very similar to those of (306), and thus is likely to be an isomer of (306). Although the reason for the isomerism is not clear, similar phenomena were observed for (253) and (254), obtained from Os$_3$(CO)$_{11}$(PFC$_2$Ph) described in Section 4.3, and so probably it has one of the two structures shown in Figure 4.49.

Complex (308) shows a $^{31}$P NMR resonance at -27.4 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of sixteen ferrocenyl protons with only one C$_5$H$_5$ ring, an ethyl group, and two hydrides. The characteristic hydride resonances indicate this complex is another member of the series Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_3$PR$_1$R$_2$)Fe(C$_5$H$_4$)] ((245), (261), (269), (278)) (Sections 4.2, 4.3, 4.5, and 4.7, respectively), and its

![Figure 4.49 Possible structures for complexes (306), (307), and (309).](image-url)
structure was determined by a single crystal X-ray diffraction study. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.50.

Crystal data: fw=1224.77, orange, prism, monoclinic system, space group P21/n (#14), a=10.356(3), b=19.514(3), c=15.630(3) Å, β=102.23(2)°, V=3086.8(9) Å³, Z=4, D_calc=2.635 g/cm³, R=0.032, R_w=0.025.

The structure of (308) is another example of the series Os₃(CO)₈(H)₂[(C₅H₃PRR₁)Fe(C₅H₄)] (RR₁=Ph₂ (245), FcPh (261), Et₂ (269), iPr₂ (278)). It consists of a closed Os₃ triangle capped on one face by an ortho- and hetero-metalated ferrocenyl moiety and a phosphine. A Fe-Os bond of 2.836(1) Å is also present. Eight terminal CO groups and two bridging
hydrides make the whole molecule electron precise. The Os-Os bond lengths vary greatly from Os(2)-Os(3) at 3.1117(7) Å to Os(1)-Os(3) at 2.8386(7) Å with Os(1)-Os(2) being intermediate at 2.8727(6) Å. The longest and shortest Os-Os bonds are each bridged by a hydride which was located in the refinement. The Os(1)-C(1) bond at 2.181(7) Å is longer than Os(3)-C(6) bond at 2.065(8) Å, but both are typical of Os-C bonds. The Os(3)-C(30) bond at 1.851(9) Å is the shortest among Os-C (carbonyl) bonds (the rest average to 1.904 Å). The Fe(1)-C(1) bond at 2.121(7) Å is longer than the other Fe(1)-C (Cp(1)) bonds (av. 2.046 Å), and Fe(1)-C(6) at 1.987(7) Å is shorter than the other Fe(1)-C (Cp(2)) bonds (av. 2.060 Å). In comparison, all Fe(2)-C distances are the same for the Cp(3) (av. 2.042 Å) and Cp(4) rings (av. 2.037 Å). The P(1)-C(2) and P(1)-C(11) bonds (av. 1.802 Å) are, as expected, shorter than P(1)-C(21) bond at 1.846(8) Å. The Cp(1) and Cp(2) planes make angles of 78.88 and 79.81° with the Os3 plane. The ring tilt angle of 2.84° between the Cp(3) and Cp(4) rings is slightly larger than that of 1.85° between the Cp(1) and Cp(2) rings. P(1) is almost in the Cp(1) and Cp(3) planes (0.0215 and 0.074 Å away respectively). Os(1) and Os(3) are 0.6879 and 1.2605 Å away respectively from the Cp(1) and Cp(2) planes. The Cp(1) and Cp(2) rings are slightly staggered with the torsion angle C(1)Os(1)Os(3)C(6) being 12.4(4)°. All the Os-C-O angles are close to linear (av. 177.8°) except for Os(2)-C(26)-O(4) which is slightly bent at 172.9(7)°.

Complex (309) shows a $^{31}$P NMR resonance at 58.0 ppm suggesting the presence of a phosphido moiety or a phosphine. The $^1$H NMR spectrum shows the presence of eight ferrocenyl protons with no C$_5$H$_5$ ring, and an intact ethyl group. The mass spectrum gives the parent ion at 1067 corresponding to a formula such as Os$_3$(CO)$_9$[((C$_5$H$_4$P)$_2$Et)Fe(C$_5$H$_4$)], and a
likely structure similar to (263) described in Section 4.3 and (300) described in Section 4.10 is shown in Figure 4.49.

Complex (310) shows two $^{31}$P NMR resonances at 116.6 and -38.0 ppm suggesting the presence of a phosphido moiety and a phosphine. The $^1$H NMR spectrum shows the presence of twenty-five ferrocenyl protons with two C$_5$H$_5$ rings, two ethyl groups, and one hydride. No satisfactory mass spectrum was obtained, but formulae such as $\text{Os}_3(\text{CO})_2(H)[(\text{C}_5\text{H}_4\text{PEtFc})\text{Fe}(\text{C}_5\text{H}_4)][(\text{C}_5\text{H}_3\text{PEt})\text{Fe}(\text{C}_5\text{H}_5)]$ (x=7 or 8) or $\text{Os}_3(\text{CO})_2(H)[(\text{C}_5\text{H}_3\text{PEtFc})\text{Fe}(\text{C}_5\text{H}_5)] [(\text{C}_5\text{H}_4\text{PEt})\text{Fe}(\text{C}_5\text{H}_4)]$ (x=7 or 8) seem likely.

Complex (311) is the diastereoisomer of complex (308) as shown by its $^{31}$P and $^1$H NMR spectra, but it was produced in very low yield.

The pyrolysis reaction of $\text{Os}_3(\text{CO})_{12}$ and PEtFc$_2$ is very complex, and many products with phosphido and/or phosphinidene moieties could not be characterized further. It should be of interest to study this pyrolysis reaction on a larger scale in order to isolate and characterize these potentially interesting compounds.

Pyrolysis of the monosubstituted complex $\text{Os}_3(\text{CO})_{11}(\text{PEtFc}_2)$ in octane for 11 h affords mainly complexes (303), (304), and (308) in addition to products showing $^{31}$P NMR resonances that have large upfield shifts at -92.8 and -111.0 ppm. Pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PEtFc}_2)$ in octane for longer time may give some of these new complexes in yields high enough for further characterization.

Overall, pyrolysis of $\text{Os}_3(\text{CO})_{12}$ with PEtFc$_2$ and of $\text{Os}_3(\text{CO})_{11}(\text{PEtFc}_2)$ shows that ferrocenyl groups are preferentially activated over ethyl groups. The reactions that ferrocenyl groups undergo are similar to those found in the pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{PFc}_2\text{Ph})$ (Section 4.3), so similar
reaction schemes can be written to account for the formation of the isolated products.

4.12 Pyrolysis of Os₃(CO)₁₂ with AsFc₂Ph

Pyrolysis of Os₃(CO)₁₁(PFc₂Ph) discussed in Section 4.3 affords many interesting products, and thus it is natural to study the analogous reaction with AsFc₂Ph.

Pyrolysis of Os₃(CO)₁₂ with AsFc₂Ph in octane for 3.5 h affords more than ten products as revealed by TLC and ¹H NMR spectroscopy. Most of the products were characterized by spectroscopic and analytical techniques. These complexes, (312) to (321), are described here.

The ¹H NMR spectrum of complex (312), Figure 4.52, shows the presence of a phenyl group and eight ferrocenyl protons with one C₅H₅ ring. The mass spectrum gives the parent ion at 1158 corresponding to a formula such as Os₃(CO)₉(AsPh)[(C₅H₃)Fe(C₅H₅)], and a structure analogous to the ferrocynne complex Os₃(CO)₉[(C₅H₃)Fe(C₅H₅)] (252), described in Section 4.3, is shown in Figure 4.51.

The ¹H NMR spectrum of complex (313) shows the presence of a C₆H₄ moiety and a ferrocenyl group. The ¹H NMR signals of the C₆H₄ moiety have a clear AA'BB' pattern, and the entire spectrum is very similar to that of the benzyne complex Os₃(CO)₉(PFc)(C₆H₄)(239) described earlier in Section 4.1. The mass spectrum gives the parent ion at 1158, the same as the previous complex (312), consistent with such a benzyne complex. A structure similar to (239) is proposed and shown in Figure 4.51.
Complex (314) shows two multiplets with the same intensity for the ferrocenyl protons in the $^1$H NMR spectrum. No satisfactory mass spectrum was obtained. The analysis does indicate low hydrogen and carbon percentages, but an X-ray diffraction study is definitely needed to solve the structure of this rather unusual complex.

The $^1$H NMR spectrum of complex (315) shows the presence of a C$_6$H$_4$ moiety, two ferrocenyl groups, and a hydride. The mass spectrum gives the parent ion at 1344 corresponding to a formula such as Os$_3$(CO)$_9$(H)(AsFc$_2$)(C$_6$H$_4$) or Os$_3$(CO)$_9$(H)(AsFc$_2$C$_6$H$_4$). An X-ray crystallographic study established it as a benzyne complex. An ORTEP diagram with 33.0% probability thermal ellipsoids is shown in Figure 4.53.

Crystal data: fw=1344.78, orange, prism, monoclinic system, space group C2/c (#15), a=31.559(5), b=15.032(4), c=16.428(3) Å, β=115.53(1)°, V=7032(2) Å$^3$, Z=8, D$_{calc}$=2.540 g/cm$^3$, R=0.038, R$_w$=0.038.

The structure of this complex is very similar to that of Os$_3$(CO)$_9$(H)(AsMe$_2$)(C$_6$H$_4$) (114b) [125] and the phosphole complex Os$_3$(CO)$_9$(H)(PC$_4$H$_2$Me$_2$)(C$_6$H$_4$) (119) described in Section 1.2.3.2 [129]. It

![Possible structures for complexes (312) and (313).](image)

Figure 4.51 Possible structures for complexes (312) and (313).
consists of an open Os$_3$ triangle capped on one face by an approximately symmetrically bound benzyne moiety. The open edge is bridged by an arsenido group (As(1)-Os(2) 2.4992(9), As(1)-Os(3) 2.510(1) Å). The Os(1)-
Os(3) bond at 2.9374(6) Å, bridged by a hydride which was located in the structure refinement, is longer than Os(1)-Os(2) at 2.8270(8) Å. Each osmium center is bonded to three terminal carbonyls, so the whole cluster is electron precise. The benzyne moiety is bonded to Os(2) and Os(3) via σ bonds (Os(2)-C(1) 2.140(8), Os(3)-C(2) 2.159(8) Å) and to Os(1) via a π bond (Os(1)-C(1) 2.412(8), Os(1)-C(2) 2.283(8) Å). The benzyne ring makes an angle of 73.88° with the Os₃ plane. The carbonyl Os(3)-C(33) bond at 1.962(9) Å is somewhat longer than the rest (av. 1.91 Å) and the Os(2)-C(32)-O(6) angle at 171(1)° is somewhat less linear than the others (av. 176.9°). The C-C bond alternation in the C(1)-C(6) ring is not apparent with
C(3)-C(4) at 1.32(1) Å being the shortest and C(1)-C(2) at 1.43(1) Å being the longest. As expected, Os(2) and Os(3) are close to coplanar with the C(1)-C(6) plane (0.1192 and -0.3517 Å away respectively). As(1) is displaced 0.6701 Å away from the Os₃ plane towards the uncapped Os₃ face. All the Fe-C (Cp rings) distances are normal. The ring tilt angle between the Cp(1) and Cp(2) rings is 2.03°, and that between the Cp(3) and Cp(4) planes is larger at 3.84° presumably due to steric interaction of that ferrocenyl group with the benzyne moiety. As(1) is slightly displaced from the Cp(1) and Cp(3) planes (0.2885 and 0.2398 Å respectively).

Complex (316) is a simple monosubstituted product Os₃(CO)₁₁ (AsFc₂Ph) characterized by ¹H NMR spectroscopy, mass spectrometry, and micro-analysis.

The ¹H NMR spectrum of complex (317), Figure 4.54, shows the presence of a symmetrical C₆H₄ moiety, two ferrocenyl groups, and a hydride. The mass spectrum gives the parent ion at 1072 corresponding to a formula such as Os₂(CO)₆(H)(AsFc₂)(C₆H₄). A likely structure is shown in Figure 4.55. This is the only dinuclear osmium benzyne complex obtained in the present study. A few literature precedents such as complexes (131) [125], (132) [125], and (135) [148,149] have been described in Section 1.2.4.

Complex (318) shows a ¹H NMR spectrum very similar to that of complex Os₃(CO)₈(H)₂[(C₅H₃PFcPh)Fe(C₅H₄)] (261) described in Section 4.3. It shows the presence of a phenyl group, seventeen ferrocenyl protons with one C₅H₅ ring, and two hydrides. The hydride chemical shifts are close to those of (261). The mass spectrum giving the parent ion at 1318, and the analysis are consistent with such a formula Os₃(CO)₈(H)₂[(C₅H₃AsFcPh)
Fe(C₅H₄)]. A proposed structure is shown in Figure 4.55. Its diastereoisomer was not observed.

The $^1$H NMR spectrum of complex (319) shows the presence of an unsymmetrical C₆H₄ moiety and a ferrocenyl group. This seems to be a benzyne complex, but the benzyne proton chemical shifts do not resemble
Figure 4.55 Possible structures for complexes (317) and (318).

Figure 4.56 300 MHz $^1$H NMR spectrum of complex (320).

those of (239) and (313), nor those of (317). It is difficult to envisage a structure without an X-ray diffraction study.
The \textsuperscript{1}H NMR spectrum of (320), Figure 4.56, shows the presence of a phenyl group, a C\textsubscript{6}H\textsubscript{4} moiety, four ferrocenyl groups, and a hydride. The mass spectrum gives the parent ion at 1838 corresponding to a formula such as Os\textsubscript{3}(CO)\textsubscript{8}(H)(AsFc\textsubscript{2}Ph)(AsFc\textsubscript{2})(C\textsubscript{6}H\textsubscript{4}) or Os\textsubscript{3}(CO)\textsubscript{8}(H)(AsFc\textsubscript{2}Ph)(AsFc\textsubscript{2}C\textsubscript{6}H\textsubscript{4}). A structure corresponding to the former formula is shown in Figure 4.57.

The \textsuperscript{1}H NMR spectrum of complex (321) shows the presence of a C\textsubscript{6}H\textsubscript{4} moiety and three ferrocenyl groups with two C\textsubscript{5}H\textsubscript{5} rings. The mass spectrum gives the parent ion at 1546 corresponding to a formula such as Os\textsubscript{3}(CO)\textsubscript{7}(AsFcC\textsubscript{6}H\textsubscript{4})[(C\textsubscript{5}H\textsubscript{4}AsFc)Fe(C\textsubscript{5}H\textsubscript{4})]. A plausible structure is shown in Figure 4.57. Since only seven CO groups are present, an Fe-Os bonding interaction is likely to be present.

![Figure 4.57 Possible structures for complexes (320) and (321).](image)

In general, the pyrolysis of Os\textsubscript{3}(CO)\textsubscript{12} with AsFc\textsubscript{2}Ph is similar to that of Os\textsubscript{3}(CO)\textsubscript{11}(PFc\textsubscript{2}Ph) discussed in Section 4.3. Phenyl orthometalation, benzyne formation, ferrocenyl ortho- and hetero-annular metalation, and ferrocyne formation take place to give the isolated products. The benzyne
complex (315) is obtained in fair yield, while the analogous complex is not formed in any appreciable quantity in the pyrolysis of Os₃(CO)₁₁(PFc₂Ph). Instead, two isomeric ferrocene complexes (257) and (258) are formed in the phosphine reaction. Such ferrocene complexes do not seem to form in the AsFc₂Ph case. Also, in the ferrocene complex (312) a phenyl group rather than a ferrocenyl group as in (252) is present. The dinuclear benzyne complex (317) is formed in the AsFc₂Ph reaction but not the PFc₂Ph reaction. Unusual complexes such as (313) and (319) have no analogues in the PFc₂Ph reaction either. However, complexes such as (253) and (254), (257) and (258), and (263) are not formed in the AsFc₂Ph reaction. The reason for the difference in reactivities of the PFc₂Ph and AsFc₂Ph systems is unclear. Reaction sequences similar to those proposed for Os₃(CO)₁₁(PFc₂Ph) discussed in Section 4.3 can be used to account for the formation of most of the isolated products.

4.13 Pyrolysis of Os₃(CO)₁₀[Fc'(PiPr₂)₂]

Pyrolysis of Os₃(CO)₁₀[Fc'(PiPr₂)₂] affords ten products with five in good yields as judged by TLC, ¹H, and ³¹P NMR spectroscopy. The characterization of these products, complexes (322) to (332), is described below.

Complex (322), a major product, shows ³¹P NMR resonances at 76.3 and 40.4 ppm with a small coupling of 2.8 Hz. The mass spectrum gives the parent ion at 1170 corresponding to the loss of one i-propyl and two CO groups from the parent. The ¹H NMR spectrum shows the presence of seven ferrocenyl protons, three intact i-propyl groups, and two hydrides
Figure 4.58 Possible structures for complexes (322) and (324).

Figure 4.59 300 MHz $^1$H NMR spectrum of complex (323).
corresponding to a formula such as \( \text{Os}_3(\text{CO})_8(\text{H})_2[(\text{C}_5\text{H}_4\text{P}^\text{IPr}_2)\text{Fe(}C_5\text{H}_3\text{P}^\text{IPr})] \) or \( \text{Os}_3(\text{CO})_8(\text{H})_2[(\text{C}_5\text{H}_3\text{P}^\text{IPr}_2)\text{Fe(}C_5\text{H}_4\text{P}^\text{IPr})] \). Both are consistent with the analytical and spectroscopic data including the small \( ^{31}\text{P-}^{31}\text{P} \) coupling constant. The exact structure can only be determined from an X-ray diffraction study, but it is believed to have one of the structures shown in Figure 4.58. B is less likely because of the presence of the strained four-membered C-C-P-Os ring.

Complex (323) shows \( ^{31}\text{P} \) NMR resonances at 16.2 and 18.0 ppm suggesting that both phosphorus atoms are probably in the form of phosphines. The mass spectrum, however, shows the parent ion at 1198, corresponding to the loss of one carbonyl and one i-propyl group from the parent. In addition, fragments are associated with the stepwise loss of nine CO and three i-propyl groups. The \( ^1\text{H} \) NMR spectrum, Figure 4.59, shows the presence of eight ferrocenyl protons, three i-propyl groups, and a hydride presumably derived from the lost i-propyl group. The most probable formula for the complex is \( \text{Os}_3(\text{CO})_9(\text{H})_1[(\text{C}_5\text{H}_4\text{P}^\text{IPr}_2)\text{Fe(}C_5\text{H}_4\text{P}^\text{IPr})] \), but there is no obvious explanation for the close NMR chemical shifts of the phosphine and phosphido resonances. The formulation was later confirmed by an X-ray crystallographic study. An ORTEP diagram of the molecule with 32.0% probability thermal ellipsoids is shown in Figure 4.60.

Crystal data: \( \text{fw}=1198.93 \), red orange, prism, triclinic system, space group \( \text{P1} \) (\#2), \( a=11.102(3) \), \( b=17.799(4) \), \( c=9.348(2) \) Å, \( \alpha=101.53(2) \), \( \beta=113.95(1) \), \( \gamma=73.16(1) \), \( V=1609(1) \) Å\(^3\), \( Z=2 \), \( D_{\text{calc}}=2.475 \) g/cm\(^3\), \( R=0.031 \), \( R_w=0.029 \).

The structure of (323) consists of a closed Os\(_3\) triangle with four carbonyls bonded to Os(3), three to Os(2), and two to Os(1). The longest Os(1)-Os(2) bond (2.9382(7) Å) is bridged by the hydride which was
located in the structure refinement and by the phosphido moiety (P(1)-Os(1) 2.404(1), P(1)-Os(2) 2.395(1) Å). Os(2)-Os(3) and Os(1)-Os(3) bonds have the lengths of 2.9055(8) and 2.8858(9) Å respectively. The Os(1)-P(2) distance at 2.368(1) Å is slightly shorter than the P(1)-Os distances. The Os-C distances for CO groups bonded to Os(3) (av. 1.938 Å) are longer than those bonded to Os(2) (av. 1.909 Å) and Os(1) (av. 1.884 Å). A similar pattern of M-C distances was also noted for Ru3(CO)8(OH)(Cl)[Fc′(PiPr2)2] (371) to be described in Section 5.9. P(1) is 1.7326 Å away from the Os3 plane, while P(2) and H(1) are 0.7338 and 0.4726 Å away respectively from the Os3 plane but on opposite sides. P(1) and P(2) are effectively in the plane of the Cp rings and are displaced away by 0.0803 and 0.0395 Å.
respectively. The two Cp rings have a small ring tilt angle of 2.11°. As expected, P-C (sp\textsuperscript{2}) distances (av. 1.812 Å) are shorter than P-C (sp\textsuperscript{3}) ones (av. 1.863 Å). Some Os-C-O angles Os(2)-C(3)-O(3) (172.6(5)*), Os(2)-C(4)-O(4) (172.2(4)*), and Os(3)-C(8)-O(8) (170.6(5)*) are somewhat less linear than the others (av. 176.7°). The Cp(1) and Cp(2) planes make angles of 24.78 and 22.92° respectively with the Os\textsubscript{3} plane. The angle between the Os\textsubscript{3} plane and the Os(1)0s(2)P(1) plane is 114.05°.

Complex (324) shows an identical mass spectrum to that of (322) and (326), but the \textsuperscript{31}P NMR resonances are at 28.2 and 6.0 ppm with a coupling of 12.8 Hz. The \textsuperscript{1}H NMR spectrum also shows the presence of only seven ferrocenyl protons, three intact i-propyl groups, and two hydrides. Thus it is also an isomer of (322) and (326). The exact structure has to rely on an X-ray diffraction study, but a proposed one is shown in Figure 4.58.

Complex (325) is produced only in low yield. It was not possible to obtain a good FAB mass spectrum because of the high molecular weight of this complex. A single \textsuperscript{31}P NMR resonance at -5.3 ppm suggests the equivalence of the two phosphorus atoms. \textsuperscript{1}H NMR spectroscopy reveals the presence of only two ferrocenyl proton signals with unusual chemical shifts (intensity 2:2), four intact i-propyl groups, and two hydride signals whose intensity corresponds to two hydrides for each resonance. Each hydride resonance is split into a doublet, not a triplet, indicating that only one phosphorus atom is attached to each Os\textsubscript{3} unit. A formula such as (Os\textsubscript{3}(CO)\textsubscript{X}(H)\textsubscript{2})\textsubscript{2}[(C\textsubscript{5}H\textsubscript{2}P\textsubscript{i}Pr\textsubscript{2})Fe(C\textsubscript{5}H\textsubscript{2}P\textsubscript{i}Pr\textsubscript{2})] could be advanced to explain the spectroscopic data. The structure of the complex was established by means of an X-ray crystallographic analysis. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.61.
Crystal data: fw=2007.69, red, prism, monoclinic system, space group, P2$_1$/c (#14), a=13.607(2), b=22.925(6), c=16.649(3) Å, β=113.00(2)$^\circ$, V=4781(2) Å$^3$, Z=4, D$_{calc}$=2.789 g/cm$^3$, R=0.031, R$_w$=0.026.

The complex is very unusual in that it contains two Os$_3$ units bridged by a bidentate phosphine and by a ferrocenyne [Fe(C$_5$H$_2$)$_2$] moiety. The structure is almost symmetrical in the solid state and in solution the two halves must be identical because only two hydride signals, two ferrocenyln
proton signals, and one $^{31}\text{P}$ resonance are observed in the NMR spectra.

Each closed Os$_3$ unit in structure (325) is capped on one face by a C$_5$ ring aryne moiety and is also coordinated equatorially to a PiPr$_2$ group attached to the other C$_5$ ring of the ferrocenyl moiety. Two hydrides are associated with each Os$_3$ unit as indicated by the $^1$H NMR spectrum, and they are apparently derived from the two meta-protons of each C$_5$ ring. Three of the total four hydrides were located in the structure refinement, and they bridge the two longer Os-Os bonds in each Os$_3$ unit, namely those Os-Os edges centered on Os(4) and Os(1) (Os(4)-Os(6) 3.0995(8), Os(4)-Os(5) 2.8315(9); Os(1)-Os(3) 3.1127(9), Os(1)-Os(2) 2.8379(8) Å). The longest Os(4)-Os(6) and Os(1)-Os(3) bonds are cis to the phosphine. This trend is observed for simple substitution products such as M$_3$(CO)$_{11}$L (M=Ru or Os, L=phosphine or arsine) [223], but in the present case these could be due to the C$_5$H$_3$ bridge. The two shortest Os-Os bonds are Os(5)-Os(6) at 2.7776(8) Å and Os(2)-Os(3) at 2.7831(7) Å. The Os-Os distances in each Os$_3$ unit are similar to those found in Os$_3$(CO)$_9$(H)$_2$(C$_6$H$_4$) (126), namely 2.751(2), 2.866(2), and 3.026(2) Å [139]. The hydrides were not located during the X-ray analysis of (126), and they were placed along the longer Os-Os bonds [139]. The two Os$_3$ plane in (325) are almost parallel with a dihedral angle of 171.0°.

The ferrocenyl moiety shows an eclipsed configuration as the torsion angles C(1)P(1)Os(1)C(8) (0.7(4)°) and C(3)Os(4)P(2)C(6) (1.1(4)°) reveal, although the two PiPr$_2$ fragments now have to be trans to each other. P(1) and P(2) are displaced 0.2703 and 0.3098 Å away from the Cp(1) and Cp(2) planes respectively, but both are displaced towards the middle of the sandwich to allow phosphine coordination. There is little distortion of the Cp ring planarity (mean deviation Cp(1) 0.0036, Cp(2) 0.0127 Å), but the
two rings have a ring tilt angle of 10.50°. Os(4) and Os(6) are situated 0.4885 and 0.2594 Å away respectively from the Cp(1) plane but in opposite directions. A similar situation holds for Os(1) and Os(3) which are located 0.5106 and 0.2234 Å away from the Cp(2) plane. The Os-C distances are consistent with σ bonding interactions involving C(3) and Os(4), C(4) and Os(6), and correspondingly between the pairs C(8)Os(1) and C(9)Os(2). There is some shortening of the Fe-Cp distances (1.630(4) and 1.632(4) Å) compared to, for example, complex (323) (1.664(3) and 1.659(2) Å). Also the Fe(1)-C(1), Fe(1)-C(2), Fe(1)-C(6), and Fe(1)-C(7) distances (av. 2.002 Å) are shorter than the rest (av. 2.070 Å). The P-C (sp²) lengths (av. 1.808 Å) are, as expected, slightly shorter than P-C (sp³) bonds (av. 1.863 Å).

Since the two halves of the molecule are very similar, discussion of the other metrical details is focused on the Os(1)Os(2)Os(3) moiety. The aryne moiety is bound to the Os₃ unit in an unsymmetrical fashion previously observed only for open clusters such as (121), (122), and (124) [131, 133-135], and the present structure represents the first report of such bonding in a closed M₃ cluster. Aryne C-Os bonds Os(1)-C(8) 2.189(8), Os(2)-C(8) 2.279(8), Os(3)-C(9) 2.095(8), and Os(2)-C(9) 2.60(1) Å indicate two σ bonds and a π bonding interaction between C(8) and Os(2), closely resembling the bonding in complexes (121), (122), and (124) described in Section 1.2.3.2. Some C-C bond lengthening in the Cp ring is present. The Cp(2) ring is tilted at an angle of 69.60° with the Os₃ plane, comparable to 63.9 and 69.0° for (126) [139]. Three CO groups each are bound to Os(2) and Os(3), and two to Os(1). The C-Os distances vary from 1.87(1) for Os(1)-C(11) to 1.94(1) Å for Os(2)-C(14).
The molecular structure of (325) may be compared with that of (126) except that in (126) the benzyne moiety is bound to the Os₃ face symmetrically (Table 1-5) and there is no phosphine bound to the cluster. The formation of (325) is a result of the oxidative addition of two adjacent (meta) C-H bonds in each C₅ ring to one Os₃ unit. Since C-H and C-P cleavage of the i-propyl group dominate the decomposition pathway of Ru₃(CO)₁₀[Fe(PiPr₂)₂] to be discussed in Section 5.9, the formation of (325) is rather unexpected. Moreover, it involves two Os₃ units. The structure of (325) suggests that it might be obtained from (Os₃(CO)₁₁)[Fe(PiPr₂)₂] and indeed an improved yield of 15% for (325) was obtained after refluxing the bridged derivative in octane for 2.5 h. Although (126) is easily obtained from benzene and Os₃(CO)₁₂ or Os₃(CO)₁₀(MeCN)₂, the reaction of ferrocene with Os₃(CO)₁₂ or Os₃(CO)₁₀(MeCN)₂ is reported to give intractable materials [181]. Evidently prior coordination of the phosphine brings the Cp rings to close proximity to the Os₃ cluster thus allowing C-H activation to occur. The formation of this ferrocicyne complex is a remarkable demonstration of this concept.

The ¹H NMR spectrum of Os₃(CO)₉(H)₂(C₆H₄) (126) shows two separate signals for the two hydrides only at low temperatures [139]. The motion that gives rise to averaged signal at higher temperatures has been studied and it involves a rapid, reversible exchange between hydrides on the Os₃ moiety and protons on the aryne ring. This process is not possible for (325) because the rings are locked in position by the coordinated phosphorus atoms and the ferrocenyl moiety, consequently sharp and well separated hydride resonances are observed at room temperature.

Complex (326) shows ³¹P NMR resonances at 70.1 and 22.6 ppm with a coupling of 18.7 Hz. The mass spectrum gives the parent ion at 1170
corresponding to the loss of an i-propyl and two CO groups from the parent. The $^1$H NMR spectrum shows the presence of, again, only seven ferrocenyl protons, three intact i-propyl groups, and two hydrides. This complex is thus the third isomer of (322), the other being (324). Its structure was solved by using X-ray crystallography. An ORTEP diagram of the molecule with 25.0% probability thermal ellipsoids is shown in Figure 4.62.

Crystal data: fw=1170.92, orange, plate, monoclinic system, space group P2$_1$/a (#14), a=14.668(2), b=14.022(2), c=15.807(3) Å, $\beta$=94.40(1)$^\circ$, V=3241.5(8) Å$^3$, Z=4, $D_{calc}$=2.399 g/cm$^3$, R=0.031, $R_w$=0.025.

The structure consists of a closed Os$_3$ triangle with one face capped by the bidentate phosphine-phosphido moiety and the metalated Cp(1)

Figure 4.62 ORTEP diagram of complex (326).
ring to which the phosphido group is attached. Eight terminal carboxyls, three each to Os(2) and Os(3), and two to Os(1), and two hydrides which were located in the structure refinement, make the complex electron precise. The Os-Os bond lengths show a large variation with Os(1)-Os(2) at 3.1038(6) Å being the longest. Os(1)-Os(3) at 2.9387(6) Å is of intermediate length, and Os(2)-Os(3) at 2.8823(8) Å is the shortest. As expected, the hydrides bridge the two longer Os-Os vectors. The phosphido moiety bridges Os(1)-Os(3) bond approximately symmetrically (Os(1)-P(1) 2.392(2), Os(3)-P(1) 2.365(2) Å), and the Os(1)Os(3)P(1) plane is almost perpendicular to the Os₃ plane (84.87°). The C(1)-Os(2) bond is trans to the carbonyl C(24)0(5) and the length 2.145(9) Å is typical of an Os-C σ bond.

The phosphine occupies a pseudo-axial position (P(2) is 1.1811 Å above the Os₃ plane). The Os-C (carbonyl) bond lengths range from 1.87(1) to 1.93(1) Å and all Os-C-O angles are close to linear.

In the ferrocenyl moiety, all Fe-C bonds are equal and normal (av. 2.05 Å). The Cp(1) plane is nearly perpendicular to the Os₃ plane (86.88°) and the two Cp rings are parallel with a small ring tilt angle of 2.58°. Both P(2) (0.0696 Å) and P(1) (0.0637 Å), and Os(2) (0.0749 Å) are only slightly displaced away from the Cp(2) and Cp(1) planes respectively.

Broadly, this structure can be compared with that of Os₃(CO)₉(μ-CO) (PMeC₆H₄) (232) which was obtained from the pyrolysis of Os₃(CO)₁₁ (PMePh₂) [132]. There are two notable differences, however: (1) the bridging carbonyl in (232) is replaced by two bridging hydrides in (326); (2) the six-membered C₆H₄ ring in (232) is replaced by a C₅H₃ ring which is also coordinated to the Fe(C₅H₄PiPr₂) moiety and this extra phosphine replaces one carbonyl.

Complex (327) was obtained in trace quantity. A 3¹P NMR resonance
at 0.0 ppm suggests the presence of two equivalent phosphines. The $^1$H NMR spectrum shows the presence of two hydrides at -16.91 (J=25.8 Hz) and -19.05 ppm (J=12.8 Hz). This complex was not characterized further, but the hydrides do resemble those of (325) both in chemical shifts and in coupling constants.

Complex (328) was also obtained in trace amounts. A $^{31}$P NMR resonance at 2.7 ppm and two hydrides at -16.78 (J=25.0 Hz) and -18.91

![Figure 4.63 400 MHz $^1$H NMR spectrum of complex (329).](image-url)
ppm (J=11.9 Hz) indicate that it is similar to (327) and to (325). Unfortunately no further data are available.

Complex (329) shows $^{31}$P NMR resonances at 268.3 and 16.5 ppm suggesting the presence of a phosphinidene moiety and a phosphine. The $^1$H NMR spectrum, Figure 4.63, shows the presence of eight ferrocenyl protons, three intact i-propyl groups with one unusually shifted, and a hydride at -21.92 ppm. The mass spectrum gives the parent ion at 1142 corresponding to the loss of one i-propyl and three CO groups from the parent. The presence of only seven CO groups in the molecule indicated by the mass spectrum assures some unusual structural features as established by an X-ray crystallographic study. An ORTEP diagram of the molecule with 32.0% probability thermal ellipsoids is shown in Figure 4.64.

Crystal data: $fw=1142.91$, orange, prism, monoclinic system, space

Figure 4.64 ORTEP diagram of complex (329).
group P2$_1$/n (#14), a=8.910(3), b=22.784(2), c=15.416(2) Å, $\beta$=98.25(2)*, $V=3097(1)$ Å$^3$, $Z=4$, $D_{\text{calcd}}=2.451$ g/cm$^3$, $R=0.032$, $R_w=0.026$.

The structure of this complex consists of a closed Os$_3$ triangle capped on one face by a phosphinidene moiety P$i$Pr. The ferrocenyl moiety (C$_5$H$_4$)Fe(C$_5$H$_4$P$i$Pr$_2$) is bonded to Os(1) alone and it acts as a five-electron donor. The Os(1)-Fe(1) distance at 2.813(1) Å is the shortest Fe (ferrocene)-M distance to be determined [316-323], and it is shorter than all the three Os-Os bonds. The Os(1)-Os(2) length at 3.0513(7) Å is considerably longer than the other two (Os(1)-Os(3) 2.8594(6), Os(2)-Os(3) 2.8715(9) Å). The hydride was not located, but presumably it bridges the longest Os(1)-Os(2) edge. The phosphinidene fragment P(1) is almost symmetrically bound to the Os$_3$ moiety (P(1)-Os(1) 2.286(1), P(1)-Os(2) 2.322(3), P(1)-Os(3) 2.312(2) Å). The Os(1)-P(2) distance at 2.305(2) Å is in the same range as those of P(1)-Os distances. C(13) is bonded to Os(1) in an axial position and has a bond length of 2.047(8) Å. The two Cp rings are slightly opened up (11.58°) and P(2) is bent 0.2502 Å towards Fe(1) side of the Cp(1) plane. The two Cp rings are also eclipsed (C(8)P(2)Os(1)C(13) torsion angle 1.6(5)°). The Fe(1)-C(8) bond at 2.109(8) Å is appreciably longer than the other Fe(1)-C (Cp(1)) distances (av. 2.048 Å). Os(1), Os(2), and Os(3) are bonded respectively to one, three, and three carbonyls. The Os-C (carbonyl) distances range from 1.85(1) for Os(1)-C(1) to 1.93(1) Å for Os(3)-C(7).

Complex (330) shows $^{31}$P NMR resonances at 59.2 and 19.2 ppm. Its mass spectrum gives the parent ion at 1240 corresponding to the loss of one carbonyl from the starting material, and fragments are associated with the loss of nine CO and three i-propyl groups. The $^1$H NMR spectrum shows the presence of eight ferrocenyl protons, four characteristic CH$_2$Me$_2$ protons,
a CH₂ multiplet, seven methyl groups, and a hydride at -13.53 ppm. These data suggest a formula such as Os₃(CO)₈(H)[(C₅H₄PiPr₂)Fe(C₅H₄PiPrCHMeCH₂CO)] for the complex. An X-ray diffraction study established the molecular structure, and an ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 4.65.

Crystal data: (330)-0.5CH₂Cl₂, fw=1284.49, yellow orange, prism, monoclinic system, space group P2₁/a (#14), a=16.268(2), b=11.298(3), c=20.649(3) Å, β=94.43(1)°, V=3784(1) Å³, Z=4, Dcalc=2.255 g/cm³, R=0.029, Rw=0.026.

The structure of (330) consists of a closed Os₃ triangle with one edge bridged by a bidentate phosphine, an acyl moiety derived from CO insertion into a β C-H activated i-propyl group, and a hydride which was located crystallographically. The acyl Os(2)-C(19)-O(1) angle of 119.4(6)° is consistent with sp² hybridization at C(19). The di(tertiary)phosphine

Figure 4.65 ORTEP diagram of complex (330).
occupies two equatorial sites. H(1), C(19), and O(1) are displaced 0.7187, 1.8012, and 1.9260 Å away, respectively, from the Os\textsubscript{3} plane but on opposite sides. This structure is similar to that of Ru\textsubscript{3}(CO)\textsubscript{8}(Cl)(OH) \[\text{Fe'(P}^\text{tPr}_2)_2\] (371) which will be described in Section 5.9 except that in (371) the Ru(1)-Ru(2) edge is open. This arrangement of the bridging ligands distorts the carbonyls bonded to Os(1) and Os(2) to staggered orientation relative to Os(3) bonded carbonyls as found in (371) described in Section 5.9.

The bridged Os(1)-Os(2) bond at 2.9250(6) Å is slightly longer than the unbridged ones (Os(1)-Os(3) 2.8610(6), Os(2)-Os(3) 2.8776(7) Å). The acyl Os(1)-O(1) (2.151(5) Å), Os(2)-C(19) (2.039(8) Å), and C(19)-O(1) (1.289(9) Å) bonds are unexceptional. P(1) and P(2) are displaced 0.2104 and 0.3011 Å away respectively from the Fe(1) side of the Cp(1) and Cp(2) planes. The ring tilt angle between the two Cp rings is 5.73°. These rings are eclipsed, and the two P-C (ferrocenyl) bonds have a torsion angle of 61.3(3)°. The Os-C (carbonyl) distances range from 1.86(1) for Os(1)-C(25) to 1.94(1) Å for Os(2)-C(26) and the latter one is probably a result of the trans influence of the Os(2)-C(19) σ bond. This Os(2)-C(26)-O(4) angle (172.7(9)°) is also somewhat less linear than the others (av. 177.7°). The Os(1)-P(1) bond at 2.389(2) Å is appreciably longer than Os(2)-P(2) at 2.325(2) Å, probably due to the formation of a stable five-membered ring at Os(2). The P-C (sp\textsuperscript{2}) bonds (av. 1.805 Å) are, as expected, shorter than P-C (sp\textsuperscript{3}) bonds (av. 1.861 Å).

Many complexes of the type Os\textsubscript{3}(CO)\textsubscript{10}(H)(X) are known [113], the unique feature of complex (230) is the presence of the bridging di(tertiary)phosphine ligand in addition to the (H)(X) bridge.
Although Ru$_3$ and Os$_3$ acyl complexes analogous to (230) are known [140, 326-330], these are usually synthesized either by the oxidative addition of aldehydes to M$_3$(CO)$_{12}$ (or to activated derivatives such as Os$_3$(CO)$_{10}$(MeCN)$_2$) [140, 328], or by nucleophilic attack of Nu$^-$ (amines, OR$^-$, R$^-$, etc) at a CO group of M$_3$(CO)$_{12}$ followed by decarbonylation and protonation [326, 329]. Insertion of a CO group into a metal-alkyl bond is involved in the formation of A and B in Equation 4.1, but these reactions involve very forcing conditions [330]. In the present study CO insertion into an Os-alkyl bond occurs under mild conditions (1 atm, 120°C) and the result is certainly unprecedented and unexpected because CO insertion is not a facile process on a third-row transition metal center. CO insertion into a more reactive methylene moiety is, however, known for both Ru$_3$ [331] and Os$_3$ clusters [332], but these reactions do not afford oxygen bonded acyl complexes and therefore the presence of external carbon monoxide is necessary to drive the reaction. The formation of (330) from its precursor is certainly an intramolecular reaction.

Complex (331) shows $^{31}$P NMR resonances at 51.0 and 18.7 ppm. The mass spectrum is identical to that of (330), while the $^1$H NMR spectrum shows the presence of eight ferrocenyl protons, four CHMe$_2$ protons, seven methyl groups, one CH$_2$ multiplet, and a hydride at -13.57 ppm. These data suggest that (331) is a diastereoisomer of (330). Complex (330) is the
major isomer (5:1) present in the pyrolysis mixture, and this can be understood as the result of a strong steric interaction between the cis methyl and i-propyl groups in the Os(2)P(2)C(17)C(18)C(19) five-membered ring in (331). Also in (330) and (331), the P(1) NMR chemical shift remains almost unchanged (by 0.5 ppm), while P(2) changes by 8.2 ppm, consistent with the change in the configuration at this C(17) atom (Figure 4.65).

Complex (332) shows $^{31}$P NMR resonances at 54.2 and 9.3 ppm with a coupling of 9.0 Hz. The $^{1}$H NMR spectrum shows a hydride at -16.70 ppm with $J_1=J_2=12$ Hz. The low yield of the complex (332) precludes further characterization, but it is likely that (332) is similar to the complex Ru$_3$(CO)$_8$(H)[(C$_5$H$_3$PPh$_2$)Fe(C$_5$H$_4$PPh$_2$)] (162) described in Section 2.3.2 [120], that is, it has a formula such as Os$_3$(CO)$_8$(H)[(C$_5$H$_3$PiPr$_2$)Fe(C$_5$H$_4$PiPr$_2$)]. It may be formed from M or 0 (Scheme 4-17).

A minor complex showing $^{31}$P NMR resonances at 154.5 and 49.2 ppm with a coupling of 70 Hz (by $^{31}$P-$^{31}$P COSY spectrum of the pyrolysis mixture) was not found in any bands eluted from the column, but it is probably complex H shown in Scheme 4-16.

Scheme 4-14 A possible reaction sequence for the pyrolysis of Os$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$].

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The formation of the ferrodicyne complex (325) (and also (327),
(328)) from Os$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$] certainly involves many steps and it is not easy to formulate a unique reaction sequence. The formation of all the other complexes from the starting material are outlined in Schemes 4-14 to 4-17. Two reaction pathways seem to account for the products of the pyrolysis of Ru$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$] to be described in Section 5.9. Both of these involve initial $\beta$ C-H activation of an i-propyl group followed by propene elimination and concomitant formation of a Ru-P bond; the essential first step being the movement of one end of the ligand from an equatorial to an axial position. Pyrolysis of Os$_3$(CO)$_{10}$Fc'(PiPr$_2$)$_2$ is more

Scheme 4-15 A possible reaction sequence for the pyrolysis of Os$_3$(CO)$_{10}$Fc'(PiPr$_2$)$_2$.  

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complicated. More products are produced, some involving CO insertion and metalation of the Cp rings. The first step of the reaction appears not only to involve movement of one phosphorus atom to form A, the analogue of the initial ruthenium intermediate, but also movement of both phosphorus atoms to form A', Scheme 4-14. In this Scheme and those below, compounds designated by letters have not been isolated or characterized.

Intermediate A can undergo $sp^3 \beta$ C-H activation at the Os(CO)$_4$ center to give B, Scheme 4-15. B loses a propene molecule readily to give C. A CO insertion into the Os-alkyl bond in B is unlikely since it is already a stable five-membered ring. C can further lose a CO to give (322) by activating one C-H bond from the C$_5$H$_4$P$_2$Pr$_2$ ring, to give D by breaking the P (phosphido)-Fc' bond, and/or to give E by forming an iron-osmium bond. D and E lose a CO to give the isolated product (329).

Intermediate A can also undergo $sp^3 \beta$ C-H activation at the Os(CO)$_3$ center to give F, Scheme 4-16. F can lose a propene molecule to afford (323) or isomerize to G; CO insertion in G affords complexes (330) and (331), a pair of diastereoisomers. The isomerization step may not be necessary, and the insertion is believed to be driven by a release of the steric interaction in F. Further CO loss from (323) results in $sp^3 \beta$ C-H activation of the i-propyl group on the phosphido moiety, a reaction similar to that proposed for the pyrolysis of Ru$_3$(CO)$_{10}$[Fc'(P$_2$Pr$_2$)$_2$] to be discussed in Section 5.9. This process is expected to be more difficult for the osmium complexes since both Os-Os and Os-P bonds are longer than Ru-Ru and Ru-P bonds, and therefore the C-H bond to be activated is not as accessible to the osmium metal center as in the ruthenium analogue. This probably accounts for the fact that (369) and (370) are the major products in the ruthenium case (Section 5.9), while here H is probably produced in
Scheme 4-16 A possible reaction sequence for the pyrolysis of
\( \text{Os}_3(\text{CO})_{10}[\text{Fc'}(\text{PiPr}_2)_2] \).

minute quantities and no I is obtained.

Turning to A', Scheme 4-17, it can undergo sp\(^3\) \( \beta \) C-H activation to give K, or ferrocenyl C-H activation to give M or O depending on which Cp ring is activated. The last two reactions may be compared to the ortho- and hetero-annular metalation of ferrocenyl moiety in complexes such as \( \text{Os}_3(\text{CO})_{11}(\text{PFC}_2\text{Ph}) \) (Schemes 4-2 to 4-4). K loses a propene molecule to give L. Further CO loss from L results in ferrocenyl C-H activation to afford (324) and (326) depending on which ring is metalated. In the alternative pathways M and O can undergo sp\(^3\) \( \beta \) C-H activation to give N and P respectively. Elimination of a propene molecule with concomitant formation of an Os-P bond gives (326) and (324) as the final isolated products.
Scheme 4-17 A possible reaction sequence for the pyrolysis of
Os$_3$(CO)$_{10}$[Fc'(PiPr)$_2$)$_2$.

Overall, the proposed Schemes 4-14 to 4-17 rationalize the formation
of the isolated complexes reasonably well. The chemistry associated with
Os$_3$(CO)$_{10}$[Fc'(PiPr)$_2$)$_2$ is apparently richer and more interesting than that of
the ruthenium analogue to be discussed in Section 5.9. Two more reaction
types, namely, CO insertion into a M-alkyl bond and ferrocenyl C-H
activation, are observed for the osmium complex but not for the ruthenium
analogue. Although sp³ C-H activation is involved in forming most of the
isolated complexes, it is clear from the ready formation of (322), (324), and
(326) that ferrocenyl C-H activation is favored over i-propyl C-H
activation. The observed predominance of sp³ C-H activation is simply due
to the low flexibility, therefore low accessibility, of the ferrocenyl moiety
as it acts as a rigid bridge between two PiPr₂ fragments. Pyrolysis of
Os₃(CO)₁₁(PFcᵢPr₂) discussed earlier in Section 4.7 is consistent with this
statement.

4.14 Pyrolysis of Os₃(CO)₁₂ with P(1-C₁₀H₇)₃

Pyrolysis of Os₃(CO)₁₂ with P(1-C₁₀H₇)₃ in octane for 24 h affords
more than eight products with three in major quantities as judged by TLC,
³¹P, and ¹H NMR spectroscopy. The characterization of these complexes,
(333) to (335), is described below.

The third band contained a complex which gives a ³¹P NMR
resonance at 79.2 ppm suggesting the presence of a phosphine. The ¹H
NMR spectrum is very complex between 7.0 and 8.2 ppm. A hydride
resonance at -20.53 ppm is present. It is probably a complex with one
naphthyl group metalated at the 8 position.

Complex (333) shows a ³¹P NMR resonance at 30.9 ppm suggesting
the presence of a phosphine. The ¹H NMR spectrum shows complex
resonances in the aromatic proton region, and the presence of two
hydrides. The hydride chemical shifts are very similar to those of (336) to be described in the next Section, and this is believed to be an analogous naphthylene complex. The mass spectrum giving the parent ion at 1207 and the micro-analysis are consistent with the expected formula $\text{Os}_3(\text{CO})_8(\text{H})_2[\text{1-C}_{10}\text{H}_7]_2\text{P}(\text{1-C}_{10}\text{H}_5)$. A most likely structure is shown in Figure 4.66.

Complex (334) shows a $^{31}\text{P}$ NMR resonance at 51.1 ppm suggesting the presence of a phosphine. The $^1\text{H}$ NMR spectrum is too complex between 6.8 to 8.3 ppm, but a hydride resonance at -18.53 ppm is present. The mass spectrum gives the parent ion at 1236 corresponding to a formula such as $\text{Os}_3(\text{CO})_9(\text{H})_1[\text{1-C}_{10}\text{H}_7]_2\text{P}(\text{1-C}_{10}\text{H}_6)$. The position of metalation is either at 2 or 8. A comparison of the hydride chemical shift with similar aryl complexes such as $\text{Os}_3(\text{CO})_9(\text{H})_1[\text{C}_5\text{H}_4\text{PPhC}_6\text{H}_4]{\text{Fe(C}_5\text{H}_5)}$ (242) (Section 4.1) favors the 2 position, and a corresponding structure is proposed as shown in Figure 4.66.

Complex (335) shows a $^{31}\text{P}$ NMR resonance at 42.4 ppm suggesting the presence of a phosphine. The $^1\text{H}$ NMR spectrum again is very complex and there is a hydride present. The mass spectrum gives the parent ion at

![Figure 4.66 Possible structures for complexes (333) and (334).](image)
suggesting a monosubstituted complex $\text{Os}_3(\text{CO})_{11}[\text{P}(1-\text{C}_{10}\text{H}_7)_3]$. The last band shows a $^{31}\text{P}$ NMR resonance at 41.9 ppm suggesting the presence of a phosphine. The $^1\text{H}$ NMR spectrum appears simple but cannot easily be analyzed. There are no hydrides present.

The formation of complex (334) involves the orthometalation of a naphthyl group in the presumed precursor (335). The formation of (333) is believed to be driven by a release of the steric interaction between the 1- and 8- positions of naphthyl groups. A more detailed discussion will be provided in Sections 5.10 and 5.11.

4.15 Pyrolysis of $\text{Os}_3(\text{CO})_{12}$ with $\text{As}(1-\text{C}_{10}\text{H}_7)_3$

Pyrolysis of $\text{Os}_3(\text{CO})_{12}$ with $\text{As}(1-\text{C}_{10}\text{H}_7)_3$ in octane for 25 h affords one major product and some minor ones as judged by TLC. The characterization of complex (336) is described below.

Complex (336) gives the parent ion at 1252 in the mass spectrum corresponding to a formula such as $\text{Os}_3(\text{CO})_8[\text{As}(1-\text{C}_{10}\text{H}_7)_3]$. The $^1\text{H}$ NMR spectrum shows the presence of only nineteen naphthyl protons and two hydrides. A formula such as $\text{Os}_3(\text{CO})_8(\text{H})_2[(1-\text{C}_{10}\text{H}_7)_2\text{As}(1-\text{C}_{10}\text{H}_5)]$ is most likely, and it was confirmed by an X-ray single crystal structure determination. An ORTEP diagram of the molecule with 25.0% probability thermal ellipsoids is shown in Figure 4.67.

Crystal data: $\text{fw}=1251.10$, yellow, prism, monoclinic system, space group C2/c (#15), $a=25.746(1)$, $b=9.688(2)$, $c=33.521(1)\ \text{Å}$, $\beta=108.647(3)^\circ$, $V=7922(2)\ \text{Å}^3$, $Z=8$, $D_{\text{calc}}=2.098\ \text{g/cm}^3$, $R=0.033$, $R_w=0.031$.

The molecular structure of (336) consists of a closed $\text{Os}_3$ triangle
Figure 4.67 ORTEP diagram of complex (336).

capped on one face by a naphthyne moiety. The aryne moiety is attached to an arsine coordinated to Os(1). There are eight terminal carboxyls, three each bonded to Os(2) and Os(3), two to Os(1), and two bridging hydrides with only one being located in the structure refinement. The Os(1)-Os(2) bond at 3.0316(6) Å is the longest and Os(2)-Os(3) at 2.7564(7) Å is the
Os(1)-Os(3) has an intermediate length of 2.8950(5) Å. H(1) bridges the Os(1)-Os(3) bond, and the other hydride is believed to bridge the shortest Os(2)-Os(3) bond rather than the longest Os(1)-Os(2) bond. This argument is based on the fact that in the analogous phosphine complex (333) described in the previous Section the two hydrides show very different couplings to the phosphine indicating that most likely one hydride is two bonds and the other three bonds away from the phosphorus atom. The whole cluster is electron precise. The naphthyne moiety is bonded to Os(1) and Os(2) via σ bonds (Os(1)-C(1) 2.112(8), Os(2)-C(2) 2.128(9) Å), and to Os(3) via a π bond (Os(3)-C(1) 2.281(8), Os(3)-C(2) 2.369(9) Å). This bonding mode is very similar to that found in Os₃(CO)₉(H)₂(C₆H₄) (126) [139]. The Os(3)-C(2) bond is ca. 0.1 Å longer than Os(3)-C(1) presumably due to the formation of the Os(1)C(1)C(10)C(9)As(1) five-membered ring. The carbonyls C(32)O(2) and C(35)O(5) trans to the Os-C (aryne) σ bonds have slightly longer Os-C (carbonyl) bonds (av. 1.94 Å) than the others which average to 1.90 Å. All the Os-C-O angles are close to linear (av. 178.4°). Os(1)-As(1) bond has a length of 2.446(1) Å. As(1) and H(1) are displaced to the opposite sides of the Os₃ plane (1.0180 and 0.9493 Å respectively). As(1) is 0.0921, 0.0408, and 0.3049 Å away respectively from the C(1)-C(10), C(11)-C(20), and C(21)-C(30) planes. Os(1) and Os(2) atoms are close to coplanar with the C(1)-C(10) plane (0.2301 and 0.0479 Å away respectively). The C(1)-C(10) plane makes an angle of 63.64° with the Os₃ plane, this value is also similar to that found in Os₃(CO)₉(H)₂(C₆H₄) (126) (63.9 and 69.0°) [139]. The C(1)Os(1)As(1)C(9) torsion angle is 4.9(3)°. As(1)-C(9)-C(10) angle at 112.5(5)° is considerably smaller than As(1)-C(9)-C(8) angle at 126.8(7)° because of ring formation.
while in the naphthyl groups the 1,8 steric interaction renders the As(1)-C(21)-C(30) angle at 125.1(7)° larger than As(1)-C(21)-C(22) at 115.0(7)°.

There is some C-C bond variation in the naphthyne moiety. For example, the C(1)-C(10) bond at 1.45(1) Å is significantly longer than C(3)-C(4) and C(7)-C(8) both at 1.34(1) Å. However the two intact naphthyl groups have similar variation. In the C(21)-C(30) moiety, for example, the C(25)-C(30) bond at 1.46(1) Å is significantly longer than C(23)-C(24) at 1.35(1) and C(28)-C(29) at 1.36(1) Å. There is little bond angle variation in the aryne ring.

Complex (336) represents the first metal cluster complex containing a naphthyne moiety. Cleavage of the C-H bond on the 8-position of a naphthyl group which has a strong steric interaction with the large arsenic atom presumably takes place first. A second C-H activation and establishment of a π bond then gives the product. The two hydrides show two sharp singlets, in contrast to that found for (126) which shows only one resonance at room temperature [139].

The complex in the fourth band gives the parent ion at 1452 in the mass spectrum corresponding to a formula such as Os₃(CO)₈[As(1-C₁₀H₇)₂]₂. There was not enough sample for ¹H NMR characterization, but no extra hydrides were found in the ¹H NMR spectrum of the reaction mixture. Electron counting requires each arsenido moiety to act as a four electron donor, that is, As(1-C₁₀H₇)(1-C₁₀H₆).

The complex in the fifth band shows the parent ion at 1554 in the mass spectrum corresponding to a formula such as Os₃(CO)₇(C₁₀H₆)[As(1-C₁₀H₇)₂]₂. This is likely a naphthyne complex analogous to (106) and (49) described in Section 1.2.3.1.
Chapter 5 Pyrolysis of Triruthenium Complexes Containing Ferrocenyl Ligands

5.1 Pyrolysis of Ru$_3$(CO)$_{11}$(PFcPh$_2$)

Pyrolysis of Ru$_3$(CO)$_{11}$(PFcPh$_2$) has been examined in a number of reaction conditions. In all, seven complexes, (337) to (343), have been characterized and they are described below. The characterization of the benzyne complex (338), which was obtained from Ru$_3$(CO)$_{12-x}$(PFcPh$_2$)$_x$ (x=1 or 2 or 3), will be described in Section 5.3.

Pyrolysis of Ru$_3$(CO)$_{11}$(PFcPh$_2$) in cyclohexane for 1 h affords four major products, complexes (337), (339), (340), and a complex showing a $^{31}$P NMR resonance at 112.7 ppm that was not found after column chromatography. The $^{31}$P NMR spectrum is shown in Figure 5.1.

![Figure 5.1 121.4 MHz $^{31}$P NMR spectrum of a product mixture.](image-url)
Complex (337) shows a $^{31}$P NMR resonance at 387.8 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum, Figure 5.2, shows the presence of a C$_6$H$_4$ moiety and a ferrocenyl group. The mass spectrum gives the parent ion at 847 corresponding to the loss of two CO groups from the parent, and therefore a formula such as Ru$_3$(CO)$_9$(PFc) (C$_6$H$_4$) is most likely. A proposed structure is shown in Figure 5.4.

Figure 5.2 300 MHz $^1$H NMR spectrum of complex (337).

Complex (339) shows a $^{31}$P NMR resonance at 408.1 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum shows the presence of a symmetrical benzyne moiety and a ferrocenyl group. The mass spectrum gives the parent ion at 1004 corresponding to a formula
such as \( \text{Ru}_4(\text{CO})_{11}(\text{PFC})(\text{C}_6\text{H}_4) \). In fact, the \(^1\text{H} \) NMR spectrum is in close agreement with that of (107c) previously described \cite{120} and the two compounds are clearly identical.

Complex (340) shows a \(^{31}\text{P} \) NMR resonance at 149.5 ppm suggesting the presence of a phosphido moiety. The \(^1\text{H} \) NMR spectrum, Figure 5.3.

Figure 5.3 300 MHz \(^1\text{H} \) NMR spectrum of complex (340).
shows the presence of a C₆H₄ moiety and a ferrocenyl group. The mass spectrum gives the parent ion at 720 corresponding to a formula such as Ru₂(CO)₈(PFcC₆H₄). Most likely the complex contains a Ru-Ru bond, and therefore a most probable structure is shown in Figure 5.4. Such CO inserted complexes are known [114].

Pyrolysis of the same starting material (Ru₃(CO)₁₁(PFcPh₂)) in cyclohexane for 3 h affords a number of new products besides complexes (337) to (340). The characterization of three such new products, complexes (341) to (343), is described below.

Complex (341) shows a ³¹P NMR resonance at 415.3 ppm suggesting the presence of a phosphinidene moiety. The ¹H NMR spectrum shows the presence of a C₆H₄ moiety and a ferrocenyl group. The mass spectrum gives the parent ion at 1163 corresponding to a formula such as Ru₅(CO)₁₃(PFc)(C₆H₄). The ³¹P NMR chemical shift difference between (339) and (341) (7.2 ppm) is similar to that between (107a) and (108a) [117, 118], and a proposed structure is shown in Figure 5.4.

![Figure 5.4 Possible structures for complexes (337), (340), and (341).](image)
Complex (342) shows two $^{31}$P NMR resonances at 390 and 162.2 ppm, Figure 5.5, suggesting the presence of a phosphinidene and a phosphido moiety. The signal at 390 ppm is rather broad at room temperature and its variable temperature behaviour is shown in Figure 5.6. There is no obvious rationale for the splitting into two signals. The $^1$H NMR spectrum shows the presence of two C$_6$H$_4$ moieties and two ferrocenyl groups. The mass spectrum gives the parent ion at 1399 corresponding to a formula such as Ru$_5$(CO)$_{11}$(PFc)(PFcC$_6$H$_4$)(C$_6$H$_4$). The structure was solved by an X-ray diffraction study. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 5.7.

Crystal data: (342)-CH$_2$Cl$_2$, $\text{fw}=1482.60$, red, irregular, monoclinic system, space group Cc (#9), $a=10.990(2)$, $b=44.840(4)$, $c=10.145(3)$ Å, $\beta=111.60(2)^\circ$, $V=4648(2)$ Å$^3$, $Z=4$, $D_{\text{calc}}=2.118$ g/cm$^3$, $R=0.031$, $R_w=0.027$.

Figure 5.5 121.4 MHz $^{31}$P NMR spectrum of complex (342).
 history of operations in the accounting department of a large corporation. The
company's financial statements are prepared on a monthly basis, and the
Accounting Department is responsible for ensuring that these statements are
accurate and timely. The department is divided into several sections, each of
which is responsible for a specific aspect of financial reporting. The

The molecular structure of (342) consists of a "square" Ru$_4$ unit
(mean deviation 0.0469 Å, torsion angles Ru(1)Ru(2)Ru(5)Ru(4) 3.60(2)°,
Ru(1)Ru(4)Ru(5)Ru(2) 3.64(2)°) sharing an edge (Ru(1)-Ru(2)) with a Ru$_3$
unit. Instead of adopting the butterfly arrangement that is more commonly
found in such systems, these two units are almost perfectly perpendicular
(91.07°). The outer face of the Ru$_4$ moiety is capped by a phosphinidene
moiety, and that of the Ru$_3$ triangle is capped by a bridging phosphido
group that is also bound to the third ruthenium atom through the
orthometalated carbon atom C(8) of the phenyl group. The phosphido

Figure 5.6 121.4 MHz variable temperature $^{31}$P NMR spectrum of
complex (342).
Figure 5.7 ORTEP diagram of complex (342).

group bridges the Ru(1)-Ru(3) bond rather than the shared edge Ru(1)-Ru(2). The inner face of the Ru4 "square" and Ru3 triangle is occupied by a novel η^6-benzyne moiety which is bound to Ru(4)-Ru(5) through carbon atoms C(1) and C(2) and bound to Ru(3) in a η^6 fashion. All carbonyls are terminal, and they are distributed three each to Ru(4) and Ru(5), two each to Ru(1) and Ru(2), and one to Ru(3). The whole cluster is electron precise.
if the benzyne moiety is considered to be a six-electron donor to Ru(3) and a two-electron donor to Ru(4)-Ru(5).

The "square" Ru$_4$ and triangular Ru$_3$ units are rather unsymmetrical and the metal-metal bonds show significant variation. This is not unexpected because the molecule is not symmetrical due to the presence of the phosphido bridge. In the Ru$_4$ unit, the Ru(2)-Ru(5) bond is rather long at 3.0515(9) Å and it is much longer than Ru(1)-Ru(4) at 2.8966(8) Å. The Ru(4)-Ru(5) distance is equal to that of Ru(1)-Ru(4), but the Ru(1)-Ru(2) bond is longer at 2.935(1) Å. In the Ru$_3$ unit, the phosphido bridged Ru(1)-Ru(3) bond is the longest at 2.976(1) Å, and Ru(2)-Ru(3) at 2.819(1) Å is the shortest which is shorter than those found in Ru$_3$(CO)$_{12}$ (av. 2.848 Å).

The $\mu_4$-phosphinidene P$_1$Fc bridges the Ru$_4$ unit slightly unsymmetrically. Thus, the P(1)-Ru(1) and P(1)-Ru(5) bonds (2.371(2) and 2.385(2) Å) are slightly shorter than the P(1)-Ru(2) and P(1)-Ru(4) distances (2.424(2) and 2.403(2) Å). These bonds are longer than the phosphido bridges P(2)-Ru(1) (2.296(2) Å) and P(2)-Ru(3) (2.271(2) Å) which are also slightly unsymmetrical.

The benzyne-ruthenium σ bonds C(1)-Ru(4) at 2.154(7) Å and C(2)-Ru(5) at 2.100(7) Å are of similar lengths to the orthometalated phenyl carbon C(8)-Ru(2) bond at 2.125(7) Å. The benzyne C(1)-C(6) ring is $\eta^6$ bonded to Ru(6) as found in $\eta^6$ arene-ruthenium complexes such as Ru$_6$C(CO)$_{14}$(1,3,5-C$_6$H$_3$Me$_3$) [344] and Ru$_4$(CO)$_9$(C$_6$H$_6$)(C$_6$H$_8$) [345]. The Ru(3)-carbon distances are slightly shorter for C(4), C(3), and C(2) (2.336(8), 2.257(7), and 2.274(7) Å respectively) than for C(1), C(5), and C(6) (2.311(7), 2.314(8), and 2.337(7) Å respectively), but the average (2.288 Å) is close to that in Ru$_6$C(CO)$_{14}$(1,3,5-C$_6$H$_3$Me$_3$) (av. 2.24 Å) and
Ru$_4$(CO)$_9$(C$_6$H$_6$)(C$_6$H$_8$) (av. 2.238 Å) [344, 345]. The Ru(3)-benzyne ring centroid distance is 1.800 Å.

The Ru-C (carbonyl) distances for those carbonyls bound to Ru(1), Ru(2), and Ru(3) (av. 1.872 Å) are shorter than those of the Ru(4) and Ru(5) bound carbonyls (av. 1.918 Å) presumably due to the higher electron density on the Ru$_3$ unit. All C-O distances are equivalent (av. 1.135 Å). Most of the Ru-C-O angles are close to linear (from 175.4(7) to 179.6(8)°), but the Ru(4)-C(38)-O(6) (171.4(8)°), Ru(4)-C(39)-O(7) (173.1(8)°), and Ru(5)-C(42)-O(10) (173.1(7)°) ones are significantly bent.

In the benzyne moiety C(1)-C(6), the planarity is little distorted (mean deviation 0.0145 Å). The Ru(4) atom is situated 0.6497 Å away from the C$_6$ plane though Ru(5) lies closer to it (0.1272 Å), and the torsion angle Ru(4)C(1)C(2)Ru(5) is 7.2(3)°. The benzyne ring makes an angle of 74.88° with the Ru$_4$ plane, and 21.50° with the Ru$_3$ plane. As expected, the Ru(4)-C(1)-C(2) (104.5(5)°), Ru(4)-C(1)-C(6) (132.6(5)°), Ru(5)-C(2)-C(1) (114.4(5)°), and Ru(5)-C(2)-C(3) (126.6(6)°) angles show a wide variation, but the internal angles of the benzyne ring are more regular (from 117.4(7) to 122.8(7)°). The C-C bond lengths in the ring range from 1.39(1) Å for C(4)-C(5) to 1.44(1) Å for C(1)-C(2) with an average of 1.415 Å. In the orthometalated phenyl C(7)-C(12) ring the C-C lengths are shorter ranging from 1.36(1) Å for C(11)-C(12) to 1.41(1) Å for C(7)-C(8) with an average of 1.385 Å. Some bond lengthening in the benzyne ring is thus present. The C(7)-C(11) ring shows little deviation from planarity (mean deviation 0.0123 Å) and both the Ru(2) and P(2) atoms are almost coplanar with the ring (0.0536 and 0.1415 Å away respectively). The C(8) atom is almost coplanar with the Ru$_4$ unit (0.0960 Å). The C(7)-C(12) ring is perpendicular to the Ru$_3$ plane (89.92°) as is found in a similar unit on
Os₃(CO)₉(µ-CO)[µ₃-PMc₆H₄]} (232) [132]. The Ru(2)-C(8)-C(7) (119.5(5)°) and Ru(2)-C(8)-C(9) (122.9(6)°) angles are close to ideal, but the P(2)-C(7)-C(8) (112.9(5)°) and P(2)-C(7)-C(12) (126.0(6)°) angles are significantly different from 120°. Within the C₆ ring, the C-C-C angles range from 117.6(7) to 121.5(8)°.

In both ferrocenyl moieties, all Fe-C (Cp rings) distances are the same and normal (av. 2.035 Å), and so are the Fe-Cp distances (av. 1.646 Å). Within the Cp rings, the C-C-C angles show little deviation from 108°. The C-C bond lengths are the same and normal except in the Cp(3) ring (C(23)-C(27)) where the C(23)-C(27) bond at 1.46(1) Å is unexpectedly longer than C(25)-C(26) and C(26)-C(27) bonds (both 1.37(1) Å). The P(1)-C(13)-C(14) and P(1)-C(13)-C(17) angles (125.7(6) and 128.2(6)°) are normal, but the P(2)-C(23)-C(24) and P(2)-C(23)-C(27) angles (131.4(6) and 122.7(6)°) are somewhat distorted. The P(1) and P(2) atoms are 0.2390 and 0.1425 Å away from Cp(1) and Cp(3) planes respectively. The Cp(1) and Cp(2) rings have a ring tilt angle of 4.22°, and the Cp(3) and Cp(4) rings have one of 2.95°.

This molecule appears to be similar to the penta-nuclear ruthenium benzyne complex Ru₅(CO)₁₃(PPh)(C₆H₄) (108a) described by Knox et al. [117, 118]. However there are two important differences: (1) In (108a) the Ru₄ and Ru₃ units are in a butterfly arrangement allowing the benzyne ring to interact with all the ruthenium atoms of the Ru₃ unit in a face-capping mode thus donating a total of six electrons, in (342) the Ru₄ and Ru₃ units are perpendicular, the benzyne can only interact with Ru(3) but it still donates six electrons. (2) The Ru₃ triangle in (342) contains an extra face-capping moiety PFc(C₆H₄).
The formation of (342) from Ru$_3$(CO)$_{11}$(PFcPh$_2$) must involve many steps including cluster fragmentation and recombination. However, centering on the phosphine ligands, it is evident that two P-C bonds have been cleaved from P(1), and one P-C bond has been cleaved from P(2). Two C-H bonds are also cleaved, one from C(8) atom, and one from the benzyne ring. The two hydrides and two phenyl groups are probably lost as two benzene molecules. Clearly only phenyl C-H and C-P bonds are attacked. It is rather surprising that compound (342) is formed in refluxing cyclohexane (3 h, 15%) since complex (108a) was obtained in refluxing toluene (18 h, 7%).

The minor complexes in the seventh, eighth, and ninth bands are presumably very interesting. For example, those showing $^{31}$P NMR resonances at 450.6, 423.5, and 420.6 ppm all contain phosphinidene moieties. The complex showing two $^{31}$P NMR resonances at 387.2 and 192.8 ppm with a coupling of 73.4 Hz contain a phosphinidene and a phosphido moiety. It may be an isomer of complex (342) differing in the orientation of the PFcC$_6$H$_4$ moiety.

Figure 5.8 Possible structures for complexes (338) and (343).
Complex (343) shows two $^{31}$P NMR resonances at 410.5 and 275.0 ppm suggesting the presence of a phosphinidene and a phosphido moiety. The $^1$H NMR spectrum shows the presence of two $C_6H_4$ moieties and two ferrocenyl groups. The mass spectrum gives the parent ion at 1268 corresponding to a formula such as $Ru_4(CO)_{10}(PFc)(PFcC_6H_4)(C_6H_4)$. In view of the structure of complex (339), a plausible structure for (343) is shown in Figure 5.8.

5.2 Pyrolysis of $Ru_3(CO)_{10}(PFcPh_2)_{2}$

Pyrolysis of $Ru_3(CO)_{10}(PFcPh_2)_{2}$ in cyclohexane for 70 min affords mainly complexes (338) and (344). These will be described in the next section: complex (344) is a symmetrical isomer of (338). The third possible isomer may also be present in the reaction mixture in small quantities. It is believed that these different isomers have different thermodynamic stabilities, and thus their relative yields depend on reaction temperature and time.

Pyrolysis of $Ru_3(CO)_{10}(PFcPh_2)_{2}$ in hexanes for 20 h affords the same products, and again (338) and (344) are the major ones.

5.3 Pyrolysis of $Ru_3(CO)_{9}(PFcPh_2)_{3}$

Pyrolysis of $Ru_3(CO)_{9}(PFcPh_2)_{3}$ in cyclohexane for 13 h affords more than ten products as judged by TLC and $^{31}$P NMR spectroscopy. The characterization of five complexes, (338), (344) to (347), will be described
below. A $^{31}$P NMR spectrum of a mixture of (338) and (344) is shown in Figure 5.9.

Complex (338) shows a $^{31}$P NMR resonance at 236.8 ppm suggesting the presence of one or two phosphido moieties. The $^1$H NMR spectrum shows the presence of two equivalent phenyl groups, two equivalent ferrocenyl groups, and a symmetrical benzyne moiety. A very strong parent ion peak at 1161 in the mass spectrum suggests that two equivalent phosphido moieties must be present and a formula such as $\text{Ru}_3(\text{CO})_7(\text{PFcPh})_2(\text{C}_6\text{H}_4)$ is very likely. In analogy with similar osmium complexes (Section 4.2), a structure in which both ferrocenyl moieties are situated on the benzyne side of the $\text{Ru}_3$ triangle is preferred, and two possibilities are shown in Figure 5.8. This new isomer was not isolated in the previous study [119].

Complex (344) was characterized to be (106b), previously described.

![Figure 5.9 121.4 MHz $^{31}$P NMR spectrum of a mixture of (338) and (344).](image)

337
by Cullen and coworkers [119]. Two $^{31}$P NMR resonances at 272.2 and 208.3 ppm with a coupling of 199.6 Hz, a $^1$H NMR spectrum showing the presence of two different ferrocenyl groups, two different phenyl groups, and an unsymmetrical benzyne moiety, and a mass spectrum virtually identical to that of (338) are all in good agreement with those reported. The crystal structure of this complex was actually re-determined, but a different space group and a different set of unit cell parameters were found. This is not unusual because the crystals were obtained from a different solvent system. A stereoview of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 5.10.

Figure 5.10 ORTEP diagram of complex (344).
Crystal data: fw=1161.59, red, prism, monoclinic system, space group P2₁/c (#14), a=13.872(3), b=9.800(3), c=31.721(2) Å, β=99.85(1)°, V=4249(2) Å³, Z=4, Dcalc=1.816 g/cm³, R=0.036, Rw=0.037.

The molecule consists of a closed Ru₃ triangle capped on one face by a benzyne moiety and bridged by a phosphido group each on two edges. The two phosphorus atoms are situated on opposite sides of the Ru₃ plane (0.6387 and 0.6520 Å away for P(1) and P(2) respectively) with P(2) towards benzyne side. The benzyne moiety is bonded to Ru(1) and Ru(3) via σ bonds (Ru(1)-C(21) 2.124(6), Ru(3)-C(22) 2.097(6) Å) and to Ru(2) via a π bond (Ru(2)-C(21) 2.337(6), Ru(2)-C(22) 2.352(6) Å), and it makes an angle of 63.79° with the Ru₃ plane. Ru(1) and Ru(3) are close to coplanar with the benzyne moiety (0.1480 and 0.0103 Å away respectively) consistent with σ interactions, while Ru(2) is displaced 2.0179 Å away from this plane. The Ru-Ru distances span an even larger range compared to (106b), namely, Ru(1)-Ru(3) at 2.9190(7) and Ru(1)-Ru(2) at 2.8051(7) Å are longer than the corresponding ones previously determined (Table 1-3), while Ru(2)-Ru(3) at 2.7054(9) Å is appreciably shorter than the corresponding one (2.7420(8) Å). The variation of the bond lengths within the benzyne ligand suggests some degree of bond localization (C(21)-C(22) 1.445(8), C(21)-C(26) 1.426(9), C(26)-C(25) 1.364(9), C(25)-C(24) 1.38(1) Å). Ru-P bond lengths are not different from those previously determined. Among the Ru-C (carbonyl) bonds, Ru(3)-C(43) at 1.98(1) Å is the longest, Ru(1)-C(39) at 1.854(7) and Ru(2)-C(41) at 1.866(8) Å are the shortest, the rest average to 1.925 Å. As previously described, the carbonyl C(45)-O(7) is semi-bridging between Ru(2) and Ru(3) as indicated by Ru(3)-C(45)-O(7) angle (166.0(6)°) and Ru(2)-Ru(3)-C(45) angle 68.6(2)° [119]. The Ru(2)-C(45) distance is relatively long at
2.690(7) Å, but is in the range where significant interaction with Ru(2) would be expected to occur. In addition to the Ru(3)-C(45)-O(7) angle of 166.0(6)°, the Ru(3)-C(43)-O(5) angle at 170.5(9)° is also somewhat smaller than the others which average to 177.8°. The ring tilt angle between the Cp(1) and Cp(2) rings is 3.84°, and that between the Cp(3) and Cp(4) rings is 2.58°. P(1) is 0.2289 and 0.0936 Å away respectively from the Cp(1) and C(27)-C(32) planes, while P(2) is 0.1786 and 0.2112 Å away respectively from the Cp(3) and C(33)-C(38) planes.

Complex (345) shows two $^{31}P$ NMR resonances at 265.1 and 208.3 ppm with a coupling of 201.6 Hz suggesting the presence of two phosphido moieties in an arrangement similar to that in (344). The $^1H$ NMR spectrum shows the presence of a C$_6$H$_4$ moiety, two phenyl groups, and two ferrocenyl groups. The mass spectrum gives the parent ion at 1190, and the fragmentation pattern is very similar to that of (338) and (344). The structure cannot be established without an X-ray diffraction study, but a comparison with Os$_3$(CO)$_8$(C$_6$H$_5$)(PPhC$_6$H$_4$)(PPh$_2$) (226), obtained from Os$_3$(CO)$_{10}$(PPh$_3$)$_2$ [67-69], indicates that complex (345) is probably analogous. Two possible structures differing in PFcPh configuration are shown in Figure 5.11.

The fifth band contains mainly two complexes and the $^{31}P$ NMR resonances suggest that both contain a phosphido moiety and a phosphine.

The isomeric complexes (346) and (347) show typical ABX $^{31}P$ NMR patterns with AB suggesting the presence of two phosphido moieties and X suggesting the presence of a phosphine. The parent ion at 1505 in the mass spectrum corresponds to the loss of one phenyl and three CO groups from Ru$_3$(CO)$_9$(PFcPh$_2$)$_3$, and the fragments are associated with the successive

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Figure 5.11 Possible structures for complex (345).

Figure 5.12 300 MHz $^1$H NMR spectrum of complexes (346) and (347).
loss of six carbonyls and the loss of PFcPh\textsubscript{2} and a phenyl group. A formula such as Ru\textsubscript{3}(CO)\textsubscript{6}(PFcPh\textsubscript{2})(PFcPh)\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}) is very likely. The \textsuperscript{1}H NMR spectrum, shown in Figure 5.12, is rather complicated, nevertheless it is consistent with the presence of six ferrocenyl groups (six C\textsubscript{5}H\textsubscript{5} singlets, three from each complex), and benzyne moieties. By analogy with complexes (338) and (344), the proposed structures for (346) and (347) are shown in Figure 5.13. \textit{P}_B has the ferrocenyl group pointing towards the benzyne side of the Ru\textsubscript{3} plane, while \textit{P}_A has two different geometrical arrangements resulting in the observed isomers. This same difference in the geometrical arrangements of \textit{P}_A gives rise to the isomeric complexes (338) and (344). It should be noted that the \textsuperscript{31}P NMR chemical shift of \textit{P}_A changes by 9.8 ppm from one isomer to the other, while \textit{P}_B and \textit{P}_X both change by only 2.2 ppm, this is consistent with the change in \textit{P}_A.

![Possible structures for complexes (346) and (347)](image)

Figure 5.13 Possible structures for complexes (346) and (347).
5.4 Pyrolysis of Ru$_3$(CO)$_{11}$(PF$_2$C$_2$Ph)

Pyrolysis of Ru$_3$(CO)$_{11}$(PF$_2$C$_2$Ph) has been studied under different reaction conditions. Pyrolysis of Ru$_3$(CO)$_{12}$ and PF$_2$C$_2$Ph in octane was also studied. In all, five complexes, (348) to (352), have been characterized. The characterization of these complexes are described below.

Pyrolysis of Ru$_3$(CO)$_{11}$(PF$_2$C$_2$Ph) in hexanes for 15 h affords four major products and some minor ones as judged by TLC and $^{31}$P NMR spectroscopy.

Complex (348) shows a $^{31}$P NMR resonance at 364.4 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum shows the presence of seventeen ferrocenyl protons with two C$_5$H$_5$ rings. The mass spectrum gives the parent ion at 1086 corresponding to a formula such as Ru$_4$(CO)$_{10}$(PF$_2$)[(C$_5$H$_3$)Fe(C$_5$H$_5$)]. Its structure may be similar to that of the tetranuclear benzyne complexes (107). This is an unprecedented formulation and an X-ray crystallographic study is needed to confirm it.

Complex (349) shows a $^{31}$P NMR resonance at 377.8 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum shows the presence of a C$_6$H$_4$ moiety and, unexpectedly, two ferrocenyl groups. The mass spectrum gives the parent ion at 1008 corresponding to the loss of three CO groups from the parent, and thus a formula such as Ru$_3$(CO)$_8$(PF$_2$C$_6$H$_4$). No obvious structures can be conceived which are consistent with all the available data, a structure determination is clearly needed.

Complex (350) shows a $^{31}$P NMR resonance at 24.6 ppm suggesting the presence of a phosphine. The $^1$H NMR spectrum shows the presence of a phenyl group, seventeen ferrocenyl protons with two C$_5$H$_5$ rings, and a hydride. The mass spectrum gives the parent ion at 1035 corresponding to
the loss of two CO groups from the parent. The structure of this complex was established by using X-ray crystallography. An ORTEP diagram with 33.0% probability thermal ellipsoids is shown in Figure 5.14.

Crystal data: fw=1033.44, red-orange, prism, triclinic system, space group P1 (#2), a=12.761(2), b=13.280(2), c=10.216(2) Å, α=93.01(1), β=98.57(1), γ=83.66(1)°, V=1700.4(4) Å³, Z=2, D_{calc}=2.018 g/cm³, R=0.029, R_w=0.030.

The molecular structure of complex (350) consists of a closed Ru₃ metal framework with a face-capping and significantly modified ferrocenyl phosphine ligand, eight terminal carboxyls, a bridging carbonyl, and a bridging hydride which was located in the structure refinement. The cluster is electron precise since an iron ruthenium bond is present. The Ru-
Ru bond distances span a large range with Ru(1)-Ru(3) being the shortest at 2.7828(6) Å, Ru(1)-Ru(2) being very long at 3.0319(6) Å, and Ru(2)-Ru(3) being of intermediate length of 2.8868(6) Å which is comparable to that in Ru₃(CO)₁₂ (2.854(4) Å) (Table 2-1). The shortest Ru-Ru bond is bridged asymmetrically by carbonyl C(27) (Ru(1)-C(27) 1.971(4)Å, Ru(3)-C(27) 2.134(4) Å, Ru(1)-C(27)-Ru(3) 85.3(2)*), and symmetrically by the orthometalated ferrocenyl carbon C(2) (Ru(1)-C(2) 2.262(4) Å, Ru(3)-C(2) 2.252(4) Å, Ru(1)-C(2)-Ru(3) 76.1(1)*). Such symmetrical bridging of an orthometalated aryl moiety is present in complex Os₃(CO)₈(H)[Ph₂PCH₂P(Ph)C₆H₄] (236) [273], but this compound is coordinatively unsaturated and undergoes a facile reversible addition reaction with CO [307]. The longest Ru-Ru bond is, as expected, bridged by the hydride. The Ru(2) and Ru(3) centers have approximate octahedral geometry, but Ru(1) center is highly distorted.

The carbonyl C-Ru distances show significant variations. The Ru(1)-C(28) (1.864(5) Å) and Ru(1)-C(29) (1.857(5) Å) bonds are the shortest presumably due to the higher electron density of the Ru(1) center compared to Ru(2) and Ru(3) centers. This probably also accounts for a shorter Ru(1)-C(27) bond than Ru(3)-C(27). The other carbonyl C-Ru distances range from 1.900(4) Å to 1.936(4) Å for Ru(3)-C(35) which occupies an axial position. The bridging carbonyl bond C(27)-O(1) at 1.185(5) Å is longer than the other carbonyl C-O distances (av. 1.137 Å). Two terminal carbonyls C(31)-O(5) and C(35)-O(9) are not linear, the Ru-C-O angles being 172.3(4) and 173.6(4)* respectively. The other Ru-C-O angles average to 177.1*, being close to linear. The bridging carbonyl angles Ru(1)-C(27)-O(1) (138.3(4)*) and Ru(3)-C(27)-O(1) (136.4(3)*) are typical of such carbonyls.
The presence of both the dangling ferrocenyl group (Fc(2): Cp(3), Cp(4)) and the significantly modified ferrocenyl moiety (Fc(1): Cp(1), Cp(2)) in the same molecule invites comparison. In Fc(2), all Fe-C bonds are the same (av. 2.042 Å) and normal, this is also reflected by normal Fe(2)-Cp(3) and Fe(2)-Cp(4) distances (1.648 and 1.654 Å respectively). In Cp(1), the Fe(1)-C(2) bond is very long at 2.182(4) Å, Fe(1)-C(1) and Fe(1)-C(3) bonds (av. 2.084 Å) are slightly lengthened, Fe(1)-C(4) and Fe(1)-C(5) bonds are normal (av. 2.045 Å). In Cp(2), Fe(1)-C(6) and Fe(1)-C(10) (av. 2.108 Å) are longer than the other three (av. 2.051 Å). The Fe(1)-Cp bonds (both 1.698 Å) are also longer than those of Fc(2) by ca. 0.05 Å. In the Cp(3) and Cp(4) rings, all C-C bonds are effectively the same and normal (av. 1.415 Å). In Fc(1), the Cp(2) ring has identical C-C bonds (av. 1.401 Å) which are probably shortened albeit insignificantly; in the Cp(1) ring, as might be expected, the C(1)-C(2) bond has been lengthened significantly (1.471(5) Å), and C(2)-C(3) (1.440(5) Å) maybe slightly lengthened, the other three (av. 1.413 Å) are normal. All C-C-C bond angles in the Fc(2) moiety (Cp(3) and Cp(4) rings) and in the Cp(2) ring of the Fc(1) moiety are normal (av. 108.0° for each of the three rings), but in the orthometalated Cp(1) ring, the C(1)-C(2)-C(3) angle at 104.1(3)° is significantly smaller than the others which range from 107.9(3) to 110.4(3) for C(2)-C(3)-C(4). Such deviations of the C-C bond lengths and C-C-C bond angles were not found in Os₃(CO)₁₀(PF₇C₅H₅)₂ (Section 6.3.2). The mean deviation of the carbon atoms from the least square planes for Cp(1) is 0.0133 Å, while those of the Cp(2), Cp(3), and Cp(4) rings are 0.0045, 0.0031, and 0.0027 Å respectively. It is also interesting to note that P(1) is close to coplanar with Cp(1) (0.0886 Å), but displaced 0.2760 Å away from the Cp(3) plane. The P(1)-C(11)-C(12) and P(1)-C(11)-C(15) angles (125.6(3) and 126.1(3)°) are
the same and ideal, but the $\text{P}(1)$-$\text{C}(1)$-$\text{C}(2)$ (120.7(3)$^\circ$) and $\text{P}(1)$-$\text{C}(1)$-$\text{C}(5)$ angles (130.0(3)$^\circ$) differ by 10$^\circ$. This is again the result of the metalation since it was not found in $\text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2$ (Section 6.4.2). The geometry around $\text{P}(1)$ is similar to that found in $\text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2$ which will be discussed in Section 6.4.2 and in $\text{PFc}_2\text{Ph}$ [346] ($\text{Ru}(2)$-$\text{P}(1)$-$\text{C}(11)$ 118.5(1)$^\circ$, $\text{Ru}(2)$-$\text{P}(1)$-$\text{C}(21)$ 117.8(1)$^\circ$, and $\text{C}(11)$-$\text{P}(1)$-$\text{C}(21)$ 101.3(3)$^\circ$).

The $\text{Cp}(3)$ and $\text{Cp}(4)$ rings have a ring tilt angle of 5.93$^\circ$, while the $\text{Cp}(1)$ and $\text{Cp}(2)$ rings have opened up considerably to an angle of 21.25$^\circ$ which is similar to that found in $\text{Ru}_3(\text{CO})_8(\text{H})[(\text{C}_5\text{H}_4\text{PPh}_2)\text{Fe}(\text{C}_5\text{H}_3\text{PPh}_2)]$ (162) [120]. The $\text{Cp}(1)$ and $\text{Cp}(2)$ planes make angles of 84.62 and 74.41$^\circ$ respectively with the $\text{Ru}_3$ plane. $\text{Ru}(2)$ is close to coplanar with the $\text{Cp}(1)$ ring (0.1048 Å).

The $\text{Ru}(1)\text{Ru}(3)\text{C}(2)$ plane makes an angle of 80.27$^\circ$ with the $\text{Ru}_3$ plane. The $\text{C}(2)$-$\text{Ru}(1)$ and $\text{C}(2)$-$\text{Ru}(3)$ bonds are slightly longer than typical $\sigma$ bonds but shorter than $\pi$ bonds, thus it is appropriate to envisage the $\text{Ru}(1)$-$\text{C}(2)$-$\text{Ru}(3)$ bonds as two electron-three center (2e-3c) bonds with the $\text{C}(2)$ atom donating one electron.

The structure of this complex is similar to that of (162) except that one carbonyl on $\text{Ru}(1)$ is replaced by a phosphine which is attached to the $\text{Cp}(2)$ ring [120]. However, three significant differences should be noted: (1) in complex (162) the orthometalated carbon is bonded to two $\text{Ru}$ atoms rather unsymmetrically (2.12(2) and 2.45(2) Å) indicating a normal $\sigma$ bond and a secondary $\pi$ interaction; (2) in complex (162) the Fe-$\text{Ru}$ bonding interaction is rather weak as indicated by the length of 3.098(3) Å, and this bond is even longer than the $\text{Ru}(1)$-$\text{Ru}(2)$ bond (3.037(2) Å); (3) in complex (162) there is no bridging or semi-bridging carbonyls. The
presence of the bridging carbonyl C(27)O(1) may be attributed to the strong electron releasing nature of the Fc groups.

Since the orthometalation of a Cp ring in forming (350) creates planar chirality, two diastereoisomers are possible for the complex. However solution NMR spectra including that of the pyrolysis mixture reveal only one hydride. There is no obvious explanation for the absence of the other diastereoisomer. Also surprising is the absence of any hydrides due to phenyl orthometalated complexes such as Ru₃(CO)₉(H)(PFc₂C₆H₄) or benzyne complex such as Ru₃(CO)₉(H)(PFc₂)(C₆H₄).

Pyrolyses of the same starting material Ru₃(CO)₁₁(PFc₂Ph) in cyclohexane for 6 h, and in toluene for 5 h afford the same products as discussed above but in different proportions. A few new complexes in small quantities were isolated from the pyrolysis reaction in toluene.

Pyrolysis of Ru₃(CO)₁₂ and PFc₂Ph in 1:1 molar ratio in octane for 3.5 h affords more than eight products as judged by TLC and ³¹P NMR spectroscopy. ¹H NMR spectroscopy revealed the absence of any hydride containing species. The characterization of two new products, complexes (351) and (352), are described below.

Complex (351) shows a ³¹P NMR resonance at 418.0 ppm suggesting the presence of a phosphinidene moiety. The ¹H NMR spectrum shows the presence of only thirteen ferrocenyl protons indicating some unusual feature in this complex. The mass spectrum gives the parent ion at 993 corresponding to a formula such as Ru₄(CO)₁₁(PFc)(C₅H₄). This novel formulation was confirmed by an X-ray diffraction study. An ORTEP diagram with 33.0% probability thermal ellipsoids is shown in Figure 5.15.

Crystal data: fw=992.48, red, prism, monoclinic system, space group
The structure of (351) consists of a metal skeleton of Ru₃ triangle sharing a Ru-Ru edge with a Ru₃P butterfly arrangement. The Ru(1)Ru(3)Ru(4) plane makes an angle of 75.86° with the Ru(2)Ru(3)Ru(4) plane. The cyclopentadienyl ring C(1)-C(5) is σ bonded to Ru(2) via C(1) and η⁵ bonded to Ru(1). The carbonyl ligands are distributed two to Ru(1), three each to Ru(2), Ru(3), and Ru(4), and the whole cluster is electron precise. The Ru(1)-Ru(4) bond is the longest at 2.9514(6) Å, Ru(1)-Ru(3) and Ru(2)-Ru(4) bonds are shorter at 2.8974(7) and 2.9199(5) Å respectively.

Figure 5.15 ORTEP diagram of complex (351).
tively, and the Ru(3)-Ru(4) bond is the shortest at 2.7874(5) Å. The phosphinidene moiety is not symmetrically bound; the Ru(4)-P(1) bond (2.393(1) Å) is longer than Ru(2)-P(1) (2.341(1) Å) which is longer than Ru(3)-P(1) (2.323(1) Å). The Ru(2)-C(1) bond at 2.086(4) Å is typical of such σ bonds. The Ru(1)-C (Cp(1)) distances show some variation with Ru(1)-C(1) and Ru(1)-C(2) bonds (av. 2.258 Å) ca. 0.04 Å longer than the other three (av. 2.214 Å), and they are longer than Fe-C bonds (Cp(2) and Cp(3)) (av. 2.047 and 2.019 Å) as expected. The Ru(1)-Cp(1) length (1.876(3) Å) is also greater than the Fe(1)-Cp(2) and Cp(3) lengths (1.644(4) and 1.646(6) Å).

The carbonyl C-Ru distances show significant variation. The Ru(2)-C(20) bond which is trans to Ru(2)-C(1) σ bond is the longest at 1.952(4) Å, Ru(2)-C(19) and Ru(3)-C(23) bonds which are trans to Ru-P(1) bonds are at av. 1.936 Å, Ru(3)-C(22), Ru(4)-C(25), and Ru(4)-C(26) bonds average to 1.913 Å, and the rest average to 1.884 Å. The Ru-C-O angles are close to linear only for carbonyls C(18), C(19), C(22), C(23), and C(24) (av. 177.8°). The rest average to 173.4° which is somewhat bent.

The planarity of the Cp(1) ring is little distorted with a mean deviation of only 0.0033 Å. The Cp(2) plane makes an angle of 30.08° with the Ru(1)Ru(3)Ru(4) plane and 75.13° with the Ru(2)Ru(3)Ru(4) plane. Ru(2) is close to coplanar with the ring (0.1003 Å away). The C(3)-C(4) bond at 1.396(6) Å may be slightly longer than the other four in the ring (av. 1.427 Å). Only the C(2)-C(1)-C(5) angle (105.0(6)°) in the ring is slightly distorted from the ideal. The ferrocenyl moiety is unexceptional and the Cp(2) and Cp(3) rings have a small ring tilt angle of 2.82°. P(1) is only 0.0742 Å away from the Cp(2) plane.
The structure may be compared to that of the (benzyne)chromium tricarbonyl complex (128) [121], and it may also be considered as a ruthenium analogue of the well known osmium benzyne complexes Os₃(CO)₉(PR)(C₆H₄) (R=Ph, Et, Me) (121) [131-133]. The difference between (128) and (351) is that in (128) the (C₆H₄)Cr(CO)₃ moiety is bonded to two Ru centers via two carbon atoms of the C₆H₄ fragment and to the third Ru atom via the chromium atom, while in (351) the (C₅H₄)Ru(CO)₂ moiety is bonded to one Ru center via one carbon atom of the C₅H₄ fragment and to the other two Ru centers via the Ru(1) atom.

Complex (352) shows a ³¹P NMR resonance at 328.5 ppm suggesting the presence of a phosphinidene moiety. The ¹H NMR spectrum shows the presence of seventeen ferrocenyl protons with two C₅H₅ rings. The mass spectrum gives the parent ion at 956 corresponding to the loss of one phenyl and two CO groups from the parent. A formula such as Ru₃(CO)₉(PFC)[(C₅H₃)Fe(C₅H₅)] is very likely, and two possible structures are shown in Figure 5.16.

Figure 5.16 Two possible structures for complex (352).
The pyrolysis of Ru$_3$(CO)$_{11}$(PFcPh$_2$) affords a number of novel complexes. Both tetra- and dinuclear complexes are formed. As expected, the reactivities are centered on phenyl groups. The pyrolysis of Ru$_3$(CO)$_{11}$(PFc$_2$Ph) is different. It gave the tetraneous benzyne complex (339) but not the trinuclear benzyne complex (337) which has been discussed in Section 5.1, a somewhat unexpected result. It did not give the dinuclear complex (340) either. The formation of the other isolated complexes (348) to (352) does seem to indicate that in this case the reactivities are centered on ferrocenyl groups. Further study to firmly characterize all the isolated products is certainly needed.

A comparison of the results of the pyrolysis of Ru$_3$(CO)$_{11}$(PFc$_2$Ph) with that of Os$_3$(CO)$_{11}$(PFc$_2$Ph), which has been described in Section 4.3, clearly shows that the two systems are rather different. The Ru$_3$ system readily undergoes cluster framework change, while the Os$_3$ system is very robust. The chemistry of the Os$_3$ system is richer, more products are formed. Orthometalation, P-C bond cleavage reactions, and Fe-M bond formation of ferrocenyl moieties are common for both systems, however there is no indication of hetero-annular metalation of such moieties in the Ru$_3$ system presumably due to the lower accessibility of the hetero C$_5$H$_5$ rings to the smaller Ru metal centers than to the larger Os metal centers. The formation of complexes such as (351) adds extra interest to the Ru$_3$ system, however.
5.5 Pyrolysis of Ru$_3$(CO)$_{12}$ with PEt$_2$Fc

Pyrolysis of Ru$_3$(CO)$_{12}$ with PEt$_2$Fc in octane for 18 h affords many products as judged by TLC and $^{31}$P NMR spectroscopy. The characterization of complexes (353) and (354) is described below.

Complex (353) shows a $^{31}$P NMR resonance at 370.4 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum shows the presence of only ethyl protons. The number of protons cannot be established with certainty. The mass spectrum gives the parent ion at 1189, but no obvious formulation can be conceived. Structure elucidation will have to rely on X-ray crystallography. While its structure may be interesting, the absence of ferrocenyl groups makes the project of lower priority.

Complex (354) shows a $^{31}$P NMR resonance at 366.8 ppm suggesting the presence of a phosphinidene moiety. The $^1$H NMR spectrum seems to show the presence of two ethyl groups and six ferrocenyl protons with a C$_5$H$_5$ ring! The mass spectrum gives the parent ion at 1137, and no obvious formulation can be conceived. Establishing the structure will again have to rely on an X-ray diffraction study.

Although most of the reaction products have not been characterized, it is clear that extensive C-P cleavage reactions have occurred. Pyrolysis of Ru$_3$(CO)$_{12}$ with PEt$_2$Fc, of Ru$_3$(CO)$_{11}$(PEt$_2$Fc), and of Ru$_3$(CO)$_{10}$(PEt$_2$Fc)$_2$ under milder reaction conditions should be studied in future research. This may lead to some unusual ferrocenyl moiety containing products.
5.6 Pyrolysis of Ru$_3$(CO)$_{12}$ with PEtFc$_2$

Pyrolysis of Ru$_3$(CO)$_{12}$ with PEtFc$_2$ in toluene for 10 h affords many products as shown by TLC and $^{31}$P NMR spectroscopy. The pyrolysis of Ru$_3$(CO)$_{11}$(PFc$_2$Ph) under similar reaction conditions, which has been described in Section 5.4, affords only a few major products. Purification of the products proved to be difficult, and so far only one complex (355) has been characterized by using X-ray crystallography. An ORTEP diagram of (355) with 33.0% probability thermal ellipsoids is shown in Figure 5.17.

![Figure 5.17 ORTEP diagram of complex (355).](image)

Crystal data: fw=993.65, dark green, prism, monoclinic system, space group C2/c (#15), a=31.831(3), b=9.904(2), c=17.536(2) Å, $\beta=99.36(1)^\circ$, Z=8, $D_{calc}=2.420$ g/cm$^3$, $R_0=0.026$, $R_w=0.024$. 

354
The molecular structure of (355) consists of a Ru$_5$P octahedron with an Et group on phosphorus and a $\eta^6$ coordinated toluene molecule on a neighbouring Ru atom. The other four Ru atoms are each coordinated to three carbonyls. The octahedron is very regular, for example, the angle between the Ru(1)Ru(2)Ru(3)Ru(4) and Ru(1)Ru(3)Ru(5)P(1) planes is 89.46°, between the Ru(1)Ru(2)Ru(3)Ru(4) and Ru(2)Ru(4)Ru(5)P(1) planes is 87.97°, and between the Ru(1)Ru(3)Ru(5)P(1) and Ru(2)Ru(4)Ru(5)P(1) planes is 89.98°. The Ru-Ru bond lengths vary slightly; the Ru(2)-Ru(5) bond at 2.8134(6) and Ru(4)-Ru(5) at 2.7902(5) Å are the shortest, the Ru(1)-Ru(4) bond at 2.8274(5), Ru(1)-Ru(2) at 2.8250(5), and Ru(3)-Ru(5) at 2.8263(5) Å are slightly longer, the Ru(1)-Ru(5) bond at 2.8678(6) Å is significantly longer, and the Ru(3)-Ru(2) bond at 2.8890(5) and Ru(3)-Ru(4) at 2.8922(5) Å are the longest. The phosphinidene bridge is unsymmetrical with P(1)-Ru(1) bond at 2.2836(9) Å being the shortest, P(1)-Ru(2) and P(1)-Ru(4) average to 2.378 Å being the longest, and P(1)-Ru(3) is at 2.3659(9) Å. The Ru(1)-C(1) distance at 2.300(4) Å is significantly longer than the others due to the steric interaction between the Me group on C(1) and the carbonyl C(9)-O(2) on Ru(2). This interaction is also reflected in the slight bending away of the Me group from the C(1)-C(6) plane (0.1111 Å). The Ru(1)-C(5) bond at 2.180(4) Å is shorter than the other four (av. 2.230 Å).

All the Ru-C (carbonyl) distances are the same with an average of 1.887 Å except Ru(4)-C(16) which is somewhat longer at 1.911(4) Å. All the Ru-C-O angles are close to linear with an average of 176.6° except for Ru(2)-C(9)-O(2) which is significantly bent at 167.1(4)° due to the steric interaction with the Me group on toluene and for Ru(3)-C(12)-O(5) which is slightly bent at 172.0(4)° due to the steric interaction with the Et group on
phosphorus atom. The C(20)-C(21) bond at 1.453(7) Å is exceptionally short and even shorter than C(1)-C(7) at 1.496(6) Å which is normal. The aromatic ring is little distorted and the average C-C bond length is 1.403 Å. P(1)-C(20) bond has a length of 1.850(4) Å, comparable to that in Os3(CO)8(H)2[(C5H3PET2)Fe(C5H4)] (269) (av. 1.831 Å) which has been described in Section 4.5 and that in Os3(CO)8(H)2[(C5H3PETFc)Fe(C5H4)] (308) (1.846(8) Å) which has been described in Section 4.11. The P(1)-C(20)-C(21) angle at 117.9(4)°, similar to 118.3(6)° in (308), is closer to 120° rather than 109.5° probably due to steric interaction with the carbonyls on Ru(3).

The structure of this complex (355) is closely related to Ru5(CO)15(μ4-PR) (R=Me, Et, Ph, Bz) [349] and Os5(CO)15(μ4-P(OMe)) [350]. The bonding of the toluene molecule is similar to that in (η6-C6H6)Ru(MeC≡CMe)Os3(CO)9 [351], Ru6(CO)11(η6-1,3,5-C6H3Me3)(η6-C6H6), and Ru6(CO)11(η6-1,3,5-C6H3Me3)2 [352].

The formation of complex (355) apparently involves many steps, but two interesting features are: (1) a solvent molecule is incorporated into the complex; (2) two ferrocenyl groups in PEtFc2 are lost via two ferrocenyl C-P bond cleavages. This indicates that ethyl groups do not undergo α or β C-H and C-P activation reactions readily, it also indicates that ferrocenyl C-H metalation is not a facile process on Ru3 clusters since any ferrocenyl C-H activation would not lead to this isolated complex.

5.7 Pyrolysis of Ru3(CO)10[Fc'(PPh2)2] [120]

Pyrolysis of Ru3(CO)10(bppf) has been previously studied [120], however no 31P NMR data are available particularly for complex (339).
which was obtained from all the three PFcPh$_2$ substituted complexes of Ru$_3$(CO)$_{12}$ and from Ru$_3$(CO)$_{11}$(PFc$_2$Ph) in the present study. Also no isomer of complex (106c) was found. In view of the results of the present studies, an isomer of such a benzyne complex is expected to form. A re-examination of the pyrolysis reaction was thus undertaken.

Pyrolysis of Ru$_3$(CO)$_{10}$(bppf) in cyclohexane for 4 h affords only three products as judged by TLC and $^3$P NMR spectroscopy. The major product, complex (356), shows two $^3$P NMR resonances at 35.0 and 3.5 ppm with a coupling of 4.5 Hz and a $^1$H NMR spectrum indicating the presence of four phenyl groups, seven ferrocenyl protons, and a hydride. Clearly this complex is Ru$_3$(CO)$_8$(H)[(C$_5$H$_3$PPh$_2$)Fe(C$_5$H$_4$PPh$_2$)], identical to complex (162) which has been discussed in Section 2.3.1 in Chapter 2 [120]. Similarly, complex (357) showing two $^3$P NMR resonances at 40.6 and 36.0 ppm with a coupling of 20.5 Hz is identified as the known complex Ru$_3$(CO)$_8$(H)[(C$_5$H$_4$PPhC$_6$H$_4$)Fe(C$_5$H$_4$PPh$_2$)] (222) described earlier in Section 2.3.1 [120]. The $^1$H NMR spectrum of (357) is in close agreement with that reported, notably the hydride signal at -16.80 ppm with coupling constants of 26.4 and 10.6 Hz. The third product isolated, complex (358), shows a single $^3$P NMR resonance at 0.0 ppm suggesting the equivalence of the two phosphorus environments. The $^1$H NMR spectrum shows the presence of four phenyl groups and eight ferrocenyl protons. By analogy with complex (371) to be discussed in Section 5.9, a formula such as Ru$_3$(CO)$_x$(H)(OH)(bppf) ($x$=8 or 9) or Ru$_3$(CO)$_x$(Cl)(OH)(bppf) ($x$=8 or 7) may be conceived. The absence of any hydride resonances in the $^1$H NMR spectrum favors the latter formula. This complex was not observed in the earlier study [120]. Presumably the compound has a structure analogous to that of (371), and it is shown in Figure 5.18.
Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{bppf})$ in cyclohexane for 40 h affords many products as judged by TLC. $^{31}\text{P}$ NMR spectroscopy revealed complex (356) as the major product, three new complexes (359), (360), and (361) in medium quantities, together with complexes (357), (358), and (362) in small quantities.

Complex (359) shows two $^{31}\text{P}$ NMR resonances at 263.9 and 215.9 ppm with a coupling of 190.7 Hz suggesting the presence of two phosphido moieties in a trans arrangement. The mass spectrum gives the parent ion at 1055 corresponding to the loss of three carbonyls from the starting material, and the fragments are clearly associated with the loss of seven carbonyls and three phenyl groups. These data and the $^1\text{H}$ NMR spectrum suggest that this complex (359) is the previously characterized complex $\text{Ru}_3(\text{CO})_7(\text{PFcPh})(\text{PPh}_2)(\text{C}_6\text{H}_4)$ (106c) which has been discussed in Section 1.2.3.1 in Chapter 1 [120].

Complex (360) shows two $^{31}\text{P}$ NMR resonances at 274.9 and 204.1 ppm with a coupling of 195.7 Hz suggesting the presence of two phosphido moieties in a trans arrangement. The mass spectrum is virtually identical to that of (359). The $^1\text{H}$ NMR spectrum shows the presence of three phenyl groups, a $\text{C}_6\text{H}_4$ moiety, and a ferrocenyl group, consistent with a formula such as $\text{Ru}_3(\text{CO})_7(\text{PFcPh})(\text{PPh}_2)(\text{C}_6\text{H}_4)$. This is clearly an isomer of the previously characterized complex (106c). Its structure is shown in Figure 5.18. Complexes (359) and (360) differ in the stereochemistry of the phosphorus center in PFcPh moiety. This complex was not isolated in the earlier study [120].

Complex (361) shows two $^{31}\text{P}$ NMR resonances at 166.9 and 111.9 ppm with a coupling of 12.8 Hz and it does not contain hydrides. It was not characterized further. This complex is presumably the previously known
complex $\text{Ru}_3(\text{CO})_9[(\text{C}_5\text{H}_4\text{PC}_6\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)]$ (223) which has been described in Section 1.2.3.1 in Chapter 1 [120].

![Figure 5.18 Possible structures for complexes (358) and (360).](image)

The new minor product, complex (362), shows two $^{31}$P NMR resonances at 184.0 and 128.4 ppm with a coupling of 15.0 Hz. The $^1$H NMR spectrum shows the presence of three phenyl groups and only seven ferrocenyl protons. The mass spectrum gives the parent ion at 1031 corresponding to the loss of one carbonyl and one benzene molecule from the parent, thus a formula such as $\text{Ru}_3(\text{CO})_9[(\text{C}_5\text{H}_4\text{PPh}_2)\text{Fe}(\text{C}_5\text{H}_3\text{PPh})]$ or $\text{Ru}_3(\text{CO})_9[(\text{C}_5\text{H}_3\text{PPh}_2)\text{Fe}(\text{C}_5\text{H}_4\text{PPh})]$ is likely. The osmium complexes (322), (325), and (326) previously described in Section 4.13 have similar formulations except that one CO being replaced by two hydrides. Without a structure determination, it is difficult to assign a structure with certainty.

In general, the results of the present study parallel those of the reported [120]. The isomer of complex (106c), complex (360), is indeed formed and has been characterized. It is surprising that no benzyne complex (107c) was isolated in the present study. This may be because the
reaction conditions in the two studies are different. The formation of complex (356) (or (162)) from Ru₃(CO)₁₀(bppf) may be due to its high thermodynamic stability under the reaction conditions because phenyl C-H metalation is clearly favored over that of ferrocenyl in the closely related system Ru₃(CO)₁₁(PFcPh₂) discussed in Section 5.1.

5.8 Pyrolysis of Ru₃(CO)₁₀[Fc'(PtBuPh)₂]

Pyrolysis of Ru₃(CO)₁₀(bppf), discussed in the previous section, showed that reactions are mainly associated with phenyl groups although a rather interesting complex (356) (or (162)) which involves a ferrocenyl C-H bond cleavage and Fe-Ru bond formation was obtained in good yield. This may be related to the lower accessibility of the ferrocenyl protons as compared to the phenyl protons. Pyrolysis of Ru₃(CO)₁₀[Fc'(PiPr₂)₂] discussed in the next section, showed that reactions in this case are associated with i-propyl groups. By using a ligand such as Fc'(PtBuPh)₂ that contains alkyl, aryl, and ferrocenyl groups, it is thus interesting to compare the reactivities of these different groups in these reactions.

Pyrolysis of Ru₃(CO)₁₀[Fc'(PtBuPh)₂] (the ligand has the meso configuration) in hexanes for 15 h affords five major products, complexes (363) to (367), as revealed by TLC, ¹H, and ³¹P NMR spectroscopy. The characterization of these five products is described below.

The minor compounds in the first and second bands were not fully identified due to insufficient material. Nonetheless these show interesting spectra; e.g., a ³¹P NMR resonance at 432.7 ppm indicates a complex with a phosphinidene moiety such as PtBu or PFc, and two resonances at 298.5
and 162.9 ppm are most likely due to phosphido moieties. These complexes could well contain benzyne or even ferrocynye moieties.

Complex (363) shows two $^{31}$P NMR resonances at 56.8 and 62.3 ppm suggesting that all the P-C bonds are intact. The mass spectrum gives the parent ion at 1042 corresponding to the loss of two CO groups from the parent. The $^1$H NMR spectrum shows the presence of two phenyl and two t-butyl groups, seven ferrocenyl protons, and a hydride. This suggests a formula such as Ru$_3$(CO)$_8$(H)[(C$_5$H$_4$P$_1$BuPh)Fe(C$_5$H$_3$P$_1$BuPh)] analogous to that of complex (356) described in the previous section. Since the phosphine ligand has the meso configuration as confirmed by the crystal structure of complex (365), two epimers are possible for complex (363) since orthometalation of a C$_5$H$_4$ moiety generates planar chirality on the ring. The two possibilities are shown in Figure 5.19. An X-ray structure analysis is required to distinguish between these two epimers.

Complex (364) shows $^{31}$P and $^1$H NMR spectra very similar to those of (363), and the mass spectra of the two complexes are identical. These strongly suggest that complexes (363) and (364) are the epimers shown in Figure 5.19.

![Figure 5.19 Possible structures for complexes (363) and (364).](image-url)
Complex (365) shows two $^{31}$P NMR resonances at 40.4 and 90.1 ppm suggesting that all the P-C bonds are intact. The mass spectrum gives the parent ion at 1042 corresponding to the loss of two carbonyls from the starting material. The $^1$H NMR spectrum shows the presence of a phenyl group, a C$_6$H$_4$ moiety, eight ferrocenyl protons, two t-butyl groups, and a hydride, and it is consistent with a formula such as Ru$_3$(CO)$_8$(H) [(C$_5$H$_4$P*BuC$_6$H$_4$)Fe(C$_5$H$_4$P*BuPh)]. A single crystal X-ray diffraction study was carried out. An ORTEP view of the molecule with 32.0% probability thermal ellipsoids is shown in Figure 5.20.

Crystal data: (365) C$_{71}$H$_{8}$, fw=1132.83, red, prism, monoclinic system, space group P2$_1$/n (214), a=15.684(2), b=14.519(4), c=20.102(2) Å, $\beta$=103.86(1)'', V=4444(1) Å$^3$, Z=4, $D_{calc}$=1.693 g/cm$^3$, R=0.033, $R_w$=0.038.

Figure 5.20 ORTEP diagram of complex (365).
The molecular structure of this complex (365) is very similar to 
\[\text{Ru}_3(\text{CO})_8(\text{H})\{\text{(C}_5\text{H}_4\text{PPPhC}_6\text{H}_4)\text{Fe(C}_5\text{H}_4\text{PPPh}_2)\}\} (222)\] which has been discussed in Section 2.3.1 [120]. It consists of a closed Ru$_3$ framework capped on one face by a phosphine and an orthometalated C$_6$H$_4$ moiety which is also $\eta^2$ bonded to Ru(1). The Ru-Ru distances span a large range with the Ru(2)-Ru(3) bond being the longest at 3.0502(7) Å which is also longer than the corresponding distance measured in (222) (3.000(2) Å). The Ru(1)-Ru(3) bond is normal at 2.8494(6) Å and the Ru(1)-Ru(2) bond is significantly shorter at 2.7402(8) Å. The hydride present in the molecule was not located in the refinement, but it presumably bridges the longest Ru(2)-Ru(3) bond. The Ru(1) and Ru(3) atoms are each bonded to three carbonyls, and Ru(2) to two, and the whole cluster is electron precise. The phosphine P(1) occupies an axial position and P(2) occupies an equatorial position. The carbonyls C(33), C(35), and C(38) occupy the axial positions on the uncapped face of the Ru$_3$ plane. The Ru(2)-C(12) bond at 2.144(5) Å is typical of such $\sigma$ bonds, and the Ru(1)-C(11) at 2.452(5) and Ru(1)-C(12) at 2.339(5) Å are consistent with a $\eta^2$ interaction between the C(11)-C(12) bond and the Ru(1) center. The Ru-C (carbonyl) bond distances are normal (av. 1.893 Å) apart from the Ru(3)-C(38) bond which is significantly longer at 1.958(6) Å, probably due to the trans influence of the P(1) moiety (P(1)-Ru(3)-C(38) 170.5(2)*). All the C-O distances are the same (av. 1.138 Å) and all the Ru-C-O angles are close to linear (av. 175.9°) except Ru(1)-C(33)-O(3) which at 168.8(6)* is somewhat bent. The Ru-P bonds (Ru(2)-P(2) 2.362(1) and Ru(3)-P(1) 2.345(1) Å) are unexceptional. The P-C bonds for sp$^2$ carbons (av. 1.825 Å) are shorter than those for sp$^3$ carbons (av. 1.907 Å) as expected.
In the ferrocenyl moiety, all Fe-C bonds are normal. The P(1) and P(2) atoms are situated 0.3186 and 0.2035 Å away respectively from the Cp(1) and Cp(2) planes. The two Cp rings are slightly opened up with a ring tilt angle of 6.00° as indicated also by the Cp(1)-Fe(1)-Cp(2) angle of 174.2(1)°.

In the C₆H₄ moiety, the C(11)-C(12), C(12)-C(13), and C(11)-C(16) bonds (av. 1.441 Å) are longer than the other three (av. 1.366 Å), and this difference is significant and greater even than that observed for the benzyne moiety in Ru₃(CO)₇(PFcPh)₂(C₆H₄) (106b) [119], indicating considerable electronic perturbation of the aromatic ring. The unperturbed C₆H₅ ring has equivalent C-C bond lengths which average to 1.382 Å. The C(11)-C(12)-C(13) angle at 113.5(4)° is also considerably smaller than 120°, the others are close to this value. The P(1) atom is displaced 0.5769 Å away from the C₆H₄ plane, while the P(2) atom is almost coplanar with the C₆H₅ plane (0.0750 Å). As expected, the Ru(2) and Ru(3) atoms are displaced 0.1886 and 0.5232 Å away respectively from the CO 1)-C(16) plane, and the C₆H₄ moiety makes an angle of 47.44° with the Ru₃ plane.

Complex (366) shows two ³¹P NMR resonances at 41.1 and 80.6 ppm suggesting that all the P-C bonds are intact. The mass spectrum gives the parent ion at 1070 corresponding to the loss of only one CO group from the starting material. The ¹H NMR spectrum shows the presence of a phenyl group, a C₆H₄ moiety, eight ferrocenyl protons, two t-butyl groups, and a hydride. These data clearly suggest a formula such as Ru₃(CO)₉(H) [(C₅H₄PBU₃C₆H₄)Fe(C₅H₄PBU₃Ph)]. A likely structure is shown in Figure 5.21.

Complex (367) shows two ³¹P NMR resonances at 22.8 and 35.0 ppm suggesting that all the P-C bonds are intact. The ¹H NMR spectrum seems to indicate the presence of nine phenyl protons, seven ferrocenyl protons,
two t-butyl groups, but no hydrides. The mass spectrum clearly gives the parent ion at 1095 which is the same as the starting material. No obvious structures can be conceived for this complex (367).

![Possible structure for complex (366)](image)

Figure 5.21 A possible structure for complex (366).

The formation of complexes (363)-(366) discussed above from the starting material Ru₃(CO)₁₀[Fe(Ph₃P)₂] is straightforward, and it involves either phenyl C-H or ferrocenyl C-H bond activation. This is very similar to the pyrolysis reactions of Ru₃(CO)₁₀(bppf) discussed above (Section 5.7). tBu groups are not involved in the reactions, and in view of the facile β C-H activation of i-propyl groups in the pyrolysis of Ru₃(CO)₁₀[Fe(Ph₃P)₂] to be discussed in the next section, it may be concluded that phenyl groups are more reactive towards C-H activation reactions. In (363) and (364), an iron-ruthenium bond is likely to be present and the structure is believed to be analogous to complex (162) discussed previously [120]. Since most of the reaction products do not involve P-C bond cleavage, it should be interesting to study the pyrolysis at elevated temperatures. Complexes such as Ru₄(CO)₁₁(PR)(C₆H₄) (R=Fc or tBu) and Ru₃(CO)₇(P₃BuFc)
(P^1BuPh)(C_6H_4) (for this complex, three or four isomers are possible) might be formed. Other interesting products may also be obtained.

5.9 Pyrolysis of Ru_3(CO)_10[Fe(PiPr_2)_2]

Pyrolysis of Ru_3(CO)_10[Fe(PiPr_2)_2] in refluxing cyclohexane for 15 h affords three products, (368), (369), and (370) in moderate yields. A minor product (371), isolated in very low yield from the reaction was also characterized. These four complexes are described below.

Complex (368) shows two ^{31}P NMR resonances at 269.4 and 67.5 ppm suggesting the presence of a phosphinidene moiety and a phosphine. The mass spectrum gives the parent ion at 861 corresponding to the loss of two carbonyl and two i-propyl groups from the starting material. The ^1H NMR spectrum shows the presence of eight ferrocenyl protons, two i-propyl groups, and two hydrides suggesting a formula such as Ru_3(CO)_8(H)_2[(C_5H_4P)Fe(C_5H_4PiPr_2)]. The structure was established by an X-ray crystallographic study. A stereo ORTEP view of the molecule with 25.0% probability thermal ellipsoids is shown in Figure 5.22.

Crystal data: fw=861.45, red orange, prism, triclinic system, space group P1 (#2), a=11.782(4), b=12.538(5), c=10.193(6) Å, α=95.70(4), β=98.70(4), γ=84.41(3)°, V=1476(1) Å^3, Z=2, D_{calc}=1.938 g/cm^3, R=0.027, R_w=0.034.

The structure consists of a Ru_3 triangle capped on one face by the phosphinidene moiety P(1) which results from the cleavage of two P-C (sp^3) bonds. Ru(2) and Ru(3) are each bonded to three carbonyls, while Ru(1) is bonded to two carbonyls and to the intact end of the bidentate
phosphine. The two hydrides were located in the refinement, and they bridge the Ru(1)-Ru(2) and Ru(1)-Ru(3) bonds respectively. These hydride bridged Ru-Ru bonds are longer (Ru(1)-Ru(2) 2.950(1) and Ru(1)-Ru(3) 2.984(2) Å) than the unbridged Ru(2)-Ru(3) bond at 2.817(1) Å. These values may be compared to those in Ru$_3$(CO)$_{12}$ (av. 2.854 Å) [194] and Ru$_3$(CO)$_{10}$(bppf) (bppf bridged Ru-Ru bond 2.9284(5) and unbridged ones 2.8600 Å) [250]. The Ru-C distances for the carbonyls that are roughly trans to the phosphinidene moiety are significantly longer than the others (Ru(2)-C(20) 1.958(3), Ru(3)-C(23) 1.954(4), Ru(1)-C(18) 1.941(3) Å; others average 1.894 Å) due to the large trans influence of the phosphinidene ligand. The ferrocenyl bridge is not unusual with the two Cp rings almost eclipsed and having a ring tilt angle of 4.21°. The Ru-P bond is longer for the phosphine (P(2)-Ru(1) 2.359(1) Å) than for the phosphinidene moiety (av. P(1)-Ru(n) 2.295 Å). P(1) and P(2) are displaced 0.1319 and 0.1996 Å away respectively from the Cp(1) and Cp(2) planes. Due to the repulsive interactions among the axial carbonyls,
all equatorial carbonyls and P(2) are significantly displaced from the idealized coplanar geometry with the Ru$_3$ plane towards the phosphinidene capped side. For example, C(17), P(2), C(21), and C(22) are 0.8591, 1.0008, 0.7265, and 0.6007 Å away respectively from the Ru$_3$ plane. The two hydrides are situated on the same side of the Ru$_3$ plane as the three axial carbonyls. Overall the structure of (368) is similar to that of the previously known complex Ru$_3$(CO)$_8$(H)$_2$(PPh)(PPh$_3$) [353], except that in this example the phosphine is situated below the Ru$_3$ plane in an axial position. Broadly, it can also be compared with complex (217) (this complex has been discussed in Section 2.3) which has an open Ru$_3$ triangle and contains no hydrides [246]. The phosphine also occupies an axial position in (217).

Complex (368) is stable towards further reaction in refluxing cyclohexane. This is probably because the movement of the phosphine to an axial position of the uncapped face cannot occur and such a motion is necessary for further C-H and/or C-P oxidative cleavage.

Complex (369) was characterized by spectroscopic and analytical techniques and by reactivity studies. The mass spectrum gives the parent ion at 903 corresponding to the loss of one i-propyl and two CO groups from the starting material. The $^{31}$P NMR resonances at 177.4 and 73.7 ppm suggest the presence of a phosphido moiety and a phosphine. The $^1$H NMR spectrum shows the presence of eight ferrocenyl protons indicating that the two hydrides do not originate from the Cp rings. The presence of peaks associated with three CHMe$_2$ groups (2.85 and 2.58 ppm) indicates that a formula such as Ru$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$P$_{1}$Pr$_2$)Fe(C$_5$H$_4$PCHMeCH$_2$)] is more likely than Ru$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$P$_{1}$Pr$_2$)Fe(C$_5$H$_4$PMe$_2$)]. A formula such as Ru$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$P$_{1}$PrCHMeCH$_2$)Fe(C$_5$H$_4$P$_{1}$Pr)] is unlikely on the basis of reaction Scheme 5-2 to be discussed later in this section. Pyrolysis of (369) in
refluxing cyclohexane for 10 h affords (368) exclusively. This reaction does not involve any intermediates as judged by TLC, and this observation further supports the assignment. The hydride-phosphorus couplings in (369) are also very close to those in (368) and the structures of (368) and (369) should be very similar. A proposed structure for (369) is shown in Figure 5.23. It consists of a closed Ru₃ triangle capped on one face by a phosphido moiety. The two bridging hydrides and eight carbonyls are presumably distributed as in (368). Since both the phosphorus atom of the phosphido moiety and the tertiary carbon atom of the CHMeCH₂ group are chiral, two diastereoisomers are possible for this complex (369). However, no evidence for the presence of isomers was found even in the ¹H and ³¹P NMR spectra of the pyrolysis mixture. The configurations of the chiral centers in (369) cannot be deduced from the available data.

![Figure 5.23 Possible structures for complexes (369) and (370).](image)

The closest known structure to that of (369) is complex (222) (Scheme 2-3) derived from Ru₃(CO)₁₀(bppf) [120]. This complex contains an orthometalated phenyl moiety and a bridging CO group rather than a β metalated i-propyl group and two bridging hydrides in (369).
closely related structure is complex (230) \((R\text{-Me})\) derived from \(\text{Os}_3(\text{CO})_{11}(\text{PMePh}_2)\) [132].

Complex (370) was also characterized by spectroscopic and analytical techniques and by comparing its spectroscopic properties with that of the osmium analogue \(\text{Os}_3(\text{CO})_7(\text{H})[(\text{C}_5\text{H}_4\text{P}^\text{iPr}_2)\text{Fe}(\text{C}_5\text{H}_4)](\text{P}^\text{iPr})\) (329) which has been described in Section 4.13. This complex (370) is less stable than (368) or (369) in solution, but it can be chromatographed in air without degassing the solvents. The mass spectrum gives the highest peak at 849 corresponding to the loss of one i-propyl and three CO groups from the starting material. The \(^{31}\text{P}\) NMR resonances at 429.3 and 53.7 ppm suggest the presence of a phosphinidene moiety and a phosphine. In view of the large \(^{31}\text{P}\) NMR chemical shift difference (160 ppm) between the phosphinidene moieties in (370) and (368), it is most likely that this complex contains a \(\mu_3\text{-P}^\text{iPr}\) rather than \(\mu_3\text{-P}^\text{Fc}^\prime\) moiety as in (368). The \(^1\text{H}\) NMR spectrum, Figure 5.24, shows the presence of three i-propyl groups, eight ferrocenyl protons, and a bridging hydride. The large down field \(^1\text{H}\) NMR chemical shift of one \(\text{CHMe}_2\) group to 3.8 ppm (the other two are at 2.5 ppm) is consistent with the presence of a unique \(\mu_3\text{-P}^\text{iPr}\) group. The ferrocenyl protons show interesting patterns with four protons significantly deshielded and four significantly shielded. This suggests considerable electronic perturbation of the ferrocenyl moiety and the possible involvement of iron-ruthenium bonding. In fact, the \(^1\text{H}\) NMR spectrum of complex (370), Figure 5.24, is very similar to that of the osmium complex (329) which has been described previously in Section 4.13 and its \(^1\text{H}\) NMR spectrum is shown in Figure 4.63. The structure of (329) was established by an X-ray crystallographic study. Complex (370) almost certainly has a formula such as \(\text{Ru}_3(\text{CO})_7(\text{H})[(\text{C}_5\text{H}_4\text{P}^\text{iPr}_2)\text{Fe}(\text{C}_5\text{H}_4)]\)
(PiPr), and a structure analogous to the osmium complex (329) is shown in Figure 5.23. This novel complex contains a five-electron donating ferroceny1 ligand $\eta^3$-P,Fe,C-(C$_5$H$_4$PiPr$_2$)Fe(C$_5$H$_4$) bonded to one ruthenium atom. Remarkably there is an iron-ruthenium and a Ru-C$_5$ (ring) $\sigma$ bond. The two Cp rings must be opened up somewhat as found in (329) (11.58°) and this probably accounts for the unusual ferroceny1 patterns in the $^1$H NMR spectra of both complexes. It is interesting to speculate that the

![Figure 5.24 300 MHz $^1$H NMR spectrum of complex (370).](image-url)
reaction of \((\text{C}_5\text{H}_4\text{PRR'})\text{Fe(}\text{C}_5\text{H}_4\text{Li)}\), which may be obtained from \(\text{R'}\text{Li}\) and \(\text{Fe(}\text{C}_5\text{H}_4\text{)}_2\text{PR}\) \([340]\) or from \((\text{C}_5\text{H}_4\text{PR}_2)\text{Fe(}\text{C}_5\text{H}_4\text{SnBu}_3)\) and \(\text{nBuLi}\) \([354]\), with unsaturated organometallic halides containing labile ligands could provide a general route to complexes containing such interesting ferrocenyl moieties. For example, \(\text{RuCl}_2(\text{PPh}_3)_3\) might react with \((\text{C}_5\text{H}_4\text{PiPr}_2)\text{Fe(}\text{C}_5\text{H}_4\text{Li)}\) to give \(\text{RuCl}(\text{PPh}_3)_2[\eta^3-(\text{C}_5\text{H}_4\text{PiPr}_2)\text{Fe(}\text{C}_5\text{H}_4)]\) by replacing a Ru-Cl bond with a Ru-C (ferrocenyl) σ bond, a PPh\(_3\) with PFc'iPr\(_2\) and by forming an Fe-Ru bond to attain a stable 18-electron structure.

A minor reaction product \((371)\) was characterized by an X-ray diffraction study. The mass spectrum gives the parent ion at 999, close to that of the starting material, but it has a different fragmentation pattern. The \(^{31}\text{P}\) NMR spectrum shows a single \(^{31}\text{P}\) NMR resonance at 20.9 ppm suggesting the presence of two equivalent phosphorus environments. The \(^1\text{H}\) NMR spectrum shows only resonances associated with the intact ligand slightly different from those of \(\text{Ru}_3(\text{CO})_{10}[\text{Fc}'(\text{PiPr}_2)_2]\). The precise formula was not established until an X-ray structure determination was carried out. An ORTEP diagram of the molecule with 50.0% probability thermal ellipsoids is shown in Figure 5.25.

Crystal data: \(\text{fw}=1001.64\), orange, prism, monoclinic system, space group \(\text{P2}_1/\text{n} \) \(#14\), \(a=16.330(2)\), \(b=11.651(2)\), \(c=19.147(3)\) Å, \(\beta=93.34(1)^\circ\), \(V=3637(1)\) Å\(^3\), \(Z=4\), \(D_{\text{calc}}=1.829\) g/cm\(^3\), \(R=0.030\), \(R_w=0.034\).

The structure of \((371)\) consists of an open Ru\(_3\) triangle with the ferrocenylphosphine Fc'\((\text{PiPr}_2)_2\), Cl, and OH groups all bridging the open edge. The bidentate phosphine occupies two equatorial positions as expected, and the Cl and OH groups are displaced towards opposite sides of the Ru\(_3\) plane. Ru\((1)\) and Ru\((2)\) are each bonded to two carbonyls and these Ru\((\text{CO})_2\) moieties adopt a staggered orientation relative to Ru\((3)\), unlike
that in Ru₃(CO)₁₂ or Ru₃(CO)₁₀(bppf). Ru(3) is bonded to four carbonyls, two being axial and two equatorial. The two Ru-Ru bond lengths, 2.8444(6) and 2.8506(7) Å, are very similar to those in Ru₃(CO)₁₂ (2.854 Å) [194] and the unbridged ones in Ru₃(CO)₁₀(bppf) (2.8600(4) Å) [250]. The Ru-C distances for Ru(1) and Ru(2) bound carbonyls (av. 1.836 Å) are significantly shorter than those of Ru(3) bound carbonyls (av. 1.925 Å) due to the strong electron releasing nature of the bridging phosphine. P-C (sp²) bonds (av. 1.823(5) Å) are slightly shorter than P-C (sp³) bonds (av. 1.861(5) Å) as expected. The two Cp rings in (371) have a ring tilt angle of 9.74° (Cp(1)-Fe-Cp(2) 171.5(1)°), larger than that in Ru₃(CO)₁₀(bppf) (Cp(1)-Fe-Cp(2) 174.6°) [250]. P(1) and P(2) are displaced 0.4286 and 0.3590 Å away respectively from the Cp(1) and Cp(2) planes.

Clusters of the type Ru₃(CO)₁₀(H)(X) (X=SR, NHR) are known [355], but they are more commonly found in Os₃ clusters [113].

Figure 5.25 ORTEP diagram of complex (371).
Os—Os edge can be closed as in Os$_3$(CO)$_{10}$(H)(SEt) [356] and Os$_3$(CO)$_{10}$(H)(COCH$_2$Ph) [357], or open as in Os$_3$(CO)$_{10}$($\mu$-OMe)$_2$ [356]. For doubly bridged Os$_3$(CO)$_{10}$(H)(X) systems, X can be a one atom, two atom, or three atom bridge. However there is no precedent for complex (371) which contains a bridging di(tertiary) phosphine in addition to the other two bridging groups.

Providing the same workup procedures are used, complex (371) can be isolated when Ru$_3$(CO)$_{10}$[Fc'(P$_1$Pr$_2$)$_2$] is refluxed in hexanes for 15 h, conditions that do not result in the formation of (368)-(370). When a trace amount of water is added to the hexane and the reaction is repeated, the product mixture contains a new compound in low yield and the $^{31}$P NMR spectrum of the reaction mixture in C$_7$D$_8$ shows a new resonance at 48.0 ppm. The $^1$H NMR spectrum shows a hydride resonance at -17.38 ppm (dd, $J_1$=15.73, $J_2$=11.63 Hz). When the same sample is examined in C$_6$D$_6$ solution the resonances of the complex (371) are recorded. These results suggest that the reaction sequence shown in Scheme 5-1 takes place. The source of Cl is probably HCl in the chlorinated solvents used for chromatography or the solvents themselves. The low yield of the reaction has mitigated against further investigation. A closely related reaction is the

![Scheme 5-1](image)

Scheme 5-1 A possible pathway for the formation of complex (371).
treatment of physisorbed Os₃(CO)₁₂ on silica with HF which affords pure Os₃(CO)₁₀(H)(OH) [358].

Scheme 5-2 and 5-3 outline pathways that account for the formation of complexes (368)-(370) from Ru₃(CO)₁₀[Fc'(PiPr₂)₂]. Compounds described by letters have not been isolated or characterized. Similar reaction schemes have been proposed for the pyrolysis of Ru₃(CO)₁₀(bppf) [120].

Movement of one end of the phosphine from an equatorial to an axial position gives A, Scheme 5-2. A β C-H activation of one i-propyl group in A by Ru(CO)₃ metal center leads to B. Elimination of a propene molecule affords C. There is strong support for such intermediates B and C. An

Scheme 5-2 Possible reaction sequence for the pyrolysis of Ru₃(CO)₁₀[Fc'(PiPr₂)₂].
osmium analogue of C, complex (323), was isolated and fully characterized by using X-ray crystallography. This complex has been described in Section 4.13. A further β C-H activation of the i-propyl group on the phosphido moiety by the Ru(CO)₄ metal center in C gives the isolated product (369) which eliminates a propene molecule to give (368). It should be noted that in the analogous osmium system discussed earlier (Section 4.13 and Scheme 4-16), no complexes corresponding to (368) and (369) were isolated indicating that complex (323) is the end product of that specific reaction pathway. This implies that the second β C-H activation of the i-propyl group on the phosphido moiety does not occur in the Os₃ system. Also in the Os₃ system, two CO inserted products are formed from an intermediate analogous to B in Scheme 5-2. In the Ru₃ system discussed here, the second β C-H activation of the i-propyl group on the phosphido moiety must be a facile and rapid process, since no B or C or CO insertion products of B are detected in the pyrolysis mixture by using ³¹P and ¹H NMR spectroscopy.

A β C-H activation of one i-propyl group in A may also occur on Ru(CO)₄ metal center to give D, Scheme 5-3. D readily loses a propene to give E. E may undergo a P-C bond cleavage to afford F which then expels another CO with concomitant formation of a Fe-Ru bond to give (370). E may also undergo Fe-Ru bond formation first to give G which then undergoes a P-C bond cleavage to give (370). Activation of the unique i-propyl group in E is not possible, so further reactions involve the ferrocenyl moiety. This scheme is similar to Scheme 4-15 discussed earlier in Section 4.13 for the analogous Os₃ system. One notable difference is that the osmium analogue of E (compound C in Scheme 4-15) also undergoes a
Scheme 5-3 Possible reaction sequence for the pyrolysis of 
Ru₃(CO)₁₀[Fe(PPr₂)₂].

ferrocenyl C-H activation to give (322), no such products are formed in the Ru₃ system.

Overall, Schemes 5-2 and 5-3 give a satisfactory rationale for the formation of complexes (368)-(370). The activation of the α C-H bonds of the i-propyl groups is not observed, in contrast with the pyrolysis of Os₃(CO)₁₁(PEt₃) which affords α C-H activated products only [263]. This is presumably due to the steric hinderance of the α C-H bonds and the unfavorable statistics (one α C-H bond as opposed to six β C-H bonds in an i-propyl group). The β C-H activation leading to (368), (369) and (370) is similar to the orthometalatation of phenylphosphine, however π bonding
interaction, benzyne formation, and reductive elimination or benzene are the major subsequent reaction pathways, while in Schemes 5-2 and 5-3 reductive elimination of propene is clearly favored over that of propane. One surprising observation is that ferrocenyl metatation does not seem to occur in this system, no analogue of complex (162) is formed. This may be due to the bulkiness of the i-propyl groups and the unfavorable statistics (four ferrocenyl C-H bonds as opposed to twenty-four i-propyl β C-H bonds).

5.10 Pyrolysis of Ru3(CO)12 with P(1-C10H7)3

Pyrolysis of Ru3(CO)12 with P(1-C10H7)3 in cyclohexane for 24 h affords two major products, complexes (372) and (373). Their characterization is described below. 31P NMR spectroscopy shows that no phosphido or phosphinidene complexes were produced.

Complex (372) shows a 31P NMR resonance at 68.7 ppm suggesting the presence of a phosphine. The 1H NMR spectrum shows the presence of nineteen naphthyl protons and two hydrides, each being a doublet. The mass spectrum gives the parent ion at 941 corresponding to a formula such as Ru3(CO)8(H)2[(1-C10H7)2P(1-C10H5)]. The hydride couplings and chemical shifts are similar to the osmium naphthyne (333) which has been described in Section 4.14. This complex (372) is almost certainly a naphthyne complex with a structure similar to that of (333) and (336). It is shown in Figure 5.26.

This complex is the first naphthyne complex on a ruthenium cluster to be described, it is also the first aryne complex on a Ru3 cluster to have a
structure analogous to the known osmium complex $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{C}_6\text{H}_4)$ (126) which has been discussed in Section 1.2.3.2.

Complex (373) shows a $^{31}\text{P}$ NMR resonance at 71.9 ppm suggesting the presence of a phosphine. The $^1\text{H}$ NMR spectrum shows the presence of only naphthyl protons. The mass spectrum gives the parent ion at 1067 corresponding to a formula such as $\text{Ru}_4(\text{CO})_9[(1-\text{C}_{10}\text{H}_7)_3\text{P}]$. No obvious structures can be proposed, and X-ray crystallography will be needed to provide the answer.

Under the mild reaction conditions (refluxing in cyclohexane), P-C bond cleavage does not seem to occur, presumably due to the ready formation of a very stable product such as complex (372). Due to the steric interaction of the hydrogen on the 8-position of the naphthyl groups and the phosphorus atoms, the C-H bonds on the 8-position are expected to be more readily activated than the ortho C-H bonds. However, orthometalation could lead to further reactions such as $\pi$ bonding of the metalated ring with the cluster, reductive elimination of naphthalene, and naphthyne formation, and it would be interesting to study this pyrolysis reaction in some different reaction conditions.

![Figure 5.26 Likely structures for complexes (372) and (374).](image-url)
5.11 Pyrolysis of Ru₃(CO)₁₂ with As(1-C₁₀H₇)₃

Pyrolysis of Ru₃(CO)₁₂ with As(1-C₁₀H₇)₃ in cyclohexane for 10 h affords one major product, complex (374), and its characterization is described in this section.

Complex (374) shows a complex ¹H NMR spectrum, Figure 5.27. A 2D proton-proton correlation NMR study seems to support the presence of nineteen naphthyl protons with one unique naphthyl group containing only five hydrogen atoms. Two hydride resonances are similar to those in complex (372) discussed above, and to the osmium naphthyne complex (336) which has been described in Section 4.15. The mass spectrum gives the parent ion at 984 consistent with a formula Ru₃(CO)₈(H)₂[(1-C₁₀H₇)₂As(1-C₁₀H₅)] expected for an analogous naphthyne complex. A structure similar to that of (336) is shown in Figure 5.26.

It is very interesting to note that naphthyne complexes of this structure are formed in all the reactions of M₃(CO)₁₂ (M=Ru or Os) with E(1-C₁₀/₁₇)₃ (E=P or As). This is a rare example of a complete series of complexes in both Ru₃ and Os₃ systems with both phosphines and arsines. The best known series of benzyne complexes for both Ru₃ and Os₃ systems are those of (106) for Ru₃ systems, (49) and (113) for Os₃ systems. However such benzyne complexes on Ru₃ systems with arsinido moieties have not yet been described.

It is also interesting to note that the naphthyne complexes from As(1-C₁₀H₇)₃ were formed in higher yields than from P(1-C₁₀H₇)₃ for both Os₃ systems (35% compared to 70%) and Ru₃ systems (50% compared to 70%). This seems to correlate with the steric interaction of the hydrogen in the 8-position with the donor atom, that is the larger arsenic atom favors
metalation at 8 position, leading to the naphthyne complexes in better yields. The naphthyne complexes from P(1-C_{10}H_{7})_3 were obtained in higher yields for the Ru_3 complex than for the Os_3 complex, this also correlates with such a 1,8 steric interaction. Although the elimination of the above discussed steric interaction is important in forming the naphthyne complexes, this 8-metalation is probably not the first step of the reaction.

Figure 5.27 300 MHz $^1$H NMR spectrum of complex (374).
5.12 Pyrolysis of Ru₃(CO)₁₂ with SFcPh

Pyrolysis of Ru₃(CO)₁₂ with SFcPh in toluene for 11 h affords three major products as judged by TLC. These products do not contain any hydrides as revealed by ¹H NMR spectroscopy, and their characterization is described here.

The first band contained two complexes as judged by TLC. Their ¹H NMR spectrum cannot readily be analyzed, and no satisfactory mass spectrum was obtained. Repeated chromatography is needed to obtain each complex pure and to elucidate their structures by using spectroscopic and analytical techniques.

The ¹H NMR spectrum of complex (375), the major product isolated from the reaction, shows the presence of a ferrocenyl group and an unusually up field shifted phenyl group. The mass spectrum gives the parent ion at 823 corresponding to a formula such as Ru₃(CO)₈(SFcPh). The unusual phenyl proton resonances are similar to those of complex (376) which will be described in the next section. In fact, its structure was revealed only after the structure of (376) was solved by an X-ray diffraction study (described in the next section). This complex (375) almost certainly has a structure analogous to (376) and is shown in Figure 5.28.

The initial objective of using SFcPh for pyrolysis studies was to compare the relative ease of ferrocenyl and phenyl C-H and C-S cleavage reactions by providing both groups with equal environments. Pyrolysis of Os₃(CO)₁₂ with SMePh gives the benzyne complex (120) in low yield [130], but similar reactions of sulfides with Ru₃(CO)₁₂ have not been studied. It was of interest therefore to assess whether the Ru₃ system would afford an analogous benzyne complex or some other new complexes involving
ferrocenyl C-H metalation perhaps even ferrocyne complexes. Clearly this reaction of Ru$_3$(CO)$_{12}$ with SFcPh does not afford any hydride containing species which would be expected to be present in either benzyne or ferrocyne complexes. Complex (375) was obtained in good yield, and it is a result of a S-Ph bond cleavage without C-H activation. The reaction sequence leading to its formation is unknown, both sulfur coordination or phenyl ring $\eta^6$ coordination are possible as the first step. It would be interesting to further characterize all the isolated products and to elucidate possible reaction pathways.

![Figure 5.28 A most likely structure of complex (375).](image)

5.13 Pyrolysis of Ru$_3$(CO)$_{12}$ with SPh$_2$

Pyrolysis of Ru$_3$(CO)$_{12}$ with SPh$_2$ in toluene for 15 h affords three products as judged by TLC. These products, somewhat unexpectedly, do not contain any hydrides as revealed by $^1$H NMR spectroscopy. The characterization of complex (376) is described below.

Complex (376) was isolated as the only major product from the
reaction in 70% yield. The $^1$H NMR spectrum, Figure 5.29, shows the presence of two phenyl groups with one being unusually up field shifted. The mass spectrum gives the parent ion at 715 corresponding to a formula such as Ru$_3$(CO)$_8$(SPh$_2$). Its structure was established by using X-ray crystallography. An ORTEP diagram of the molecule with 33.0% probability thermal ellipsoids is shown in Figure 5.30.

Crystal data: fw=713.56, yellow orange, prism, orthorhombic system, space group P2$_1$2$_1$2$_1$ (*19), a=13.733(4), b=19.886(2), c=8.140(3) Å, V=2223(1) Å$^3$, Z=4, D$_{calc}$=2.132 g/cm$^3$, R=0.025, R$_{w}$=0.021.

The structure of (376) consists of an open Ru$_3$ triangle with the open edge bridged by a η$^1$ and η$^6$ bonded aryl C$_6$H$_5$ moiety. The Ru(1)-Ru(2)-
Ru(3) angle is 86.80(2)° and the Ru(1)Ru(2)Ru(3)C(1) torsion angle is very small at 4.8(1)°. The Ru(2)-Ru(3) edge is bridged by a thiolate SPh moiety. Ru(1) is bonded to two carbonyls, Ru(2) and Ru(3) are each bonded to three carbonyls, thus the whole cluster is electron precise. The Ru(1) center has a typical three-leg piano stool geometry, and the other two Ru centers have approximate octahedral geometry. The sulfur center is chiral and the C₆H₅ group is anti to the σ,π bonded C₆H₅ moiety as expected for such a structure. The thiolate bridged Ru(2)-Ru(3) bond at 2.7691(8) Å is much shorter than the unbridged Ru(1)-Ru(2) bond at 2.9093(6) Å, and the thiolate bridge is symmetrical (2.392(1) and 2.394(1) Å respectively). The aryl C(1)-C(6) ring is bonded to Ru(3) via a σ bond of length 2.119(4) Å and η⁶ bonded to Ru(1). The Ru(1)-C (C(1)-C(6) ring) distances range

Figure 5.30 ORTEP diagram of complex (376).
from 2.266(5) to 2.308(5) Å with an average of 2.286 Å.

The carbonyl C-Ru distances show some variation. The Ru(3)-C(20) bond which is trans to the Ru(3)-C(1) σ bond and the Ru(2)-C(16) bond are the longest (av. 1.936 Å), the Ru(1)-C(13) and Ru(1)-C(14) bonds are the shortest (av. 1.855 Å), and the rest average to 1.888 Å. All C-O bonds are normal ranging from 1.121(6) to 1.155(6) Å. All Ru-C-O angles are close to linear with an average of 177.9°.

The planarity of the C(1)-C(6) ring is little distorted with a mean deviation of only 0.0081 Å, and the ring plane makes an angle of 82.15° with the Ru(1)Ru(2)Ru(3) plane and of 71.99° with the Ru(2)Ru(3)S(1) plane. The Ru(3) atom is only slightly displaced away from the ring plane (0.2173 Å). There is noticeable C-C bond lengthening in the ring; the C(1)-C(2), C(1)-C(6), and C(2)-C(3) bonds (av. 1.428 Å) are longer than the other three (av. 1.395 Å), and these should be compared to the C-C bonds in the C(7)-C(12) ring (av. 1.379 Å). While all C-C-C angles in the C(7)-C(12) ring are close to 120°, the C(2)-C(1)-C(6) angle of 113.3(4)° is significantly smaller than the rest (from 117.6(4) to 123.7(4)°). The Ru(2)Ru(3)S(1) plane is perpendicular to the Ru(1)Ru(2)Ru(3) plane (86.96°) and S(1) is 0.2431 Å away from the C(7)-C(12) plane.

The formation of complex (376) from Ru3(CO)12 and SPh2 was not expected. As discussed in Chapter 2, orthometalation of phenyl groups is a well known and presumably facile process for arylphosphines or arsines, and it is also expected to be facile for arylsulfides. More surprising is that a phenyl C-S bond is cleaved while all the C-H bonds remain intact.

Complex (376) was obtained in high yield, and the reaction may likely be extended to other sulfides which will allow the preparation of many analogues of (376). It should also be interesting to investigate the
pyrolysis of Ru$_3$(CO)$_{12}$ and also Os$_3$(CO)$_{12}$ with bidentate sulfides such as CH$_2$(SPh)$_2$, Fe'(SPh)$_2$, and mixed phosphine sulfide ligands such as (C$_5$H$_4$PPh$_2$)Fe(C$_5$H$_4$SPh).
Chapter 6 Syntheses and Characterization of Ferrocenyl Ligands and Their Triosmium and Triruthenium Complexes

6.1 Syntheses and Characterization of Ferrocenyl Ligands

6.1.1 Syntheses of ferrocenyl ligands

A series of ferrocenyl ligands, in particular, ferrocenylphosphines, -arsines, and -sulfides were prepared by the reaction of mono- or dilithiated ferrocenes with appropriate reagents such as halophosphines, haloarsines, and disulfides. The yields for bidentate ligands Fc'(PR₂)₂ (R=Ph, iPr, Et) and Fc'(SR₂)₂ (R=Ph, Me) are reasonably high as expected because 1,1'-dilithiated ferrocene is known to form in high yield. The ferrocenophane ligand Fc'PPh was obtained from PPhCl₂ and Fe(C₅H₄Li)₂ only in 25% yield, lower than that reported [338-340]. The yields for monodentate ligands PFcPh₂, PEt₂Fc, PFciPr₂, PtBu₂Fc, SFcPh, and SFc₂ are moderate to low since stoichiometric monolithiation of ferrocene is more difficult to achieve. Repeated chromatography is often necessary to obtain pure products. The ligands PFc₂Ph, PnBuFcPh, PEtFc₂, and AsFc₂Ph were obtained in low yields, and chromatographic separation is very difficult and time consuming. In the course of the preparation of PFc₂Ph, a diastereoisomeric pair of the ligand Fc'(PFcPh)₂ was obtained. Likewise in the course of the preparation of PEtFc₂, diastereoisomers of Fc'(PEtFc)₂ were obtained. The reaction of monolithiated ferrocene with sulfur afforded FcSSFc and Fc'(SSFc)(SFc) in addition to the desired [3]-
ferrocenophane $\text{Fc'S}_3$. The reaction of $\text{PFc}_2\text{Ph}$ with sulfur is almost quantitative affording $\text{S-PFc}_2\text{Ph}$. Triferrocenylstibine was also prepared in low yield from $\text{SbCl}_3$ and $\text{FcLi}$. In all the preparations mentioned above, substantial amounts of ferrocene (10-25%) were recovered.

6.1.2 Characterization of the ferrocenyl ligands

The ferrocenyl ligands were obtained as orange, dark orange, or yellow solids except for $\text{PEt}_2\text{Fc}$, $\text{PFc}_1\text{Pr}_2$, $\text{Fc'(PEt}_2\text{)}_2$, and $\text{Fc'(SMe)}_2$ which are orange oils and $\text{Fc'PPh}$ which is a dark red solid. In solutions most of the phosphine ligands are easily oxidized by air, but in the solid state they are reasonably stable. The $[1]$-ferrocenophane $\text{Fc'PPh}$ is not very stable even in the solid state and decomposes to dark intractable materials. The oily phosphines $\text{PEt}_2\text{Fc}$, $\text{PFc}_1\text{Pr}_2$, and $\text{Fc'(PEt}_2\text{)}_2$ are also less stable than the others. All the ligands prepared in the present study can be column chromatographed with reasonable ease to obtain pure samples. In the case of $\text{PFc}_2\text{Ph}$, $\text{PEtFc}_2$, $\text{Fc'PPh}$, and $\text{PtBu}_2\text{Fc}$, care should be taken since these are more easily oxidized especially on a silica column.

The characterization of these ferrocenyl ligands is straightforward. In the $^1\text{H}$ NMR spectra, the unsubstituted Cp ring protons appear as a sharp singlet between 3.96 and 4.29 ppm, the substituted ring protons appear between 3.91 and 4.51 ppm as two multiplets of 3:1 as in $\text{SFc}_2$, $\text{PEtFc}_2$, and $\text{PnBuFcPh}$, as two multiplets of 1:1 as in $\text{SbFc}_3$, $\text{SFcPh}$, $\text{PFCPh}_2$, $\text{PEt}_2\text{Fc}$, and $\text{PFc}_1\text{Pr}_2$, as three multiplets of 2:1:1 as in $\text{PtBu}_2\text{Fc}$, and as four multiplets of 1:1:1:1 as in $\text{PFc}_2\text{Ph}$ and $\text{SPFc}_2\text{Ph}$. The same protons in the bidentate ligands appear between 4.68 and 4.01 ppm as two multiplets (or singlets) of 1:1 such as in $\text{Fc'(PPh}_2\text{)}_2$, $\text{Fc'(PiPr}_2\text{)}_2$, and $\text{Fc'(SMe)}_2$, or as three multiplets of 1:1:2 such as in $\text{Fc'(PEt}_2\text{)}_2$. Ethyl protons resonate between
1.50 and 2.13 ppm for methylene protons and between 0.95 and 1.22 ppm for methyl protons. The CH$_2$ protons appear as quartets due to couplings to three methyl protons (J=7 to 8 Hz), and the CH$_3$ protons appear as triplets of doublets due to couplings to one phosphorus (J=14 to 18 Hz) and to the CH$_2$ protons. i-Propyl protons resonate between 1.85 and 1.62 ppm for CH protons, and between 1.26 and 1.11 ppm for CH$_3$ protons. The CH protons appear as two overlapping septets due to couplings to one phosphorus and six methyl protons. The CH$_3$ protons appear as doublets of doublets due to couplings to one phosphorus and one CH proton. It is interesting to note that in Fc'(P$_2$iPr)$_2$, all methyl protons appear as one doublet of doublet, while in PFciPr$_2$ these protons appear as two doublets of doublets since the magnetic environments of two methyl groups in each i-propyl group are different. t-Butyl protons in P'tBu$_2$Fc resonate at 1.15 ppm as a doublet due to coupling to phosphorus (J=11.0 Hz).

The $^{31}$P NMR spectra of ferrocenylyphosphines show one sharp singlet. Their chemical shifts agree well with those calculated by using the empirical equation (6.1) for tertiary phosphines [359]:

$$
\delta = -62 + \sum_{n=1}^{3} \sigma_n^P \quad (6.1)
$$

wherein $\sigma^P$ are constants that are assigned to and characteristic of the group. Values for the following groups are [359-361]: Et, 14; iPr, 27; nBu, 10; tBu, 41; Ph, 18. The $\sigma^P$ value for a ferrocenyl group derived from the measured chemical shifts of PFcPh$_2$, PFc$_2$Ph, PEt$_2$Fc, PEtFc$_2$, PFciPr$_2$, P$n$BuFcPh, and P'tBu$_2$Fc by using the above equation are 9.1, 6.9, 7.9, 6.8, 8.6, 6.3, and 7.8 ppm, respectively. An average value of 7.6 is thus
obtained for a ferrocenyl group. The calculated chemical shift values based on this value by using equation (6.1), the experimental values, and their differences for the above seven ferrocenylphosphines are tabulated in Table 6-1. The agreement is quite good, and this value can be used to predict the \( ^{31}\text{P} \) NMR chemical shift of a new ferrocenylphosphine if \( \sigma^p \) values for the other groups attached are known. The bidentate ligands have very similar chemical shifts to their monodentate analogues. For example, \( \text{Fc}'(\text{PiPr}_2)_2 \) and \( \text{PFc}i\text{Pr}_2 \) differ by only 0.5 ppm. Likewise, \( \text{Fc}'(\text{PPh}_2)_2 \) and \( \text{PFc}Ph_2 \) differ by 0.7 ppm, \( \text{Fc}'(\text{P}^i\text{Bu}_2)_2 \) and \( \text{P}^i\text{Bu}_2\text{Fc} \) differ by 1.3 ppm.

Table 6-1 Comparison of measured and calculated \( ^{31}\text{P} \) NMR chemical shifts

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Calculated (ppm)</th>
<th>Experimental (ppm)</th>
<th>Difference (calc.-exp.) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFcPh_2</td>
<td>-18.4</td>
<td>-16.9</td>
<td>-1.5</td>
</tr>
<tr>
<td>PFc_2Ph</td>
<td>-28.8</td>
<td>-30.3</td>
<td>+1.5</td>
</tr>
<tr>
<td>PET_2Fc</td>
<td>-26.4</td>
<td>-26.1</td>
<td>-0.3</td>
</tr>
<tr>
<td>PETFc_2</td>
<td>-32.8</td>
<td>-34.5</td>
<td>+1.7</td>
</tr>
<tr>
<td>PFciPr_2</td>
<td>-0.4</td>
<td>+0.6</td>
<td>-1.0</td>
</tr>
<tr>
<td>PnBuFcPh</td>
<td>-26.4</td>
<td>-27.7</td>
<td>+1.3</td>
</tr>
<tr>
<td>P^iBu_2Fc</td>
<td>+27.6</td>
<td>+27.8</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

The \( ^{13}\text{C} \) NMR spectra of PFcPh_2 and PnBuFcPh were recorded. The ferrocenyl carbons appear as three doublets from substituted \( \text{C}_5\text{H}_4 \) rings.
and a singlet from unsubstituted C₅H₅ rings. The most deshielded resonances at 75.8 ppm (J=6.1 Hz) for PFcPh₂ and 73.2 ppm (J=5.8 Hz) for PnBuFcPh are assigned to the carbons ortho to the site of substitution. The resonances at 72.8 ppm (J=14.8 Hz) for PFcPh₂ and 70.4 ppm (J=14.6 Hz) for PnBuFcPh are due to the ipso carbons because of the largest $^{31}\text{P}-^{13}\text{C}$ couplings. The carbons meta to the site of substitution resonate at 70.7 ppm for PFcPh₂ and 69.9 ppm for PnBuFcPh both with a coupling of 3.8 Hz. The unsubstituted Cp ring carbons resonate at 69.0 ppm.

Electron impact mass spectrometry proved to be very useful in characterizing these ferrocenyl ligands. All the ligands studied show parent ion peaks, and these peaks are also base peaks for the following ligands: PFcPh₂, PFc₂Ph, Fc'(PFcPh)₂, Fc'PPh, SFcPh, Fc'(SPh)₂, Fc'(SMe)₂, Fc'S₃, SFc₂, and SPFc₂Ph. The desorption chemical ionization (DCI) mass spectrum of SbFc₃ gives 491, which corresponds to SbFc²⁺, as the base peak. The most common fragments observed in the mass spectra of these ligands (>20% intensity relative to the base peak) are: (M-Ph)⁺, (M-Et)⁺, (M-nBu)⁺, (M-¹Bu)⁺,Fc₂⁺ (370), PFc₂Cp₃⁺ (336), Fe₂Cp₃⁺ (307), PFcPh⁺ (293), AsFc⁺ (260), Fc'P₂⁺ (246), Fe₂Cp₂⁺ (242), PFc⁺ (216), SFc⁺ (217), FeCp₂⁺ (186), FeCp⁺ (121), PhH⁺ (78), Fe⁺ (56). Table 6-2 lists the major mass spectrum peaks of these ligands and the corresponding ions.

It is interesting to note that PFcPh₂ gives (M-Ph)⁺, Fc⁺, and Ph⁺ as the major fragments, while SFcPh gives (M-Cp)⁺, Cp₂⁺, and Fe⁺ as the major fragments suggesting that S-C bonds are probably stronger than P-C bonds. A comparison of the major fragments of PFc₂Ph with those of SFc₂ leads to the same conclusion.
Table 6-2 Major features of the EI mass spectra of ferrocenyl ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Major mass spectra peaks and the corresponding ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFcPh2</td>
<td>370 (M+, base peak), 293 ((M-Ph)+), 186 (FcH+), 78 (PhH+)</td>
</tr>
<tr>
<td>PFc2Ph</td>
<td>478 (M+, base peak), 401 ((M-Ph)+), 304 (Fe2Cp3+), 239 (Fe2Cp2+), 216 (PFc+), 121 (FeCp+), 56 (Fe+)</td>
</tr>
<tr>
<td>PET2Fc</td>
<td>274 (M+), 245 ((M-Et)+), 217 (PFc+, base peak), 121 (FeCp+)</td>
</tr>
<tr>
<td>PFciPr2</td>
<td>302 (M+), 217 (PFc+), 186 (FcH+)</td>
</tr>
<tr>
<td>PnBuFcPh</td>
<td>350 (M+), 293 ((M-nBu)+), 216 (PFc+, base peak), 121 (FeCp+)</td>
</tr>
<tr>
<td>P1Bu2Fc</td>
<td>330 (M+), 273 ((M-tBu)+), 217 (PFc+, base peak), 186 (FcH+), 121 (FeCp+), 56 (Fe+)</td>
</tr>
<tr>
<td>PETFc2</td>
<td>430 (M+), 401 ((M-Et)+, base peak), 215 (PFc+), 186 (FcH+), 121 (FeCp+), 56 (Fe+)</td>
</tr>
<tr>
<td>AsFc2Ph</td>
<td>522 (M+), 445 ((M-Ph)+), 370 (Fc2+, base peak), 304 (Fe2Cp3+), 260 (AsFc+), 121 (FeCp+)</td>
</tr>
<tr>
<td>SFcPh</td>
<td>294 (M+, base peak), 228 ((M-Cp)+), 129 (Cp2+), 56 (Fe+)</td>
</tr>
<tr>
<td>SFc2</td>
<td>402 (M+, base peak), 304 (Fe2Cp3+), 272 (Scp2Fe2+), 121 (FeCp+), 96 (Scp+), 56 (Fe+)</td>
</tr>
<tr>
<td>SPFc2Ph</td>
<td>510 (M+, base peak), 433 ((M-Ph)+), 325 ((M-Fc)+), 248 (SPFc+), 186 (FcH+)</td>
</tr>
<tr>
<td>Compound</td>
<td>Mass Spectrum Details</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>SbFc₃</td>
<td>676 (M⁺), 491 ((M-Fc)⁺, base peak), 304 (Fe₂Cp₃⁺), 187 (FcH⁺), 121 (FeCp⁺ and/or Sb⁺)</td>
</tr>
<tr>
<td>Fc'(PFcPh)₂</td>
<td>770 (M⁺, base peak), 304 (Fe₂Cp₃⁺), 293 (PFcPh⁺)</td>
</tr>
<tr>
<td>Fc'PPh</td>
<td>292 (M⁺, base peak), 226 ((M-Cp)⁺), 186 (FcH⁺), 170</td>
</tr>
<tr>
<td></td>
<td>170 (PhPCp⁺), 121 (FeCp⁺)</td>
</tr>
<tr>
<td>Fc'(PiPr₂)₂</td>
<td>418 (M⁺), 375 ((M-iPr)⁺, base peak), 334 ((M-2iPr)⁺), 246 (Fc'P₂⁺), 186 (FcH⁺), 121 (FeCp⁺), 56 (Fe⁺)</td>
</tr>
<tr>
<td>Fc'(SPh)₂</td>
<td>402 (M⁺, base peak)</td>
</tr>
<tr>
<td>Fc'(SMe)₂</td>
<td>278 (M⁺, base peak), 263 ((M-Me)⁺), 121 (FeCp⁺)</td>
</tr>
<tr>
<td>FcSSFc</td>
<td>434 (M⁺), 217 (SFc⁺, base peak), 186 (FcH⁺), 152 (SCpFe⁺), 121 (FeCp⁺), 97 (SCp⁺), 56 (Fe⁺)</td>
</tr>
<tr>
<td>Fc'(SSFc)(SFc)</td>
<td>434 ((M-SFc)⁺), 304 (Fe₂Cp₃⁺), 272 (SCp₂Fe₂⁺), 218 (SFc⁺, base peak), 186 (FcH⁺), 152 (SCpFe⁺), 121 (FeCp⁺), 97 (SCp⁺), 56 (Fe⁺)</td>
</tr>
<tr>
<td>Fc'S₃</td>
<td>280 (M⁺, base peak), 216 (SFc⁺), 184 (Fc⁺), 96 (SCp⁺)</td>
</tr>
</tbody>
</table>

Cone angle is an important and useful concept introduced by Tolman [362] to describe quantitatively the steric bulk of a phosphine. Phosphine ligands, as mentioned in Section 2.1, are one of the most important classes of ligands in organometallic chemistry. A great advantage of this class of ligand is the possibility of modifying electronically and sterically the groups attached to phosphorus, so as to "tune" their chemistry. Ferrocenyl groups
are strongly electron releasing, but steric bulkiness is another important characteristic.

The cone angle of PFc₃ has been determined previously from the crystal structure of Ru(CO)₄(PFc₃) [250, 315], the value is 178° only slightly smaller than 182° of PtBu₃. From the known cone angles [363] of PnBu₃, PPh₃, PEt₃, and PiPr₃, the cone angles for the ferrocenylyphosphine ligands used in this work can be calculated using equation \( \theta = \frac{2}{3} \sum \theta_i / 2 \), i=1,2,3 [250]. The results are (for comparison, the value for PiPr₃ is 160°):

\[
\begin{align*}
\text{PEt₂Fc,} & \quad 147° \\
\text{PEtFc₂,} & \quad 163° \\
\text{PnBuFcPh,} & \quad 152° \\
\text{PFcPh₂,} & \quad 156° \\
\text{PFcPh₂,} & \quad 156° \\
\text{PFc₂Ph,} & \quad 167° \\
\text{PiPr₂Fc,} & \quad 166° \\
\text{PFc₂Ph,} & \quad 168° \\
\text{PiBu₂Fc,} & \quad 181°
\end{align*}
\]

Clearly, these ferrocenylyphosphines are rather bulky. Even the least bulky ligand PEt₂Fc is more bulky than PPh₃ whose cone angle is 145° [363].

6.2 Syntheses and Characterization of Triosmium Ferrocenylphosphine Complexes

6.2.1 Syntheses of triosmium ferrocenylphosphine complexes

Mono- and di-substituted triosmium ferrocenylphosphine carbonyl complexes Os₃(CO)₁₂-xLₓ (x=1 or 2) were prepared via Os₃(CO)₁₂-x(MeCN)ₓ (x=1 or 2). Me₃NO was used as a CO labilizing reagent in the syntheses of the MeCN derivatives which were used in situ to reduce the preparation time and number of isolation steps. The reactions of these labile intermediates with appropriate amounts of ligands (stoichiometric or slight excess to eliminate excess of Me₃NO which may be present in the reaction.
mixture) generally afford good yields (50-75%) of the desired products. In this manner, the complexes Os$_3$(CO)$_{11}$L (L=PFcPh$_2$, PFc$_2$Ph, PEt$_2$Fc, PFciPr$_2$, PtBu$_2$Fc, PEtFc$_2$) and Os$_3$(CO)$_{10}$L$_2$ (L=PFcPh$_2$, PFc$_2$Ph, PEt$_2$Fc, PFciPr$_2$, PEtFc$_2$) were prepared and characterized. The 1:1 reaction of Os$_3$(CO)$_{12}$ with PFciPr$_2$ affords, unexpectedly, also the di- and tri-substituted products Os$_3$(CO)$_{10}$(PFciPr$_2$)$_2$ and Os$_3$(CO)$_9$(PFciPr$_2$)$_3$. The reactions of Os$_3$(CO)$_{12}$ with PEtFc$_2$ or PEt$_2$Fc, in 1:1 molar ratio, affords some disubstituted complexes Os$_3$(CO)$_{10}$(PEtFc$_2$)$_2$ (15%) and Os$_3$(CO)$_{10}$(PEt$_2$Fc)$_2$ (15%).

The reaction of the bidentate ligand Fc'(PiPr$_2$)$_2$ with Os$_3$(CO)$_{12}$ in 1:1 molar ratio in refluxing toluene for 4 h afforded the desired product Os$_3$(CO)$_{10}$(Fc'(PiPr$_2$)$_2$) in 70% yield. Unexpectedly, a complex with the bidentate ligand bridging two Os$_3$ units, (Os$_3$(CO)$_{11}$)$_2$(Fc'(PiPr$_2$)$_2$), was also obtained in 20% yield.

6.2.2 Characterization of triosmium ferrocenylphosphine complexes

The triosmium ferrocenylphosphine complexes described above are stable crystalline solids soluble in CH$_2$Cl$_2$, toluene, and cyclohexane. Os$_3$(CO)$_{11}$(PtBu$_2$Fc) seems to be unstable in solution, especially if left on silica column overnight probably due to the steric bulk of the phosphine (cone angle 181°). These compounds are orange, reddish orange, or red in colour, and there are only subtle differences between the colour of the mono- and the di-substituted complexes of the same ligand. The purification of these products is relatively easy by using column chromatography and satisfactory elemental analyses are more readily obtained than for the ruthenium complexes to be described in the next section.
The $^{31}$P NMR chemical shift change of the ferrocenylphosphines upon coordination to Os$_3$ clusters is generally in the range of 4 to 20 ppm downfield. For example, the chemical shift changes for the following complexes from their respective free ligands are (ppm): Os$_3$(CO)$_{11}$(PFcPh$_2$), 6.3; Os$_3$(CO)$_{11}$(PFc$_2$Ph), 7.5; Os$_3$(CO)$_{11}$(PFc$_2$Pr$_2$), 18.1; Os$_3$(CO)$_{10}$[Fe'($^{3}$Pr$_2$)$_2$], 7.2; Os$_3$(CO)$_{11}$(PET$_2$Fc)$_2$, 12.7; Os$_3$(CO)$_{11}$(P$^{t}$Bu$_2$Fc)$_2$, 15.8.

The $^1$H NMR spectra of these triosmium complexes are similar to those of the free ligands except that the resonances are generally downfield shifted. For example, the ferrocenyl proton resonances for Os$_3$(CO)$_{11}$(PET$_2$Fc) are at 4.52 and 4.28 ppm compared to 4.28, 4.21, and 4.17 ppm in PET$_2$Fc, similar resonances for Os$_3$(CO)$_{11}$(P$^{t}$Bu$_2$Fc) are at 4.58, 4.55, and 4.28 ppm compared to 4.41, 4.28, and 4.20 ppm in P$^{t}$Bu$_2$Fc. Resonances of the other protons are similarly downfield shifted. For example, the CHMe$_2$ protons in Os$_3$(CO)$_{11}$(PFc$_2$Pr$_2$) resonate at 2.36 ppm compared to 1.62 ppm in PFc$_2$Pr$_2$. The CH$_2$ protons in Os$_3$(CO)$_{11}$(PET$_2$Fc) appear as complex overlapping multiplets compared to a quartet in PET$_2$Fc. The same CH$_2$ protons in Os$_3$(CO)$_{11}$(PET$_2$Fc)$_2$ appear as a quartet, the same as in the free ligand. The Me protons in Os$_3$(CO)$_{11}$(PFc$_2$Pr$_2$) appear as two doublets of doublets similar to those in the free ligand. The Me protons in Os$_3$(CO)$_{10}$[Fe'($^{3}$Pr$_2$)$_2$] appear as one doublet of doublet as in the free ligand, however, the same resonances in (Os$_3$(CO)$_{11}$)$_2$[Fe'($^{3}$Pr$_2$)$_2$] appear as two doublets of doublets similar to those in Os$_3$(CO)$_{11}$(PFc$_2$Pr$_2$).

The $^{13}$C NMR spectra were obtained for Os$_3$(CO)$_{10}$(PFcPh$_2$)$_2$, Os$_3$(CO)$_{11}$(PFc$_2$Pr$_2$)$_2$, and Os$_3$(CO)$_{11}$(PET$_2$Fc)$_2$. The chemical shifts for the substituted Cp ring carbons in these complexes are slightly changed but the couplings are greatly increased. For example, the ipso carbon resonances change from 72.8 ppm in PFcPh$_2$ to 82.0 ppm in
Os$_3$(CO)$_{10}$(PFcPh$_2$)$_2$, and the coupling increases from 14.8 Hz in PFcPh$_2$ to 58.8 Hz in the complex. The ortho carbons are upfield shifted from 75.8 to 73.8 ppm and the coupling increases from 6.1 to 11.5 Hz. The meta carbons and unsubstituted Cp ring carbons are little affected in chemical shifts, but the coupling of the meta carbons increases from 3.8 to 8.0 Hz.

The fast atom bombardment mass spectra of these triosmium substitution complexes all show molecular ion peaks even for (Os$_3$(CO)$_{11}$)$_2$ [Fc'(PiPr$_2$)$_2$] which has a molecular weight at around 2170. The molecular ions are also the most abundant ions for Os$_3$(CO)$_{10}$L$_2$ (L=PFcPh$_2$, PFc$_2$Ph, PEtFc$_2$), Os$_3$(CO)$_{11}$L (L=PEt$_2$Fc and PEtFc$_2$), and Os$_3$(CO)$_{10}$ [Fc'(PiPr$_2$)$_2$]. This seems to indicate that the molecular ions become more stable towards fragmentation as the degree of substitution increases and as the ligands become more electron donating. The base peak for Os$_3$(CO)$_{11}$(PFcPh$_2$) is (M-11CO)$^+$ and for Os$_3$(CO)$_{11}$(PFc$_2$Ph) is (M-2CO)$^+$. The base peak for Os$_3$(CO)$_{11}$(PFc'iPr$_2$) is (M-2iPr)$^+$, for Os$_3$(CO)$_{11}$(P^'Bu$_2$Fc) is (M-2^'Bu-8CO)$^+$ ((M^-Bu-10CO)$^+$ is unlikely), and for (Os$_3$(CO)$_{11}$)$_2$ [Fc'(PiPr$_2$)$_2$] is (M-CO)$^+$. The fragmentation patterns are generally associated with successive losses of ten or eleven CO groups. The loss of phenyl groups is often observed, the loss of ferrocenyl groups however is rare. In the complexes with PEtFc$_2$ and PEt$_2$Fc ligands, the loss of ethyl groups is observed but can not be differentiated from the loss of CO groups. In the complexes of the PFc'iPr$_2$ ligand, the fragmentation pattern is rather complex, a combination of the loss of CO (28), methyl (15), and/or i-propyl groups (43, equivalent to CO+Me) gives many peaks. For complex Os$_3$(CO)$_{11}$(P^'Bu$_2$Fc), the competitive and/or successive loss of CO (28) and ^'Bu (57) groups gives the observed spectrum.
6.3 Syntheses and Characterization of Triruthenium Ferrocenylphosphine Complexes

6.3.1 Syntheses of triruthenium ferrocenylphosphine complexes

The reactions of Ru$_3$(CO)$_{12}$ with PFcPh$_2$, PFc$_2$Ph, PFc$_{1}$Pr$_2$, PEtFc$_2$, PEt$_2$Fc, P$_{1}$Bu$_2$Fc, P$_n$BuFcPh, Fc'(PPh$_2$)$_2$, Fc'(PFcPh)$_2$, Fc'(P$_{1}$BuPh)$_2$, and Fc'(P$_{1}$Pr$_2$)$_2$ have been studied in addition to the reactions of Ru$_3$(CO)$_{10}$[Fc'(P$_{1}$Pr$_2$)$_2$] with PFc$_2$Ph and PEtFc$_2$.

The monosubstituted complexes Ru$_3$(CO)$_{11}$L (L-PFcPh$_2$, PFc$_2$Ph, PFc$_{1}$Pr$_2$, P$_n$BuFcPh) were prepared by using stoichiometric quantities of Ru$_3$(CO)$_{12}$ and the appropriate ligands and by using sodium benzophenone radical anions as catalyst [203-208]. The yields are high for PFcPh$_2$ (80%) and P$_n$BuFcPh (75%), but only moderate for PFc$_2$Ph and PFc$_{1}$Pr$_2$ (both 55%). In both of the last two reactions, considerable yields of the disubstituted complexes (30%) were isolated. It should be noted that the BPK catalyzed reaction is extremely air sensitive, and it was observed that a green (rather than purple) solution also catalyzed the reaction, but many more products were formed as revealed by $^{31}$P NMR spectroscopy.

The monosubstituted complexes Ru$_3$(CO)$_{11}$L (L-PEt$_2$Fc and P$_{1}$Bu$_2$Fc) were obtained unexpectedly in moderate yields (50 and 60% respectively) via thermal reactions by using two equivalents of ligand. P$_{1}$Bu$_2$Fc is an extremely bulky ligand (cone angle 181°) (Section 6.1), and the formation of the monosubstituted product is not unexpected under such reaction conditions, but there is no rationale for the formation of Ru$_3$(CO)$_{11}$(PEt$_2$Fc). The trisubstituted complex should predominate in the reaction of PEt$_2$Fc.

The reaction of Ru$_3$(CO)$_{12}$ with PFcPh$_2$ in 1:2 molar ratio using BPK as catalyst gives a complex mixture of all three substitution complexes with
the disubstituted complex predominating.

The thermal reactions of Ru₃(CO)₁₂ with PFcPh₂, PFc₂Ph, and PFcPr₂ in 1:3 molar ratio afford corresponding trisubstituted complexes in 60%, 45%, and 35% yields, respectively. The bulkiness of PFc₂Ph and PFcPr₂ compared to that of PFcPh₂ presumably accounts for the decreased yields.

The bidentate ferrocenyiphosphine complexes Ru₃(CO)₁₀(L-L) (L-L=Fc'(PPh₂)₂, Fc(PFcPh)₂, Fc'(P'BuPh)₂, and Fc'(PiPr₂)₂) were prepared by using a 1:1 molar ratio of Ru₃(CO)₁₂ and the appropriate ligand with PPN⁺Cl⁻ as catalyst. The yields for Fc'(PFcPh)₂, Fc'(PiPr₂)₂, and Fc'(P'BuPh)₂ are higher than that for Fc'(PPh₂)₂. The BPK catalyzed reactions of Fc'(PPh₂)₂ or Fc'(P'BuPh)₂ with Ru₃(CO)₁₂ gave incredibly complex mixtures as revealed by TLC and ³¹P NMR spectroscopy. This is not understood, but presumably it is because the electron transfer intermediates decompose before subsequent reactions can take place.

The thermal reaction of Ru₃(CO)₁₀[Fc'(PiPr₂)₂] with PFc₂Ph in hexanes gives a very good yield of the desired product. Both ligands in the product are very bulky, however the bidentate ligand occupies two neighbouring positions on two adjacent Ru atoms in Ru₃(CO)₁₀[Fc'(PiPr₂)₂], so the third substitution readily takes place on the third Ru atom, most likely via a dissociative pathway. These reactions are surprisingly facile as demonstrated by the reaction of Ru₃(CO)₁₀[Fc'(PiPr₂)₂] with PEtFc₂ at room temperature for 5 days (45%).

6.3.2 Characterization of triruthenium ferrocenyiphosphine complexes

In general, these triruthenium ferrocenyiphosphine complexes are stable in air in the solid state. The complexes of the monodentate ligands are not very stable in air in solution. More highly substituted complexes
with more bulky phosphines are even less stable. However, the bidentate phosphine complexes are more stable. The monosubstituted complexes are orange in colour. The disubstituted monodentate phosphine complexes are pink red, purple, purple red, and pink, and the bidentate phosphine complexes are all red in colour. The trisubstituted complexes are dark purple, pink red, or dark red. The $R_f$ values (rate of flow) on TLC plates decreases as the degree of substitution increases. Because more highly substituted complexes are often considerably slower to elute and more susceptible to decomposition, column chromatography should be performed in as a short time as possible (in some cases, the pink red or purple spots on TLC plates disappear in 1 h). Overall, these triruthenium complexes are less stable than the osmium analogues, more polar, and more difficult to purify.

The $^{31}P$ NMR chemical shift changes of the ferrocenylphosphines upon coordination to Ru$_3$ clusters are in the range of 35 to 50 ppm downfield, greater than that in the Os$_3$ system discussed in Section 6.2.2. For example, the chemical shift changes for the following complexes from their respective free ligands are (ppm): Ru$_3$(CO)$_{11}$(PFc$_2$Ph), 46.1; Ru$_3$(CO)$_{11}$(PtBu$_2$Fc), 48.3; Ru$_3$(CO)$_{11}$[Fc'(PPr$_2$)$_2$], 41.2; Ru$_3$(CO)$_9$[Fc'(PPr$_2$)$_2$](PFc$_2$Ph), 37.5, 35.9, 44.0; Ru$_3$(CO)$_9$(PFcPh$_2$)$_3$, 45.8.

The change of the $^1H$ NMR resonances of these ruthenium complexes as compared to those of the free ligands is similar to that of the Os$_3$ complexes, the magnitude of change is also similar. For example, ferrocenyl proton resonances at 4.26, 4.22, 4.14, 4.05, and 3.91 ppm in PFc$_2$Ph change to 4.52, 4.46, 4.34, 4.14, and 4.10 ppm in Ru$_3$(CO)$_{11}$(PFc$_2$Ph). The resonances of other protons such as phenyl and i-propyl protons are similarly changed as in the osmium complexes. For example, the CH proton
resonances in PFciPr2 and Ru3(CO)11(PFcPr2) are at 1.62 and 2.33 ppm respectively differing by 0.71 ppm, the CH2 proton resonances in PEt2Fc as a quartet at 1.60 ppm change to complex multiplets in Ru3(CO)11(PET2Fc) at 2.24-1.94 ppm.

The fast atom bombardment mass spectra of these triruthenium complexes were more difficult to obtain than those of the Os3 complexes. The monosubstituted complexes such as Ru3(CO)11L (L=PFcPh2, PFc2Ph, PEt2Fc, PFciPr2, PnBuFcPh, PETFc2, PiBu2Fc) all show molecular ions, but only in one case (PETFc2) is the molecular ion also the most abundant ion. The others give as base peaks (M-8CO-Ph)+ for Ru3(CO)11L (L=PFcPh2 and PFc2Ph), (M-4CO)+ or (M-3CO-Et)+ or (M-2CO-2Et)+ for Ru3(CO)11(PET2Fc), (M-CO-2iPr)+ for Ru3(CO)11(PFciPr2), (M-11CO-2tBu-Cp)+ for Ru3(CO)11(PiBu2Fc), and (M-nBu-CO)+ or (M-3CO)+ for Ru3(CO)11(PnBuFcPh). Among the disubstituted complexes, only Ru3(CO)10(PFcPh2)2 and Ru3(CO)10(PFcPr2)2 give satisfactory mass spectra that show molecular ions. Ru3(CO)10(PFc2Ph)2 does not give any meaningful spectrum despite repeated attempts. Among the trisubstituted complexes only Ru3(CO)9(PFcPh2)3 gives a good spectrum. The major fragments correspond to (M-CO)+, (M-PFcPh2-5CO)+, (M-PFcPh2-6CO)+, and (M-PFcPh2-Ph-8CO)+ (base peak). These differences may be due to the bulkiness of PFc2Ph and PFciPr2 (cone angles 167 and 166° respectively) compared to PFcPh2 (cone angle 156°) (Section 6.1.2).

The bidentate phosphine complexes Ru3(CO)10(L-L) (L-L=Fc(PPh2)2, Fc(PFcPh)2, Fc(PiBuPh)2, and Fc(PiPr2)2) all give reasonable mass spectra that show molecular ions. The base peaks for the first two complexes are (M-2CO)+. The base peak for Ru3(CO)10[Fc'(PiBuPh)2] is (M-2tBu-CO)+ and for Ru3(CO)10[Fc'(PiPr2)2] is (M-2iPr-CO)+.
6.4 Structures of Triosmium and Triruthenium Ferrocenyl-phosphine Complexes

6.4.1 Isomerism in the disubstituted complexes M₃(CO)₁₀L₂

The structures of the complexes of the types M₃(CO)₁₁L, M₃(CO)₉L₃, M₃(CO)₁₀(L-L), (M₃(CO)₁₁)₂(L-L), and M₃(CO)₉(L-L)L' are straightforward and they should have structures as discussed in Section 2.2. The structures of the disubstituted complexes are more complex and merit further discussion.

A rather unexpected aspect of these studies of the reactions of these ferrocenylphosphines with Ru₃(CO)₁₂ and Os₃(CO)₁₂ is the frequent occurrence of isomerism in the disubstituted products. An extensive structural study of Ru₃ and Os₃ phosphine complexes showed that the disubstituted complexes usually adopt the symmetrical structure [221]. This is explained by the tendency of these ligands (usually bulky) to keep away from each other as much as possible. There were earlier indications of unsymmetrical and symmetrical type of isomerism in Os₃ complexes with less bulky ligands such as PEt₃ and PMe₂Ph (cone angles 132 and 122° respectively) [254, 259, 364]. This isomerism would also be aided by longer Os-Os and Os-P bonds relative to Ru-Ru and Ru-P bonds respectively. The ferrocenylphosphines used in this work are much more bulky than PEt₃ or PMe₂Ph (the least bulky PEt₂Fc has a cone angle of 147°) (Section 6.1). The formation of the unsymmetrical isomers is therefore totally unexpected especially in the Ru₃ system. This phenomenon can only be attributed to electronic effects. The ³¹P NMR spectra of the unsymmetrical isomers show two sharp resonances, two relatively broad resonances, or one broad resonance. This is understood as:
(1) The phosphorus atoms are directly bonded to the metal centers and they are naturally more sensitive to the change of coordination environments; (2) The different appearances of the $^{31}$P NMR spectra are due to the fluxional process shown in Scheme 6-1 (axial CO groups are omitted for clarity).

![Scheme 6-1 An exchange pathway of two unsymmetrical structures.](image)

Strongly electron donating ligands such as ferrocenylphosphines have higher trans effects. The ligands tend to adopt the unsymmetrical structure to avoid the large trans labilizing effects the two phosphines would have on each other via a metal-metal bond in a symmetrical structure (377a). Overall then, steric hindrance favors the symmetrical structure (377a), while trans labilizing effects favor the unsymmetrical structure (377b).
Due to the electronic effects only the unsymmetrical isomers of \( \text{Os}_3(\text{CO})_{10}(\text{PFcPh}_2)_2 \) and \( \text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \) were formed as described above. However, in the analogous \( \text{Ru}_3 \) complexes, steric effects become more severe (\( \text{Ru-Ru} \) and \( \text{Ru-P} \) bonds are shorter than \( \text{Os-Os} \) and \( \text{Os-P} \) bonds respectively), and this makes the same ligands appear more bulky and mixtures of the symmetrical and unsymmetrical isomers were obtained. The fluxional process shown in Scheme 6-1 is slower for \( \text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \) than for \( \text{Os}_3(\text{CO})_{10}(\text{PFcPh}_2)_2 \) thus the \(^{31}\text{P} \) NMR spectrum of the former is well resolved into two peaks but still broad, while that of the latter shows only one broad resonance due to faster exchange.

6.4.2 Molecular structure of \( \text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \) (378)

The reaction of \( \text{Os}_3(\text{CO})_{10}(\text{MeCN})_2 \) with \( \text{PFc}_2\text{Ph} \) in 1:2 molar ratio gives a good yield of the expected product \( 1,2-\text{Os}_3(\text{CO})_{10}(\text{PFc}_2\text{Ph})_2 \). The \(^{31}\text{P} \) NMR spectrum of this complex shows two signals of equal intensity in a number of different solvents clearly showing it to be the unexpected unsymmetrical isomer. An X-ray diffraction study was carried out to confirm this novel finding. An ORTEP diagram with 33.0% probability thermal ellipsoids is shown in Figure 6.1.

Crystal data: \( M = 1806.99 \), orange, prism, monoclinic system, space group \( C2/c \) (#15), \( a=27.846(4), b=11.253(4), c=38.520(3) \) Å, \( \beta=107.813(9) \), \( V=11492(5) \) Å\(^3\), \( Z=8 \), \( D_{calc}=2.089 \) g/cm\(^3\), \( R=0.030 \), \( R_w=0.027 \).

The structure of (378) consists of a closed \( \text{Os}_3 \) triangle and is like \( \text{Os}_3(\text{CO})_{12} \) with one CO group on Os(1) and Os(2) replaced by the phosphine ligand \( \text{PFc}_2\text{Ph} \). The Os-Os distances are as usual with Os(2)-Os(3) (2.893(1) Å) being slightly shorter than the other two (2.9237(6) and 2.9259(9) Å). Such bond alternation is not surprising since both the Os(1)-Os(3) and
Os(1)-Os(2) bonds are cis to a bulky phosphine PFc2Ph. Similar lengthening was observed in monosubstituted phosphine and arsine complexes of the type M₃(CO)₁₁₄ (M=Ru or Os, L=phosphine or arsine), but not in complexes of the type M₃(CO)₁₀L₂ (M=Ru or Os, L=phosphine or arsine) since all these disubstituted complexes adopt the symmetrical structure (377a). In (378) the two bulky phosphines adopt the unsymmetrical arrangement and they occupy two equatorial coordination sites. Surprisingly, both phosphines are distorted slightly towards one side of the Os₃ plane (0.4491 Å for P(1) and 0.3369 Å for P(2)). One equatorial carbonyl (C(59)) also lies on the same

Figure 6.1 ORTEP diagram of complex (378).
side of the Os₃ plane (by 0.3213 Å) as P(1) and P(2), while the other three alternating equatorial carbonyls (C(53), C(56), C(60)) are situated on the other side of the Os₃ plane (by 0.3227, 0.3106, and 0.2167 Å respectively). As a consequence the six axial carbonyls are distorted from their idealized positions. On the P(1), P(2), and C(59) side of the Os₃ plane, C(54), C(57), and C(61) have moved towards Os(2), Os(3), and Os(1), respectively (C(54)-Os(1)-Os(2) 80.8(3)°, C(57)-Os(2)-Os(3) 83.1(3)°, C(61)-Os(3)-Os(1) 81.4(3)°). On the other side of the Os₃ plane, a compensating motion of C(55), C(58), and C(62) occurs towards Os(3), Os(1), and Os(2), respectively (C(55)-Os(1)-Os(3) 83.4(3)°, C(58)-Os(2)-Os(1) 81.3(3)°, C(62)-Os(3)-Os(2) 85.5(3)°).

The Os(1)-C(53) and Os(2)-C(56) bond distances (1.87(1) and 1.88(1) Å respectively) are probably shorter than the other Os-C distances (av. 1.935 Å), while all the C-O distances are the same and normal (av. 1.14 Å) and all the Os-C-O bonds are close to linear (av. 175°). Both Os-P distances are the same and normal (2.353(2) and 2.359(3) Å). All Fe-C distances are equal as are the Fe-Cp distances. The Cp rings in each ferrocenyl group are parallel with small ring tilt angles (2.48° for Fc(1), 3.27° for Fc(3)) as found for free PFC₂Ph ligand (2.1 and 1.6° respectively) [346], but the values for Fc(2) and Fc(4) are larger than usual (6.75 and 9.06° respectively). These unusually large values are also indicated by the Cp-Fe-Cp angles (Cp(3)-Fe(2)-Cp(4) 173.5(4)° and Cp(7)-Fe(4)-Cp(8) 172.7(4)°, while Cp(1)-Fe(1)-Cp(2) 177.0(2)° and Cp(5)-Fe(3)-Cp(6) 176.4(3)° are usual). There is no obvious explanation for this difference.

In each ferrocenyl moiety the two Cp rings are approximately eclipsed as found in free ligand [346]. The coordination of the phosphorus atom to the cluster has no influence on the CPC angles which are less than
the ideal tetrahedral angle of 109.5°, being 100.2(4), 99.1(4), and 100.7(4)°
for P(1), 100.2(4), 99.5(4), and 103.0(4)° for P(2). These values are the
same as in the non-coordinated ligand (101.0(5), 98.6(5), and 100.0(5)°)
[346].

As discussed in Section 2.2, many phosphine complexes of the type
M₃(CO)₁₀L₂ are known but, as discussed above, few are reported to be of
structures other than (377a). The present complex (378) is the first
molecule of structure (377b) to be characterized in the solid state.

6.5 General Comments on the Pyrolytic Reactions and
Characterization of Pyrolysis Products

6.5.1 General comments

Two general methods were used for the pyrolytic studies described
in Chapters 4 and 5. The first involves heating an appropriately
substituted complex, and the second one involves heating Ru₃(CO)₁₂ or
Os₃(CO)₁₂ with the appropriate amount of a ligand of interest. The first
method is preferable for Ru₃ and Os₃ complexes containing strongly
binding ferrocenylphosphines which are not too bulky, and the second
method is preferable for weakly binding ligands such as SFcPh and SPh₂
and for extremely bulky ligands such as P¹Bu₂Fc and P(1-C₁₀H₇)₃. For such
weak coordinating and/or very bulky ligands, the preparation of the
simple substitution complexes is more difficult or even impossible. Also for
such ligands, the direct pyrolysis is not likely to afford products that
contain or are derived from two or more ligand moieties.
Purification of the pyrolysis products is best achieved by column chromatography. Most of the products are stable for such operations. It should be noted that most of the pyrolysis reactions afford some very polar (presumably mononuclear products) or decomposition products which do not come off the column. Since many of the products are formed in low yields (5-15%), repeated chromatography is seldom used to isolate minor products because there is often insufficient material for such an operation.

The colour of the ruthenium complexes is often yellow, orange, red, dark red, or sometimes green, and the colour of the osmium complexes is often yellow, orange, or green. Most of the products are stable in the solid state, and as observed for the substitution complexes, the osmium complexes are generally more readily crystallized, more stable, but less soluble in common organic solvents than the ruthenium compounds. In terms of characterization of these products, the osmium compounds again more readily give satisfactory analyses and good mass spectra than the ruthenium complexes. In the FAB mass spectra, the successive loss of CO, iPr, tBu, Me, and Ph groups where appropriate is the main feature. Osmium complexes are apparently more robust than ruthenium complexes. For example, complex (329) discussed in Section 4.13 gave a good mass spectrum with the molecular ion, while the ruthenium analogue (370) discussed in Section 5.9 did not give the parent ion.

6.5.2 $^1$H NMR spectra of the pyrolysis products

The $^1$H NMR spectra of these complexes are very structure dependent, and only complexes with the same structures make useful comparisons. The ferrocenyl proton resonances in the series of complexes
Os₃(CO)₈(H)₂[(C₅H₃PR₂)Fe(C₅H₄)] appearing as seven separate signals are very characteristic. For example, such resonances in (245) (R₂-Ph₂) at 5.12 (2H), 4.62, 4.27, 3.98, 3.16, and 2.97 ppm are similar to 5.41, 5.12, 4.77, 4.31, 4.24, 4.12, and 3.08 ppm in (278) (R₂-iPr₂). The other most useful features in the ¹H NMR spectra are sharp singlets for C₅H₅ ring protons, doublets of doublet for CHMe₂ protons, an AA’BB’ or ABCD pattern for C₆H₄ protons, two overlapping septets for CHMe₂ protons, sharp strong doublets for CMe₃ protons, and triplets of doublet for CH₂Me protons. The breadth of the ferrocenyl chemical shift region is also highly useful.

As many of the pyrolysis products contain one or two hydrides, the hydride resonances are particularly useful for comparing two similar structures in the absence of Infra-red spectroscopic data. For example, in the series of complexes Os₃(CO)₈(H)₂[(C₅H₃PR₂)Fe(C₅H₄)], the hydride resonances, summarized in Table 6-3, are similar in chemical shifts and couplings indicating that these are characteristic of the structure type.

The hydride resonances for the series of naphthyne complexes of the formula M₃(CO)₈[(1-C₁₀H₇)₂E(1-C₁₀H₅)] are shown in Table 6-4. The hydride chemical shifts are similar for the two Os₃ complexes, and for the two Ru₃ complexes, but both hydrides in the Ru₃ complexes are downfield shifted by ca. 1.5 ppm from the corresponding Os₃ complexes. The ¹H-³¹P couplings for the hydride that is three bonds away from the phosphorus is little changed (by 0.4 Hz) from the Os₃ complex (333) to the Ru₃ complex (372), while that for the hydride which is two bonds away increased by 6.6 Hz from (333) to (372).

The hydride resonance in complex Os₃(CO)₇(H)(μ₃-PiPr)₃(C₅H₄PiPr₂)Fe(C₅H₄)] (329) at -21.92 ppm with couplings of 13.9 and 7.6 Hz is slightly downfield shifted to -21.02 ppm in the ruthenium analogue (370) with
increased couplings of 22.8 and 9.0 Hz respectively.

Table 6-3 $^{31}$P and hydride NMR resonances for complexes $\text{Os}_3(\text{CO})_8(\text{H})_2\text{[(C}_5\text{H}_3\text{PR}_2)\text{Fe}(\text{C}_5\text{H}_4)]}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P NMR chemical shifts (ppm)</th>
<th>hydride chemical shifts (ppm) and hydride-phosphorus couplings (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(245) $\text{R}_2=\text{Ph}_2$</td>
<td>-6.0</td>
<td>-12.23, $J=4.2$ -16.94, $J=13.4$</td>
</tr>
<tr>
<td>(261) $\text{R}_2=\text{FcPh}$</td>
<td>-20.4</td>
<td>-12.13, $J=4.5$ -16.91, $J=12.5$</td>
</tr>
<tr>
<td>(262) $\text{R}_2=\text{FcPh}$</td>
<td>-22.0</td>
<td>-12.16, $J=3.9$ -17.05, $J=13.0$</td>
</tr>
<tr>
<td>(269) $\text{R}_2=\text{Et}_2$</td>
<td>-22.7</td>
<td>-12.22, $J=4.5$ -17.39, $J=11.4$</td>
</tr>
<tr>
<td>(278) $\text{R}_2=\text{iPr}_2$</td>
<td>2.5</td>
<td>-12.07, $J=4.1$ -17.13, $J=12.0$</td>
</tr>
<tr>
<td>(289) $\text{R}_2=\text{nBuPh}$</td>
<td>-16.1</td>
<td>-12.14, $J=4.8$ -16.99, $J=12.9$</td>
</tr>
<tr>
<td>(290) $\text{R}_2=\text{nBuPh}$</td>
<td>-17.7</td>
<td>-12.30, $J=4.5$ -17.06, $J=12.0$</td>
</tr>
<tr>
<td>(308) $\text{R}_2=\text{EtFc}$</td>
<td>-27.4</td>
<td>-12.13, $J=4.3$ -17.04, $J=12.3$</td>
</tr>
<tr>
<td>(311) $\text{R}_2=\text{EtFc}$</td>
<td>-26.5</td>
<td>-12.17, $J=3.9$ -17.45, $J=11.7$</td>
</tr>
</tbody>
</table>
Table 6-4 Hydride resonances for complexes $\text{M}_3(\text{CO})_8[(\text{1-C}_{10}\text{H}_7)_2\text{E}(\text{1-C}_{10}\text{H}_5)]$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydride chemical shifts (ppm) and hydride-phosphorus couplings (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(333) $\text{M}=\text{Os}, \text{E}=\text{P}$</td>
<td>$-17.59, J=5.6$</td>
</tr>
<tr>
<td>(336) $\text{M}=\text{Os}, \text{E}=\text{As}$</td>
<td>$-17.69$</td>
</tr>
<tr>
<td>(372) $\text{M}=\text{Ru}, \text{E}=\text{P}$</td>
<td>$-15.78, J=5.2$</td>
</tr>
<tr>
<td>(374) $\text{M}=\text{Ru}, \text{E}=\text{As}$</td>
<td>$-15.93$</td>
</tr>
</tbody>
</table>

Another series of complexes of the general formula $\text{Os}_3(\text{CO})_{10}(\text{H})_2 [(\text{C}_{5}\text{H}_4\text{PR}_2)\text{Fe(C}_{5}\text{H}_3)]$ show similar hydride chemical shifts and couplings characteristic of this structure type, Table 6-5.

Except in a few complexes such as (244) (hydride resonance at -5.43 ppm), all hydrides are probably bridging between two metal atoms. In some $\text{Os}_3$ cluster complexes such as (269) and (334), two pairs of satellite peaks can be observed beside the main hydride resonances indicating couplings to two $^{187}\text{Os}$ nuclei thus supporting the bridging bonding mode of
the hydrides.

A general observation in the $^1$H NMR spectra of these hydride containing species is that the hydrides appear as sharp resonances except in complexes (276) and (305). For example, a series of complexes containing an α doubly-metalated alkyl group on a ferrocenylphosphine, $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{EtFcPCMe})$ (267), $\text{Os}_3(\text{CO})_8(\text{PET}_2\text{Fc})(\text{H})_2(\text{EtFcPCMe})$ (271) and (272), $\text{Os}_3(\text{CO})_8(\text{PnBuFcPh})(\text{H})_2(\text{FcPhPCnPr})$ (293) and (294), all exhibit sharp and well resolved hydride signals, while the literature precedents such as $\text{Os}_3(\text{CO})_9(\text{H})_2(W_2\text{PCR})$ (227) and $\text{Os}_3(\text{CO})_8(\text{PR}_3)(\text{H})_2(R'R_2\text{PCR})$ (228).

Table 6-5 $^{31}$P and hydride NMR resonances for complexes $\text{Os}_3(\text{CO})_{10}(\text{H})_2 [(\text{C}_5\text{H}_4\text{PR}_2)\text{Fe}(\text{C}_5\text{H}_3)]$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P chemical shifts (ppm)</th>
<th>Hydride chemical shifts (ppm) and hydride-phosphorus couplings (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(253) $\text{R}_2=\text{FcPh}$</td>
<td>-24.2</td>
<td>-16.86, $J=29.6$</td>
</tr>
<tr>
<td>(254) $\text{R}_2=\text{FcPh}$</td>
<td>-33.3</td>
<td>-17.25, $J=30.5$</td>
</tr>
<tr>
<td>(275) $\text{R}_2=\text{iPr}_2$</td>
<td>0.0</td>
<td>-17.21, $J=28.0$</td>
</tr>
<tr>
<td>(306) $\text{R}_2=\text{EtFc}$</td>
<td>-31.3</td>
<td>-17.15, $J=27.3$</td>
</tr>
<tr>
<td>(307) $\text{R}_2=\text{EtFc}$</td>
<td>-32.9</td>
<td>-17.10, $J=27.6$</td>
</tr>
</tbody>
</table>
discussed in Section 4.5 (Table 4-1) exhibit sharp resonances only at low temperature [263]. The naphthyne complexes $M_3(CO)_8(H)_2[(1-C_{10}H_7)_2E(1-C_{10}H_5)]$ (M=Os, E=P, (333); Os, As, (336); Ru, P, (372); Ru, As, (374)) also show very sharp hydride resonances, in contrast with the analogous benzyne complex $Os_3(CO)_9(H)_2(C_6H_4)$ (126) which shows only one hydride resonance at room temperature [139]. A further example is the arsenido benzyne complex $Os_3(CO)_9(H)(AsFc_2)(C_6H_4)$ (315) which shows a sharp singlet for the hydride, while the analogous complex $Os_3(CO)_9(H)(AsMe_2)(C_6H_4)$ (114b) shows a broad resonance at room temperature [126].

6.5.3 $^{31}P$ NMR spectra of the pyrolysis products

$^{31}P$ NMR spectroscopy proved to be a very powerful technique in characterizing these pyrolysis products containing various moieties of phosphorus especially in the ruthenium complexes because of its greater chemical shift range from 450 to -50 ppm in the present investigation compared to that in the osmium complexes from 210 to -100 ppm.

Carty et al. in their excellent article have made a qualitative analysis of the factors that influence the chemical shifts of phosphinidene and phosphido moieties [365]. These include the metal atom, the nature of M-M and M-P interactions associated with M-P-M angles, changes in angles and stereochemistry at the phosphorus atom, involvent of p and d orbitals in bonding, and finally the number and orientation of other ligands on the metal. Because of these complications, only comparisons between analogous structures can be made with any degree of confidence.

In the pyrolysis products of the series $Os_3(CO)_8(H)_2[(C_5H_3PR_2)Fe(C_5H_4)]$ and $Os_3(CO)_10(H)_2[(C_5H_4PR_2)Fe(C_5H_3)]$, the $^{31}P$ NMR chemical shifts as shown in Tables 6-3 and 6-5 respectively show the same type of
variation with groups $R_2$ as observed for the free ligands discussed in Section 6.1.

In the osmium cluster complexes, the chemical shift differences between phosphinidene moieties and phosphines are generally readily recognizable. For example, in complex $\text{Os}_3(\text{CO})_9(\text{PPh}_2)(\text{PPh})(\text{C}_6\text{H}_4)$ (239), the $^{31}\text{P}$ NMR chemical shifts are 207.3 ppm. In the ferrocyan complex $\text{Os}_3(\text{CO})_9(\text{PR})[[(\text{C}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_5)] (\text{R}=\text{Fc}, \text{Bn}, \text{nBu})$, the $^{31}\text{P}$ NMR chemical shifts are also readily recognizable (189.8 and 209.8 ppm respectively). Another example is complex $\text{Os}_3(\text{CO})_7(\text{H})(\mu_3-P\text{Pr})[[\text{C}_5\text{H}_4\text{P}\text{Pr}_2]\text{Fe}(\text{C}_5\text{H}_4)]$ (329) in which the phosphinidene moiety shows a resonance at 268.3 ppm, while the phosphine resonates at 16.5 ppm. The chemical shifts of the phosphido moieties are generally less readily recognizable. For example, the $^{31}\text{P}$ NMR chemical shift for the ferrocyan complex $\text{Os}_3(\text{CO})_8(\text{H})(\text{PPr}_2)[[(\text{C}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_5)] (274)$ is at 203.9 ppm (in the range of phosphinidene resonances), those in the complex $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{H})(\text{PPh})(\text{C}_6\text{H}_4)$ (248) are at 42.3 and -13.6 ppm for the phosphido moiety and the phosphine respectively, while those in the complex $\text{Os}_3(\text{CO})_9(\text{H})[[\text{C}_5\text{H}_4\text{PPr}\text{Fe}(\text{C}_5\text{H}_4\text{PPr}_2)] (323)$ are at 16.2 and 18.0 ppm for the phosphido moiety and for the phosphine. In complexes of similar structures, the $^{31}\text{P}$ NMR chemical shifts for such phosphido moieties show consistency. For example, in the ferrocyan complexes $\text{Os}_3(\text{CO})_8(\text{H})(\text{PR}_2)[[(\text{C}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_5)] (\text{R}_2=\text{FcPh}, \text{Bn}, \text{EtFc})$, such shifts are at 146.9, 150.2, and 148.5 ppm, respectively. In the symmetrical benzyne complexes $\text{Os}_3(\text{CO})_7(\text{PR}_2)_2(\text{C}_6\text{H}_4)$ (R2=FcPh, 246; nBuF, 291), the chemical shifts are at 157.8 and 151.3 ppm respectively. In complexes
Os₃(CO)₉(µ-CO)[(C₅H₃PR)Fe(C₅H₅)] (R-Fe, (255); nBu, (285); tBu, (299)), the chemical shifts are at 43.5, 56.7, and 52.3 ppm, respectively.

In the ruthenium complexes, the chemical shifts for both phosphinidene and phosphido moieties are readily recognizable. For example, the phosphinidene moiety in the complex Ru₃(CO)₇(H)(µ₃-PiPr) [(C₅H₄PiPr₂)Fe(C₅H₄)] (370) resonates at 429.3 ppm (the osmium analogue (329) at 268.3 ppm), in Ru₄(CO)₁₁(PFc)(C₅H₄) (351) at 418.0 ppm, in Ru₃(CO)₉(PFc)(C₆H₄) (337) at 387.8 ppm (the osmium analogue (239) at 207.3 ppm), and in Ru₃(CO)₈(H)₂[(C₅H₄P)Fe(C₅H₄PiPc₂)] (368) at 269.4 ppm. The phosphido moiety in complex Ru₅(CO)₁¹(PFc)(PFcC₆H₄)(C₆H₄) (342) resonates at 162.2 ppm, in Ru₂(CO)₇(PFcC₆H₄CO) (340) at 149.5 ppm, and in Ru₃(CO)₈(H)₂[(C₅H₄PCHMeCH₂)Fe(C₅H₄PiPr₂)] (369) at 177.4 ppm.

In the series of complexes containing two phosphido moieties, the ³¹P NMR resonances are downfield shifted more than those mentioned above. For example, the unsymmetrical benzyne complex Ru₃(CO)₇(PFcPh)₂(C₆H₄) (344) shows two resonances at 272.2 and 208.3 ppm with a coupling of 199.6 Hz (the osmium analogue (247) at 187.3 and 143.8 ppm with a coupling of 166 Hz), and Ru₃(CO)₇(PFcPh)(PPh₂)(C₆H₄) shows resonances at 263.9 and 215.9 ppm with a coupling of 190.7 Hz for one isomer (359), at 274.9 and 204.1 ppm with a coupling of 195.7 Hz for the other (360). Complexes Ru₃(CO)₈(C₆H₅)(PFcPh)(PFcC₆H₄) (345) and Ru₃(CO)₆(PFcPh₂)(PFcPh)₂(C₆H₄) (346) and (347) are similar.

A good example of the chemical shift changes for phosphinidene and phosphido moieties is seen in the complexes (368) to (370) obtained from Ru₃(CO)₁₀[Fc'('PiPr₂)₂]. The chemical shift for the phosphine in each molecule remains little changed in (368), (369), and (370) (67.5, 73.7, and 53.7 ppm, respectively), while the chemical shift for the phosphido moiety
in (369) is 177.4 ppm: the shifts of the phosphinidene moieties in (368) and (370) are at 269.4 and 429.3 ppm respectively.

6.6 Iron (ferrocene)-metal Bonding Interactions in Triosmium and Triruthenium Complexes

A discussion of Fe (ferrocene)-M bonding interactions is appropriate in view of the widespread occurrence of such interactions found in the Os₃ and Ru₃ clusters in this study.

The role of the central metal atom in electrophilic substitution reactions of metallocenes especially ferrocenes has been under discussion for a long time. Rosenblum et al. [366] postulated that the iron atom is the site of the initial attack of the electrophile to form an intermediate such as (379) in Scheme 6-2.

The unusually highly shielded ¹H NMR resonances observed for ferrocene in boron trifluoride hydrate [367] and trifluoromethanesulfonic acid [368] (2.1 and 2.25 ppm respectively) provide some evidence for the existence of structures such as (379). The basicity of ruthenocene RuCp₂ and ferrocene FeCp₂ towards proton was also known [369]. In 1972 Hendrickson et al. found that electrochemical oxidation of RuCp₂ at a mercury anode gave the mercury-bridged cation [Cp₂Ru-Hg-RuCp₂]²⁺ (380) which was characterized by spectroscopic and analytical techniques [370]. At the same time, the structures of two ruthenocene mercuric adducts appeared [371], and a Ru-Hg bond of 2.74 Å was found. Reactions of FeCp₂ with HgX₂ (X=Cl, Br) also gave various adducts [371]. IR and Raman
Scheme 6-2 A postulated electrophilic substitution reaction pathway involving initial attack of the electrophiles on the central metal atom.

Spectroscopic studies suggest the presence of Ru-Hg and Fe-Hg bonds [372]. A later electronic spectroscopic study also supported the presence of such metal-metal interactions in these mercuric halide adducts [373]. Weak Fe-E (E=P, Ge, or Si) interactions were also suggested for ferrocenophanes Fe(C₅H₄)₂PPh and Fe(C₅H₄)₂EPh₂ (E=Ge or Si) [374, 375] because of the somewhat short Fe-E distances.

Mossbauer spectroscopic studies provided strong evidences for Fe-Hg interactions in the ferrocene mercuric halide adducts mentioned above [376]. Similar studies on the adducts of [2]-ferrocenophane and 1,1,2,2-tetramethyl-[2]-ferrocenophane with SnCl₄ [377] and HgX₂ (X=Cl⁻, I⁻, CN⁻) [378] also gave evidence for Fe-Sn and Fe-Hg interactions. Such a study indicated the protonation of the iron atom by HAuCl₄ [379].

As previously mentioned in various sections of Chapters 4 and 5, Fe (ferrocene)-M bonding interactions are also known for Cu, Ag, Au, Ru, and particularly Pd and Pt. The gold complex [(C₅H₅)Fe(C₅H₄Au₂(PPh₃)₂)]⁺ (381)
shows a Fe-Au bond of 2.818 Å [321]. The two Au-C bonds are asymmetrical (2.13 and 2.27 Å respectively) and the two Cp rings are opened up considerably to a ring tilt angle of 16°. The copper and silver complexes (382a) and (382b) (R=CH2NMe2), derived from 2-lithio-1-(dimethylamino-methyl)ferrocene and copper or silver iodide, are isostructural [322, 323]. A Fe-Cu distance of 2.945(5) Å in (382a) and Fe-Ag distance of 3.091(3) Å in (382b) are thought to indicate some weak bonding interactions between these atoms. In both structures, the Cu-C and Ag-C bonds are symmetrical, and the Cp ring tilt angles are similar (6.5° for (382a) and 8.1° for (382b)) as well.

Seyferth et al. isolated an unexpected complex (Ph3P)PdFe(SC5H4)2 (383a) from the reaction of Pd(PPh3)4 with 1,2,3-trithia-[3]ferrocenophane [317]. An X-ray analysis revealed that a Fe-Pd bond distance of 2.878(1) Å was present and that the Cp rings had opened up considerably to a ring tilt angle of 19.6°. This Fe-Pd bonding interaction, though possibly weak, appears necessary to give Pd a favorable 16-electron configuration. The analogous Pt complex (383b) was also characterized by an X-ray diffraction study [320]. A Fe-Pt bond distance of 2.935(2) Å is present, and the Cp rings have a ring tilt angle of 21.0(7)°. Spectroscopic data have indicated such interactions of Fe or Ru in metallocenes to Pd or Pt in a series of complexes of the general formula M(C5H4X)2M'(PPh3) (M=Fe or Ru, X=S or Se, M’-Pd or Pt) [320]. These complexes were obtained by reacting M(C5H4XH)2 or M(C5H4X)2X with M'(PPh3)4. Spectroscopic studies have also indicated Fe-Pd interactions in ferrocenophane complexes such as (384) which was obtained from 1,5,9-trithia-[9]ferrocenophane and (MeCN)4Pd (BF4)2 [319]. The reactions of the same palladium precursor complex with Fe(C5H4SR)2 or Fe(C5H4PPh2)2 in the presence of PPh3 give complexes such
as (385) and (386) which are also shown to contain Fe-Pd interactions by spectroscopic techniques [318].

The ruthenium cluster complex (162) which contains a Fe-Ru bond of 3.097(3) Å has been described previously in Section 2.3.1. This was the only known cluster compound showing such an iron (ferrocene)-metal inter-action prior to the present study. The interaction must be weak in view of the very long Fe-Ru bond distance.

In this work, four types of Ru₃ and/or Os₃ cluster complexes containing strong Fe-Os or Fe-Ru interactions have been structurally characterized. The best characterized series of complexes have the formula
Os₃(CO)₈(H)₂[(C₅H₃PR₂)Fe(C₅H₄)] (R₂=Ph₂, (245); FcPh, (261) and (262); Et₂, (269); iPr₂, (278); nBuPh, (289) and (290); EtFc, (308) and (311)) and Os₃(CO)₈(H)₂[(C₅H₃AsFcPh)Fe(C₅H₄)] (318). Five structures ((245), (261), (269), (278), and (308)) determined by using X-ray crystallography reveal very short Fe-Os bond distances ranging from 2.826(1) to 2.858(1) Å. The hetero-annular metalated Cp rings have shorter C-Os bonds (from 2.065(8) to 2.08(1) Å) than those of the orthometalated Cp rings (from 2.148(6) to 2.181(7) Å). In all these five complexes, the Cp rings in the ferrocenyl moiety which is involved in Fe-Os bonding have very small ring tilt angles from 1.26 to 2.24°. In complexes (261) and (308), such angles (2.24 and 1.85° respectively) are even smaller than those in the dangling ferrocenyl moieties (5.93 and 2.84° respectively).

The second series of complexes have the formula Os₃(CO)₉(C₅H₄PR)Fe(C₅H₄)] (R=Fc, (263); nBu, (284); Ph, (300); Et, (309)). The structures of complexes (263) and (300) determined by using X-ray crystallography reveal relatively short Fe-Os distances of 2.994(2) and 2.974(1) Å respectively. The metalated Cp rings have C-Os bonds of 2.051(9) and 2.050(8) Å respectively. In this series of complexes, the Cp
rings in the ferrocenyl moiety which is involved in Fe-Os interaction have larger ring tilt angles of 8.83° and 9.04° respectively than in the first series. For comparison, the Cp rings in the dangling ferrocenyl moiety in (263) has a ring tilt angle of 3.20°. Another interesting feature in these complexes is the presence of two semi-bridging CO groups.

The third type of complexes containing very strong Fe-M interactions have the formula \( \text{M}_3(\text{CO})_7(\text{H})(\mu_3-\text{PiPr})[(\text{C}_5\text{H}_4\text{PiPr}_2)\text{Fe}(\text{C}_5\text{H}_4)] \) (M=Os, (329); M=Ru, (370)) and the structures of (329) as determined by an X-ray diffraction study reveals a Fe-Os bond of 2.813(1) Å, the shortest measured to date. The metalated Cp ring has a C-Os bond length of 2.047(8) Å, and the two Cp rings have a ring tilt angle of 11.58°, greater than those in the two series discussed above.

The last type of complex (350) has the formula Ru\(_3\)(CO)\(_8(\mu-\text{CO})(\text{H}){[(\text{C}_5\text{H}_3\text{PFcPh})\text{Fe}(\text{C}_5\text{H}_5)]]\) A structure determination reveals a Fe-Ru bond length of 2.9853(7) Å. The orthometalated carbon atom bridges one Ru-Ru edge symmetrically (2.252(4) and 2.262(4) Å). The two Cp rings in the ferrocenyl moiety which is involved in Fe-Ru interaction have a ring tilt angle of 21.25°, greater than those in the other three types of complexes discussed above (for comparison, the ring tilt angle for the Cp rings in the dangling ferrocenyl moiety is 5.93°). This unusually large ring tilt angle may be a result of the greater flexibility of a \( \text{C}_5\text{H}_5 \) ring as compared to a \( \text{C}_5\text{H}_4 \) or \( \text{C}_5\text{H}_3 \) ring. Overall, there seems to be no correlation between the Cp ring tilt angles and the Fe-M bond distances.

Two complexes of the formula Os\(_3(\text{CO})_9(\text{H}){[(\text{C}_5\text{H}_4\text{PR}_2)\text{Fe}(\text{C}_5\text{H}_4)]} \) (R\(_2\)=FcPh, (260); tBu\(_2\), (297)) and complex Os\(_3(\text{CO})_7(\text{AsFcC}_6\text{H}_4){[(\text{C}_5\text{H}_4\text{AsFcPh})\text{Fe}(\text{C}_5\text{H}_4)]} \) (321) probably also contain Fe-Os bonding interactions.
PART FOUR: SUMMARY AND FUTURE PROSPECTS
Chapter 7 Summary and Future Prospects

7.1 Summary of the Present Work

As discussed earlier in Chapter 1, a considerable number of transition metals are known to form benzyne complexes. The bonding modes of benzyne include $\eta^2$, $\eta^4$, and $\eta^6$, and the benzyne moiety may be associated with one to six metal atoms. However, prior to the present studies, essentially nothing was known about the existence of the organometallic aryne analogues, ferrocyne $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_3)$, and ferrodicyne $\text{Fe}(\text{C}_5\text{H}_3)_2$. In addition, few studies have been carried out in thermal reactions involving ligands containing ferrocenyl groups and metal cluster compounds, reactions which could conceivably lead to the trapping of the organometallic arynes on the cluster [119, 120].

In the present investigation, ferrocenyl-phosphines and -arsines have been studied as potential ligand system for stabilizing ferrocyne and ferrodicyne on osmium or ruthenium clusters and also as a source of ferrocenyl group to study their reaction with the same cluster species. Firstly, a large number of ferrocenyl ligands, especially ferrocenyl-phosphines, such as $\text{PFc}_2\text{Ph}$, $\text{PEtFc}_2$, $\text{PET}_2\text{Fc}$, $\text{PFc}^\text{iPr}_2$, $\text{AsFc}_2\text{Ph}$, $\text{Fc'PPh}$, $\text{Fc'P}^\text{iPr}_2\text{Fc}$, $\text{FcSPh}$, and $\text{SbFc}_3$ were prepared and characterized by spectroscopic and analytical techniques.

Secondly, the substitution reactions of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ with most of the phosphine ligands were studied in order to prepare and characterize complexes for further study. More than twenty substitution
complexes were prepared and characterized by spectroscopic and analytical techniques. Some examples are \( \text{Ru}_3(\text{CO})_{11}\text{(PFcPr}_2)\), \( \text{Ru}_3(\text{CO})_{10}\text{(PFc}_2\text{Ph})_2\), \( \text{Ru}_3(\text{CO})_9\text{(PFcPh}_2)\text{)_3}\), \( \text{Ru}_3(\text{CO})_{10}[\text{Fc'}(\text{PiPr}_2)_2]\text{(PFc}_2\text{Ph)}\), \( \text{Os}_3(\text{CO})_{11}\text{(PETFc}_2)\), \( \text{Os}_3(\text{CO})_{10}\text{(PFc}_2\text{Ph})_2\), \( \text{Os}_3(\text{CO})_{10}[\text{Fc'}(\text{PiPr}_2)_2]\), and \( \{\text{Os}_3(\text{CO})_{11}\text{(PFcPr}_2)\text{)_2}\). The discovery of the occurrence of symmetrical and unsymmetrical isomers of the disubstituted complexes \( \text{Ru}_3(\text{CO})_{10}\text{L}_2\) and \( \text{Os}_3(\text{CO})_{10}\text{L}_2\) was an unexpected result. This phenomenon has been rationalized in terms of the electronic effects of these ferrocenylyphosphines. The structure of one unsymmetrical isomer, \( \text{Os}_3(\text{CO})_{10}\text{(PFc}_2\text{Ph})_2\) (378) (Section 6.4.2), was determined by an X-ray crystallographic study: this is the only solid state structure of the type.

Thirdly, the pyrolytic reactions of the ligands and ruthenium or osmium clusters were studied by using two general methods. The first involves refluxing the appropriately substituted complexes such as \( \text{Os}_3(\text{CO})_{10}[\text{Fc'}(\text{PiPr}_2)_2]\) and \( \text{Ru}_3(\text{CO})_{11}\text{(PFc}_2\text{Ph)}\) in a suitable organic solvent. The second involves refluxing \( \text{Ru}_3(\text{CO})_{12}\) or \( \text{Os}_3(\text{CO})_{12}\) with the appropriate ligand under similar conditions. The latter method is particularly useful for ligands that are weakly coordinating or extremely bulky such as AsFc2Ph, FcSPh, and As(1-C10H7)3.

More than twenty substituted complexes were subjected to pyrolytic studies and about one hundred and twenty new complexes were prepared and characterized by using analytical and spectroscopic methods. In addition, more than ten pyrolytic reactions between \( \text{Ru}_3(\text{CO})_{12}\) or \( \text{Os}_3(\text{CO})_{12}\) and an appropriate ligand have been carried out and many more new products were isolated and characterized. In all, over thirty complexes have been characterized by X-ray crystallographic analyses and over
thirty more are waiting to be processed because they are believed to have novel and interesting structures. These complexes are summarized below.

Ferrocyne and Ferrodicyne Complexes

The series of ferrocyne complexes $\text{Os}_3(\text{CO})_9(\text{R})[\text{(C}_5\text{H}_3)\text{Fe(C}_5\text{H}_5)]$ (R = Fc, (252); nBu, (281)) (Sections 4.3 and 4.8 respectively) and $\text{Os}_3(\text{CO})_9(\text{AsPh})[\text{(C}_5\text{H}_3)\text{Fe(C}_5\text{H}_5)]$ (312) (Section 4.12), derived via metalation of one C-H and two C-P (As) bonds, were characterized. The structure as determined for (252) by using X-ray crystallography reveals an open Os$_3$ triangle capped on one face by a $\mu_3$ phosphinidene moiety and on the other by a symmetrically bound ferrocyne moiety. It is the first complex of an aryne to show such symmetrical bonding to an open Os$_3$ system. Also, the FeCp fragment on the aryne moiety points away from the middle Os center thus precluding any Fe-Os interaction. In contrast, the (benzyne)chromium tricarbonyl complex (130) described in Section 1.2.3.2, has a Cr-Ru bond.

Another series of ferrocyne complexes $\text{Os}_3(\text{CO})_8(\text{H})(\text{PR}_2)[\text{(C}_5\text{H}_3)\text{Fe(C}_5\text{H}_5)]$ (R$_2$ = FcPh, (257) and (258); iPr$_2$, (274); EtFc, (303) and (304)) (Sections 4.3, 4.7, and 4.11, respectively), derived via metalation of one C-H and one C-P bond, was also characterized by spectroscopic and analytical techniques. These complexes contain closed Os$_3$ triangles with a phosphido moiety and a hydride bridging two edges. The bonding mode of the ferrocyne and the orientation of the FeCp fragment on ferrocyne are unknown in the absence of a structure determination.

The remarkable ferrodicyne complex $\text{Os}_3(\text{CO})_8(\text{H})_2[\text{(C}_5\text{H}_2\text{PiPr}_2)\text{Fe(C}_5\text{H}_2\text{PiPr}_2)]$ (325) (Section 4.13) was also prepared and characterized. The structure, as determined by an X-ray diffraction study, contains two Os$_3$ units linked by the ferrodicyne moiety and in each unit the C$_5$H$_2$ ring is
bound to a closed Os₃ fragment. This molecule is also the first complex of an aryne to show unsymmetrical bonding to a closed Os₃ system.

The novel ruthenium ferrocyn complexes Ru₃(CO)₉(PFc)((C₅H₃)Fe(C₅H₅)) (352) and Ru₄(CO)₁₀(PFc)((C₅H₃)Fe(C₅H₅)) (348) (both in Section 5.4) were characterized by spectroscopic and analytical techniques.

Complexes with Fe-Os (Ru) Bonding Interactions

One unexpected feature of this study was the discovery of a number of classes of compounds in which the iron atom of a ferrocenyl moiety is involved in metal-metal bonding. Five types of complexes, a total of twenty compounds, containing such Fe-Os (Ru) bonding interactions have been characterized and four types by crystallographic studies.

The most remarkable series of complexes Os₃(CO)₈(H)₂(C₅H₃PR₂)Fe(C₅H₄)] (R₂=Ph₂, (245); FcPh, (261) and (262); Et₂, (269); iPr₂, (278); nBuPh, (289) and (290); EtFc, (308) and (311)) (Sections 4.2, 4.3, 4.5, 4.7, 4.9, and 4.11, respectively) and Os₃(CO)₈(H)₂[(C₅H₃AsFcPh)Fe(C₅H₄)] (318) (Section 4.12) are derived via the metalation of two ferrocenyl C-H bonds in a ferrocenyl group, one from each Cp ring, and the formation of a Fe-Os bond. This series of complexes was not formed in the ruthenium system or by the pyrolysis of Os₃(CO)₁₂ with PtBu₂Fc. Five of these complexes ((245), (261), (269), (278), and (308)) were structurally characterized and shown to contain Fe-Os bond distances ranging from 2.826(1) to 2.858(1) Å.

The second series of complexes is Os₃(CO)₉[(C₅H₄PR)Fe(C₅H₄)] (R-Fc, (263); nBu, (284); Ph, (300); Et, (309)) (Sections 4.3, 4.8, 4.10, and 4.11, respectively). The complex (300) was derived from the ferrocenophane Fe(C₅H₄)₂PPh containing two strained P-C bonds via a P-C bond cleavage and the formation of a Fe-Os bond. The other three complexes are derived
from ferrocenylphosphines via metalation of a ferrocenyl hetero-annular 
C-H bond, reductive elimination of a benzene or ethane molecule, and the 
formation of a Fe-Os bond. The complexes (263) and (300) were 
structurally characterized by using X-ray crystallography and shown to 
have Fe-Os bond distances of 2.994(2) and 2.974(1) Å respectively.

The third series of complexes M₃(CO)₇(H)(µ₃⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻‥

The fourth type of complex Ru₃(CO)₈(μ⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻‥

The fifth type of complex Os₃(CO)₉(H)(µ⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻‥

The last type of complex Os₃(CO)₉(H)(µ⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻‥

The last type of complex Os₃(CO)₉(H)(µ⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻┅
Other Aryne Complexes

The complex Ru$_5$(CO)$_{11}$(PFC)(PFcC$_6$H$_4$)(C$_6$H$_4$)$_{(342)}$ (Section 5.1), a new and unusual benzyne complex, was structurally characterized. It consists of a butterfly Ru$_5$ assembly with the outer face of the Ru$_4$ square capped by a $\mu_4$ phosphinidene moiety, the outer face of the Ru$_3$ triangle capped by a $\mu_3$ PFcC$_6$H$_4$ moiety, and the common face occupied by a benzyne moiety which is bound to the two unshared Ru atoms of the Ru$_4$ square via $\sigma$ bonds and to the unshared Ru atom of the Ru$_3$ triangle via all the six carbon atoms. This complex may be regarded as a derivative of the otherwise unknown (benzyne)ruthenium dicarbonyl moiety.

A remarkable series of naphthyne complexes M$_3$(CO)$_8$(H)$_2$[(1-C$_{10}$H$_7$)$_2$E(1-C$_{10}$H$_5$)] (M=Os, E=P, (334); Os, As, (336); Ru, P, (372); Ru, As, (374)) (Sections 4.14, 4.15, 5.10, and 5.11, respectively), derived via metalation of two adjacent C-H bonds of a naphthyl group and formation of a $\eta^2$ bond to the cluster, were characterized by spectroscopic and analytical techniques. The structure as determined for (336) by using X-ray crystallography consists of a closed M$_3$ triangle capped on one face by a symmetrically bound naphthyne moiety which is attached to the phosphorus or arsenic atom. These are the first known naphthyne complexes of Os$_3$ and Ru$_3$ clusters.

The dinuclear benzyne complex Os$_2$(CO)$_6$(H)(AsFc$_2$)(C$_6$H$_4$)$_{(317)}$ (Section 4.12), similar to (131) described in Section 1.2.4, was characterized. The Ru-Ru bond is bridged by a $\mu_2$ benzyne moiety, an arsinido moiety, and a hydride.

The tetranuclear benzyne complex Ru$_4$(CO)$_{11}$(PFc)(C$_6$H$_4$)$_{(339)}$ (Section 4.1), which contains a Ru$_4$ square capped on one face by a symmetrically bound $\mu_4$ benzyne moiety (six electron donor) and on the
other by a \( \mu_4 \) phosphinidene moiety, was previously known \[120\]. The pentanuclear benzyne complex \( \text{Ru}_5(\text{CO})_{13}(\text{PFc})(\text{C}_6\text{H}_4) \) (341) (Section 5.1) is analogous to complexes (107) described in Section 1.2.3.1. The structure consists of a butterfly \( \text{Ru}_5 \) assembly with the outer face of the \( \text{Ru}_4 \) square capped by a \( \mu_4 \) phosphinidene moiety, and the common face of the \( \text{Ru}_4 \) square and \( \text{Ru}_3 \) triangle capped by a symmetrically bound \( \mu_5 \) benzyne moiety which acts as an eight electron donor.

Three well known series of benzyne complexes were prepared and characterized. The structure of complexes (239), (315), and (344) from the three series were determined.

The first series of benzyne complexes includes \( \text{Os}_3(\text{CO})_9(\text{PFc})(\text{C}_6\text{H}_4) \) (239) (Section 4.1), \( \text{Os}_3(\text{CO})_9(\text{AsFc})(\text{C}_6\text{H}_4) \) (313) (Section 4.12), \( \text{Os}_3(\text{CO})_8(\text{PFcPh}_2)(\text{PFc})(\text{C}_6\text{H}_4) \) (250) (Section 4.2), and \( \text{Ru}_3(\text{CO})_9(\text{PFc})(\text{C}_6\text{H}_4) \) (337) (Section 5.1). The structure consists of an open \( \text{M}_3 \) triangle capped on one face by an unsymmetrically bound benzyne moiety and on the other by a \( \mu_3 \) phosphinidene or arsinidene moiety. The complex (337) is the first example of such a benzyne structure on a \( \text{Ru}_3 \) cluster.

The second series of benzyne complexes includes \( \text{Os}_3(\text{CO})_9(\text{H})(\text{AsFc}_2) \) (\( \text{C}_6\text{H}_4 \)) (315) (Section 4.12), \( \text{Os}_3(\text{CO})_8(\text{AsFc}_2\text{Ph})(\text{H})(\text{AsFc}_2)(\text{C}_6\text{H}_4) \) (320) (Section 4.12), and \( \text{Os}_3(\text{CO})_8(\text{PFcPh}_2)(\text{H})(\text{PFcPh})(\text{C}_6\text{H}_4) \) ((248) and (249)) (Section 4.2). The structure consists of an open \( \text{Os}_3 \) triangle capped on one face by a symmetrically bound benzyne moiety and bridged on the open edge by a phosphido or arsinido moiety.

The third series of benzyne complexes includes \( \text{Os}_3(\text{CO})_7(\text{PFcPh})_2 \) (\( \text{C}_6\text{H}_4 \)) ((246) and (247)) (Section 4.2), \( \text{Os}_3(\text{CO})_7(\text{PnBuFc})_2(\text{C}_6\text{H}_4) \) ((291) and (292)) (Section 4.8), \( \text{Ru}_3(\text{CO})_7(\text{PFcPh})_2(\text{C}_6\text{H}_4) \) ((338) and (344)) (Section 5.3), \( \text{Ru}_3(\text{CO})_7(\text{PFcPh})(\text{PPh}_2)(\text{C}_6\text{H}_4) \) ((359) and (360)) (Section 5.7), and \( \text{Ru}_3(\text{CO})_6 \)
(PFcPh$_2$)(PFcPh)$_2$(C$_6$H$_4$) ((346) and (347)) (Section 5.3). The structure consists of a closed M$_3$ triangle capped on one face by a symmetrically bound benzyne moiety and bridged on two edges by a phosphido moiety. Complexes (344) and (359) were previously known [119, 120], however their isomers (338) and (360) respectively were isolated and characterized in this study. Such isomers were obtained for all the complexes in this series, however the third possible isomer of Os$_3$(CO)$_7$(PFcPh)$_2$(C$_6$H$_4$), Os$_3$(CO)$_7$(P$_{n}$BuFc)$_2$(C$_6$H$_4$), and Ru$_3$(CO)$_7$(PFcPh)$_2$(C$_6$H$_4$) was not isolated.

Other Interesting Complexes

Complex Ru$_4$(CO)$_{11}$(PFc)(C$_5$H$_4$) (351) (Section 5.4), is the first cluster complex that contains a C$_5$H$_4$ moiety derived from a ferrocenyl group. This group transfer reaction is unprecedented under such mild conditions. The structure is best regarded as an open Ru$_3$ triangle capped on one face by a $\mu_3$ phosphinidene moiety and on the other by a $(C_5H_4)Ru(CO)_2$ moiety. This unique Ru atom bridges a Ru-Ru bond of the triangle, and the C$_5$H$_4$ moiety is $\sigma$ bonded to the third Ru atom of the triangle.

Complex Ru$_3$(CO)$_8$(SPh)(C$_6$H$_5$) (376) (Section 5.13) derived via S-C activation from SPh$_2$ without C-H activation, a rather uncommon happening for an unstrained ligand, was characterized by using X-ray crystallography. The structure consists of an open Ru$_3$ triangle with the SPh moiety bridging a closed edge, and the C$_6$H$_5$ moiety bridging the open edge via a $\sigma$ bond to the Ru atom which is also bridged by the SPh moiety and via a $\pi$ bond to the other. The SFc analogue (376) was also characterized (Section 5.12).

Complexes Os$_3$(CO)$_8$(H)$_2$((C$_5$H$_4$P$i$Pr$_2$)Fe(C$_5$H$_4$P$i$PrCH$_2$MeCH$_2$CO)) ((330) and (331)) (Section 4.13), derived via $\beta$ C-H activation of an i-propyl group.
followed by a CO insertion into the Os-C bond, were characterized by spectroscopic and analytical techniques. The structure of (330) as determined by using X-ray crystallography reveals a closed Os$_3$ triangle bridged on one edge by a di(tertiary)phosphine, a hydride, and a bridging acyl moiety. A dinuclear ruthenium complex Ru$_2$(CO)$_7$(PFC$_6$H$_4$CO) (340) (Section 5.1), which contains a $\eta^1$ acyl moiety resulting from the insertion of a CO group into a Ru-C (aryl) bond, was also characterized.

Complex Os$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$PiPr)$_2$Fe(C$_5$H$_3$PiPr)] (326) (Section 4.13), derived from Os$_3$(CO)$_{10}$[Fe(Pr$_2$)$_2$] via metalation of a $\beta$ C-H bond of an i-propyl group, loss of a propene molecule, and metalation of a Cp ring, was structurally characterized. Two isomeric complexes (322) and (324) were also characterized (Section 4.13).

Complex Os$_3$(CO)$_9$(H)$_2$[(C$_5$H$_4$PiPr)$_2$Fe(C$_5$H$_3$PiPr)$_2$] (323) (Section 4.13), derived via metalation of a $\beta$ C-H bond of an i-propyl group and loss of a propene molecule, was characterized by using X-ray crystallography. The hydride, di(tertiary)phosphine, and the phosphido moiety bridge the same Os-Os edge.

Complex Os$_3$(CO)$_9$(H)$_2$[(C$_5$H$_4$PiBuCMe$_2$CH$_2$)Fe(C$_5$H$_4$)] (295) (Section 4.9), derived via metalation of a $\beta$ C-H bond of a t-butyl group and metalation of a ferrocenyl hetero-annular C-H bond, was characterized by spectroscopic and analytical techniques.

Complex Ru$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$PCHMeCH$_2$)Fe(C$_5$H$_4$PiPr)$_2$] (369) (Section 5.9) is derived via metalation of two $\beta$ C-H bonds of two i-propyl groups on the same phosphorus atom and reductive elimination of a propene molecule. Complex Ru$_3$(CO)$_8$(H)$_2$[(C$_5$H$_4$P)Fe(C$_5$H$_4$PiPr)$_2$] (368) (Section 5.9), derived via a further reductive elimination of a propene molecule in (369),
was characterized by an X-ray crystallographic analysis. The structure consists of a closed Ru₃ triangle capped by a phosphinidene moiety.

One series of complexes Os₃(CO)₉(H)(PR₂C₆H₄) (R₂=FcPh, (242); Fc₂, (256); nBuFc, (287) and (288)) (Sections 4.1, 4.4, and 4.8, respectively), Os₃(CO)₈(PFcPh₂)(H)(PFcPhC₆H₄) (251) (Section 4.2), and Ru₃(CO)₈(H) [(C₅H₄P₁BuPh)Fe(C₅H₄P₁BuC₆H₄)] (365) (Section 5.8) were characterized. The structure was determined for (242), (251), and (365), and it is similar to (231), (224), and (221), respectively described in Section 2.3. The metalated C₆H₄ ring has a η² bonding interaction with the cluster.

The other series of complexes Os₃(CO)₁₀(H)(PR₂C₆H₄) (R₂=FcPh, (243); Fc₂, (259)) (Sections 4.1 and 4.3 respectively), Os₃(CO)₉(PFc₂Ph)(H)(PFc₂C₆H₄) (266) (Section 4.4), and Ru₃(CO)₉(H)[(C₅H₄P₁BuPh)Fe(C₅H₄P₁BuC₆H₄)] (366) (Section 5.8) containing an orthometalated phenyl moiety were also characterized. These differ from the above series in that the metalated C₆H₄ moiety does not interact with the cluster as in (225) described in Section 2.3.2.

The series of complexes Os₃(CO)₁₀(H)[(C₅H₄PR₂)Fe(C₅H₄)] (R₂=Ph₂, (244); FcPh, (264) and (265); iPr₂, (280)) (Sections 4.1, 4.4, and 4.7, respectively) containing a hetero-annular metalated ferrocenyl moiety were characterized.

The series of complexes Os₃(CO)₁₀(H)₂[(C₅H₄PR₂)Fe(C₅H₃)] (R₂=FcPh, (253) and (254); iPr₂, (275); EtFc, (306) and (307)) (Sections 4.3, 4.7, and 4.11, respectively) and Os₃(CO)₉(PEt₂Fc)(H)₂[(C₅H₄PEt₂)Fe(C₅H₃)] (273) (Section 4.6), derived via ferrocenyl hetero-annular double metalation, were characterized by spectroscopic and analytical techniques.

The series of complexes Os₃(CO)₉(H)[(C₅H₃PR₂)Fe(C₅H₅)] (R₂=Et₂, (270); iPr₂, (279); nBuPh, (282) and (283); tBu₂, (298); EtFc, (301) and
(302)) (Sections 4.5, 4.6, 4.8, 4.9, and 4.11, respectively), derived via orthometalation of a ferrocenyl group and formation of a $\eta^2$ bond of the C$_5$H$_3$ moiety with the cluster, were characterized.

The series of complexes Os$_3$(CO)$_9$($\mu$-CO)[(C$_5$H$_3$PiPr)Fe(C$_5$H$_5$)] (R=Fc, (255); iPr, (277); nBu, (285); tBu, (299)) (Sections 4.3, 4.7, 4.8, and 4.9, respectively), derived via orthometalation of a ferrocenyl group and reductive elimination of a benzene or propane or 2-methylpropane molecule, were characterized by spectroscopic and analytical techniques. Complex Os$_3$(CO)$_9$(H)$_2$[(C$_5$H$_3$PiPr)Fe(C$_5$H$_5$)] (276) (Section 4.7) is closely related.

Complexes Ru$_3$(CO)$_8$(H)[](C$_5$H$_3$PiBuPh)Fe(C$_5$H$_4$PiBuPh)] ((363) and (364)) (Section 5.8), derived via metalation of a ferrocenyl C-H bond, are analogous to complex (162) described in Section 2.3.1.

Complexes Os$_3$(CO)$_9$(H)$_2$(EtFcPCMe) (267) (Section 4.5), Os$_3$(CO)$_8$(PEt$_2$Fc)(H)$_2$(EtFcPCMe) ((271) and (272)) (Section 4.6), and Os$_3$(CO)$_8$(PnBuFcPh)(H)$_2$(FcPhPCnPr) ((293) and (294)) (Section 4.8), derived via double $\alpha$ metalation of one Et or nBu group, were characterized. These are analogous to (227) and (228) described in Section 2.3.2.

Pyrolysis Reaction Sequences

Detailed reaction sequences were proposed for the pyrolyses of complexes such as Ru$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$] (Section 5.9), Os$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$] (Section 4.13), Os$_3$(CO)$_{11}$(PFc$_2$Ph) (Section 4.3), Os$_3$(CO)$_{11}$(PEt$_2$Fc) (Section 4.5), and Os$_3$(CO)$_{11}$(PFc$i$Pr$_2$) (Section 4.7). The reactivity differences between similar complexes such as Ru$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$] and Os$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$], Os$_3$(CO)$_{11}$(PFc$_2$Ph) and Os$_3$(CO)$_{11}$(PFc$_2$Ph), Os$_3$(CO)$_{11}$(PFc$i$Pr$_2$) and Os$_3$(CO)$_{10}$[Fc'(PiPr$_2$)$_2$], Os$_3$(CO)$_{11}$(PEt$_2$Fc) and Os$_3$(CO)$_{11}$(PFc$i$Pr$_2$) were
discussed in terms of various factors such as electronic, steric, and statistical effects.

i-Propyl groups were found to undergo facile β C-H activation and subsequent P-C activation reactions on Os₃ clusters, ethyl (and n-butyl) groups undergo α C-H activation, and all these alkyl groups are very resistant to direct reductive elimination. Ferrocenyl groups readily undergo metalation on both Cp rings, Fe-Os bond formation, and sometimes P-Fc cleavage, and the ease of C-H activation is comparable to that of phenyl groups. The P-Ph cleavage reaction, however, is much more facile than P-Fc cleavage. The reactivities of ferrocenyl groups vary with the donor atom, with the nature of the group (monodentate, bidentate, ferrocenophane), and with the other groups attached to the donor atom(s).

In reactions involving Ru₃ clusters the trinuclear core is often absent in the products, and dinuclear, tetranuclear, pentanuclear species result. i-Propyl groups were also found to undergo β C-H activation with subsequent P-C cleavage. However i-propyl groups on monodentate ligands such as PFciPr₂ and Et groups seem to be very resistant to both C-H activation and P-C cleavage. Ferrocenyl groups undergo orthometalation, Fe-Ru bond formation, and P-Fc cleavage, but not hetero-annular metalation.

An important implication of this work is that phosphines are rather labile on these cluster complexes presumably because of the presence of a metal triangular face [299]. Phenyl, ferrocenyl, alkyl groups all undergo intramolecular C-H and often C-P(As) oxidative addition reactions. This imposes some limitations on the use of these phosphine ligands to prepare cluster derivatives of known structures, for example, as catalytic precursors.
7.2 Suggestions for Future Work

The study described in this thesis has opened up a vast field in which work can be undertaken in the future. Selected aspects will be discussed in the order of presentation in the thesis.

Relating to ferrocenyl ligands, Wright [354] has demonstrated the great promise of Fe(η⁵-C₅H₄SnBu₃)₂ as a precursor to monodentate ligands, to various mixed bidentate ligands, and to various chiral ligands with various combinations of chiralities. This new methodology should be fully explored in order to prepare the monodentate ligands used in this work: considerable improvement in the yields is to be expected. Other monodentate ligands such as PFc₃, AsFc₃, and PFc₂Me should be more easily available for subsequent substitution and pyrolysis studies, and for use in other areas of organometallic chemistry. Chiral monodentate ferrocenylphosphines such as PnBuFcPh, PFcMePh may be of interest for study in asymmetric synthesis and catalysis. Pyrolysis reaction studies involving such optically pure ligands should provide mechanistic information because of the chirality built into the products. Bidentate ligands of the type (C₅H₄PR₂)Fe(C₅H₄PR₂), (C₅H₄PR₂)Fe(C₅H₄AsR₂), and (C₅H₄PR₂)Fe(C₅H₄SR') are also interesting for use in a systematic study of various bond cleavage reactions. The design of novel chiral ferrocenyl ligands particularly of bidentate ligands with same or different donor atoms is also of interest.

Relating to the substitution complexes, the isomerism phenomena observed for the disubstituted complexes should be studied in greater detail in order to have a better understanding of the factors governing the formation and distribution of these isomers. A detailed mechanistic study
on the substitution reactions should be performed. Potential advantages to carry out such a study are that the reactions may readily be monitored by IR, UV-vis, and/or $^{31}$P NMR spectroscopic methods, and that ferrocenylphosphines with various steric and electronic effects are readily available. Such a study should include thermal reactions, various catalyzed reactions especially those with BPK and PPN$^+$Cl$^-$ as catalysts, and room temperature reactions. Some of the reactions may be studied with complexes such as $\text{M}_3(\text{CO})_{11}\text{L}$, $\text{M}_3(\text{CO})_{10}\text{L}_2$, and $\text{M}_3(\text{CO})_{10}(\text{L-L})$. It is also interesting to study these substitution reactions using mixed ligands such as the reaction of $\text{Ru}_3(\text{CO})_{11}$(PFcPh$_2$) with PEtFc$_2$. Mixed metal clusters such as FeOs$_2$(CO)$_{12}$ and Ru$_2$Os(CO)$_{12}$ provide even more interesting systems for such studies. Room temperature reactions of the symmetrical and unsymmetrical isomers of the same formula $\text{M}_3(\text{CO})_{10}\text{L}_2$ respectively with a third ligand may provide insights on the mechanism of the third substitution reaction. For isomerism and $^{31}$P NMR in particular variable temperature NMR studies, mixed ligand complexes such as $\text{M}_3(\text{CO})_9$(L-L')L$, $\text{M}_3(\text{CO})_9$LL'L$, $\text{M}_3(\text{CO})_{10}$LL', and mixed metal complexes are particularly suitable. A study of the reactions of $\text{Ru}_3(\text{CO})_{12}$ and Os$_3$(CO)$_{12}$ with ferricenium ligands such as [PFc$_2$PPr$_2$]$^+$ and [Fc'PPh$_2$)$_2$]$^+$ is also of special interest.

Other spectroscopic techniques that may be studied systematically include UV-vis and Mossbauer spectroscopy, cyclic voltammetry (the ligands deserve this study too), and in particular IR spectroscopy which is sadly missing in this work. These studies will provide a better understanding of the spectroscopic, electronic, and molecular properties of these complexes.
A particularly interesting study by using $^{13}$C NMR spectroscopy to investigate the dynamic processes of the CO groups in these cluster complexes may be undertaken when more samples and more sensitive spectrometers become available. This presumably is the best method to study the motion of the CO groups either in the solid state or in solution. A wide range of structure types of these complexes are available, thus variable temperature $^{13}$C NMR studies should provide deeper insights to the behaviour of CO groups in different structures.

Relating to the pyrolysis reactions, much remains to be done. First of all, complexes that are not well, poorly, or not at all characterized should be characterized to the best degree possible. X-ray crystal structure determinations should be performed wherever possible for new types of complexes. As more complexes from a reaction are identified, detailed and more credible reaction pathways can be elucidated. For simpler systems (those which afford a few products, e.g. $\text{Os}_3(\text{CO})_{11}(\text{PEt}_2\text{Fc})$, $\text{Os}_3(\text{CO})_{12}+\text{Fc}^+\text{PPh}$), it may be possible to perform mechanistic studies. For complex systems (those which afford many products, e.g. $\text{Os}_3(\text{CO})_{12}+\text{PEtFc}_2$ or $\text{PnBuFcPh}$), such a study may not be possible, however pyrolysis of individual products under identical conditions should be studied to confirm or establish the reaction pathways.

Techniques such as UV-vis and Mossbauer spectroscopy (especially for compounds containing Fe-Ru and Fe-Os bonding interactions), cyclic voltammetry, and especially IR spectroscopy may be studied to obtain information on the spectroscopic, electronic, and molecular properties of these complexes. Since the number of complexes available to a certain structure type is much more limited than in simple substitution complexes, a systematic $^{31}$P and $^1$H NMR (especially hydrides) study is not possible.
However, a $^{13}$C NMR study of the CO groups in these complexes will be particularly interesting and useful.

Theoretical calculations may be performed on the ferrocyne and ferrodicyne complexes ((252) and (325)), and on the complexes containing Fe-M bonding interactions. Such studies should provide a molecular basis for understanding the bonding interactions in these complexes and should offer guidelines for stabilizing further reactive fragments.

For those products that are obtained in moderate to good yields, their chemistry should be explored in the future. For example, reactions of benzyne complexes such as (239) and (315), ferrocyne complex (252), complexes (300) and (269) containing Fe-Os bonds with various reagents such as CO, PR$_3$, acetylene may be studied. Those complexes containing weaker Fe-M bonds are particularly interesting for such studies in relation to catalysis. The Fe-M bond may be reversibly formed and ruptured thus allowing a coordination site to be readily accessible. In such studies, some novel reactivities may be discovered and interesting products obtained.

Pyrolyses of the following ligands with M$_3$(CO)$_{12}$ are of special interest for future work: SFc$_2$, PFc$_3$, and AsFc$_3$ (for preparing other ferrocyne complexes especially on Ru$_3$ clusters), Fc'(SPh)$_2$ (for C-H and S-C bond cleavage reactions), P(CH$_2$Ph)$_3$ and P(OPh)$_3$ (for preparing complexes similar to the naphthyne complexes (336) described earlier in Section 4.15), PR$_2$Ph (R=alkyl) with Ru$_3$(CO)$_{12}$ (for preparing ruthenium analogues of the osmium benzyne complexes (119) described in Section 1.2.3.2), P(C$_6$F$_5$)$_3$ and P(C$_6$F$_5$)$_2$Ph (for C-F bond activation and preparing unusual benzyne complexes), Fc'(PPh$_2$)(PMe$_2$) (for testing the first step of all the reaction sequences proposed, that is the movement of a phosphine to an axial position).
Pyrolytic studies of mixed metal systems provide special interest due to various bonding possibilities.

Some other interesting reactions that may be studied in the future have been suggested in various sections of Chapters 4 and 5. Deserving special attention are the reactions of various [1]-ferrocenophanes such as Fe'AsPh, Fe'PPh(-S) with Ru3(CO)12 and Os3(CO)12.

Another related study that could give interesting results involves the reactions of lithioferrocenes with metal cluster carbonyls. The reactions of aryl- and alkyl-lithium compounds with metal cluster carbonyl compounds have been little studied. The reaction of PhLi with Ru3(CO)12 affords complexes such as Ru3(CO)9(H)[C6H5C(C6H4)] (387) [380] whose structure is similar to that of (242) described in Section 4.1. The reactions of (C5H4Li)Fe(C5H5), (C5H4Li)2Fe, (C5H4Li)Fe(C5H4PR2) [354], and (C5H4Li)Fe(C5H4SnBU3) [354] (which can be further lithiated) should be very interesting.

Finally, heating a complex such as H3Os3(CO)9(µ3-CFc) may lead to a ferrocyne complex such as (388) which can be regarded as a ferrocyne complex derived from methylferrocene. This is based on a reversible interconversion of the benzylidyne and methylbenzyne complexes [381].
7.3 Approaches to Mononuclear Ferrocyne Complexes

In principle, most of the methods used to prepare mononuclear benzyne complexes described in Chapter 1 can be applied to the preparation of analogous derivatives of ferrocyne and ferrodicyne. However, only a number of methods are practical for various reasons such as the lack of a good synthetic route to 1,2-diiodoferroocene. The most promising ones are as follows.

(1) Heating metallocene complexes of group 4 metals such as Cp₂ZrFc₂, Cp₂TiFc₂, and Cp₂Zr(Fc)(Me) under appropriate conditions in the presence of PMe₃, an approach used to prepare the reactive benzyne complex (70) described in Section 1.2.2.1 [87], should lead to ferrocyne complexes. A more elegant variation of this sequence is shown in Scheme 7-1 in which the "PMe₃" stabilizing donor is built into the ligand.

(2) Heating pentamethylcyclopentadienyl complexes of group 5 metals such as Cp*Nb(Fc)Me₃ and Cp₂*TaFc₂, an approach used to prepare the benzyne complexes (78), (79), and (81) described in Section 1.2.2.1 [95-97], should lead to ferrocyne complexes.

(3) Reactions of mono-lithiated ferrocenes with pentahalides of group 5 and 6 metals such as NbCl₅ and WCl₅, a reaction that leads to the

Scheme 7-1 A hypothetical route to a ferrocyne complex.

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benzyne complexes (88) and (89) described in Section 1.2.2.1 [98-103], should lead to ferrocyne and bis(ferrocyne) complexes.

(4) Heating tetrakis(trimethylphosphine) ruthenium complexes such as \((\text{PMe}_3)_4\text{Ru(Me)(Fc)}\) and \((\text{PMe}_3)_4\text{RuFc}_2\), an approach used to prepare the benzyne complex (98) described in Section 1.2.2.2 [111], should lead to ferrocyne complexes.

The preparation of all the above precursors requires a convenient and high yield route to mono-lithiated ferrocenes. This has become readily accessible starting from \(\text{Fc}^+(\text{SnBu}_3)_2\) [354], and great success in these unexplored territories may be anticipated.

7.4 Other Topics of Interest

Some further variations on the theme of this work can be conceived:

(1) Pyrolysis of other interesting metal cluster systems

The pyrolysis reactions studied in this work may be extended to other metal cluster systems such as \(\text{Ru}_3(\text{CO})_{11}^-\) [382], \(\text{Co}_4(\text{CO})_{12}\), \(\text{Ru}_5\text{N}(\text{CO})_{14}^-\), and \(\text{Os}_5\text{C}(\text{CO})_{16}\) in which the structures, the metal atoms, the nuclearity, the ancillary ligands, and the charge of the clusters can be altered.

(2) Phosphines of other organometallic moieties

The ferrocenyl moieties on the phosphine ligands studied in this work as a source of ferrocyne could be replaced by various other organometallic moieties. For example, Cullen et al. [121, 144, 145] have had considerable success with phosphines containing \((\text{C}_6\text{H}_5)\text{Cr(CO)}_3\) moieties as
a source of (benzyne)chromium tricarbonyl (Section 1.2.3.2). Two classes of organometallic groups are of special interest for this type of study.

The first class consists of various types of sandwich compounds such as (C₅H₅)₂Cr, (C₅H₅)₂Co, (C₆H₆)₂Cr, (C₅H₅)Co(C₄H₄), (C₆H₆)Mn(C₅H₅), (C₇H₇)Ti(C₅H₅) in which the metal atoms, the electronic states of the metals, and the aromatic rings can be changed. Some phosphines containing these moieties such as (C₆H₅PPh₂)₂Cr [383] and (C₆H₅PMe₂)Cr(C₆H₆) [384] are known. Otherwise the preparation of unknown phosphines of this sort may be a major challenge to carrying out such a study.

The second class consists of half sandwich compounds such as (C₅H₅)Mn(CO)₃, (C₄H₄)Fe(CO)₃, (C₆H₆)Ru(dppm), and (C₅H₅)Ni(NO) in which the metal atoms, the aromatic rings, and the ancillary ligands attached to the metal may be changed. Novel reactions, structures, and bondings can be expected in the future from reactions involving phosphine or arsine derivatives of these species.

In particular such pyrolysis studies may lead to complexes containing novel aryne moieties such as (C₅H₃)Mn(CO)₃ (389), (C₄H₂)Fe(CO)₃ (390), (C₆H₄)Cr(C₆H₆) (391), and (C₆H₄)₂Cr (392) which may or may not require metal-metal interaction for stabilization. The interactions of the aryne metal atoms with those on the clusters may be rather general.

![Structures](389) (390) (391) (392)
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