‘It is like a finger, pointing away to the moon. 

Don’t concentrate on the finger, or you will miss all the heavenly glory.....’

Bruce Lee
The Synthesis, Co-ordination Chemistry and Catalytic Applications of Phosphine Ligands Containing Long-Chain Perfluoro-Alkyl Groups

Thesis submitted for the degree of
Doctor of Philosophy
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by

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Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between October 1995 and August 1998. The work has not been submitted, and is not presently being submitted, for any other degree at this or any other university.

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Abstract

A review is presented of the use of catalytic liquid-liquid biphase systems containing a perfluorinated phase, commonly referred to as ‘fluorous biphase systems’ or F.B.S. catalysis.

The phosphines PPh₃₋ₓ(C₆H₄-x-C₆F₁₃)ₓ, PPh₃₋ₓ(C₆H₄-p-C₆F₁₃)ₓ and PPh₃₋ₓ(C₆H₄-m-C₆F₁₃)ₓ, where x = 1, 2 and 3, have been synthesised and fully characterised by ¹H, ¹⁹F and ³¹P NMR spectroscopy, mass spectroscopy and elemental analysis, with a view to assessing their potential for use in F.B.S. catalysis. The crystal structures of O=P(C₆H₄-m-C₆F₁₃)₃ and Cl-P(C₆H₄-o-C₆F₁₃)₂ are also reported. The synthetic route to P(C₆H₄C₆F₁₃)₃ represents an improvement on the literature preparation.

These phosphines have been reacted with a variety of transition metals to form complexes of the type cis- and trans-[MCl₂L₂] (M = Pt, Pd), trans-[MCl(CO)L₂] (M = Rh, Ir), [RhCp*Cl₂L] and [RhClL₃]. These complexes have all been isolated and fully characterised, except for the complexes [RhClL₃], which have not been isolated, but whose solution chemistry is described. The crystal structures of the complexes cis-[PtCl₂(PPh₂C₂H₄C₆F₁₃)₂] and trans-[RhCl(CO)(P{C₂H₄C₆F₁₃}₃)₂] are also reported.

All of the complexes described above have been extensively investigated using a variety of analytical techniques including ³¹P, ¹⁹F and ¹H NMR spectroscopy, mass spectroscopy and IR spectroscopy. The results from an EXAFS spectroscopic study on some of these complexes is included as an appendix to this work.

The electronic and steric influence of the perfluorinated chains on the reactivity and behaviour of both the free phosphines and the metal complexes has been evaluated from the nature of the products isolated, from a comparison of their spectroscopic and structural data with those for related metal-phosphine complexes and, for the complexes trans-[IrCl(CO)L₂], from a kinetic study on the rate of O₂ addition.

Preliminary catalytic hydrogenation and hydroformylation studies have been carried out using the complexes [RhClL₃] and [RhH(CO)L₃] respectively, where L = phosphine. These catalytic species were generated in situ and the study involved the use of F.B.S. catalysis. The effect of the variation of the phosphine type, the solvents and the reaction conditions, has been examined in terms of reaction rate, product selectivity and product/catalyst separation. The potential of F.B.S. catalysis using phosphine ligands has been assessed.
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Abbreviations

δ  Chemical shift
Δ  Heat
ν  Stretching frequency
δE  Energy difference
5S-PYCA  2-Pyrrolidone-5(S)-carboxylate
AA  Atomic absorption
acac  2,4-Pentanedione
Ad  Adamantyl
AIBN  Azo-isobutyronitrile
Ar  Aryl fragment
atm  Atmosphere
bipy  2,2'-Bipyridine
bp  Boiling point
Bu  Butyl
cod  1,5-Cyclooctadiene
COSY  Correlated spectroscopy
Cp*  Pentamethylcyclopentadienyl
Cyclam  1,4,7,11-Tetraazacyclotetradecane
d  Doublet
dd  Doublet of doublets
DMF  N,N-Dimethyl formamide
DMSO  Dimethysulphoxide
dt  Doublet of triplets
E  Energy
EA.  Elemental analysis
ee.  Enantiomeric excess
equiv  Molar equivalent
Et  Ethyl
EXAFS  Extended X-ray adsorption fine structure
F.B.S.  Fluorous biphasic system
FC-72  Commercially available (3M) fluorocarbon liquid consisting mostly of isomers of C₆F₁₄ (bp 56 °C)

Fig.  Figure
GC  Gas chromatography
HOMO  Highest occupied molecular orbital
hr  Hour
Hz  Hertz
iPr  iso-Propanol
IR  Infra red
J  Coupling constant
k  Rate constant
LUMO  Lowest unoccupied molecular orbital
Me  Methyl
MO  Molecular orbital
mp  Melting point
NMR  Nuclear magnetic resonance
PFMC  Perfluoromethylcyclohexane
Ph  Phenyl
PP1  Perfluorohexane
PP3  Perfluoro-1,3-dimethylcyclohexane
ppm  Parts per million
Pr  Propyl
r.d.s.  Rate determining step
R  Undefined molecular fragment
Rf  Undefined fluorinated molecular fragment
RT.  Room Temperature
t  Triplet
t₁/₂  Reaction half-life
TACN  1,4,7-Triazacyclononane
tert  Tertiary
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<td>Tol</td>
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Chapter 1

Introduction

1.1 Catalysis: An Overview

Catalysis is a term frequently used by chemists to describe any process in which a chemical reaction is made to go faster via the addition of some ‘agent’ (or catalyst) to the reaction mixture. Although many thousands of catalytic substances are used in both research and industrial chemistry, all of them work basically in the same way; by bringing the two reagents together such that their alignment and their energies are optimal for a reaction to occur. In any chemical reaction, there is a threshold energy level which must be reached in order for the reaction to take place. This energy, the ‘activation energy’, is required in order to overcome the electronic and steric repulsion which occurs when the two (or more) reactants are brought together. It is often the case that, although the energy of the product(s) is less than that of the reactants (ie. the reaction is thermodynamically favourable), the activation energy is large enough to prevent the reaction from occurring to any useful extent. The role of the catalyst is essentially to provide an alternative, energetically favourable pathway by which the reagents can ‘come together’ to form the product. It is important to note that a catalyst cannot alter the thermodynamic profile of a given reaction. That is to say, if the reaction will not occur for thermodynamic reasons, then the addition of a catalyst will not make the reaction work. The catalyst will, however, reduce the activation energy required for a reaction to occur, and so, if a given reaction is extremely slow due to the presence of a large activation energy, then the addition of a catalyst will speed it up, often increasing the rate dramatically. The catalyst works by combining with the reagents to form reactive, short-lived intermediates in which the reagent fragments are ideally positioned, both spacially and energetically, to react with each other and give the desired product(s). The catalyst, meanwhile, returns to its original
state and experiences no net change over the course of the reaction. Today, the majority of bulk chemical processes use catalysts and research into novel catalytic methods continues to be driven by the desire for economic, social and environmental progress. Over the last 170 or so years this area of chemistry has developed from poorly understood laboratory observations\(^{(1)(2)}\) to the world-wide multi-billion pound industry which we see today.

The first recorded examples of catalysis\(^{(3)}\) were concerned with reactions of gases at metal surfaces, such as the reaction of ammonia over an iron oxide catalyst to give oxides of nitrogen, and these reactions would today be classed as heterogeneously catalysed processes. Homogeneous catalysis is relatively modern, probably the first example of which was the hydroformylation of olefins using a soluble cobalt carbonyl catalyst, performed by O.Roelen in 1938.\(^{(4)}\)

Heterogeneous catalysis, often using metals or metal oxides, is generally preferred for use in industrial processes. This is due in large part to the inherent stability and robustness of these ionic, macro-molecular catalysts, and also to the facile separation of reaction products from catalyst which this type of process allows.\(^{(5)}\) Homogeneous catalysis is more favoured when high selectivity is the major consideration and, hence, is used extensively in pharmaceutical and fine chemical synthesis. It is apparent then, that both techniques have inherent advantages\(^{(7)(7)}\) and the successful chemist will recognise this and select a catalyst accordingly.

Over recent years, however, chemists have been looking increasingly towards catalytic systems which can utilise the key advantages of both heterogeneous and homogeneous catalysis, and the work presented in this thesis is concerned with one such technique. The concept is essentially based on a two phase system which, upon heating, becomes monophasic, and is popularly referred to as 'fluorous biphase system', or F.B.S. catalysis.

1.2 Heterogeneous or Homogeneous Catalysis?

It is useful when considering catalysis to look at the fundamental characteristics of homogeneous and heterogeneous catalysis in order to fully appreciate the
advantages and drawbacks offered by each. A homogeneous reaction is a process where the reactants and catalyst(s) are present in a single phase. In the majority of cases this means a solution, i.e. a liquid phase. It may be that during the course of the reaction, materials precipitate or crystallise out of solution, but the actual chemical reaction of one species with another to form a product (or an intermediate) occurs in a solution in which both reagents and catalyst are dissolved. The hydroformylation of olefins using transition metal catalysts is an example of a

Scheme 1.1  Mechanism of olefin hydroformylation using [RhH(CO)(PPh3)3]

![Diagram of the mechanism of olefin hydroformylation using [RhH(CO)(PPh3)3]](image-url)
homogeneous reaction which is carried out extensively, both in small scale laboratory preparations\(^{(74)}\) and also on an industrial scale\(^{(6)}\) (see Scheme 1.1). The reaction takes place via a series of intermediate steps\(^{(76)}\), all of which involve either bond formation or dissociation at the catalytic metal centre. The metal atom is usually present in solution and is surrounded by ligands which stabilise this atom and ‘hold’ it in solution whilst the reaction takes place. The reagents in this particular example are \(\text{H}_2\) gas, \(\text{CO}\) gas and an olefin (liquid or gaseous). At the moment of reaction all of the reagents are in solution and so there is no crossing of phase boundaries. Since all of the components involved in the reaction are present in a single phase (usually in solution), monitoring the reaction is straightforward. NMR or IR spectroscopy, for example, can be used to follow one particular species as the reaction progresses\(^{(75)}\) and so, in many cases, the mechanism can be elucidated. This in turn means that the modification of catalysts, reagents and conditions can be tailored to fit the known mechanism, and improvements in rate, selectivity and yield can be achieved in a logical and predictable manner. This approach to catalyst design has led to the development of catalysts which give excellent selectivity to one product and so are ideal for processes which use expensive starting materials and for the synthesis of high quality pharmaceuticals where purity is essential.

Phosphine ligands play a major role in homogeneous catalysis. The ability of phosphines to both donate electron density from a \(\sigma\)-orbital and simultaneously accept electron density into a \(\pi\)-orbital (see Section 3.1), means that these ligands are extremely versatile and can stabilise metal centres in a variety of different oxidation states.\(^{(79,80)}\) The electronic properties of a phosphine can be modified by changing the groups attached to the phosphorus\(^{(81,82)}\) and this means that they can be synthesised to specifically match the electronic requirements of a particular reaction. Asymmetry can be incorporated into phosphines via the addition of chiral groups\(^{(25)}\) and multidentate, chelating phosphines can be used to introduce more stability to a metal complex, or to alter its steric profile.\(^{(83,84)}\) The solubility of metal complexes can also be tailored to a certain degree, again, by changing the groups attached to the phosphorus,\(^{(51,34,25)}\) and the combination of these factors make phosphines an ideal choice of ligand for use in many homogeneous catalytic processes.
It follows from the above explanation that heterogeneous catalysis may be defined by one or more of the reagents being in a different phase to that of the catalyst at the moment of reaction. An example is the Haber process where $\text{H}_2$ gas and $\text{N}_2$ gas react over a mixed metal oxide catalyst to form $\text{NH}_3$. At the moment of reaction, the gaseous species are adsorbed on to the surface of a solid catalyst, where the reaction takes place, and the $\text{NH}_3$ product then desorbs and returns to the gas phase. This type of reaction is much more difficult to follow than a reaction occurring in solution for a number of reasons. Firstly, it is practically impossible to trace the ‘path’ of one of the reactants through the course of the reaction since analytical techniques used to monitor reactants in the gas phase are not applicable when those reactants adsorb onto the solid surface of the catalyst. Secondly, the characterisation of surface species is inherently more difficult than that of solution species since reaction only takes place at the surface of the solid and so only a monolayer of molecules can be investigated. Using radiation to look at this surface is problematic, as a solid support will often adsorb radiation energy to a greater degree than a solution and so detection is difficult. Finally, there is no ‘averaging’ of species as tends to occur in solution, so there may be many different surface species adsorbing gaseous molecules in many different ways, hence, it is difficult to interpret data after it has been collected. For these reasons, the study and design of heterogeneous catalysts is often approached in a less rigorous manner than that of homogeneous (solution) catalysts and, as a consequence, heterogeneous catalysts are usually much less selective than their homogeneous counterparts. For the production of bulk chemicals, however, this lack of selectivity is more than compensated for by the economic advantages of using heterogeneous catalysis. Many of these large scale processes use metal oxide catalysts (e.g. $\text{Fe}_3\text{O}_4$, $\text{CaO}$, $\text{MgO}$, $\text{Al}_2\text{O}_3$ etc.) which are cheap and which have robust, ionic structures. Also, this type of catalyst is almost always solid, whereas the reactants and products are generally liquid or gaseous, and so, separation of products from catalyst can easily be achieved. These factors hold obvious appeal where significant tonnages are required and, for these reasons, heterogeneous catalysts tend to be used in large-scale industrial processes.
1.3 New Approaches to Catalysis

Many chemists in recent years have attempted to design processes which can draw upon the key advantages of homogeneous and heterogeneous catalysis. The appeal of a system which could offer the selectivity of a homogeneous, solution process and the ease of separation of products from catalyst found in heterogeneous processes, is obvious. A number of such processes have been developed, including polymer supported catalysts, aqueous/organic biphasic catalysis and fluorous biphasic catalysis. These processes are discussed, in turn, below.

1.3.1 Polymer Supported Catalysts

Many industrial catalysts are, strictly speaking, supported catalysts. Often the support medium is a zeolite or a similar porous inorganic material such as silicon oxide or aluminium oxide. The majority of catalysts of this type contain active sites which are poorly characterised and reactions proceed via mechanisms which are not fully understood, and so, these processes still retain the inherent characteristics of traditional heterogeneous catalysis described earlier.\(^{(12)}\)

In the case of polymer supported catalysts, however, the active site is often a fully characterised metal complex whose solution chemistry is well known, and which has been attached to a structurally characterised polymer via specific covalent or ionic bonds. The polymer support can be used in solution and the chemistry occurring at the catalytic sites is basically homogeneous, solution chemistry, and so, all the benefits of the classical homogeneous catalyst still apply.\(^{(11)}\) It is not a requirement that the polymer itself is soluble in the reaction media, since, as long as the ligands immediately surrounding the metal centre are soluble, the metal is essentially ‘bathed’ by solvent and reactants and so homogeneous chemistry can still occur at the active sites. Separation of products from catalyst is simple, as the insoluble polymer and, hence the attached catalyst, can be removed from the reaction mixture by filtration. When the
polymer is soluble, addition of a non-solvent or a change of temperature may allow precipitation of the polymer, which can subsequently be separated by filtration.

Bergbreiter et al. used Rh(II) metal centres which were attached to polyethylene via carboxylic acid groups to perform the cyclopropanation of olefins (8) (see Scheme 1.2). These reactions were performed in toluene at 100 °C. Under these conditions the polymer support is soluble. Upon cooling to 25 °C, however, the polymer precipitated out of solution and was recovered by filtration.

The potential for enantioselectivity using this type of pseudo-homogeneous catalysis was exploited when Bergbreiter subsequently used a similar catalyst

Scheme 1.2  Cyclopropanation of olefins using a polythene-supported Rh(II) catalyst

![Scheme 1.2 Cyclopropanation of olefins using a polythene-supported Rh(II) catalyst](image)

Scheme 1.3  Asymmetric intramolecular cyclopropanation of 3-methyl,2-buten,1-yl diazoacetate using a polythene-supported rhodium catalyst

![Scheme 1.3 Asymmetric intramolecular cyclopropanation of 3-methyl,2-buten,1-yl diazoacetate using a polythene-supported rhodium catalyst](image)

5S-PYCA = 2-pyrrolidone-5(S)-carboxylate
PE = Polyethylene
containing chiral ancillary ligands to perform the highly stereo-selective intramolecular cyclopropanation of 3-methyl,2-buten,1-yl diazoacetate (98% ee) (see Scheme 1.3). Again, the polymer was removed by cooling followed by filtration.

Gilbertson et al.\textsuperscript{(10)} used rhodium centres bound via peptide chains to polystyrene beads to catalyse the hydrogenation of a prochiral enamide in 100% yield (see Scheme 1.4). In this case, the polystyrene beads were not soluble in the reaction medium and were separated from the products by filtration.

Scheme 1.4 Hydrogenation of a prochiral enamide using a polystyrene-supported rhodium catalyst

These experiments clearly demonstrate the application of heterogeneous separation to what are essentially homogeneous catalytic processes.

1.3.2 Organic-Aqueous Biphasic Catalysis

The use of liquid-liquid biphasic systems in which the catalyst is selectively soluble in one phase and the products/reagents selectively soluble in the other provides another method of applying facile separation to complex pseudo-homogeneous reactions. The most intensively researched system of this type, to-date, is the aqueous/organic biphase.

The potential for using selectively water-soluble, catalytic, transition-metal species in aqueous/organic biphasic systems was first realised in 1974 by researchers working for Rhone-Poulenc who quickly took out patents on the processes which they developed.\textsuperscript{(13a-d)} Further research revealed that the selectivity which could be achieved using rhodium-based, water-soluble catalysts for the hydroformylation of
olefins, meant that this process was efficient enough to be used on an industrial scale. The ease of separation of products from catalyst which this system allowed was a major factor in the decision to develop this process.\textsuperscript{(14)} The solubilisation of the metal was achieved using trisulphonated triphenylphosphine (TPPTS) (see Fig. 1.5), and the process went on stream as a joint venture with Ruhrchemie AG in July 1984.\textsuperscript{(15)}

In a biphasic system of this type, the reaction cannot be truly homogeneous since, by definition, the catalyst is in a different phase to that of the reagents. It is thought that the reaction normally occurs either at the phase boundary or in the aqueous phase.\textsuperscript{(26)} However, the yields and regioselectivities achieved using biphasic systems\textsuperscript{14,15,16} suggest that the chemistry follows essentially the same route as that in the analogous homogeneous reactions. This means that the advantages of homogeneous catalysis can be exploited without the traditional separation problems.

The applications of aqueous/organic biphasic catalysis are now many and varied, and much research is currently being carried out in order to exploit the potential of this type of system.\textsuperscript{19,20} For example Okano \textit{et al} have used a heptane/water biphasic in the carbonyl allylation of aldehydes\textsuperscript{21} (see Scheme 1.6). These reactions proceed in good yield (up to 98\%) and the organic layer containing the products is easily separated from the aqueous layer containing the catalyst and tin compounds. Plasserand and Süss-Fink have used a dicationic, water-soluble,
Scheme 1.6 Biphasic carbonyl allylation of aldehydes using a water-soluble palladium phosphine catalyst

\[
\begin{array}{c}
\text{X} + \text{ArCHO} + \text{SnCl}_2 \\
\text{PdCl}_2\text{L}_2 \\
\text{H}_2\text{O/heptane}
\end{array}
\Rightarrow
\begin{array}{c}
\text{OH} \\
\text{Ar} \\
\text{R}
\end{array}
\]

\[X = \text{Cl, OH}\]

\[L = \text{Ph}_2\text{P}
\]

Scheme 1.6 Biphasic hydrogenation of benzene using a water-soluble, ruthenium cluster

\[R = \text{for example CH}_3, \text{C}_2\text{H}_4, \text{NO}_3\]
One of the great advantages of homogeneous catalysis is the enantiomeric selectivity which can be achieved using specifically designed complexes in solution.\(^{(24)}\) Herrmann et al. attempted to perform asymmetric hydroformylation using watersoluble catalysts in an aqueous/organic biphasic.\(^{(25)}\) A chiral auxiliary was prepared by the straightforward sulphonation of the well-known diphosphine, NAPHOS (see Fig. 1.8), which, upon incorporation of six NaSO\(_3\) groups at various points around the aromatic frame, was rendered water soluble. The catalyst was prepared \textit{in situ} from \([\text{Rh(CO)}\(_2\)(acac)]\) and was used in a methanol-water/toluene biphasic. Styrene was hydroformylated with good regioselectivity (95\%) and an enantioselectivity of 18\% ee. This represents a significant drop in enantioselectivity compared to that observed in the analogous monophasic homogeneous system (34\% ee) and other attempts at asymmetric catalysis under aqueous biphasic conditions have shown a similar decrease in ee's.\(^{(26)/(28)}\) However, these results demonstrate that the potential to perform optically selective reactions in an aqueous/organic biphasic does exist.

Fig 1.8  \hspace{1cm} NAPHOS, an asymmetric diphosphine

One possible reason for this lowering of enantiomeric selectivity is the effect of solvation of water on intermediate species. If an enantiomeric excess is to be achieved, then there must be an energy difference between the two intermediates which give rise to the two enantiomeric products, that is to say, one must be energetically favoured. This energy difference may be influenced by solvation with certain solvents producing a larger energy gap than others. It has been postulated by Amrani and Sinou\(^{(27)}\) that
the solvation of water results in a small energy change, causing the two intermediate species to be close in energy. This, in turn, results in rather small enantiomeric excesses.

Catalysis under aqueous/organic biphasic conditions, in many circumstances, confers the advantages of heterogeneous separation to homogeneous reactions. However, the reduction in optical selectivity and the fact that hydrolytically sensitive reagents, such as phosphites, cannot be used in these systems, means that the usefulness of the technique is limited.

1.3.3 The Fluorous Biphase

A fluorous biphasic system consists of a highly fluorinated organic (or ‘fluorous’) solvent and another organic solvent (or mixture of solvents) which is immiscible with the fluorous solvent. The catalyst is modified to be preferentially soluble in the fluorous phase, while the products and reactants are preferentially soluble in the organic phase. Perfluorinated organic solvents are non-polar relative to protio, organic solvents, and have low intermolecular forces. They are generally very stable, non-toxic, and do not pose a threat to the environment, and so are an ideal choice for use in catalytic systems. Most common organic solvents are immiscible with perfluorinated solvents. This is probably due to the low level of electrostatic interaction between the non-polar, fluorous molecules and the more polarisable protio solvents. The exceptions to this rule are organic solvents of low polarity, such as alkanes and ethers, which are generally miscible with perfluorinated solvents at room temperature, and this is not unexpected on the principle of ‘like dissolves like’. A comparison of some physical properties of two perfluorinated solvents with their protio analogues is given in Table 1.1. The principle of immiscibility of phases which allows easy separation of products from reactants is essentially identical to that used in an aqueous/organic biphasic. The key advantage of the fluorous biphase is that, when the two phases are heated to a particular temperature, they can become fully miscible, and the reactants and catalyst can then react in a homogeneous environment. The temperature at which miscibility
Table 1.1  Some physical properties of two perfluorinated solvents and their perprotio analogues

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molecular Mass</th>
<th>Boiling Point (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoro-1,3-dimethylcyclohexane</td>
<td>400</td>
<td>101</td>
<td>1.828</td>
</tr>
<tr>
<td>1,3-Dimethylcyclohexane</td>
<td>112</td>
<td>120</td>
<td>0.784</td>
</tr>
<tr>
<td>1-Bromoperfluorooctane</td>
<td>499</td>
<td>142</td>
<td>1.930</td>
</tr>
<tr>
<td>Octane</td>
<td>114</td>
<td>125</td>
<td>0.703</td>
</tr>
</tbody>
</table>

occurs is highly dependent upon the solvents used, although for most common organic solvents, the system will become monophasic somewhere between 20 and 150 °C (at ambient pressure). When the catalysis is complete, the system can be cooled and the two phases separated, leaving the catalyst in the fluorous phase and the reaction products in the organic phase.

The first attempts at fluorous biphasic catalysis were made by Horváth and Rabáí in 1994. The hydroformylation of 1-decene was performed under moderately high temperature and pressure (10 bar, 100 °C) using a biphasic system consisting of toluene and perfluoromethylcyclohexane. GC analysis of the separated phases revealed reasonable conversion rates (84% in 24 hrs) and, more importantly, it was established that leaching of the catalyst into the organic layer did not appear to take place. The catalyst used in this instance was [HRh(CO){P(C₂H₄C₆F₁₃)₃}]₃, made in situ from [Rh(CO)₂(acac)] and 40 molar equivalents of P(C₂H₄C₆F₁₃)₃ (see Fig. 1.9). The three C₆F₁₃ tails enable this phosphine to ‘anchor’ the catalyst in the fluorous phase. The purpose of the C₂H₄ ‘spacer’ groups is to reduce the electron-withdrawing effect of the fluorous tails, such that there is still sufficient electron density on the phosphorus atom for it to co-ordinate effectively to potentially catalytic metal centres.

In 1995 Horváth and Rabáí went on to describe oxidation reactions performed in the fluorous biphasic, employing fluorous soluble cobalt and iron species. The yields and selectivities produced in these experiments were generally poor, however,
the work demonstrated the varied potential of the technique. It is, perhaps, surprising that these initial oxidation studies were not more successful as oxygen is highly soluble in perfluorinated solvents\(^{(32)}\)\(^{(47)}\) and several examples of fluorous biphasic oxidations have since appeared in the literature. For example Pozzi \textit{et al} attempted to synthesise oxidation catalysts based on manganese tetraarylporphyrin structures.\(^{(36)}\) Metallo-tetraarylporphyrins are well known catalysts for hydrocarbon oxidation reactions\(^{(37)}\) and the activity of this type of catalyst often increases if electron withdrawing groups are attached to the porphyrin ring.\(^{(44)}\) Pozzi successfully incorporated n-C\(_7\)F\(_{15}\) chains into the porphyrin ring (see Fig. 1.10) via amido bonds, and the catalytic activity of the manganese (III) species was increased. However, the complexes were not soluble in in fluorous solvents and so could not be used in fluorous biphasic catalysis. These porphyrins were subsequently modified by removing the amido bond and adding an extra CF\(_2\) linkage in its place\(^{(38)}\) (see Fig. 1.11). This family of porphyrin rings was synthesised by condensation of aromatic perfluoroaldehydes with pyrrole, according to Lindsey’s procedure,\(^{(39)}\) but the rings were still found to be insoluble in fluorous media. This work demonstrates the difficulty involved in adapting known catalytic/ligand systems to the fluorous biphasic.
Although three C₆F₁₃ chains are sufficient to solubilise phosphines and some related complexes, considerably more CF₂₅ units are required to make larger organic moieties soluble in perfluorinated solvents, and this can involve difficult and expensive synthetic procedures. Pozzi et al. succeeded in rendering the porphyrin group fluorous soluble by incorporating eight C₈F₁₇ ponytails on to the ring via condensation of a substituted pyrrole ring (see Fig. 1.12). On co-ordination of this modified porphyrin derivative to cobalt, a fluorous-soluble Co(II) complex was obtained. This complex (see Fig. 1.13) was found to be an efficient catalyst for the fluorous biphasic epoxidation of alkenes by molecular oxygen, using 2-methylpropanal as a reducing agent. Alkene epoxidations in up to 100% yield were achieved with, in some cases, greater than 95% selectivity. The reactions were carried out in a biphasic system consisting of MeCN and perfluorohexane. The system was not heated, and the two
phases remained immiscible throughout the reactions. The catalyst was recovered by
decantation of the two phases and was subsequently re-used without loss of activity or
selectivity.

Fig. 1.11 Modified porphyrin derivatives

As for Fig 1.10 except Ar =

[Chemical structure]

or

or

or

Fig. 1.12 Modified porphyrin derivative

As figure 1.10 but Ar =

[Chemical structure]
Pozzi then turned his attention towards the functionalisation of azamacrocycles in an effort to find a simpler route to fluorous soluble oxidation catalysts. The compound 1,4,8,11-Tetraazacyclotetradecane (cyclam) was modified by attaching (per)fluorooxyalkylenic chains to each of the four nitrogens in the ring (see Fig. 1.14). This fluorous-soluble ligand was then co-ordinated to copper and cobalt to give two catalytically active fluorous soluble-complexes. These catalysts were found to oxidise cyclooctane and cyclohexene with molecular oxygen under fluorous biphasic conditions (using the liquid substrate as the organic phase).

However, the selectivity was not particularly good, and both the alcohol and the ketone products were formed in all cases. The biphasic system was not heated during the reaction and the catalysts were successfully recovered and re-used, with a small drop in catalytic activity on the second run.
Fig. 1.14  Cyclam derivatised with perfluorinated chains

RfH2CO(H2C)2
N
N
N
(\text{CH}_2)_{20}OCH_2R_f

\text{Cyclam}
CH_3CN
Na_2CO_3
reflux 24hrs

R_fCH_2O(CH_2)_{20}TS

R_fH_2CO(H_2C)_{2}N
N
N
(\text{CH}_2)_{20}OCH_2R_f

R_f= \text{CF}_2(O\text{CF}(\text{CF}_3)\text{CF}_2)_q(\text{OCF}_2)_p\text{OCF}_3
\quad \text{Av. } q=3.38
\quad \text{Av. } p=0.11

Fish et al. also attempted to exploit the high solubility of oxygen in perfluorinated solvents by functionalising 1,4,7-triazacyclononane with C_3H_6C_8F_{17} chains\textsuperscript{(45)} in order to solubilise potential oxidation catalysts in fluorous solvents (see Fig. 1.15 Tris-n-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN)

R_f
\quad R_f
\quad \text{R}_f= \text{C}_8\text{F}_{17}
This macrocyclic ligand was then allowed to react with the fluoro-ponytailed carboxylate synthons \([\text{Mn}^{2+}(\text{O}_2\text{C}(\text{CH}_2)_2\text{C}_8\text{F}_{17})_2]\) and \([\text{Co}^{2+}(\text{O}_2\text{C}(\text{CH}_2)_2\text{C}_8\text{F}_{17})_2]\) in order to produce complexes of the type \([(\text{F}_{17}\text{C}_8\{\text{CH}_2\}_2\text{CO}_2)\text{M}^{2+}(\text{R}_7\text{TACN})]\) (M = Co or Mn). These catalysts were used to oxidise alkenes in the presence of tert-butyl hydroperoxide and molecular oxygen. This type of reaction is usually carried out in a monophasic homogeneous process and separation of the Mn catalyst has been found to be very difficult under these conditions.\(^{(46)}\) Fish used the alkene substrate as the organic phase and perfluoroheptane as the fluorous phase and the experiments were performed under 1 atm \(\text{O}_2\) gas. The yields of alcohols and ketones were respectable and separation of products from catalyst was achieved very simply with no discernible leaching of the catalyst into the organic layer.

The high solubility of oxygen in perfluorinated solvents was also exploited by Knochel \textit{et al.} in order to oxidise organoboranes and zinc organometallics\(^{(48)-(49)}\) under heterogeneous conditions. The liquid reactants were simply added to a fluorous solvent which was cooled to around 0 °C and saturated with oxygen, and the products were separated by decantation. No fluorous soluble catalyst was used, however, in many cases the reaction rates and selectivities were dramatically improved due to the relatively high oxygen content in solution.

Knochel went on to synthesise three transition metal catalysts which were soluble in the fluorous phase, two of which were oxidation catalysts,\(^{(50)}\) and the third, a palladium-based, carbon-carbon bond formation catalyst.\(^{(51)}\) The oxidation catalysts, one of which contained ruthenium and the other nickel, both used functionalised acac type ligands in order to render them fluorous soluble (see Fig. 1.16). The nickel catalyst was used to oxidise aldehydes to carboxylic acids and also to oxidise sulphides to sulphoxides and sulphones (see Scheme 1.17). The aldehyde oxidation tolerates several functional groups (ester, chloride, ether), works for aliphatic and aromatic aldehydes, and gives yields of 71-87%. The ruthenium-based catalyst was used to epoxidise alkenes and was found to give excellent selectivity, epoxidising only disubstituted double bonds (see Scheme 1.18). Both of these
Fluorous-soluble Ru and Ni complexes containing derivatised acac ligands

Scheme 1.17 Oxidation of sulphides to sulphoxides and sulphones using fluorous-soluble Ni catalyst

Scheme 1.18 Selective alkene epoxidation using fluorous soluble Ru catalyst

catalysts were used under homogeneous conditions. A biphasic mixture consisting of 5 cm$^3$ toluene and 5 cm$^3$ either C$_8$F$_{17}$Br or perfluorodecalin was heated to 50-60 °C, at which temperature the solvents become miscible. On completion of the reaction, the monophasic mixture was cooled to 0 °C and the two phases separated by decantation. Very little leaching of the catalytic species was found to occur, and re-use of the
fluorous layer, containing the catalyst, resulted in a 17% drop in yield (for the oxidation of p-chlorobenzaldehyde) after six runs.

Catalytic, fluorous-biphasic, carbon-carbon coupling reactions were performed by Knochel using a palladium (0) catalyst to couple aryl-zinc bromides with aryl-iodides (see Scheme 1.19). The metal was rendered soluble in the fluorous phase by the phosphine P(C₆H₄-p-C₆F₁₃)₃. Biaryl product yields were typically greater than 90%, however, when the previously reported phosphine P(C₂H₄C₆F₁₃)₃ was used, no catalytic activity was observed. This difference in reactivity is due, presumably, to the variation of electronic density on the phosphorus atoms resulting from the different 'spacer' groups used to insulate the phosphorus from the electron-withdrawing effect of the perfluorinated chain. The reactions

Scheme 1.19 Carbon-carbon coupling reactions using a fluorous-soluble Pd phosphine catalyst

\[
\begin{align*}
\text{Ar} & \quad \text{ZnBr} \quad P(C₆H₄-p-C₆F₁₃)₃ \quad 0.6\text{mol}\% \\
+ & \quad \text{[Pd(dba)₂]} \quad 0.15\text{mol}\% \\
\text{Ar}^2 & \quad \text{Tol/C₈F₁₇Br} \quad 60°C \quad 0.2-0.5\text{hrs}
\end{align*}
\]

were again performed under homogeneous conditions consisting of a monophasic mixture of toluene and 1-bromoperfluorooctane at 60 °C and, upon cooling, the catalyst was easily separated from the products. Re-use of the catalyst in the fluorous layer resulted in no significant change in yield. The successful application of the fluorous biphasic to this process is particularly interesting as most C-C coupling reactions of this type require relatively large quantities of a costly palladium catalyst (1-5 mol%) and removal of palladium from the reaction products.

The Stille reaction is an important transition metal catalysed cross-coupling reaction which is regularly used in organic synthesis. The reaction involves using a palladium catalyst to couple two organic moieties, one of which is bound to a trialkyl tin compound (see Scheme 1.20). The reaction is very useful as the tin reagents are reasonably air- and moisture-stable, can be easily synthesised and purified, and
Scheme 1.20 The Stille reaction

$$\begin{align*}
R^2 & \xrightarrow{[\text{Pd}]} R^2^1 \\
+ & \\
^1R & \xrightarrow{\text{Sn(alkyl)}_3} X \xrightarrow{\text{Sn(alkyl)}_3}
\end{align*}$$

tolerate a wide variety of functional groups. Problems are encountered, however, with separation of the products from the toxic tin compounds.

Curran has developed a fluorous soluble trialkyl tin species (see Fig. 1.21) which has been used in Stille reactions with some success.\(^{(56)}\) The reactions are carried out under homogeneous conditions using a DMF/C\(_6\)H\(_5\)CF\(_3\) mixture as the solvent. Upon completion of the reaction, water and FC-72 (a fluorocarbon liquid consisting mostly of isomers of C\(_6\)F\(_{14}\)) are added to form a three-phase mixture, and the fluorous-derivatised tin chloride can be recovered in very high yield (99%) from

Fig 1.21  Fluorous-soluble, trialkyl-tin reagent
Scheme 1.22  Reduction of adamantylbromide using a fluorous-soluble trialkyl-tin hydride

\[
\begin{align*}
\text{Ad-} & \quad \text{Br} \\
+ & \\
\text{(C}_6\text{F}_{13}\text{C}_2\text{H}_4)_3\text{SnH} & \quad \text{reflux} \\
\text{Ad-} & \quad \text{H}
\end{align*}
\]

Curran went on to use the corresponding trialkyl-tin hydride reagent (as Fig. 1.21 where \(R = H\)) under similar conditions to perform reductions\(^{58}\) (see Scheme 1.22). By rendering the tin reagents fluorous soluble, the separation problems are overcome and the facile recycling means that toxic tin compounds are not disposed of and potential environmental problems are avoided.

After Horváth's initial success with the hydroformylation of alkenes,\(^{34}\) he went on to look at rhodium-catalysed hydroboration under fluorous biphasic conditions.\(^{59}\) Hydroboration reactions can be catalysed by a variety of metal complexes,\(^{60}\) however, these catalytic species are often destroyed during the subsequent oxidation step to yield the alcohol products. Horváth used a fluorous-soluble Wilkinson's catalyst analogue, \([\text{RhCl}(\text{P}\{\text{C}_2\text{H}_4\text{F}_{13}\}_3)_3]\), in order to perform the hydroboration of several alkenes and alkynes (see Scheme 1.23). The liquid reactants were used as the organic phase and, upon completion of the reaction, were extracted into THF or benzene wherein the oxidation step \((\text{H}_2\text{O}_2/\text{NaOH})\) was performed. Using this technique, no decomposition of the catalyst was observed, and re-use of the fluorous layer containing the catalyst resulted in minimal loss of activity. Horváth found that particularly low catalyst concentrations \((0.01 \text{ mol%})\) could be used effectively in this reaction, however, it was also noted that the rates of reaction were slower than when the analogous complex \([\text{RhCl}(\text{PPh}_3)_3]\) was used under homogeneous, but otherwise identical, conditions.
In collaboration with Guillevic, Horváth went on to synthesise a fluorous soluble Vaska's complex analogue, again employing the phosphine $P(C_2H_4C_6F_{13})_3$. This was structurally characterised using single crystal X-ray crystallographic methods, and was found to be isostructural with the rhodium analogue $\text{trans-}[\text{RhCl(CO)}\{P(C_2H_4C_6F_{13})_3\}]_2$. Further analogous complexes were synthesised (see Fig. 1.24) in order that comparisons could be made between the physical and chemical properties of fluorous derivatised and underivatised metal complexes, and also to attempt to establish how the fluorous ponytails affect the behaviour of the complexes. As part of this study a comparison of carbonyl stretching

**Fig. 1.24** Vaska’s complex analogues containing derivatised and underivatised phophine ligands. See Table 1.2 for definition of M and L.
Table 1.2  carbonyl stretching frequencies of Vaska's complex analogues

<table>
<thead>
<tr>
<th>Complex</th>
<th>v(C=O) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L= P(C₂H₄C₆F₁₃)₃ M= Ir</td>
</tr>
<tr>
<td>2</td>
<td>L= PPh₃        M= Ir</td>
</tr>
<tr>
<td>3</td>
<td>L= P(C₂H₄C₆H₁₃)₃ M= Ir</td>
</tr>
<tr>
<td>4</td>
<td>L= P(C₂H₄C₆F₁₃)₃ M= Rh</td>
</tr>
</tbody>
</table>

frequencies was made (see Table 1.2), and this clearly shows that the 'spacer' does not entirely insulate the metal from the electron withdrawing effect of the perfluorinated chains. Relative rates of oxidative addition of CH₃I, H₂ and O₂ to the iridium complexes⁶³ were also examined (see Scheme 1.25). It was established that the reaction of CH₃I with trans-[IrCl(CO){P(C₂H₄C₆F₁₃)₃}₂] proceeded via a free radical pathway, as opposed to the SN₂-like mechanism observed for the reaction of trans-[IrCl(CO){PPPh₃}₂] with primary alkyl halides.⁶⁴ The rates of addition of H₂ and O₂ were slower for trans-[IrCl(CO){P(C₂H₄C₆F₁₃)₃}₂] than for the analogous complexes where L=PPh₃ or P(C₆H₁₇)₃, and this supports the suggestion that the electron density on the iridium atom is reduced due to the electron-withdrawing effect of the fluorous ponytails. Surprisingly, the addition of O₂ to trans-[IrCl(CO){P(C₂H₄C₆F₁₃)₃}₂] proceeded more quickly in THF than in CF₃C₆F₁₁ as solvent, despite the higher solubility of O₂ in the latter. It was postulated that this may be due to the non-polar nature of the CF₃C₆F₁₁ resulting in less stabilisation of the transition state for the oxidative addition relative to free O₂ and the trans-[IrCl(CO){P(C₂H₄C₆F₁₃)₃}₂] species.

Scheme 1.25  Oxidative addition of a molecule XY to Vaska's complex analogue

```
L      CO
 Ir      Cl  
         L
               X--Y

L      CO
 Ir      Cl  
         L
               OC
               Cl
```

25
Despite the interest in this area of chemistry, so far only one article has appeared in which the fluorous biphase has been applied to asymmetric catalysis. Pozzi et al. have developed chiral fluorous-soluble salen type ligands which have been used to perform asymmetric epoxidation of alkenes (see Scheme 1.26). These ligands were used in the synthesis of fluorous-soluble manganese complexes, the protio analogues of which are known to be asymmetric epoxidation catalysts.\(^{(67)}\) Under biphasic conditions at 20 °C, it was found that, with most alkenes, significant ee's were not produced. In the case of indene, however, an ee of 92% was achieved. Although the asymmetry of the ligand was not transferred as well as was hoped, the experiments showed that enantioselectivity can potentially be achieved in the fluorous biphase.

Scheme 1.26  Fluorous-soluble salen ligand containing perfluorinated chains

\[
\begin{align*}
R - R &= -(\text{CH}_2)_{4}^- \\
\text{or } R &= \text{Ph}
\end{align*}
\]

In an effort to expand the number of potential applications of the fluorous biphase, Bergbreiter et al. have synthesised a polymer support which is soluble in perfluorinated solvents and which contains reactive sites suitable for attaching metal atoms. Hughes et al. have developed cyclopentadienyl ligands with fluorinated ponytails attached to the ring and Vierling et al. have synthesised ferrocenes containing perfluoroalkylated side chains.\(^{(70)}\) Perfluoroalkylated reagents are also proving to be useful in other areas of chemistry and the recent review articles which examine the F.B.S. concept certainly suggest that the various applications
of the fluorous biphas e will play an important role in preparative and catalytic chemistry in the future.

1.4 Outline of Thesis

This thesis describes the synthesis of a number of phosphines containing perfluorinated chains, some of which are soluble in perfluorinated solvents. These phosphines were co-ordinated to a variety of metal centres, and the influence of the perfluorinated chains on the metal complex examined using various analytical techniques. Some catalytic reactions were performed in the fluorous biphas e, and the effect of using different solvent systems was investigated in terms of reaction rate, selectivity and potential for product catalyst separation.
References for Chapter 1

(b) Rhône-Poulenc Industrie (E.Kuntz), FR 2,349,562 (1976).
(c) Rhône-Poulenc (E.Kuntz), FR 2,338,253 (1976).


Chapter 2

Synthesis of Ligands

2.1 Synthesis of Alkyl Ligands

In order to examine the chemistry of fluorous biphase systems, it was first necessary to synthesise ligands which could be used to solubilise potentially catalytic complexes in perfluorinated solvents. It was decided that the most suitable ligands to look at were tertiary phosphine ligands containing long chain perfluoroalkyl chains. This choice was made on the grounds that phosphines are extremely versatile and can be used in a wide variety of catalytic processes, including hydrogenation, hydroformylation, decarbonylation, oligomerisation, oxidation, and alkene activation and are also suitable for modification into asymmetric ligands for use in chiral catalysis. In addition to this flexibility, phosphine ligands had already been shown to be useful fluorous biphase ligands by Horváth et al. who performed preliminary catalytic studies using the phosphines P(C$_2$H$_4$C$_6$F$_{13}$)$_3$ (3) and P(C$_2$H$_4$C$_8$F$_{17}$)$_3$ (3a). Phosphine (3) had been synthesised previously using PH$_3$ (see Scheme 2.1). This synthetic route is not ideal since PH$_3$ is highly toxic and notoriously difficult to handle and, also, the reaction yield is rather low (26%). It was decided to attempt to synthesise (3) via the corresponding Grignard reagent of the
perfluoroalkyl iodide starting material (see Scheme 2.2). This Grignard reagent could

Scheme 2.2 Synthesis of perfluorinated Grignard reagent IMgC\(_2\)H\(_4\)C\(_6\)F\(_{13}\)

then be used to perform nucleophilic attack on a suitable phosphorus(III) halide, thus
eliminating the need to handle PH\(_3\). Surprisingly, Horváth et al. used a similar
Grignard route to synthesise the related phosphine (3a),\(^{(10)}\) although no reference was
made to any attempt, successful or otherwise, to use this route to synthesise (3).

Precedent can be found in the literature for the formation of Grignard reagents
of the type R\(_f\)MgX where R\(_f\) is a perfluorinated alkyl group\(^{(12)(13)(14)}\) and, also, of the
type R\(_f\)CH\(_2\)CH\(_2\)MgX\(^{(15)}\) where an ethyl ‘spacer’ is included. It has been shown,
however, that highly fluorinated organo-magnesium reagents are susceptible to thermal
decomposition\(^{(16)}\) to give the corresponding olefin products (see Scheme 2.3), although
the introduction of the C\(_2\)H\(_4\) ‘spacer’ group significantly improves their stability.\(^{(17)}\)

Scheme 2.3 Thermal decomposition of perfluoro-Grignard reagents

Bearing in mind the limited amount of data available on fluorous soluble
ligands, it was decided that it would be useful to prepare the family of phosphines
PPh\(_x\)(C\(_2\)H\(_4\)C\(_6\)F\(_{13}\))\(_{3-x}\) where x = 0, 1 or 2. It seemed unlikely that all three phosphines
would be of practical use in fluorous biphasic catalysis, however, comparison of the
behaviour and properties of the ligands was thought likely to be a good source of
information about the influence of perfluorinated chains on the chemistry of F.B.S.
ligands.
2.1.1 Synthesis of \( \text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}) \) (1)

The synthesis of the Grignard reagent, \( \text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{MgI} \), was attempted via the dropwise addition of \( \text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{I} \) to an excess of Mg turnings using dry diethyl ether as the solvent. The glassware was scrupulously dried (24 hrs, 80 °C) and great care was taken to ensure that the reaction was performed anaerobically. However, after addition of \( \text{PPh}_2\text{Cl} \), none of the expected product could be detected and this continued to be the case when the ether was heated to reflux in an attempt to initiate the reaction. In order to overcome this lack of activity 1,2-dibromoethane was used as an entrainer, to clean and activate the magnesium. It is believed that this compound reacts with the magnesium to give 2-bromoethylmagnesiumbromide which rapidly eliminates magnesium (II) bromide, producing ethylene\(^\text{(18)}\) (see Scheme 2.4). The magnesium (II) bromide then goes on to react with the less active alkyl iodide.\(^\text{(19)}\) The attraction of using 1,2-dibromoethane as an entrainer, rather than another alkyl halide such as methyl iodide,\(^\text{(20)}\) is that a second, extraneous Grignard reagent is not formed, since the ethylene gas is inert to further reaction. This activation of the magnesium proved to be very effective and addition of two drops of 1,2-dibromoethane was enough to 'kickstart' the reaction, after which the heat produced by the exothermic process was sufficient to keep it progressing throughout the dropwise addition. When the Grignard formation was complete, chlorodiphenylphosphine was added directly into the reaction flask, however, this resulted in the formation of a yellowish, sticky substance which prevented the stirrer bead from turning and, hence, hampered further reaction progress. The insoluble nature of this by-product prevented characterisation,
although it is possible that it may have been a polymeric phosphorus species, the formation of which was catalysed by the excess of magnesium metal still present in the flask. Evidence for this postulation comes from the fact that, when the Grignard reagent was transferred to a second flask (via a cannular) before addition of the chlorodiphenylphosphine, the sticky by-product did not appear and the reaction proceeded smoothly (see Scheme 2.5). After working up, the phosphine was purified using column chromatography. Due to the suspected air sensitivity of the product, it was necessary to maintain an inert atmosphere throughout the purification process and this resulted in the procedure being difficult and time consuming. It was noted that most of the by-products tended to stick to the alumina and remain close to the top of the column, and so this procedure was later modified to entail passing the product through a separating funnel which was half filled with alumina. This flash chromatography was much simpler to perform but still removed the majority of the impurities. Finally, any remaining traces of perfluoroalkyliodide starting material

Scheme 2.5 Reaction of fluorinated Grignard reagent with chlorodiphenyl phosphine

\[
\text{ClPPh}_2 + \text{F}_{13}\text{C}_6\text{H}_4\text{C}_2\text{Mgl} \xrightarrow{\text{ether, RT, N}_2} \text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}) + \text{MgICl}
\]

Fig. 2.6 1H,1H,2H,2H-perfluoroctyl diphenyl phosphine (1)
were removed by heating to 60 °C under dynamic vacuum for 2 hrs. The product (1) (see Fig. 2.6) was isolated as a white solid. As was expected, this phosphine was not preferentially soluble in perfluorinated solvents.

**2.1.2 Synthesis of PPh(C_2H_4C_6F_{13})_2 (2)**

The synthesis of (2) was performed using the same route as for (1). The only modification to the procedure was that slightly less than the stoichiometric amount of dichlorophenyl phosphine was used, in an effort to ensure that no mono-substituted product was formed (see Scheme 2.7). The product was isolated as a white solid and solubility tests showed that this phosphine was also insoluble in perfluorinated solvents (see Fig. 2.8).

Scheme 2.7  Reaction of dichlorophenyl phosphine with an excess of fluoro-Grignard reagent

\[
\text{Cl}_2\text{PPh} + \text{XS}\text{F}_{13}\text{C}_6\text{H}_4\text{C}_2\text{Mgl} \rightarrow \text{PPh(C}_2\text{H}_4\text{C}_6\text{F}_{13})_2
\]

**2.1.3 Synthesis of P(C_2H_4C_6F_{13})_3 (3)**

Phosphine (3) was successfully synthesised using essentially the same procedure as used for (2) and this fairly simple preparation resulted in a 50% yield, considerably better than that reported for the previously reported route.\(^9\) The product (see Fig. 2.9) was isolated as a colourless oil which partially solidified after several days storage in a Schlenk flask under N\(_2\). The melting point of (3) was determined to be around 25 °C and this presented handling difficulties since, at room temperature, it
Fig. 2.8  Bis(1H,1H,2H,2H-perfluorooctyl) phenyl phosphine (2)

Fig. 2.9  Tris(1H,1H,2H,2H-perfluorooctyl) phosphine (3)
is a very oily solid. Cooling the Schlenk flask with cardice and, hence, solidifying the phosphine before removal proved to be the most convenient handling method. Phosphine (3) was found to be preferentially soluble in perfluorinated solvents.

2.1.4 Attempted Synthesis of PPh₂(C₂H₄C₈F₁₇) (4)

The synthesis of (4) was also attempted using the Grignard method detailed above. A similar route has been used by Horváth et al. to make the related compound P(C₂H₄C₈F₁₇)₃. However, despite repeated attempts, the synthesis was unsuccessful and no evidence for the formation of (4) could be found. It appeared that the Grignard reagent was decomposing before it could react with the chlorophosphine, possibly to give an olefinic compound, and this decomposition product then went on to dimerise in some way. The mass spectrum of the products from this reaction showed a large peak at 1088 mass units which was almost certainly due to some sort of dimeric product, since the starting material has a molecular mass of only 574 mass units. It is not clear, however, what the structure or the mechanism of decomposition actually is. Supporting evidence for the postulation that the Grignard reagent was decomposing comes from the fact that the ³¹P NMR spectrum of the reaction products showed a doublet at δₚ 16 ppm, with a coupling constant of 450 Hz. This is characteristic of ¹Jₚₚ coupling in PPh₂(O)H, and suggests that this compound was being formed during the hydrolysis work up (see Scheme 2.10) and the Grignard reagent was not reacting at all with the chlorodiphenyl phosphine.

Scheme 2.10 Hydrolysis of chlorodiphenyl phosphine

\[ \text{H}_2\text{O} + \text{PPh}_2\text{Cl} \rightarrow \text{Ph}_2\text{POH} \]
2.2 Synthesis of Para-Substituted Aryl Phosphines

The alkyl phosphines (1-3) provide a good basis on which to examine the influence of the C_6F_{13} groups upon the chemistry of this type of ligand. Nevertheless it was decided that the synthesis of further ligands of the general formula PPh_x(C_6H_4-p-C_6F_{13})_{3-x} (x=0,1 or 2) which incorporated aromatic 'spacer' groups, would be valuable in providing a comparison against which the alkyl phosphines (1-3) could be examined. It was hoped that both the increased size and the delocalised nature of the C_6H_4 unit would result in it being more effective at insulating the phosphorus from the electronic effects of the perfluorinated tails, than the C_2H_4 unit. It also seemed probable that aryl-substituted phosphines of this type would be of greater use in catalytic reactions than the alkyl phosphines, reflecting the trend shown by their protio analogues. The synthetic route of choice was, again, the nucleophilic attack of the aryl fragment on the relevent phosphorus halide (see Scheme 2.11). In this case, the organolithium reagent was used rather than the Grignard reagent, since it is well known that aryl Grignard reagents are often difficult to prepare.\(^{23}\)

Scheme 2.11 Nucleophilic attack of aromatic carbanion on chlorophosphine

![Diagram of nucleophilic attack of aromatic carbanion on chlorophosphine](image)

2.2.1 Synthesis of PPh_2(C_6H_4-p-C_6F_{13}) (5)

The first step in the synthesis was the coupling of the C_6F_{13} chain to the aryl ring. This was achieved via the one-pot, copper mediated coupling of perfluorohexyl iodide with 1-bromo-4-iodobenzene (see Scheme 2.12). This route to fluoroalkyl substituted aromatic compounds was first proposed by McLoughlin and Thrower\(^{24}\) and has since been investigated by Chen \textit{et al.}\(^{25\text{a}}\text{b}\) The resulting
bromoaryl species (see Fig. 2.13) was then allowed to react with n-butyllithium at -78 °C. Halogen metal exchange (see Scheme 2.14) produced the lithiated aryl fragment,

Scheme 2.12 Copper-mediated coupling of perfluoroalkyl iodide with aryl iodide

\[
\begin{align*}
(1) & \quad R_fI & \xrightarrow{\text{Cu, bipy, DMSO}} & \quad R_fCuL_3 + ICuL_3 \\
& \quad C_6H_{13}F & \text{80°C} & \\
(2) & \quad R_fCuL_3 & \xrightarrow{\text{Arl}} & \quad ArCuL_2 \\
& & & \quad ArR_f + ICuL_3 \\
\end{align*}
\]

Where L= solvent or bipy

Fig. 2.13 1-Bromo-4-perfluorohexyl benzene

![1-Bromo-4-perfluorohexyl benzene](image)

Scheme 2.14 Halogen-metal exchange in the reaction of BuLi with 1-bromo-4-perfluorohexyl benzene

\[
RLi + R'X \xrightarrow{} R'Li + RX
\]

and slow addition of chlorodiphenyl phosphine followed by a gradual warming to room temperature, resulted in the formation of (5) (see Fig. 2.15). Purification was achieved by anaerobic flash chromatography as with (1-3), followed by distillation in a Kugelröhr oven. The phosphine was isolated as a white solid and was found not to be preferentially soluble in perfluorinated solvents.
2.2.2 Synthesis of PPh(C₆H₄-p-C₆F₁₃)₂ (6)

The synthesis of (6) was performed using the same route as that used for (5). As with (2), slightly less than the stoichiometric amount of dichlorophenylphosphine was used in order to prevent formation of the mono-substituted product. The phosphine (see Fig. 2.16) was isolated as a white solid which was found not to be preferentially soluble in perfluorinated solvents.
2.2.3 Synthesis of $\text{P(C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_3$ (7)

The synthesis was carried out following the same general procedure as that used to make (6). It was found to be beneficial to allow the reaction mixture to warm up to around -50 °C after the addition of the n-butyllithium to the substituted arylbromide. This was to ensure that the halogen-metal exchange had occurred and that there was no n-butyllithium remaining in the reaction mixture. When this temperature increase was not allowed to happen, the products contained a significant amount of a second species, in which an n-butyl group had coupled with the phosphorus trichloride, as well as two substituted aryl groups (see Scheme 2.17). The product was isolated as a white solid (see Fig 2.18) and, as expected, was found to be preferentially soluble in perfluorinated solvents.

Scheme 2.17 Side reaction of butyl group with $\text{PCl(C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2$

\[
\text{BuLi} + R_1\text{C}_6\text{H}_4\text{Li} \xrightarrow{\text{PCl}_3\ -78^\circ\text{C}} \text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_2\text{(C}_4\text{H}_9)\]

Fig. 2.18 Tris(4-perfluorohexylphenyl) phosphine (7)
2.3 Synthesis of Meta-Substituted Aryl Phosphines

A series of phosphines of the type PPh₄(C₆H₄-m-C₆F₁₃)₃-x (x = 0, 1 or 2) was synthesised, following essentially the procedure given for (5-7). It was hoped that these phosphines would provide useful information about how the insulating ability of the C₆H₄ spacer varied when the position of substitution on the ring was changed and, also, allow the steric implications of substitution in the meta-position to be examined. The aryl starting material used was 1-bromo-3-iodobenzene, hence, the resulting phosphines were substituted with C₆F₁₃ chains in the meta- rather than the para-position (see Fig. 2.19).

Fig 2.19 3-Perfluorohexylphenyl diphenyl phosphine (8), Bis(3-perfluorohexylphenyl) phenyl phosphine (9) and Tris(3-perfluorohexyl-phenyl) phosphine (10)
Phosphines (8-10) were all isolated as white solids. Phosphine (10) is preferentially soluble in perfluorinated solvents.

### 2.3.1 Crystal Structure of $\text{O}=\text{P} (\text{C}_6\text{H}_4\text{m-C}_6\text{F}_{13})_3$

Crystals of the oxide of (10) were obtained by slow evaporation of a solution of (10) in chloroform and the structure was solved using X-Ray crystallographic methods (see Fig. 2.20).

Fig. 2.20  Crystal structure of (10)
Table 2.1 Selected bond lengths and angles for (10) and O=PPh₃

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å) or angle (°) in (10)</th>
<th>Length (Å) or angle (°) in O=PPh₃ (29)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)-O(1)</td>
<td>1.49(2)</td>
<td>1.46(1)</td>
</tr>
<tr>
<td>P(1)-C(13)</td>
<td>1.84(2)</td>
<td>1.77(1)</td>
</tr>
<tr>
<td>P(1)-C(25)</td>
<td>1.77(2)</td>
<td>1.77(1)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.84(2)</td>
<td>1.75(1)</td>
</tr>
<tr>
<td>C(25)-P(1)-C(13)</td>
<td>106.7(10)</td>
<td>107.2(7)</td>
</tr>
<tr>
<td>C(25)-P(1)-C(1)</td>
<td>106.0(10)</td>
<td>106.5(7)</td>
</tr>
<tr>
<td>C(13)-P(1)-C(1)</td>
<td>105.0(10)</td>
<td>107.6(6)</td>
</tr>
</tbody>
</table>

Fig. 2.21 Crystal packing diagram for (10)
The bond data in Table 2.1 shows that the P-O and P-C bonds in (10) are, within experimental error, similar in length to those found in triphenylphosphine oxide.\(^{(29)}\) This suggests that the electron density available for bonding on the phosphorus in (10) is not significantly affected by the perfluorinated chains. There is no significant change in the geometry of the groups around the phosphorus atom in (10) compared to that of triphenylphosphine. This implies that there is no significant steric repulsion between the chains on adjacent phenyl rings. The fluorines on the ends of the fluorinated tails of adjacent molecules are unusually close, and the tails appear to line up in order to accommodate these interactions. This results in the ‘tail to tail’ arrangement seen in the unit cell of (10) (see Fig. 2.21).

The synthesis of phosphines (1-3) and (5-10), as described above, has been published,\(^{(49)}\) along with the synthetic routes to several other phosphorus-based ligands containing perfluorinated chains.

### 2.4 Attempted Synthesis of P(C\(_6\)H\(_4\)-p-C\(_2\)H\(_4\)C\(_6\)F\(_{13}\))\(_3\) (11)

Phosphine (11) has been synthesised by Leitner \textit{et al.}\(^{(28)}\) for use as a ligand in catalytic systems which use super-critical CO\(_2\) as the solvent, since the non-polar nature of the fluorous chains results in the phosphine being highly soluble in this medium. Attempts were made to synthesise this ligand for use in fluorous biphasic systems, however, the preparation by Leitner \textit{et al.}\(^{(28)}\) was reported as a communication, with very little experimental detail and, despite repeated attempts, the synthesis was unsuccessful. The major stumbling block occurred during the preparation of the substituted aryl moiety, BrC\(_6\)H\(_4\)C\(_2\)H\(_4\)C\(_6\)F\(_3\). This was attempted using a copper-catalysed coupling reaction of the aryl-Grignard reagent with the perfluoroalkyliodide (see Scheme 2.22). Disappointingly, the reaction showed very poor selectivity and, although the \(^1\)H NMR of the product mixture revealed traces of the desired product, the major products resulted from unwanted side reactions.
Scheme 2.22 Mixture of products formed in the reaction of BrC₆H₄Br with IC₂H₄C₆F₁₃

2.5 Synthesis and Crystal Structure of PCl(C₆H₄-ο-C₆F₁₃)₂ (12)

In order to examine the effect of substitution in the ortho-position, the synthesis of P(C₆H₄-ο-C₆F₁₃)₃ was attempted. The aryl precursor, 1-ido-2-bromobenzene, was synthesised using the copper-mediated coupling reaction described earlier. The yield was lower than expected and this was thought to be due to the unfavourable steric interaction of the C₆F₁₃ group with the adjacent bromine (see Scheme 2.23). The substituted arylbromide was allowed to react with n-butyllithium, followed by phosphorus trichloride at low temperature (-60 °C) and then brought to room temperature over a period of several hours. After purification, the product was isolated as a whitish, thick, oily solid. Characterisation was attempted using ¹⁹F and ³¹P NMR, but both techniques gave unexpectedly complex spectra. The ³¹P NMR spectrum consisted of a highly complex eleven-line multiplet at δₚ 80 ppm (see Fig. 2.26), and the ¹⁹F NMR spectrum (see Fig. 2.27) showed a series of multiplets which were clearly quite different to the general pattern previously observed for the C₆F₁₃ moieties. The compound was fully characterised when crystals
Scheme 2.23  Reaction of 1-iodo,2-bromo benzene with perfluorohexyliodide

were grown by slow evaporation of a solution of (12) in acetone, and the structure was solved using X-Ray crystallographic methods (see Fig. 2.24).

Fig. 2.24  Crystal structure of (12)
Table 2.2 Selected bond lengths and angles for (12)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å) or angle (°) in (12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C (average)</td>
<td>1.85</td>
</tr>
<tr>
<td>P-Cl</td>
<td>2.09</td>
</tr>
<tr>
<td>C(1)-P-C(13)</td>
<td>102.3</td>
</tr>
<tr>
<td>C(1)-P-Cl</td>
<td>97.9</td>
</tr>
<tr>
<td>C(13)-P-Cl</td>
<td>100.2</td>
</tr>
</tbody>
</table>

Fig. 2.25 Crystal packing diagram for (12)

The data in Table 2.2 indicates that the geometry around the phosphorus atom is distorted tetrahedral, with one site occupied by a lone pair. The bond angles shown are of a comparable size to those found in PCl₃ (100°) and PPh₂H (100.8°) and this suggests that there is no significant steric repulsion resulting from the chains, despite the apparent crowding around the phosphorus. The close approach of the fluorine atoms on the ends of the chains, to those on adjacent chains, is similar to that observed
in (10) and appears to be a significant factor in the crystal packing of this type of compound (see Fig.2.25).

The vast majority of phosphorus(III) compounds of the type PCIR$_2$ are prepared using carefully controlled conditions,$^{30}$ since the P-Cl bond is generally reactive and, unless precautions are taken, the PCIR$_2$ product will react further to give PR$_3$R'. The conditions used during the synthesis of (12) would be expected to push the reaction through to the formation of PR$_3$, but, in this case one of the P-Cl bonds has remained intact. The probable reason for this P-Cl bond stability is the protection afforded by the perfluorinated chains which are orientated in such a way as to partially envelope the phosphorus, hence preventing further nucleophilic attack by a third, bulky, arylbromide fragment.

After examining the structure of (12), it was suggested that the unusual complexity of the $^{31}$P and $^{19}$F NMR spectra of this compound was due to through-space coupling between the fluorines on the chains and the phosphorus.$^{99}$ In an attempt to prove this, the $^{31}$P NMR spectrum was simulated using gNMR v4.0 (NMR simulation software package). Unfortunately, the extensive coupling proved to be too complex to simulate fully and the best attempt is shown in Fig 2.26 (bottom spectrum) along with the actual $^{31}$P NMR spectrum (top spectrum). The $^{19}$F NMR spectrum could not be simulated, partly due to its complexity and, also, because some impurity peaks are present. The actual $^{19}$F NMR spectrum for (12) is shown in Fig. 2.27 (see Fig. 2.28 for a 'typical' $^{19}$F NMR signal pattern for C$_6$F$_{13}$ chain). The simulated $^{31}$P NMR spectrum is based on a spin system in which the fluorines on the $\alpha$- and $\beta$-carbons in each of the two chains exhibit significant coupling to the phosphorus. It is thought that the fluorine atoms on the $\delta$- and $\varepsilon$-carbons (see Section 5.5.1 for definition of carbon atoms) also exhibit significant coupling to the phosphorus and this coupling is thought to be the cause of the fine splitting seen in the actual spectrum, but, unfortunately, the software used to perform the simulation could not accommodate this level of complexity. The simulation data suggests that the two fluorines on each of the two $\alpha$-carbons in the chain show different $^4J_{PF}$ coupling constants, although the two pairs of fluorine atoms on the two different chains are equivalent. Thus, F(7A) and F(7B) are inequivalent as are F(19A) and (F19B), but F(7A) and F(19A) are
equivalent, as are F(7B) and F(19B) (see Fig. 2.24). This pattern of equivalent pairs of fluorines is thought to continue along the chains.

This coupling pattern fits in with the crystal structure, where it would be expected that the two fluorines on each carbon would be different distances from the phosphorus and, hence, would exhibit different magnitudes of through-space coupling. The major feature to note in the $^{19}$F spectrum (see Fig. 2.27) is the complex splitting patterns which are present in the region -97 to -120 ppm. Typically, this region of the spectrum shows simple multiplet resonances for the fluorine atoms on the $\alpha$- and $\beta$-carbons of the $C_6F_{13}$ chain (see Fig 2.28). Clearly, the chemical shift and the multiplicity of these peaks has been significantly altered by the through-space P-F coupling described above.

Phosphine (12) was found to be insoluble in perfluorinated solvents, and consequently, is of no practical use in the fluorous biphase. However, it may be that
this unusual compound has other applications, possibly in the area of phosphenium\textsuperscript{(31)} chemistry.

Fig. 2.27 $^{19}$F NMR spectrum of PCl(C$_6$H$_4$-o-C$_6$F$_{13}$)$_2$ (12)

2.6 Characterisation of Phosphines

Phosphines (1-3) and (5-10) were characterised using a combination of $^{31}$P, $^1$H and $^{19}$F NMR spectroscopy, mass spectroscopy and elemental analysis. Phosphine (12) was characterised using $^{31}$P, $^1$H and $^{19}$F NMR spectroscopy and mass spectroscopy. All of the phosphines showed parent ions [M$^+$] in their mass spectra and several also exhibited peaks due to [M+O]$^+$. These oxidised species were found to be present in the mass spectra even when the NMR spectra showed no sign of phosphine oxide, and so, it is assumed that oxidation occurred during the sample loading procedure. The $^{31}$P NMR spectra gave a singlet in all cases (see Section 2.8), except for (12), where a complex multiplet was observed (see Section 2.5). The $^{19}$F NMR spectra exhibited an almost identical pattern of signals for phosphines (1-3) and (5-10) (see Fig. 2.28). The chemical shifts of the CF$_{2/3}$ units do not vary significantly from

53
phosphine to phosphine and, similarly, the $^2J_{hf}$ and $^2J_{ff}$ coupling constants are of almost identical magnitude in all cases. The CF$_2$H resonances have been assigned using $^{19}$F-$^{19}$F COSY experiments$^{(49)}$. Exceptionally, again, compound (12) gave a complex pattern of signals due, presumably, to through-space coupling of the fluorines with the phosphorus (see Section 2.5). The $^1$H NMR spectra are slightly more informative than the $^{19}$F NMR spectra for compounds of this type. In the case of phosphines (1-3), the C$_2$H$_4$ resonances are found as multiplets. Phosphines (5-10) generally show complex multiplets in the aryl region, the exception being the tri-substituted phosphine (7), in which the aryl protons give rise to a doublet (H's 3 and 5) and a virtual triplet (H's 2 and 6). For full characterisation data on these compounds, see Section 5.5.

Fig. 2.28 ‘Typical’ signal pattern in the $^{19}$F NMR spectrum of a compound containing a C$_6$F$_{13}$ chain. Peak integration is shown
2.7 Bonding in Phosphines

There is no one description of the bonding in phosphines which can satisfactorily explain all of the variations in bond lengths and angles which are observed experimentally. The direct valence approach\(^{(33)}\) and VSEPRT,\(^{(34)}\) can account for the simplest of observations, however, both models are unsatisfactory when applied to more complex examples. The most useful explanation is that based on the Walsh MO diagram\(^{(35),(36)}\) shown in Fig. 2.29. The difficulty in describing bonding in phosphines arises when considering why the PR\(_3\) unit is generally pyramidal, whereas the NR\(_3\) unit generally has a more planar geometry. Fig. 2.29 shows a comparison between the relative energies of the molecular orbitals in the planar case, involving p orbitals (on the left) and the pyramidal case, involving sp hybridised orbitals (on the right). Phosphorus has five electrons available for bonding, so, if it contributes one electron to each of three covalent bonds, then these three electron pairs, plus the remaining lone pair on the phosphorus atom, will occupy the four lowest energy molecular orbitals. As is evident in the diagram, the HOMO in the pyramidal case is lower in energy than that in the planar case. The difference in energy is denoted by \(E\). It has been shown that the amount of stabilisation, \(E\), of the HOMO in the pyramidal geometry, depends inversely on the energy gap, \(\Delta E\), between the HOMO and the LUMO in the planar geometry. This energy gap is, in turn, influenced by the nature of the central atom (size, electronegativity, etc) and by the nature of the R groups. The energy gap is generally smaller for phosphorus than for nitrogen, hence, the stabilisation, \(E\), is greater for phosphorus and, as a consequence, phosphines tend to be more pyramidal than amines. The major drawback of this theory is that the factors which affect the energy difference, \(\Delta E\), are many and varied and, in order to make any valid predictions about the geometry of particular phosphines, very complex orbital calculations must be carried out.\(^{(38)}\) The theory is useful, however, as a general tool for rationalising the observed geometry of phosphines and, also, for describing the complexity of the bonding and, hence, illustrating why simple trends are not observed when considering phosphine bond angles.
Steric factors also play a role in determining the geometry of phosphines. Steric repulsion between the groups bound to the phosphorus results in an increase in observed bond angle and this effect can be very significant in phosphines containing particularly bulky groups. The widest C-P-C angle observed for a phosphine to date is 109.7° in trimesitylphosphine.\(^{(40)}\)
2.8 Discussion of $^{31}$P NMR Data for Phosphines (1-3) and (5-10)

Table 2.3 shows the $^{31}$P NMR chemical shifts for the groups of phosphines (1-3) and (5-10) and also shows comparative data for several structurally related protio phosphines.

Table 2.3 Chemical shifts of (1-3),(5-10) and other, related phosphines

<table>
<thead>
<tr>
<th>R</th>
<th>$C_2H_4C_6F_{13}$</th>
<th>$C_2H_5$</th>
<th>$C_6H_4-p-C_6F_{13}$</th>
<th>$C_6H_4-m-C_6F_{13}$</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$R</td>
<td>-16.0</td>
<td>-12.0</td>
<td>-5.0</td>
<td>-4.8</td>
<td>-5.0</td>
</tr>
<tr>
<td>PPhR$_2$</td>
<td>-23.0</td>
<td>-16.0</td>
<td>-5.4</td>
<td>-5.0</td>
<td>-5.0</td>
</tr>
<tr>
<td>PR$_3$</td>
<td>-25.0</td>
<td>-20.4</td>
<td>-6.0</td>
<td>-6.0</td>
<td>-5.0</td>
</tr>
</tbody>
</table>

Table 2.3 shows that the shifts of the phosphines containing $C_2H_4$ spacer groups are of significantly lower frequency than those of the analogous phosphines where the $C_2H_4C_6F_{13}$ unit(s) is replaced by an ethyl group(s). The shifts of the phosphines containing $C_6H_4$ spacer groups, however, are very similar to that of triphenylphosphine, even when three perfluorinated chains are present. The position of the chain on the aryl ring does not appear to have any significant effect on the chemical shift. This suggests that the aryl spacer groups are more effective at reducing the electronic influence of the perfluorinated chains than the alkyl spacer groups. It is not useful to attempt to interpret the chemical shifts in terms of the electron-withdrawing effect of the groups attached to the phosphorus, since $^{31}$P chemical shifts have been shown to be dependant on several contributary factors, including steric effects and molecular orbital occupancy, as well as electronegativity.\textsuperscript{(42)}
2.9 Discussion of Air Sensitivity of the Phosphines

Phosphines (1-3) all react with molecular oxygen to give the corresponding phosphine oxide if exposed to air. The air sensitivity increases with increasing substitution; (1) oxidising after several weeks, (2) after a few days and (3) after only a few hours exposure. Phosphines (5-10) also react with molecular oxygen if left in air. However, the aryl spacer group used in these phosphines insulates the phosphorus from the electronic effects of the perfluorinated chains more effectively than the alkyl group used in (1-3) and, consequently, the air sensitivity of (5-10) is less pronounced. The tris-substituted phosphines (7 and 10) oxidise after several days’ exposure to air, the bis-substituted (6 and 9) after several weeks, and the mono-substituted phosphines (5 and 8) show only small amounts (<10%) of oxide after several months. It should be noted that the above oxidation rates are for the phosphines in their pure, solid state. The rates of oxidation are dramatically increased if the phosphines are exposed to air whilst in solution.

It has been noted before that the introduction of electron-withdrawing groups (namely CF₃ groups) on to the phenyl rings of triphenylphosphine, causes an increase in reactivity towards molecular oxygen.⁴³⁴⁴ This is, perhaps, surprising, since the electron-withdrawing effect of these groups should reduce the electron density on the phosphorus atom and this may be expected to lessen the ability of the phosphorus atom to form a bond with oxygen and, hence, reduce the air sensitivity of the phosphine. This apparently anomalous behaviour can be rationalised if the nature of the P=O bond and the mechanism of its formation is considered. The bond is formed not by nucleophilic attack of the phosphorus atom on dioxygen, but by a free radical process.⁴⁵ This means that the electron density on the phosphorus atom is not a major consideration in the bond formation. Secondly, the P=O bond consists of some σ-overlap between the sp³ phosphorus orbital and the oxygen sp² orbital,⁴⁶ and also significant π-overlap resulting from electron density in p-orbitals on the oxygen back-donating into available orbitals on the phosphorus. (These orbitals may be d-orbitals,⁴⁶ although recent work⁴⁷⁴⁸ has shown that, in phosphorus-to-metal bonding, the π back-bonding from the metal goes into σ*3d hybrid-orbitals on the phosphorus, and this seems likely to be the case with the P=O bond). Since the P=O
bond involves electron-density transfer both from phosphorus to oxygen (σ-bonding), and from oxygen to phosphorus (π-bonding), decreasing the electron density on the phosphorus atom could either weaken or strengthen the bond depending on the relative size of the contributions from each bonding mode. Indeed, both effects have been observed in the platinum-phosphorus bond, the nature of which is believed to be similar to that of the P=O bond. This means that the amount of electron density on the phosphorus cannot be directly correlated with either the ease of formation, or the strength of the P=O bond. Hence, the air sensitivity of phosphines cannot be predicted by looking at the electron-withdrawing effect of its substituents.
References for Chapter 2


Chapter 3

The Co-ordination Chemistry of the Ligands

3.1 Bonding in Metal Phosphines

Metal phosphine complexes are used extensively as homogeneous catalysts by both academic and industrial chemists. The ability of metal phosphine complexes to perform such a wide variety of catalytic processes (see Section 2.1) is due largely to the nature of the metal-phosphorus bond. This bond is required to break in order to create vacant co-ordination sites and, hence, initiate reactions, and then to reform in order to stabilise the metal in its 'resting' state. The bond is also required, in most cases, to stabilise the metal centre in at least two different oxidation states, as the oxidative addition and reductive elimination steps occur. According to the currently accepted model of the metal-phosphorus bond, the lone pair on the phosphorus forms a σ-bond by donating electron-density into empty d-orbitals on the metal, whilst electron-density from filled d-orbitals on the metal is donated into 3dσ*-hybrid orbitals on the phosphorus, forming a π-bond (see Fig. 3.1). This model can be used effectively to rationalise the versatility of the metal-phosphorus bond. Electron density is donated in both directions, from the metal to the phosphorus and vice versa. This means that, if the metal centre is in a high oxidation state and has little electron density in its d-orbitals, then the σ-bond, formed by donation of the lone-pair on the phosphorus, will be predominant. If, however, the metal is in a low oxidation state and has lots of electron density in its d-orbitals, then the π-backbonding into the 3dσ*-orbitals on the phosphorus will be predominant. In this way, the metal-phosphorus bond can adapt to the electronic requirements of the metal in a catalytic cycle and, consequently, phosphines make excellent ligands for use in transition metal catalysis.
The electronic properties of the groups on the phosphine will, obviously, have an effect on the 'electronic adaptability' of the phosphine.

Fig. 3.1  a) Phosphorus-to-metal σ-bonding and metal-to-phosphorus π-bonding

b) Mixing of σ*- and 3d-orbitals on phosphine to give 3dσ*-hybrid, π-acceptor LUMOs

Alkyl groups, for example, push electron density on to the phosphorus and this results in the formation of strong σ-bonds between the metal and the phosphine. This
generally leads to decreased catalytic activity because the phosphine is less labile and, hence, vacant sites are not readily created. Also, the strong σ-donor character of the phosphine means that the metal is stabilised to a greater degree in higher oxidation states (for example following oxidative addition), and similar stability of both high and low oxidation states is generally required for a successful catalytic cycle.\(^9\) In some cases, however, increasing the electron density on the phosphorus can be beneficial to a catalytic cycle, and this is particularly true for many alkane carboxylation reactions\(^{10\text{-}11}\) Scheme 3.2 shows two of the key steps in this type of reaction. The formation of the 14-electron species \([\text{RhCl(P}_{R3}\text{)}_2]\) and the subsequent oxidative addition of \(R'H\) to give the Rh(III) intermediate happen much more quickly when the metal is stabilised by electron-rich ligands and, for this reason, alkyl-phosphines are often used in this reaction.\(^{12}\) Similarly, some catalytic reactions, particularly hydroformylation reactions,\(^{13\text{-}14}\) are found to proceed faster if electron-poor, π-acidic phosphites are used. This type of ligand stabilises the metal centre in much the same way as carbon monoxide,\(^{15}\) and, as such, is often used to stabilise metals in low oxidation states.\(^{16}\) Work is currently being carried out to try to synthesise phosphines with electron-withdrawing properties similar to those of phosphites.\(^{17}\) It is anticipated that these ligands will show the same activity as the related phosphites, whilst the removal of the oxygen will make them more robust and, consequently, more useful.

The \(C_6F_{13}\) tails which are present in phosphines (1-3) and (5-10), were expected to have an electron-withdrawing effect, the magnitude of which would be determined by the efficiency of the ‘spacer’ group. In order to examine the reactivity of the phosphines and to probe their electronic and bonding characteristics, extensive
co-ordination chemistry was carried out with a variety of metal centres. Preliminary catalytic studies, consisting of hydrogenation and hydroformylation reactions, have also been performed using metal complexes containing these ligands. These experiments were carried out in order to establish what effect the perfluorinated tails have upon the catalytic activity of complexes into which the ligands are incorporated and, also, to look at the usefulness of various F.B.S solvent systems. These studies are described and discussed fully in Chapter 4.

The metal complexes described here were characterised by a combination of $^1$H, $^{31}$P and $^{19}$F NMR spectroscopy, IR spectroscopy, Mass spectrometry, elemental analysis and, in two cases, X-ray crystallography. For full characterisation data see Chapter 5.

### 3.2 Complexes of the Type [PtCl$_2$L$_2$]

Platinum-195 (abundance 33%, spin 1/2) provides a useful NMR ‘handle’ with which to investigate phosphines. The magnitude of the coupling between the platinum and the phosphorus can yield information on both the geometry of the complex$^{(18)}$ and, also, the electronic properties of the phosphine ligand$^{(19)}$ (see Section 3.2.5).

* cis-*[PtCl$_2$(MeCN)$_2$]$^{(20)}$ is a convenient starting material for making square planar complexes of the type [PtCl$_2$L$_2$], since it is reasonably soluble in most common organic solvents, and the MeCN ligands are easily displaced by most phosphorus-based ligands under relatively mild conditions (see Scheme 3.3). The starting material has a *cis*-arrangement$^{(21)}$ and this geometry is observed in the bisphosphine product in the majority of cases. The *cis*-product is thought to be the kinetic product and, in

![Scheme 3.3 Preparation of complexes of the type cis-[PtCl$_2$L$_2$]](image-url)
most cases, cis-trans isomerisation can be achieved by heating,\(^{(22)}\) or irradiation.\(^{(23)}\)
Complexes of this type have been used as catalysts for various reactions including hydrogenation, hydroformylation and polymerisation,\(^{(40)}\) and so, are of interest as potential fluorous-biphase catalysts.

3.2.1 Reactions of \(\text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})\) (1), \(\text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\) (2) and \(\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\)
(3) with cis-[PtCl\(_2\)(MeCN)]

The reactions of ligands (1) and (2) with cis-[PtCl\(_2\)(MeCN)]\(_2\)] in refluxing dichloromethane produced, as expected, cis-[PtCl\(_2\)(PPh\(_2\)(C\(_2\)H\(_4\)C\(_6\)F\(_{13}\))_2\)] (13) and cis-[PtCl\(_2\)(PPh{C\(_2\)H\(_4\)C\(_6\)F\(_{13}\)}_2)] (14) in good yield (see Fig. 3.5). The complexes were initially characterised using \(^{31}\text{P}\) NMR spectroscopy, the spectrum of each showing a singlet with the expected platinum satellites. The Pt-P coupling constants for (13) and (14) were found to be 3630 Hz (see Fig. 3.4) and 3518 Hz respectively. These values are typical for cis-complexes of this type \(^{1}J_{\text{PtP}}\) for cis-[PtCl\(_2\)L\(_2\)], where L is a tertiary phosphine, generally falls in the region 3200-3700 Hz\(^{(18)}\). Support for the

Fig. 3.4 \(^{31}\text{P}\) NMR spectrum of cis-[PtCl\(_2\)(PPh\(_2\)C\(_2\)H\(_4\)C\(_6\)F\(_{13}\))_2\)] (13) showing \(^{195}\text{Pt}\) satellites
cis-geometries also came from the infra-red spectra of the complexes. Both spectra showed two bands in the region 290-370 cm$^{-1}$ assigned as Pt-Cl stretches, and this is highly suggestive of the cis-formulation.$^{(26)}$ In the case of the analogous trans-complexes, only one IR active band is observed in this region, and so, IR spectroscopy can be used to distinguish between the two isomers. This distinct difference in the IR spectra of cis- and trans-square planar d$^8$ complexes of the type [MX$_2$L$_2$], is due to the different symmetry of the two isomers. The cis-complexes belong to the symmetry point group C$_2v$, whilst the trans-complexes belong to the more symmetrical D$_{2h}$ point group. Using group theory, it can be shown that the cis-isomers have two IR-active M-Cl vibrations (symmetric and asymmetric stretches) whilst the trans-isomers have only one (asymmetric stretch).$^{(94)}$

Fig. 3.5  cis-[Platinum dichloride bis(1H,1H,2H,2H-perfluorooctyl diphenyl phosphine)] (13), cis-[Platinum dichloride bis(bis(1H,1H,2H,2H-perfluorooctyl) phenyl phosphine)] (14) and trans-[Platinum dichloride bis(tris(1H,1H,2H,2H-perfluorooctyl) phosphine)] (15)

Due to the air-sensitivity of P(C$_2$H$_4$C$_6$F$_{13}$)$_3$ (3), this phosphine was allowed to react with cis-[PtCl$_2$(MeCN)$_2$] in a Schlenk flask under N$_2$ gas. Whilst it is possible to use a refluxing solvent in a closed system, it does require a more complex experimental procedure, and in this case it was decided to perform the reaction at room
temperature. Surprisingly, the trans-product was formed (see Fig. 3.5), despite the fact that milder conditions than those used in the synthesis of (13) and (14), were employed. It is likely that the steric interaction between the two large, tri-substituted phosphines results in the cis-product being unstable and this effect forces the complex to adopt the less sterically hindered trans-geometry. The structure was characterised using $^{31}\text{P}$ NMR spectroscopy, which showed a singlet with a $J_{\text{Pt-P}}$ coupling constant of 2491 Hz ($J_{\text{Pt-P}}$ for trans-[PtCl$_2$L$_2$] where L is a tertiary phosphine, generally falls in the region 2300-2800$^{(18)}$) and IR spectroscopy, which showed one active band at 346-362 cm$^{-1}$, typical for a trans-structure of this type.$^{(27)}$ Although ligand (3) is preferentially soluble in perfluorinated solvents, the complex, (15), is not, and so has no real potential for use in fluorous-biphase catalysis.

### 3.2.2 Crystal Structure of cis-[PtCl$_2$(PPh$_2$C$_2$H$_4$C$_6$F$_{13}$)$_2$] (13)

Crystals of (13) were obtained by slow evaporation of a solution of the complex in acetone, and the structure was determined using single crystal X-ray crystallographic methods (see Fig. 3.6). A comparison of selected bond lengths and angles from (13) with those of cis-[PtCl$_2$(PPh$_2$Me)$_2$] is made in Table 3.1. As can be seen from Table 3.1, there are no significant variations in bond length between the two structures. This implies that the electron-withdrawing effect of the perfluorinated chains does not have a major impact on the electron density available for bonding on the phosphorus atoms in (13). There is however some difference in the geometric arrangement of the ligands in the two complexes. This is most noticeable in the C-P-C bond angles. In the case of (13), both phosphines each exhibit two C-P-C angles which are approximately equal in magnitude ($\sim$100° and $\sim$102° respectively) while the third is noticeably larger ($\sim$106° and $\sim$108° respectively). In cis-[PtCl$_2$(PPh$_2$Me)$_2$], a similar pattern exists, but here, the two similar angles in each phosphine ($\sim$106° in both cases) are larger than the other, noticeably smaller angle ($\sim$100° in both cases). It seems likely that the increased asymmetry in complex (13) relative to that in cis-[PtCl$_2$(PPh$_2$Me)$_2$], is due, in large part, to the steric effect of the C$_2$H$_4$C$_6$F$_{13}$ group. This, in contrast to the methyl unit in cis-[PtCl$_2$(PPh$_2$Me)$_2$], is very bulky, and so, has a
significant influence on the geometry of the phosphine. Also, the electron-withdrawing ability of the perfluorinated chain may contribute to this asymmetry by causing localised fluctuations in electron density around the phosphorus.

Fig. 3.6 Crystal structure of \textit{cis-}[PtCl}_2(PPh}_2C}_2H}_4C}_6F_(13)2] \textit{(13)}
Table 3.1 Selected bond lengths and angles for cis-[PtCl₂(PPh₂C₂H₄C₆Fj₃)₂] (13) and cis-[PtCl₂(PPh₂Me)₂]⁵⁴

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å) or angle (°)</th>
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<tbody>
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<td></td>
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<td>Pt(1)-P(2)</td>
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<td>P(1)-C(1a)</td>
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<tr>
<td>C(21)-P(1)-C(11)</td>
<td>100.6(6)</td>
</tr>
<tr>
<td>C(11)-P(1)-C(1a)</td>
<td>106.0(7)</td>
</tr>
<tr>
<td>C(31)-P(2)-C(1)</td>
<td>102.0(6)</td>
</tr>
<tr>
<td>C(41)-P(2)-C(1)</td>
<td>102.3(7)</td>
</tr>
<tr>
<td>C(31)-P(2)-C(41)</td>
<td>108.1(7)</td>
</tr>
</tbody>
</table>

The fluorine atoms at the ends of one of the tails are quite disordered and so their exact positions are not defined. However, it appears that there is a close approach between the terminal CF₃ groups on the fluorous chains of adjacent molecules (see Fig. 3.7). These F-F, intermolecular distances are of the order of 1.8-1.9 Å (F-F bond distance is 1.417 Å²⁵⁵), and it seems that these intermolecular fluorine-fluorine interactions play a significant role in the crystal packing of this type of complex. As
can be seen in Fig. 3.7, the molecules align themselves such that the ends of adjacent tails from different molecules are arranged in an almost linear fashion. This effect is also observed in the crystal packing of \([\text{RhCl}(\text{CO})\{\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}_2]\) (see Section 3.4).

**Fig. 3.7** Crystal packing diagram for (13)

---

### 3.2.3 Reactions of \(\text{PPh}_2(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})\) (5) and \(\text{PPh}(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})_2\) (6) with \(\text{cis-}\)[\(\text{PtCl}_2(\text{MeCN})_2\)]

Ligands (5) and (6) were each allowed to react with \(\text{cis-}\)[\(\text{PtCl}_2(\text{MeCN})_2\)] in refluxing dichloromethane, giving the expected products, \(\text{cis-}\)[\(\text{PtCl}_2(\text{PPh}_2\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})_2\)] (16) and \(\text{cis-}\)[\(\text{PtCl}_2(\text{PPh}\{\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13}\}_2)_2\)] (17) in good yield (see Fig. 3.8). The structures were confirmed using \(^{31}\text{P}\) NMR and IR spectroscopy, as described above.

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Fig. 3.8 cis-[Platinum dichloride bis(4-perfluorohexylphenyl diphenyl phosphine)] (16) and cis-[Platinum dichloride bis(bis{4-perfluorohexylphenyl} phenyl phosphine)] (17)

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} \quad \text{Cl} \\
\text{Cl} & \quad \text{PPh}_2(C_6H_4-p-C_6F_{13}) \quad \text{PPh}_2(C_6H_4-p-C_6F_{13})_2
\end{align*}
\]

(16)

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} \\
\text{Cl} & \quad \text{PPh}_2(C_6H_4-p-C_6F_{13})_2
\end{align*}
\]

(17)

3.2.4 Reactions of PPh2(C6H4-m-C6F13) (8), PPh(C6H4-m-C6F13)2 (9) and P(C6H4-m-C6F13)3 (10) with cis-[PtCl2(MeCN)2]

Ligands (8), (9) and (10) were each allowed to react with cis-[PtCl2(MeCN)2] in refluxing dichloromethane for 8 hours. In the case of (8) and (9), the reaction products, [PtCl2(PPh2C6H4-m-C6F13)2] (19) and [PtCl2(PPh(C6H4-m-C6F13)2)2] (20) were both found to be mixtures of the cis- and trans-isomers (see Fig. 3.9). In each case, the two different phosphorus environments produced two singlets in the 31P NMR spectrum, both with platinum satellites. Although relative solubility, line broadening and relaxation factors limit the value of quantitative analysis using 31P NMR spectroscopy, integration of the peaks in the 31P NMR spectrum for (19) indicated a 3:2 ratio of cis- to trans-product, whilst that for (20) suggested the cis- to trans-ratio was 1:3. The higher proportion of trans-product found for complex (20), is probably due to the extra steric bulk of the di-substituted phosphine (9), making the relative trans/cis energetics for (20) different to those for (19). The isomers could not be successfully separated by recrystallisation, however, the isomeric mixtures were found to be analytically pure. In the case of (10), the product, [PtCl2(P{C6H4-m-C6F13}3)]2 (21) was found to be exclusively trans, continuing the apparent trend exhibited by (8) and (9) (see Fig. 3.9).
Fig. 3.9  [Platinum dichloride bis(3-perfluorohexylphenyl diphenyl phosphine)] (19), [Platinum dichloride bis(bis{3-perfluorohexylphenyl} phenyl phosphine)] (20) and trans-[Platinum dichloride bis(tris{3-perfluorohexylphenyl} phosphine)] (21)

For comparison, the complex [PtCl₂(P{C₆H₄-p-C₆F₁₃})₃] (18) (synthesised by Dr. Alison Stuart) was formed with a cis- to trans-ratio of 6:1 by refluxing in dichloromethane for 2 hours (see Fig. 3.10). It was thought possible that the longer reaction times employed in the synthesis of (19-21) may have been responsible for their increased tendency to form the trans-isomer relative to (16-18). In order to check this hypothesis, the reaction of PPh₂(C₂H₄C₆F₁₃) (1) with cis-[PtCl₂(MeCN)₂] was repeated, and was refluxed in dichloromethane for > 8 hrs. The resulting complex [PtCl₂(PPh₂C₂H₄C₆F₁₃)₂] (13), was found to be entirely the cis-isomer and
this suggests that the formation of the trans-isomers of complexes (19-21) was not due to the extended reaction period. It is likely, therefore, that the structure of the phosphines is the main factor in determining the geometry of the products. In the case of (19-21), the phosphines are substituted in the meta-position, which means that there is more potential for steric interaction between two adjacent cis-phosphines than is the case with the corresponding para-substituted phosphines, in which the C₆F₁₃ groups point directly away from the phosphorus. No attempt has been made to measure the cone angles(29) of the phosphines, although it seems reasonable to predict that the cone angle of the meta-substituted phosphines would be greater than that of the corresponding para-substituted phosphines. The preferential formation of the trans-isomers of (19-21) relative to (16-18), although not conclusive, appears to support this suggestion. Complex (21) was found not to be preferentially soluble in perfluorinated solvents, as was complex (18),(28) despite the fact that the free phosphines in each case are preferentially soluble in fluorous solvents.

3.2.5 Discussion of ³¹P NMR Data for the [PtCl₂L₂] Complexes (13-21)

³¹P NMR data are particularly useful for the characterisation of complexes of the type [PtCl₂L₂] where L is a phosphorus based ligand. Platinum-195 (abundance 33%) has a nuclear spin of 1/2, and so, couples to the phosphorus giving a doublet which appears in the spectrum as satellites flanking the most intense absorption. Table 3.2 contains ³¹P NMR spectroscopic data for the complexes (13-21).
### Table 3.2 $^{31}$P NMR data for the [PtCl$_2$L$_2$] complexes (13-21)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_P$ (ppm)</th>
<th>$^1J_{P-P}$ (Hz)</th>
<th>$\delta_P$ of free phosphine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$C$<em>6$F$</em>{13}$)$_2$] (13)$^b$</td>
<td>5.8</td>
<td>3630</td>
<td>-16.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$C$<em>6$F$</em>{13}$)$_2$] (14)$^b$</td>
<td>-0.6</td>
<td>3518</td>
<td>-23.0</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(P'C$_6$H$_4$C$<em>6$F$</em>{13}$)$_2$] (15)$^c$</td>
<td>11.8</td>
<td>2491</td>
<td>-25.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$-p-C$<em>6$F$</em>{13}$)$_2$] (16)</td>
<td>14.6</td>
<td>3653</td>
<td>-5.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$-p-C$<em>6$F$</em>{13}$)$_2$] (17)</td>
<td>14.6</td>
<td>3635</td>
<td>-5.4</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(P'C$_6$H$_4$-p-C$<em>6$F$</em>{13}$)$_2$] (18)$^c$</td>
<td>15.5</td>
<td>3631</td>
<td>-6.0</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(P'C$_6$H$_4$-p-C$<em>6$F$</em>{13}$)$_2$] (18)$^c$</td>
<td>22.8</td>
<td>2719</td>
<td>-6.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$m-C$<em>6$F$</em>{13}$)$_2$] (19)</td>
<td>15.3</td>
<td>3633</td>
<td>-4.8</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(PPh$_2$C$_6$H$_4$m-C$<em>6$F$</em>{13}$)$_2$] (19)</td>
<td>21.2</td>
<td>2646</td>
<td>-4.8</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$m-C$<em>6$F$</em>{13}$)$_2$] (20)</td>
<td>15.8</td>
<td>3602</td>
<td>-5.0</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(PPh$_2$C$_6$H$_4$m-C$<em>6$F$</em>{13}$)$_2$] (20)</td>
<td>21.8</td>
<td>2696</td>
<td>-5.0</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(P'C$_6$H$_4$m-C$<em>6$F$</em>{13}$)$_2$] (21)$^d$</td>
<td>21.8</td>
<td>2723</td>
<td>-6.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_3$)$_2$]$^d$</td>
<td>14.5</td>
<td>3672</td>
<td>-5.0</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(PPh$_3$)$_2$]$^d$</td>
<td>20.4</td>
<td>2635</td>
<td>-5.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_2$Et)$_2$]$^f$</td>
<td>9.8</td>
<td>3640</td>
<td>-12.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PPh$_3$Et)$_2$]$^f$</td>
<td>3.3</td>
<td>3530</td>
<td>-16.0</td>
</tr>
<tr>
<td>cis-[PtCl$_2$(PEt$_3$)$_2$]$^f$</td>
<td>12.3</td>
<td>2400</td>
<td>-20.4</td>
</tr>
</tbody>
</table>

---

$a$ Spectra run in CDCl$_3$  
$b$ Spectrum run in CD$_2$Cl$_2$  
$c$ Spectrum run in d$_6$ acetone  
$d$ Spectrum run in C$_6$H$_5$CF$_3$ with D$_2$O sleeve  
$e$ Synthesised for comparative purposes  
$^f$ From ref (18)

The $^1J_{P-P}$ coupling constant can be used to assign the structure of the complex,\(^{(26)(30)}\) since the magnitude of the coupling falls into clearly defined regions for the two different isomers (3200-3700 Hz for the cis-isomer, 2200-2700 Hz for the trans-isomer). The magnitude of the $^1J_{P-P}$ coupling constant in this type of complex, is
thought to be directly related to the bond length and, hence, the bond strength,\(^{(31)}\) such that an increase in bond strength results in a larger coupling constant. It has been shown that the major contribution to variation in the coupling constant is variation in the s-character of the bonding molecular orbitals in both the platinum and the phosphorus, and this variation is, itself, related to the strength of the \(\sigma\)-component of the bond.\(^{(19)(30)}\) In the \(\text{cis}\)-arrangement, the geometry of the two phosphorus atoms means that they can undergo \(\pi\)-bonding with three of the metals d-orbitals, (dxy, dzy and dxz) but, in the \(\text{trans}\)-arrangement, the geometry is such that only two of the metals d-orbitals are available for \(\pi\)-bonding.\(^{(33)}\) Because of the synergic nature of the M-P bond\(^{(32)}\) this increased \(\pi\)-overlap in the \(\text{cis}\)-isomer results in a corresponding increase in the \(\sigma\)-component of the M-P bond and, hence, a larger \(J_{\text{PP}}\) coupling constant is observed for the \(\text{cis}\)-isomer than for the \(\text{trans}\)-isomer. A further contributary factor to the variation of \(J_{\text{PP}}\) in \(\text{cis/\text{trans}}\)-complexes of this type is the \(\text{trans-effect}\).\(^{(35)(36)(80)}\) In the \(\text{cis}\)-arrangement, the phosphine is \(\text{trans}\) to a chloride which has a relatively small \(\text{trans-effect}\), so the M-P bond is not weakened to any great extent, whereas, in the \(\text{trans}\)-arrangement, the phosphine is \(\text{trans}\) to another phosphine, which has a relatively large \(\text{trans-effect}\),\(^{(35)}\) and so the M-P bond is weakened significantly. Although the exact reasons for this effect are not known, it is thought that the underlying cause is the difference in electronegativity of the ligands. It has been noted, for example, that in square planar Pt (II) dichloride complexes, the Pt-Cl bond strength increases with increasing electronegativity of the ligand \(\text{trans}\) to it, and this observation has been quantitatively expressed by McWeeny \textit{et al.}\(^{(37)}\) for a variety of ligands.

Two further trends are apparent in the \(J_{\text{PP}}\) coupling constants shown in Table 3.2. The first is that, in the \(\text{cis}\)-isomers, there is a decrease in the magnitude of \(J_{\text{PP}}\) as the number of fluorous chains on the groups attached to the phosphorus increases. A similar effect has been observed previously in Pt (II) dichloride complexes containing a range of \textit{para}-substituted aryl phosphines,\(^{(19)}\) and is probably due to the decrease in \(\sigma\)-bonding caused by the electron-withdrawing tails pulling electron density away from the phosphorus and, hence, decreasing its ability to donate \(\sigma\)-electron density to the metal. The second trend is that, in the \(\text{trans}\)-complexes, there is an increase in \(J_{\text{PP}}\) as the number of fluorous chains increases. A similar trend exists in the compounds.
trans-[PtCl₂L₂], where L is a phosphine of the type PR₃ and R is an alkyl group. In this case, the ¹Jₚₚ coupling constant increases with decreasing electron-donating ability, i.e. PbU₃ < PPr₃ < PEt₃.³⁴ It is difficult to rationalise these trends, and no satisfactory explanation can be found in the literature. It appears, however, that there is a distinct difference in the way in which mutually-trans metal-phosphorus bonds are affected by variation in the electronic character of the groups attached to the phosphorus, when compared to metal-phosphorus bonds which are trans to chlorides. It also seems likely that this effect is related to the trans-effect described above. In the case where the phosphorus is trans to a chloride, the electronegativity of the chloride causes electron-density to flow through the σ-bonds, from the phosphorus towards the chloride. This effect presumably results in the σ-component of the M-P bond being relatively strong, in the sense that there is significant s-electron character in the M-P bond. As the electron-withdrawing substituents are added to the phosphorus, the major effect is that the ability of the phosphorus to donate electron density to this σ-bond is reduced, and so there is a corresponding reduction in the s-electron character of the M-P bond. In the case where the phosphines are mutually-trans, the electronegativity of both ligands is the same, and so, there is no longer a flow of σ-electron density in either direction. The M-P σ-bond, therefore, is weaker and, hence, it is probable that metal to phosphorus π-back-bonding is more important in this type of bond. As the electron-withdrawing groups are added to the phosphorus, the major effect is that the metal to phosphorus π-backbonding is increased, since the P-M σ-bond cannot polarise to any great extent as it can when it is trans to a chloride. This increase in metal to phosphorus π-back-bonding induces a δ⁺ charge on the metal, and so, in accordance with the synergic nature of the bond, the σ-component is slightly strengthened resulting in an increase in the s-electron character of the bond and an increase in ¹Jₚₚ. This explanation can be used to rationalise the observed trends, although this is an area of co-ordination chemistry which is poorly understood, and extensive research into the trans-effect and other, seemingly related effects, is required in order to establish exactly what is happening in bonding stuctures of this type.
3.3 Complexes of the Type \([\text{PdCl}_2\text{L}_2]\)

Trans-\([\text{PdCl}_2(\text{MeCN})_2]\) is a convenient starting material for synthesising complexes of the type \([\text{PdCl}_2\text{L}_2]\), since it readily undergoes ligand metathesis, resulting in the replacement of the acetonitrile groups with phosphine ligands\(^{(38)}\) (see Scheme 3.11). When \(L\) is a tertiary phosphine, the resulting palladium(II) dichloride.

Scheme 3.11 Preparation of complexes of the type \(\text{trans-}[\text{PdCl}_2\text{L}_2]\)

\[
\begin{align*}
\text{MeCN} & \quad \text{Cl} \\
\text{Pd} & \quad \text{Cl} \\
\text{Cl} & \quad \text{NCMe} \\
\text{Pd} & \quad \text{Cl} \\
\text{L} & \quad \text{Cl}
\end{align*}
\]

bisphosphine complexes almost always adopt a \(\text{trans}\) geometry\(^{(39)}\), although a few examples of \(\text{cis}\)-complexes do exist\(^{(38)}\). Palladium complexes of this type are not as conveniently characterised as the corresponding platinum complexes since there are no spin active isotopes of palladium and, hence, the \(^{31}\text{P}\) NMR spectra show only a singlet. However, as outlined above, \(\text{cis}\)- and \(\text{trans}\)-isomers can be distinguished using IR spectroscopy\(^{(26)}\). Complexes of the type \([\text{PdCl}_2\text{L}_2]\) have been shown to be effective catalysts for the carbonylation of olefins\(^{(41)}\) and various other C-C bond formation reactions\(^{(42)}\).

3.3.1 Reactions of \(\text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})\) (1), \(\text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\) (2) and \(\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\) (3) with \(\text{trans-}[\text{PdCl}_2(\text{MeCN})_2]\)

Phosphines (1-3) were each allowed to react with \(\text{trans-}[\text{PdCl}_2(\text{MeCN})_2]\) in dichloromethane, under \(\text{N}_2\). In the case of phosphines (1) and (2), the reactions were complete after refluxing for 2 hours, yielding \(\text{trans-}[\text{PdCl}_2(\text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2)]\) (22) and \(\text{trans-}[\text{PdCl}_2(\text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2)_2]\) (23) respectively (see Fig. 3.12). In the case of (3) Schlenk techniques were used due to the air-sensitivity of the phosphine, and so, refluxing the solvent was not practical. However, the reaction still proceeded.
smoothly, and trans-[PdCl₂(P{C₂H₄C₆F₁₃}₃)₂] (24) was produced after 2 hours (see Fig 3.12). Complexes (22-24) were all isolated as fine yellow powders. The solubility of all three was surprisingly low in common organic solvents, and this resulted in their purification being slightly problematic. Complex (24) was found to be preferentially soluble in perfluorinated solvents. This was, perhaps, surprising, since the analogous platinum complex, trans-[PtCl₂(P{C₃H₆C₆F₁₃}₃)₂] (15), showed no significant solubility in fluorous media. Structurally, these two complexes are very similar, and the radii of the metal centres are also thought to be of similar magnitudes (0.80 Å in both cases for the M²⁺ ion⁹⁵) and so the reason for this difference in solubility is not clear.

Fig. 3.12  trans-[Palladium dichloride bis(1H,1H,2H,2H-perfluoroctyl diphenyl phosphine)] (22), trans-[Palladium dichloride bis{bis-(1H,1H,2H,2H-perfluoroctyl) phenyl phosphine]} (23) and trans-[Palladium dichloride bis(tris{1H,1H,2H,2H-perfluoroctyl phosphine)] (24)

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3.3.2 Reactions of PPh₂(C₆H₄-p-C₆F₁₃) (5), PPh(C₆H₄-p-C₆F₁₃)₂ (6) and P(C₆H₄-p-C₆F₁₃)₃ (7) with trans-[PdCl₂(MeCN)₂]

Phosphines (5-7) were all allowed to react with trans-[PdCl₂(MeCN)₂] in refluxing dichloromethane for 2 hours, under N₂. The resulting complexes, trans-[PdCl₂(PPh₂C₆H₄-p-C₆F₁₃)₂] (25), trans-[PdCl₂(PPh{C₆H₄-p-C₆F₁₃}₂)₂] (26) and trans-[PdCl₂(P{C₆H₄-p-C₆F₁₃}₃)₂] (see Fig. 3.13), all exhibited the expected single band at 350-370 cm⁻¹ in their IR spectra, confirming their trans-structure. Purification was achieved simply by washing with warm hexane, and all of the complexes were isolated as fine yellow powders. It was expected that complex (27) would be preferentially soluble in perfluorinated solvents, since this is the case for the analogous complex (24), in which L is the triply substituted phosphine P(C₂H₄C₆F₁₃)₃ (3). It was found, however, that (27) is insoluble in perfluorinated solvents, and this suggests that P(C₆H₄-p-C₆F₁₃)₃ (7) is less efficient at solubilising metal complexes than P(C₂H₄C₆F₁₃)₃ (3). This difference in solubility is almost certainly caused by the
differences in the size and structure of the spacer groups in the phosphines. The rather small, non-polar, aliphatic, \( \text{C}_2\text{H}_4 \) spacer in (3), is more easily held in the fluorous media than the larger, aromatic, \( \text{C}_6\text{H}_4 \) group in (7). This obvious difference in fluorous solubility of the compound \( \text{trans-}[\text{PdCl}_2\text{L}_2] \) when \( \text{L} \) is (3) compared to when \( \text{L} \) is (7), is unique and this behaviour was not observed with any of the other types of complexes examined. Typically, if a compound \( [\text{MX}_n\text{L}_m] \) is fluorous soluble when \( \text{L} \) is (3), then it is also fluorous soluble when \( \text{L} \) is (7), and \text{vice versa}. The differing solubility observed in these two palladium complexes suggests that the metal is, in terms of fluorous solubility, a borderline case and this effect, coupled with the insolubility of the platinum complexes (15, 18 and 21) and the observed solubility of the iridium and rhodium complexes (see sections 3.4 and 3.7), suggests that there may be a trend in the inherent fluorous solubility of the metal centres in the order Pt < Pd < Rh, Ir. A second possibility is that the observed increase in fluorous solubility of the rhodium and iridium complexes is due to the ligands around the metal, since the rhodium and iridium complexes contain one chloride and one carbonyl group, rather than the two chlorides in the platinum and palladium complexes.

### 3.4 Complexes of the Type \( \text{trans-}[\text{RhCl(CO)}\text{L}_2] \)

Rhodium metal complexes are used extensively in catalysis, particularly homogeneous catalysis, and this catalytic potential, coupled with the NMR ‘handle’ provided by \(^{103}\text{Rh} \) (spin 1/2, abundance 100%), makes rhodium an obvious choice for use in the synthesis of potential fluorous biphase catalysts. Indeed, the first reported F.B.S. catalysis experiments were performed using a rhodium based catalyst.\(^{96}\) Square-planar, \( \text{d}^8 \) complexes of the type \( [\text{MCl(CO)}\text{L}_2] \) (M is Rh or Ir) are particularly useful for examining the properties of phosphines, since the stretching frequency of the carbonyl group (\( \nu \text{C}≡\text{O} \)) is sensitive to the electronic influence of the ligands,\(^{44k45}\) and can be readily observed using infra-red spectroscopy. The synthetic route of choice to this type of complex is via the reaction of the chloride-bridged, dimeric species \( [\text{RhCl(CO)}\text{L}_2]_2 \) with the free phosphine\(^{46}\) (see Scheme 3.14). The resultant rhodium (I) complexes always adopt a \text{trans} geometry, are usually air-stable, and are
3.4.1 Reactions of PPh$_2$(C$_2$H$_4$C$_6$F$_{13}$) (1), PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$ (2) and P(C$_2$H$_4$C$_6$F$_{13}$)$_3$ (3) with [RhCl(CO)$_2$]$_2$

Ligands (1) and (2) were each allowed to react with [RhCl(CO)$_2$]$_2$ in refluxing dichloromethane for 2 hours. The solvent was removed in vacuo, yielding a yellow solid in both cases. The product from the reaction of (1), trans-[RhCl(CO)(PPh$_2$C$_2$H$_4$C$_6$F$_{13}$)$_2$] (28) (see Fig. 3.15), was washed with hexane. This removed the excess of phosphine. Since the complex itself was also slightly soluble in hexane the observed yield was low (50%). The product from the reaction of (2), trans-[RhCl(CO)(PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$)$_2$] (29) (see Fig. 3.15) was purified by recrystallisation from dichloromethane and ethanol at 0 °C. Although the complex was air-stable and pure (by EA), it was slightly sticky, and this made it difficult to handle. This stickiness was observed for several complexes containing perfluorinated chains, although, in most cases, the effect was not significant and did not cause handling problems. The fairly high air-sensitivity of phosphine (3) means that it must be handled under nitrogen at all times, and, for this reason, the reaction of (3) with [RhCl(CO)$_2$]$_2$ was performed using Schlenk techniques in thoroughly dried and degassed dichloromethane. The reaction was performed at room temperature, rather than in refluxing solvent, because of the constraints imposed by using a closed system. However, this did not appear to affect the reaction progress, and the reaction was complete after 2 hours. Removal of the solvent in vacuo revealed a very sticky, brown
solid, which adhered to the sides of the flask. This was triturated with hexane for 30 minutes and this cleaned it very effectively, yielding a fine, light-brown powder which was recovered by filtration. The brown colour of the product suggested that the reaction had not been successful, since complexes of the type trans-[RhCl(CO)L2] are almost always yellow.\(^{(48)}\) The \(^{31}\)P NMR spectrum of the product, however, showed the expected doublet (due to Rh-P coupling), and further characterisation of the complex using mass spectroscopy, IR spectroscopy and elemental analysis, confirmed that it was the expected, square-planar, trans-[RhCl(CO)\(\{\text{P}\left\{\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}\right\}_3\}\)\(_2\)] (30) (see Fig. 3.15). Complex (30) was found to be preferentially soluble in perfluorinated solvents.

![Fig. 3.15](image)

\[\text{trans-}[\text{Rhodium carbonyl chloride bis(1H,1H,2H,2H-perfluorooctyl diphenyl phosphine)}] \ (28), \ \text{trans-}[\text{Rhodium carbonyl chloride bis(1H,1H,2H,2H-perfluorooctyl phenyl phosphine)}] \ (29) \text{ and trans-}[\text{Rhodium carbonyl chloride bis(tris-1H,1H,2H,2H-perfluorooctyl phosphine)}] \ (30)\]

\[\begin{align*}
\text{(28)} & : \text{Cl} & \text{P} & \text{Rh} & \text{CO} & \text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}) & \text{Cl} \\
\text{(29)} & : \text{Cl} & \text{P} & \text{Rh} & \text{CO} & \text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2 \\
\text{(30)} & : \text{Cl} & \text{P} & \text{Rh} & \text{CO} & \text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3 \\
\end{align*}\]

3.4.2 Crystal Structure of trans-[RhCl(CO)\(\{\text{P}\left\{\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}\right\}_3\}\)\(_2\)] (30)

Slow evaporation of a solution of (30) in PP3, produced crystals which were suitable for crystallographic characterisation. The resulting crystal structure (see Fig. 84)
3.16) has been published,\(^{(52)}\) and was the first example in the literature of a fully characterised, fluorous-soluble complex. The geometry around the rhodium is very similar to that previously observed in complexes of the type trans-[RhCl(CO)L\(_2\)], where L is a monodentate phosphine.\(^{(49)(50)(51)}\) During the course of this work, the crystal structure of complex (30) was also published by Horváth et al.,\(^{(90)}\) along with the crystal structure of the iridium analogue trans-[IrCl(CO)(P{C\(_2\)H\(_4\)C\(_6\)F\(_3\)}\(_3\))][\(_2\)]. The structure reported for (30) is practically identical to that reported here, and the iridium analogue, whilst displaying some slight differences in bond length, is also very similar (even in the positioning of the fluorous tails) and shows no remarkable features.

Fig. 3.16 Crystal structure of trans-[RhCl(CO)(P{C\(_2\)H\(_4\)C\(_6\)F\(_3\)}\(_3\))][\(_2\)] (30)
Table 3.3 Selected bond lengths and angles for *trans-*
[RhCl(CO)(P(C\textsubscript{2}H\textsubscript{4}C\textsubscript{6}F\textsubscript{13})\textsubscript{3})\textsubscript{2}] (30) and *trans-*[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}]\textsuperscript{(51)}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å) or angle (°)</th>
<th>in (30)</th>
<th>in <em>trans-</em>[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(1)-P(1)</td>
<td>2.300(2)</td>
<td>2.307(1)</td>
<td></td>
</tr>
<tr>
<td>Rh(1)-P(2)</td>
<td>2.304(2)</td>
<td>2.309(1)</td>
<td></td>
</tr>
<tr>
<td>Rh(1)-C(1)</td>
<td>1.807(5)</td>
<td>1.770(4)</td>
<td></td>
</tr>
<tr>
<td>Rh(1)-Cl(1)</td>
<td>2.356(2)</td>
<td>2.354(1)</td>
<td></td>
</tr>
<tr>
<td>P(1)-C(2)</td>
<td>1.835(6)</td>
<td>1.810(4)</td>
<td></td>
</tr>
<tr>
<td>P(1)-C(10)</td>
<td>1.833(5)</td>
<td>1.795(4)</td>
<td></td>
</tr>
<tr>
<td>P(1)-C(18)</td>
<td>1.830(5)</td>
<td>1.789(4)</td>
<td></td>
</tr>
<tr>
<td>C(1)-O(1)</td>
<td>1.152(6)</td>
<td>1.146(4)</td>
<td></td>
</tr>
<tr>
<td>C(1)-Rh(1)-P(1)</td>
<td>94.2(2)</td>
<td>91.0(1)</td>
<td></td>
</tr>
<tr>
<td>P(1)-Rh(1)-P(2)</td>
<td>172.07(5)</td>
<td>177.2(0)</td>
<td></td>
</tr>
<tr>
<td>P(1)-Rh(1)-Cl(1)</td>
<td>85.54(6)</td>
<td>89.3(0)</td>
<td></td>
</tr>
<tr>
<td>C(1)-Rh(1)-P(2)</td>
<td>93.7(2)</td>
<td>91.6(1)</td>
<td></td>
</tr>
<tr>
<td>C(1)-Rh(1)-Cl(1)</td>
<td>179.7(2)</td>
<td>179.4(1)</td>
<td></td>
</tr>
<tr>
<td>P(2)-Rh(1)-Cl(1)</td>
<td>86.53(6)</td>
<td>88.1(0)</td>
<td></td>
</tr>
<tr>
<td>C(2)-P(1)-C(10)</td>
<td>102.4(3)</td>
<td>101.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(10)-P(1)-C(18)</td>
<td>103.9(3)</td>
<td>104.5(3)</td>
<td></td>
</tr>
<tr>
<td>C(2)-P(1)-C(18)</td>
<td>102.8(3)</td>
<td>102.9(2)</td>
<td></td>
</tr>
</tbody>
</table>

The rhodium-phosphorus and rhodium-chloride bonds are quite short relative to those in other complexes of this type, and are close to those found in *trans-*[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}]\textsuperscript{(51)} (see Table 3.3). There is a general overall increase in the bond lengths of (30) as compared to those found in *trans-*[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}], and this is particularly noticeable in the P-C bonds. This is probably due to the electron-withdrawing effect of the tails, pulling electron-density away from the phosphorus and reducing the amount of electron overlap in the bonds. It is perhaps surprising that the...
C≡O bond in (30) is not significantly shorter than that in trans-[RhCl(CO)(PMe₃)₂], as it might reasonably be expected that the reduced electron-density on the rhodium centre would result in less metal-phosphorus π-backbonding and, hence, less electron-density in the π*-antibonding orbitals of the C≡O in (30) relative to that in trans-[RhCl(CO)(PMe₃)₂]. This does not appear to be the case, although, IR studies have confirmed that the C≡O unit in (30) is quite strong as expected (see Section 3.4.7).

The geometry around the rhodium differs significantly between the two complexes, although this is not surprising given the quite different steric requirements of the two phosphines. The fluorous chains on phosphine (3) appear to align themselves in two different ways. Two of the chains on each phosphorus spiral above and below the Cl-Rh-CO axis, in a similar fashion to that observed for fully fluorinated hydrocarbons.(97)
whist the third points away from the other two, in the direction of the chloride. The latter two chains are slightly bent at the third carbon and this bending causes them to point up and down, respectively. There is some disorder in the fluorine atoms at the ends of the chains. However, Fig. 3.17 clearly shows that, as with cis-

\[ \text{[PtCl}_2(\text{PPh}_2\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2] \]

(13) (see Fig. 3.7), the molecules arrange themselves in the unit cell such that the ends of the tails on adjacent molecules are aligned. This crystal structure illustrates how fluorous phosphines such as (3) can form a perfluorinated 'shell' around the metal centre and it is easy to see why complexes of this type are soluble in perfluorinated solvents.

3.4.3 Reactions of \( \text{PPh}_2(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13}) \) (5), \( \text{PPh}(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})_2 \) (6) and \( \text{P}(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})_3 \) (7) with \( \text{[RhCl(CO)]}_2 \)

Ligands (5-7) were each allowed to react with \( \text{[RhCl(CO)]}_2 \) in refluxing dichloromethane for 2 hours, after which time the solvent was removed \textit{in vacuo}, and

Fig. 3.18 \( \text{trans-[Rhodium carbonyl chloride bis(4-perfluorohexylphenyl diphenyl phosphine)]} \) (31), \( \text{trans-[Rhodium carbonyl chloride bis(bis[4-perfluorohexylphenyl] phenyl phosphine)]} \) (32) and \( \text{trans-[Rhodium carbonyl chloride bis(tris-4-perfluorohexylphenyl phosphine)]} \) (33)

\[
\begin{align*}
\text{Cl} & \quad \text{Rh} & \quad \text{PPh}_2(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13}) & \quad \text{Cl} \\
(p-\text{C}_6\text{F}_{13}\text{C}_6\text{H}_4)\text{Ph}_2\text{P} & \quad \text{CO} & \quad (p-\text{C}_6\text{F}_{13}\text{C}_6\text{H}_4)\text{Ph}_2\text{P} & \quad \text{CO}
\end{align*}
\]

(31) (32)

\[
\begin{align*}
\text{Cl} & \quad \text{Rh} & \quad \text{P}(\text{C}_6\text{H}_4-p-\text{C}_6\text{F}_{13})_3 \\
(p-\text{C}_6\text{F}_{13}\text{C}_6\text{H}_4)_3\text{P} & \quad \text{CO}
\end{align*}
\]

(33)
the resulting yellow complexes, \( \text{trans-}[\text{RhCl(CO)}(\text{PPh}_2\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2] \) (31), \( \text{trans-}[\text{RhCl(CO)}(\text{PPh}\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2]_2 \) (32) and \( \text{trans-}[\text{RhCl(CO)}(\text{P}\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_3]_2 \) (33) (see Fig. 3.18), were washed with hexane. Characterisation using \(^{19}\text{F}\) and \(^1\text{H}\) NMR and mass spectroscopy suggested that all three reactions had been successful. The \( ^{31}\text{P}\) NMR spectra, however, whilst showing the expected doublet for (32) and (33), showed a very broad hump for (31). This unexpected result was further investigated using variable temperature \( ^{31}\text{P}\) NMR spectroscopy (see Section 3.4.4). Complex (33) was found to be preferentially soluble in perfluorinated solvents.

3.4.4 \( ^{31}\text{P}\) NMR Spectroscopy Study of \( \text{trans-}[\text{RhCl(CO)}(\text{PPh}_2\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2] \) (31)

As described above, the \( ^{31}\text{P}\) NMR spectrum of complex (31), as well as exhibiting a sharp singlet at the correct chemical shift for the phosphine oxide, also showed a very broad hump, rather than the expected doublet (due to Rh-P coupling). The broad signal was indicative of some kind of exchange process, and so, the \( ^{31}\text{P}\) NMR spectrum was run again at lower temperature. As the temperature was lowered, the NMR signal resolved into the expected doublet (see Fig. 3.19) and this confirmed that an exchange process was indeed occurring. This was thought to be unusual, since none of the previously synthesised complexes of the type \( \text{trans-}[\text{RhCl(CO)}L_2] \) had shown this behaviour. When \( \text{trans-}[\text{RhCl(CO)}(\text{PPh}_3)_2] \) was prepared later for comparative purposes, however, it was discovered that this also exhibited a similar exchange process.

The mechanism of this exchange process is not known, although it seems likely that a dissociative process is occurring. This is supported by the fact that signal broadening occurs even when there is no excess phosphine present, making any five co-ordinate species unlikely. It is probable that one of the phosphines is lost from the rhodium centre, resulting in the formation of free phosphine and a three co-ordinate species \( [\text{RhCl(CO)}L] \), (see Fig. 3.20). The phosphine is then re-coordinated to give the square-planar complex. Due to limitations in the solubility of (31), it was not
Fig. 3.19 \( ^{31}\text{P} \) NMR spectrum of (31) at a range of temperatures. The sharp peak which shifts from \( \delta_p \approx 28.5 \) to \( \approx 30.5 \) (directly under the doublet) is due to phosphine oxide. The change in chemical shift suggested that the resonance frequency of this species was significantly affected by the temperature.

possible to run the NMR spectrum at a high enough temperature to provide any conclusive data. It was established, however, that as the temperature is increased, the broad hump at \( \delta_p \approx 30 \) ppm, shifts slightly to low frequency. This fits in with the
proposed mechanism, since the increased temperature would lead to increased ligand
dissociation, and so the broad, averaged signal would be expected to move to lower
frequency, that is, towards the chemical shift of the free ligand (-5 ppm). The

![Fig. 3.20 Suggested exchange mechanism for (31)](https://example.com/fig320.png)

timescale of this exchange process is such that the NMR spectrometer cannot
differentiate between the different species in solution, and this results in a broad signal
appearing in the room-temperature spectrum. Cooling the sample to 233 K effectively
slows this exchange process down, hence, the doublet due to the \textit{trans}-[RhCl(CO)L₂]
becomes clearly visible. The lack of any other relevant signals suggests that the
dissociation does not occur to any significant degree at low temperature.

3.4.5 Reactions of PPh₂(C₆H₄-m-C₆F₁₃) (8), PPh(C₆H₄-m-C₆F₁₃)₂ (9)
and P(C₆H₄-m-C₆F₁₃)₃ (10) with [RhCl(CO)₂]

The three \textit{meta}-substituted aryl phosphines (8-10), were each allowed to react
with [RhCl(CO)₂]₂ following the same procedure given for (5-7). The three
complexes, \textit{trans}-[RhCl(CO)(PPh₂C₆H₄-m-C₆F₁₃)₂] (34), \textit{trans}-[RhCl(CO)(PPh{C₆H₄-
m-C₆F₁₃}₂)₂] (35) and \textit{trans}-[RhCl(CO)(P{C₆H₄-m-C₆F₁₃}₃)₂] (36) (see Fig. 3.21),
were all isolated as yellow powders. The ³¹P NMR spectrum of (34) showed a broad
signal, similar to that observed for (31) and, upon cooling to 233 K, this signal also
resolved into the expected doublet. Complex (36) was found to be preferentially
soluble in perfluorinated solvents.
3.4.6 Discussion of $^{31}$P NMR Data for the \([\text{RhCl(CO)L}_2]\) Complexes (28-36)

The $^{1}J_{\text{RHP}}$ coupling constants for complexes (28-36) generally increase as more fluororous chains are added to the phosphine (See Table 3.4). Phosphine (3) appears not to follow this trend, since $^{1}J_{\text{RHP}}$ when \(L\) is (3), is smaller than when \(L\) is (1) or (2), however, it is still 8 Hz larger than when \(L\) is PEt$_3$, and this is a more satisfactory comparison, since phosphines (1) and (2) contain phenyl groups, which clearly exert considerable influence on the magnitude of $^{1}J_{\text{RHP}}$. This trend of increasing coupling constant with decreasing electron-density on the phosphorus has been observed previously in this class of complex\(^{(54)}\) and mirrors the trend found in the complexes \(\text{trans-[PtCl}_2\text{L}_2]\) (see Section 3.2.5). It has been proposed that the increase in $^{1}J_{\text{RHP}}$ with decreasing electron-density on the phosphorus is due to metal-phosphorus back-bonding.\(^{(54)}\) As the electron density on the phosphorus decreases, its ability to act as a \(\pi\)-acid increases and, hence, the metal-phosphorus bond is
Table 3.4  $^{31}$P NMR data for complexes (28-36)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_p$ (ppm)</th>
<th>$^1J_{RHP}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$trans$-[RhCl(CO)(PPh$_2$C$_2$H$_4$C$<em>6$F$</em>{13}$)$_2$] (28)</td>
<td>24.5</td>
<td>125</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh(C$_2$H$_4$C$<em>6$F$</em>{13}$)$_2$)] (29)</td>
<td>22.8</td>
<td>125</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(P(C$_2$H$_6$C$<em>6$F$</em>{13}$)$_2$)] (30)</td>
<td>22.8</td>
<td>122</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh$_2$C$_6$H$<em>4$H$</em>{13}$)$_2$] (31)$^b$</td>
<td>30.0</td>
<td>127</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh(C$_6$H$<em>4$H$</em>{13}$)$_2$)] (32)</td>
<td>29.9</td>
<td>129</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(P(C$_6$H$<em>4$H$</em>{13}$)$_2$)] (33)</td>
<td>30.0</td>
<td>131</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh$_2$C$_6$H$<em>4$H$</em>{13}$)$_2$] (34)$^b$</td>
<td>29.7</td>
<td>128</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh(C$_6$H$<em>4$H$</em>{13}$)$_2$)] (35)</td>
<td>29.9</td>
<td>129</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(P(C$_6$H$<em>4$H$</em>{13}$)$_2$)] (36)$^c$</td>
<td>31.8</td>
<td>132</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PPh$_3$)$_2$]$_d$</td>
<td>29.5</td>
<td>125</td>
</tr>
<tr>
<td>$trans$-[RhCl(CO)(PEt$_3$)$_2$]$^e$</td>
<td>23.6</td>
<td>117</td>
</tr>
</tbody>
</table>

$^a$ Spectra run in CDCl$_3$  $^b$ Spectrum run at 233 K  $^c$ Spectrum run in d$_6$ acetone  $^d$ Synthesised for comparative purposes  $^e$ From ref (53)

strengthened, leading to larger $^1J_{RHP}$ coupling constants. This explanation is entirely plausible and certainly agrees with experimental observations made here. However, it is in direct contrast to the trend observed by Pringle and Cobley$^{19}$ in the complexes $cis$-[PtCl$_2$L$_2$] (see Section 3.2.5), where increased phosphine electronegativity leads to a decrease in the magnitude of $^1J_{RHP}$. These observations support the suggestion that there is a difference in the nature of the metal-phosphorus bonds in $cis$- and $trans$-bisphosphine, square-planar, d$^8$ complexes (see Section 3.2.5). Phosphorus to metal $\sigma$-bonding appears to be more dominant in mutually-$cis$ metal-phosphorus bonds, whereas, in mutually-$trans$ metal-phosphorus bonds, it is metal to phosphorus $\pi$-bonding which is more important. As with the compounds, [PtCl$_2$L$_2$], it is difficult to rationalise this behaviour and it is a further example of how the influence of the trans ligand on metal-ligand bonding is not yet fully understood.$^{35(36)(56)(80)}$
3.4.7 Discussion of Carbonyl Stretching Frequencies in the [RhCl(CO)L₂] Complexes (28-36)

The bonding of the carbon-monoxide unit to metal centres (see Fig. 3.22) is such that the stretching frequency, $\nu$ (C=O), is sensitive to variations in electron-density on the metal centre and, consequently, to the electronic properties of other ligands which are bonded to the metal. The $\pi$-component of the bond consists of electron-density which is donated from the metal d-orbitals into $\pi^*$-orbitals on the C=O unit. Since the latter are anti-bonding orbitals, the strength of the C=O bond decreases with increasing metal-phosphorus $\pi$-bonding and vice-versa.

Fig. 3.22 Metal-carbonyl bonding in transition metal complexes

Carbon to metal $\sigma$-bonding

Metal to carbon $\pi$-bonding

Table 3.5 shows the carbonyl stretching frequencies found for complexes (28-36). It is evident from the data in Table 3.5 that, as the number of perfluorinated chains on the phosphine increases, so the C=O bond strength increases and $\nu$ (C=O) increases. Increasing C=O bond strength with decreasing electron-density on the phosphorus is very much in agreement with metal-carbonyl bonding theory, and has been observed previously. The increase in $\nu$ (C=O) is not uniform. The introduction of the
Table 3.5 Carbonyl stretching frequencies for complexes (28-36)

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(C=O) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (28)</td>
<td>1981</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(PPh₃)₂]b</td>
<td>1965</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(P{C₆H₄-p-C₆F₁₃})₃]c</td>
<td>1953</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(P{C₆H₄-p-C₆F₁₃})₂]d</td>
<td>1990</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(C=O) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (29)</td>
<td>1983</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(P{C₆H₄-p-C₆F₁₃})₂] (30)</td>
<td>1992</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄-p-C₆F₁₃)₂] (31)</td>
<td>1982</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄-p-C₆F₁₃)₂] (32)</td>
<td>1983</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(P{C₆H₄-m-C₆F₁₃})₂] (33)</td>
<td>1993</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄-m-C₆F₁₃)₂] (34)</td>
<td>1980</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(PPh₂C₂H₄-m-C₆F₁₃)₂] (35)</td>
<td>1984</td>
</tr>
<tr>
<td>trans-[RhCl(CO)(P{C₆H₄-m-C₆F₁₃})₂] (36)</td>
<td>1992</td>
</tr>
</tbody>
</table>

a Spectra run in nujol  
b From ref (45)  
c From ref (57)  
d Spectrum run in CH₂Cl₂ solution

first fluororous tail produces a large increase (15-20 cm⁻¹), the second a very small increase (1-4 cm⁻¹), and the third, an increase of intermediate magnitude (~10 cm⁻¹). The similarity between the data for complexes (31-33) and (34-36) suggests that the C₆F₁₃ units have a similar effect on the electron-density of the phosphorus, whether they are in the para- or the meta-position on the aryl ring. Comparison of the data for (33), (36) and trans-[RhCl(CO)L₂] where L is P(C₆H₄-p-CF₃)₃, suggests that the C₆F₁₃ units have a slightly greater electron-withdrawing effect on the phosphorus than that exerted by a para-CF₃ group.
3.5 Complexes of the Type [RhCp*Cl$_2$L]

Complexes of the type [RhCp*Cl$_2$L] are generally of considerable interest to co-ordination chemists. They are easily synthesised$^{(60)}$ by the reaction of the dimeric species [RhCp*Cl$_2$]$^{(61,62)}$ with a ligand L (phosphine, carbonyl, nitrogen donor, etc.) under mild conditions (see Scheme 3.23). The resulting rhodium (III) 'piano-stool' complexes are usually air-stable, easy to handle and, often, crystalline. The $^{103}$Rh and the Cp* protons both provide useful NMR 'handles', and the generally good solubility of these complexes in common organic solvents makes characterisation and purification fairly straightforward. Complexes of this type have been used as hydrogenation catalysts$^{(63)}$ and, also, in carbon-fluorine bond activation reactions.$^{(64)}$

3.5.1 Reactions of PPh$_2$(C$_2$H$_4$C$_6$F$_{13}$) (1), PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$ (2) and P(C$_2$H$_4$C$_6$F$_{13}$)$_3$ (3) with [RhCp*Cl$_2$]

Phosphines (1-3) were each allowed to react with [RhCp*Cl$_2$]$_2$ in ethanol for 1 hour. In the case of phosphines (1) and (2), the ethanol was refluxing, and the experiments were performed under a stream of N$_2$. In the case of (3), the reaction was performed anaerobically using Schlenk techniques. For this reason, the ethanol could not be refluxed and the reaction was undertaken at room temperature. Removal of the solvent in vacuo, gave the complexes, [RhCp*Cl$_2$(PPh$_2$C$_2$H$_4$C$_6$F$_{13}$)] (37),
[RhCp*Cl2(PPh(C2H4C6F13)2)] (38) and [RhCp*Cl2(P(C2H4C6F13)3)] (39), respectively as reddish orange powders (see Fig. 3.24). Washing the complexes with hexane was sufficient for purification of (37) and (38), whereas recrystallisation from dichloromethane and hexane was required to remove all of the impurity peaks from the ¹H, ¹⁹F and ³¹P NMR spectra of (39). All three complexes were found to be insoluble in perfluorinated solvents, and this confirmed the expectation that coordination of one phosphine containing perfluorinated chains is not sufficient to solubilise a metal centre and its surrounding ligands, even when the phosphine used has three fluorous tails. All three complexes were found to be stable in air.
3.5.2 Reactions of \( \text{PPh}_2(\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13}) \) (5), \( \text{PPh}(\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2 \) (6) and \( \text{P}(\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_3 \) (7) with \([\text{RhCp}^*\text{Cl}_2]\) 

The reactions of ligands (5-7) with \([\text{RhCp}^*\text{Cl}_2]\) were performed in refluxing ethanol under \( \text{N}_2 \), following the same procedure as that used for (1-3). The resulting complexes, \([\text{RhCp}^*\text{Cl}_2(\text{PPh}_2\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})]\) (40), \([\text{RhCp}^*\text{Cl}_2(\text{PPh}(\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_2)]\) (41) and \([\text{RhCp}^*\text{Cl}_2(\text{P}(\text{C}_6\text{H}_4\text{-p-C}_6\text{F}_{13})_3)]\) (42) (see Fig. 3.25), were all recrystallised from dichloromethane and hexane. All are air-stable reddish orange powders and none is soluble in perfluorinated solvents.

Fig. 3.25  [Rhodium pentamethylcyclopentadienyl dichloride (4-perfluorohexylphenyl) diphenyl phosphine] (40), [Rhodium pentamethylcyclopentadienyl dichloride bis(4-perfluorohexylphenyl) phenyl phosphine] (41) and [Rhodium pentamethylcyclopentadienyl dichloride tris(4-perfluorohexylphenyl) phosphine] (42)
3.5.3 Reactions of PPh$_2$(C$_6$H$_4$-m-C$_6$F$_{13}$) (8), PPh(C$_6$H$_4$-m-C$_6$F$_{13}$)$_2$ (9) and P(C$_6$H$_4$-m-C$_6$F$_{13}$)$_3$ (10) with [RhCp*Cl$_2$]

The reactions of ligands (8-10) with [RhCp*Cl$_2$]$_2$ were performed following the same procedure as that used for (5-7). The resulting reddish orange complexes, [RhCp*Cl$_2$(PPh$_2$(C$_6$H$_4$-m-C$_6$F$_{13}$))] (43), [RhCp*Cl$_2$(PPh(C$_6$H$_4$-m-C$_6$F$_{13}$)$_2$)] (44) and [RhCp*Cl$_2$(P(C$_6$H$_4$-m-C$_6$F$_{13}$)$_3$)] (45) (see Fig. 3.26), are all air-stable and none is soluble in perfluorinated solvents.

Fig. 3.26 [Rhodium pentamethylcyclopentadienyl dichloride (3-perfluorohexylphenyl) diphenyl phosphine] (43), [Rhodium pentamethylcyclopentadienyl dichloride bis(3-perfluorohexylphenyl) phenyl phosphine] (44) and [Rhodium pentamethylcyclopentadienyl dichloride tris(3-perfluorohexylphenyl) phosphine] (45)
3.5.4 Discussion of $^{31}$P NMR Data for the $[\text{RhCp}^*\text{Cl}_2\text{L}]$ Complexes (37-45)

Table 3.6  $^{31}$P NMR data for complexes (37-45)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{1}J_{\text{RhP}}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13})]$ (37)</td>
<td>144</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2[\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13}]_2)]$ (38)</td>
<td>146</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{P}[\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13}]_3)]$ (39)</td>
<td>147</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2\text{C}_6\text{H}_4-p-\text{C}<em>6\text{F}</em>{13})]$ (40)</td>
<td>146</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2[\text{C}_6\text{H}_4-p-\text{C}<em>6\text{F}</em>{13}]_2)]$ (41)</td>
<td>146</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{P}[\text{C}_6\text{H}_4-p-\text{C}<em>6\text{F}</em>{13}]_3)]$ (42)</td>
<td>147</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2\text{C}_6\text{H}_4-m-\text{C}<em>6\text{F}</em>{13})]$ (43)</td>
<td>144</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_2[\text{C}_6\text{H}_4-m-\text{C}<em>6\text{F}</em>{13}]_2)]$ (44)</td>
<td>147</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{P}[\text{C}_6\text{H}_4-m-\text{C}<em>6\text{F}</em>{13}]_3)]$ (45)</td>
<td>147</td>
</tr>
<tr>
<td>$[\text{RhCp}^*\text{Cl}_2(\text{PPh}_3)]^b$</td>
<td>144</td>
</tr>
</tbody>
</table>

*a  Spectra run in CDCl$_3$  
*b  Synthesised for comparative purposes

Table 3.6 shows that, there is no significant change in the coupling constant $^{1}J_{\text{RhP}}$ with variation in L. This suggests that the bonding in this type of complex is not as sensitive to changes in the electronic properties of the phosphine as in complexes of the type $\text{trans-[RhCl(CO)L}_2\text{]}$ (see Section 3.4.6). It is difficult to be sure of the cause of this decrease in variation of the coupling constants $^{1}J_{\text{RhP}}$, since there are two key differences between the two classes of complex. Firstly, in the complexes, $\text{trans-[RhCl(CO)L}_2\text{]}$, the rhodium is formally in the +1 oxidation state, whilst, in the complexes $[\text{RhCp}^*\text{Cl}_2\text{L}]$, it is formally in the +3 oxidation state. Secondly, the geometry of the two complexes is different, (square-planar for $\text{trans-[RhCl(CO)L}_2\text{]}$, pseudo-octahedral for $[\text{RhCp}^*\text{Cl}_2\text{L}]$) and this means that the relative energies of the molecular orbitals involved in the bonding are different.** The extent of these influences is difficult to quantify and, consequently, no definitive conclusions can be
drawn about the lack of variation of $^1J_{RP}$ with variation of the phosphine in these complexes.

3.6 Complexes of the Type [RhClL₃]

The complex [RhCl(PPh₃)₃] ('Wilkinson's Complex') was first synthesised by Wilkinson et al. in 1966. It was found to be an extremely useful complex in the field of homogeneous hydrogenation, exhibiting unusually high catalytic rates under relatively mild conditions. Since the publication of the original paper, the complex has been used extensively in a wide variety of laboratory-based, catalytic systems, and has been shown to be an active catalyst when the triphenylphosphine ligands are replaced by other tertiary phosphines. There is more than one preparatory route to Wilkinson's complex and its related analogues, however, probably the most convenient route is via the reaction of the free phosphine with the chloride-bridged, rhodium dimer [RhCl(𝐶₂𝐻₄)₂]₂ (see Scheme 3.27). The phosphines very quickly replace the ethylene ligands and break the chloride bridges. The reaction is fast, even at room temperature, and the free ethylene bubbles out of the solution, making purification simple. For these reasons, this route is ideal for the in situ preparation of catalytic species (see Section 4.2). The complex [RhCl(PPh₃)₃] is an air-stable solid, but when other phosphines are used, the resulting complexes are often unstable in air.

As with all rhodium-phosphine complexes, $^{31}$P NMR is a useful characterisation tool. These complexes give a very distinctive signal consisting of a doublet of doublets...
and a doublet of triplets, both of which normally fall within the region 0-60 ppm.\(^{(73)}\)
The doublet of triplets is produced by the resonance signal from the phosphine (a),
being split by the two equivalent, mutually-\textit{trans} phosphines (b), and also by the
rhodium (see Fig. 3.28).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.28}
\caption{Chemically equivalent phosphines in Wilkinson’s complex analogues}
\end{figure}

The doublet of doublets is produced by the resonance signal for the two equivalent
phosphines (b) being split by phosphine (a), and by the rhodium.

3.6.1 Reactions of \(\text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})\) (1), \(\text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\) (2) and \(\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\) (3) with \([\text{RhCl}(\text{C}_2\text{H}_4)_2]\)_2

Phosphine (1) was allowed to react with \([\text{RhCl}(\text{C}_2\text{H}_4)_2]\)_2 under anaerobic
conditions using dry, degassed dichloromethane as the solvent. The reaction was
performed at room temperature and the ethylene was released from the solution as
soon as the two reagents were brought together. After 1 hour, the dichloromethane
was removed \textit{in vacuo}, leaving a brown, oily solid. This solid was triturated in hexane
for 1 hour (under \(\text{N}_2\)) and then filtered to give a light-brown powder. At this point the
product was exposed to air whilst an NMR sample was prepared. The \(^{31}\text{P}\) NMR
spectrum showed the expected doublet of doublets and doublet of triplets (37 and 24
ppm respectively). The spectrum also showed a second signal consisting of another
doublet of doublets and another doublet of triplets. This second signal was shifted to
low frequency by around 15 ppm (25 and 10 ppm for the doublet of doublets and the
doublet of triplets respectively), and was of approximately equal intensity to the first,
expected signal (see Fig. 3.29a). The \(J_{\text{RhP}}\) and \(J_{\text{PP}}\) coupling constants for the second
signal were smaller than those for the first signal (see Table 3.7). The spectrum was run again after leaving the NMR tube open to the air for 2 hours. This time, only the second, lower frequency signal was visible, the original signal having disappeared completely (see Fig. 3.29b). The likely explanation for these unusual NMR spectra is that the Wilkinson's analogue (46) was, indeed, formed in the reaction, but this reacted further with O₂ to give the octahedral, Rh (III) complex [RhCl(O₂)L₃] (47), where L is PPh₂(C₂H₄C₆F₁₃) (see Fig. 3.30). The triphenylphosphine complex has been made previously by bubbling oxygen through a solution of [RhCl(PPh₃)₃] (Wilkinson's complex). The shift to higher frequency
in $\delta_p$ and the reduction in $^{1}J_{RhP}$ and $^{2}J_{PP}$ are characteristic of the increase in formal oxidation state of the metal from +1 to +3.$^{(74)}$

Scheme 3.30  Addition of dioxygen to Wilkinson's complex analogue

\[
\begin{align*}
\text{L} & = \text{tertiary phosphine} \\
\end{align*}
\]

Phosphines (2) and (3) were both allowed to react with $[\text{RhCl(C_2H_4)_2}]_2$ using anaerobic Schlenk techniques. Despite the precautions taken in the experimental procedure, the only products were sticky brown oils which, upon analysis, proved to be mostly phosphine oxide. It was apparent that, if $[\text{RhCl_L}_3]$ species were being produced, their decomposition was so fast that they could not be detected. In an effort to establish what was happening, the reactions were performed in an NMR tube under anaerobic conditions. This permitted the $^{31}$P NMR spectrum to be taken immediately. In the case of phosphine (3), this showed the expected doublet of doublets and doublet of triplets, (see Table 3.7). However, after 2 hours, this signal had begun to be replaced by several new peaks, one of which was due to the phosphine oxide, while another doublet was tentatively assigned to the chloride bridged, dimeric species $[\text{L}_2\text{Rh(μ-Cl)}_2\text{RhL}_2]$ (48) (see Fig. 3.31). The analogous species in which $\text{L}$ is triphenylphosphine, has been noted before in solutions of $[\text{RhCl(PPh}_3)_3]^{(66,76,77)}$, and the values of $\delta_p$, $^{1}J_{RhP}$ and $^{2}J_{PP}$ for this complex are similar to those for the reaction mixture described above (see Table 3.7). In the case of phosphine (2), the $^{31}$P NMR spectrum showed no signals due to $[\text{RhCl_L}_3]$. A doublet of doublets and a doublet of triplets were visible, but were shifted to low frequency by around 10 ppm, and $^{1}J_{RhP}$ and $^{2}J_{PP}$ were smaller than expected (see Table 3.7). These signals were probably due to an octahedral, dioxygen adduct, similar to (47). Other impurity peaks were also
Chloride bridged, dimeric rhodium species formed upon decomposition of Wilkinson complex analogues

![Fig. 3.31](image)

L = tertiary phosphine

visible, including peaks due to phosphine oxide and to the dimeric species described above.

During the course of this work, the complex, [RhCl(P{C₂H₄C₆F₁₃})₃], was synthesised and isolated by Horváth et al. (⁹⁸) and was successfully used as an F.B.S. hydroboration catalyst. This demonstrates complexes of this type can be successfully synthesised and also suggests that, under the correct conditions, they are stable. Unfortunately, despite repeated attempts, this synthesis and isolation could not be achieved here.

### 3.6.2 Reactions of PPh₂(C₆H₄-p-C₆F₁₃) (5), PPh(C₆H₄-p-C₆F₁₃)₂ (6) and P(C₆H₄-p-C₆F₁₃)₃ (7) with [RhCl(C₂H₄)₂]

These reactions were performed under anaerobic conditions using Schlenk apparatus. However, as with phosphines (2) and (3), no product was successfully isolated. Again, the experiments were repeated in an NMR tube and, in the case of (5) and (7), spectra were obtained which exhibited the expected signals due to the Wilkinson’s analogue (see Table 3.7). After several hours, peaks due to phosphine oxide and other impurities, including a dimeric species analogous to (48), began to appear. These complexes were stable in solution for a considerably longer period than
those containing phosphines (2) and (3). In the case of phosphine (6), only signals due to phosphine oxide, and the dimeric species analogous to (48), were visible.

3.6.3 Reaction of \( \text{P(C}_6\text{H}_4\text{-m-C}_6\text{F}_{13})_3 \) (10) with \([\text{RhCl(C}_2\text{H}_4)_2]_2\)

As with phosphine (7), phosphine (10) reacted with \([\text{RhCl(C}_2\text{H}_4)_2]_2\) in an NMR tube to give the Wilkinson’s complex analogue, and this remained stable in solution for several hours (see Table 3.7).

3.6.4 Reactions of \( \text{P(C}_6\text{H}_4\text{-p-CF}_3)_3 \) and \( \text{P(C}_6\text{H}_4\text{-m-CF}_3)_3 \) with \([\text{RhCl(C}_2\text{H}_4)_2]_2\)

The phosphines \( \text{P(C}_6\text{H}_4\text{-p-CF}_3)_3 \) and \( \text{P(C}_6\text{H}_4\text{-m-CF}_3)_3 \) were allowed to react with \([\text{RhCl(C}_2\text{H}_4)_2]_2\) for comparative purposes. The reactions were performed in NMR tubes and the \( ^{31}\text{P} \) NMR spectra showed that both phosphines formed the expected Wilkinson’s complex analogue. These were stable in solution for significantly longer than those described above, with peaks due to the dimeric species analogous to (48), and the respective phosphine oxides, beginning to appear around 12 hours later (see Table 3.7).

3.6.5 Discussion of the Reactions of Phosphines (1-3), (5-7), (10), \( \text{P(C}_6\text{H}_4\text{-p-CF}_3)_3 \) and \( \text{P(C}_6\text{H}_4\text{-m-CF}_3)_3 \) with \([\text{RhCl(C}_2\text{H}_4)_2]_2\)

It is evident that Wilkinson’s analogues which contain phosphines with perfluorinated tails decompose in solution after a period of several hours. Decomposition appears to involve the formation of phosphine oxide and the dimeric species, \([\text{RhL}_2(\mu-\text{Cl})_2\text{RhL}_2]\), and, in some cases, evidence for the formation of \([\text{RhCl(O}_2\text{)}\text{L}_3]\) is also observed. It seems possible that the mechanism for decomposition is initiated by oxidative addition of \( \text{O}_2 \), which then reacts with one or two phosphines to form the phosphine oxide (see Scheme 3.32). As the phosphine is oxidised, the remaining rhodium fragments form bridged, dimeric species in order to
maintain their electron count. As a result, peaks due to phosphine oxide and the
dimeric species, grow with time, whilst peaks due to the Wilkinson’s analogue (and

Scheme 3.32 Possible decomposition mechanism for Wilkinson’s complex analogues

its dioxygen adduct) disappear. The rate of growth of the phosphine oxide peak for all
the phosphines containing fluororous tails, is greater during this decomposition process
than it is when the free phosphines are simply left in solution and exposed to air. This
suggests that the rhodium centre actually catalyses the oxidation of the phosphines,
and this fits in with the possible mechanism given above. The complexes containing
phosphines with three aryl groups \{(5-7, 10), P(C_6H_4-p-CF_3)3 and P(C_6H_4-m-CF_3)3\}
appear to be the more stable of the Wilkinson’s analogues. These remain stable in
solution for several hours when L is (5-7) or (10), and considerably longer when L is
P(C_6H_4-p-CF_3)3 or P(C_6H_4-m-CF_3)3. The complex [RhCl(PPh_3)3] is stable for a few
days in solution, but will react to give the octahedral dioxygen adduct if O_2 is bubbled
through the solution for 2 minutes.\(^{75}\) It can be seen, therefore, that there is a
significant increase in the rate of decomposition when fluororous chains are introduced
into the molecule.

The most puzzling aspect of the decomposition of these complexes, is that
phosphine oxides were produced even though the reactions were performed under
anaerobic conditions. A possible explanation is that minute traces of oxygen which are
inevitably present, react very quickly with the phosphines due to the auto-catalytic
behaviour which the complexes appear to exhibit. A more acceptable explanation is
based on the fact that perfluorinated solvents have a very high affinity for molecular
oxygen \(^{78}\)(\(^{79}\) see Section 1.5). It seemed likely, therefore, that the long,
perfluorinated chains on the phosphines might also exhibit an affinity for molecular
oxygen, and that oxygen which was 'dissolved' in the fluorous tails, might be responsible for the decomposition reactions. This idea is reinforced by the fact that the Wilkinson's analogues where L was P(C₆H₄-p-CF₃)_3 or P(C₆H₄-m-CF₃)_3 appeared to remain stable in solution for longer than those where L contained a C₆F₁₃ tail. It is very difficult to remove all of the dissolved oxygen from a perfluorinated solvent, such as PP₃, although several freeze, pump, thaw cycles are usually adequate to prevent oxidations. With this in mind, the reaction of P(C₆H₄-p-C₆F₁₃)_3 (7) and [RhCl(C₂H₄)₂]₂ was repeated. A solution of (7) in PP₃ was made up in a Schlenk flask, and this solution was given three freeze, pump, thaw cycles, to remove any oxygen which may have been present in the fluorous tails. A solution of [RhCl₂(C₂H₄)₂]₂ in CH₂Cl₂ was also made up and given one freeze, pump, thaw cycle. The two solutions were then combined using a syringe, and the resulting biphasic mixture was subjected to one, final freeze, pump, thaw cycle. The mixture was then stirred for several minutes, during which time the yellow colour (due to the rhodium) was transferred into the lower, fluorous phase. A small sample of this fluorous layer was carefully removed and sealed under nitrogen in an NMR tube (4 mm). The tube was inserted into a D₂O 'sleeve' (5 mm NMR tube containing D₂O) and a ³¹P NMR spectrum taken. As expected, the doublet of doublets and the doublet of triplets due to the Wilkinson's analogue were clearly visible, and a large singlet due to free phosphine was also present (an excess of phosphine was used). ³¹P NMR spectra of this sample were taken at regular time intervals over the next few days, and no significant growth of new peaks was observed for 48 hrs. After this time, a peak due to the phosphine oxide began very slowly to emerge. These observations certainly suggest that O₂ gas 'trapped' in the fluorous chains may well have been responsible for the decomposition of the Wilkinson's complex analogues, since when the ligand was thoroughly degassed before use, the lifetime of the complex in solution was dramatically increased. Further evidence for this postulation was found when a seemingly related effect was observed during the reaction of Vaska's complex analogues containing perfluorinated tails with O₂, and this is discussed in detail in Section 3.7.5.

Complexes of the type [RhClL₃] generated in situ, have been used to perform the fluorous biphasic hydrogenation of styrene and this is described in Section 4.2.
3.6.6 Discussion of $^{31}$P NMR Data for Complexes of the Type $[\text{RhClL}_3]$ and Their Decomposition Products

Table 3.7 $^{31}$P NMR data for Wilkinson’s complex analogues and related species

<table>
<thead>
<tr>
<th>L</th>
<th>$[\text{RhClL}_3]$</th>
<th>$[\text{RhCl(O}_2)_3]$</th>
<th>$[\text{L}_2\text{Rh(μ-Cl)}_2\text{RhL}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PPh}_2(\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13})$ (1)</td>
<td>$dd(825.2^1 J_{\text{RhPh}} 138 \text{ Hz}$  (2^1 J_{\text{RhPh}} 40 \text{ Hz})$  (dt(836.7^1 J_{\text{RhPa}} 187 \text{ Hz}$  (2^1 J_{\text{RhPa}} 40 \text{ Hz})$</td>
<td>$dd(69.6^1 J_{\text{RhPa}} 97 \text{ Hz}$  (2^1 J_{\text{RhPa}} 25 \text{ Hz})$  (dt(825.3^1 J_{\text{RhPa}} 152 \text{ Hz}$  (2^1 J_{\text{RhPa}} 25 \text{ Hz})$</td>
<td>Not observed</td>
</tr>
<tr>
<td>$\text{PPh}(\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13})_2$ (2)</td>
<td>Not observed</td>
<td>$dd(69.5^1 J_{\text{RhPa}} 95 \text{ Hz}$  (2^1 J_{\text{RhPa}} 28 \text{ Hz})$  (dt(820.2^1 J_{\text{RhPa}} 152 \text{ Hz}$  (2^1 J_{\text{RhPa}} 28 \text{ Hz})$</td>
<td>$d(833.3^1 J_{\text{RhPa}} 194 \text{ Hz})$</td>
</tr>
<tr>
<td>$\text{P}(\text{C}_2\text{H}_4\text{C}<em>6\text{F}</em>{13})_3$ (3)</td>
<td>$dd(814.0^1 J_{\text{RhPa}} 135 \text{ Hz}$  (2^1 J_{\text{RhPa}} 40 \text{ Hz})$  (dt(827.5^1 J_{\text{RhPa}} 184 \text{ Hz}$  (2^1 J_{\text{RhPa}} 40 \text{ Hz})$</td>
<td>$d(834.3^1 J_{\text{RhPa}} 193 \text{ Hz})$</td>
<td>Not observed</td>
</tr>
<tr>
<td>$\text{PPh}_2(\text{C}_2\text{H}_4\text{p-C}<em>6\text{F}</em>{13})$ (5)</td>
<td>$dd(830.9^1 J_{\text{RhPa}} 143 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$  (dt(847.8^1 J_{\text{RhPa}} 191 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$</td>
<td>Not observed</td>
<td>Not observed</td>
</tr>
<tr>
<td>$\text{PPh}(\text{C}_2\text{H}_4\text{p-C}<em>6\text{F}</em>{13})_2$ (6)</td>
<td>Not observed</td>
<td>Not observed</td>
<td>$d(850.0^1 J_{\text{RhPa}} 193 \text{ Hz})$</td>
</tr>
<tr>
<td>$\text{P}(\text{C}_6\text{H}_4\text{p-C}<em>6\text{F}</em>{13})_3$ (7)</td>
<td>$dd(831.7^1 J_{\text{RhPa}} 144 \text{ Hz}$  (2^1 J_{\text{RhPa}} 37 \text{ Hz})$  (dt(848.0^1 J_{\text{RhPa}} 190 \text{ Hz}$  (2^1 J_{\text{RhPa}} 37 \text{ Hz})$</td>
<td>Not observed</td>
<td>$d(852.4^1 J_{\text{RhPa}} 195 \text{ Hz})$</td>
</tr>
<tr>
<td>$\text{P}(\text{C}_6\text{H}_4\text{m-C}<em>6\text{F}</em>{13})_3$ (10)</td>
<td>$dd(837.5^1 J_{\text{RhPa}} 142 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$  (dt(850.3^1 J_{\text{RhPa}} 189 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$</td>
<td>Not observed</td>
<td>Not observed</td>
</tr>
<tr>
<td>$\text{P}(\text{C}_6\text{H}_4\text{p-CF}_3)_3$</td>
<td>$dd(833.0^1 J_{\text{RhPa}} 143 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$  (dt(849.0^1 J_{\text{RhPa}} 189 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$</td>
<td>Not observed</td>
<td>$d(852.3^1 J_{\text{RhPa}} 194 \text{ Hz})$</td>
</tr>
<tr>
<td>$\text{P}(\text{C}_6\text{H}_4\text{m-CF}_3)_3$</td>
<td>$dd(837.3^1 J_{\text{RhPa}} 142 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$  (dt(850.5^1 J_{\text{RhPa}} 188 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$</td>
<td>Not observed</td>
<td>$d(854.3^1 J_{\text{RhPa}} 195 \text{ Hz})$</td>
</tr>
<tr>
<td>$\text{PPh}_3$</td>
<td>$dd(830.3^1 J_{\text{RhPa}} 143 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$  (dt(847.3^1 J_{\text{RhPa}} 188 \text{ Hz}$  (2^1 J_{\text{RhPa}} 38 \text{ Hz})$</td>
<td>Not observed</td>
<td>$d(851.9^1 J_{\text{RhPa}} 193 \text{ Hz})$</td>
</tr>
</tbody>
</table>

\(a\) Spectra run in CDCl$_3$  \(b\) Synthesised for comparative purposes  \(c\) Spectrum run in PP3 with D$_2$O sleeve  \(d\) From ref (77)
It is clear from the data in Table 3.7 that there is no significant variation of \( J_{\text{RhP}} \) or \( J_{\text{PP}} \) in the complexes where the phosphines contain three aryl rings, even when three fluorous tails are present (phosphines (7) and (10)). There is a slight decrease in the magnitude of the \( J_{\text{RhP}} \) coupling constants when phosphines containing \( \text{C}_2\text{H}_4\text{C}_6\text{F}_{13} \) units are used, (phosphines (1-3)) however, this effect is very small and is probably due to the change from aryl to alkyl groups on the phosphorus, rather than being directly associated with the presence of the \( \text{C}_6\text{F}_{13} \) units themselves. As earlier noted for the complexes \([\text{RhCp}^*\text{Cl}_2L]\) (see Section 3.5.4), the NMR spectral parameters are insensitive to electronic variations in the phosphine ligands. In every case, the mutually-trans phosphines show a smaller Rh-P coupling constant (\( J_{\text{RHP}} \)) than the phosphine trans to the chloride (\( J_{\text{RHP}} \)). This is a similar effect to that observed in the complexes \([\text{PtCl}_2\text{L}_2]\) (see Section 3.2.5), and can be rationalised by invoking the trans effect, since phosphines have a greater trans-effect than chlorides; that is to say that the bond trans to a metal-phosphorus bond is weakened to a greater extent than a bond trans to a metal-chloride bond.

3.7 Complexes of the Type trans-[IrCl(CO)L₂]

Complexes of the type, trans-[IrCl(CO)L₂] (Vaska's complex analogues), are very useful tools with which to examine the electronic effects of a ligand L upon the electronic profile and reactivity of the iridium metal centre. What makes these complexes particularly useful is, firstly, they tend to undergo oxidative addition.

Scheme 3.33 Oxidative addition to Vaska's complex analogues
(see Scheme 3.33) at a rate which is conveniently measured\textsuperscript{(82)(84)} and, secondly, many
different oxidative addition reactions have been examined in detail, using different
ligands and different halides on the iridium centre. There is, therefore, an abundance
of data in the literature with which any rate studies can be quantitatively compared.\textsuperscript{(83)}
There are several synthetic routes to Vaska's complex analogues, most of which
involve the reduction of an iridium (III) or iridium (IV) precursor.\textsuperscript{(85)(86)(87)} Probably
the most convenient synthetic pathway, however, is via the iridium (I), dimeric,
starting material, \([\text{IrCl(cod)}]_2\), which will normally react with a tertiary phosphine and
carbon monoxide at room temperature to give the desired complex in high yield\textsuperscript{(88)} (see
Scheme 3.34).

Scheme 3.34 Preparation of complexes of the type \(\text{trans-}[\text{IrCl(CO)L}_2]\)

\[\text{trans-}[\text{IrCl(CO)L}_2]\]

\(\text{31P NMR spectroscopy is not as useful a characterisation technique for this}

class of complex as it is for the analogous rhodium complexes, since iridium is not spin
active, and so, no metal-phosphorus coupling is observed. IR spectroscopy, however,
can be used to look at the stretching frequency of the carbonyl unit and, as with the
complexes \(\text{trans-}[\text{RhCl(CO)L}_2]\) (see Section 3.4), this is a very useful way of
investigating the electronic properties of the metal centre and, hence, of the ligands.
Rates of oxidative addition to the metal centre can also be conveniently studied using
IR spectroscopy, since the carbonyl stretching frequency increases by around 35 cm\(^{-1}\)
on oxidation of the iridium (I) to iridium (III).\textsuperscript{(82)} This means that the rate of oxidation
can be directly monitored via the growth rate of the Ir(III) \(v(\text{C=O})\) peak.
3.7.1 Reactions of PPh$_2$(C$_2$H$_4$C$_6$F$_{13}$) (1), PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$ (2) and P(C$_2$H$_4$C$_6$F$_{13}$)$_3$ (3) with [IrCl(cod)]$_2$

The reactions of the phosphines (1-3) with [IrCl(cod)]$_2$ were each carried out using anaerobic Schlenk techniques. The relevant phosphate and the iridium starting material were dissolved in dry, degassed THF in a Schlenk flask, under nitrogen. The nitrogen was then replaced with one atmosphere pressure of carbon monoxide, and the mixture stirred vigorously for 30 minutes. In all cases, the colour of the solution changed, within a few minutes, from the reddish orange colour imparted by the [IrCl(cod)]$_2$ starting material, to the bright greenish-yellow colour which is characteristic of Vaska’s complex analogues. This colour change is a useful indication of reaction progress and, as such, adds to the appeal of this particular

Fig. 3.35  trans-[Iridium carbonyl chloride bis(1H,1H,2H,2H-perfluorooctyl diphenyl phosphate)] (49), trans-[Iridium carbonyl chloride bis(bis{1H,1H,2H,2H-perfluorooctyl} phenyl phosphate)] (50) and trans-[Iridium carbonyl chloride bis(tris{1H,1H,2H,2H-perfluorooctyl} phosphate)] (51)

\[
\text{Cl} \quad \text{PPh}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}) \quad \text{Cl} \quad \text{PPh}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2 \\
(\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4)_2\text{P} \quad \text{CO} \quad (\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4)_2\text{PhP} \quad \text{CO}
\]

(49) \hspace{2cm} (50)

\[
\text{Cl} \quad \text{P(C}_2\text{H}_4\text{C}_6\text{F}_{13})_3 \\
(\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4)_3\text{P} \quad \text{CO}
\]

(51)
synthetic route. The resulting complexes _trans-_[IrCl(CO)(PPh₂C₆H₄C₆F₁₃)]₂ (49), _trans-_[IrCl(CO)(PPh{C₆H₄C₆F₁₃})₂] (50) and _trans-_[IrCl(CO)(P{C₆H₄C₆F₁₃})₃] (51) (see Fig. 3.35) were all isolated as bright greenish yellow powders, after washing with hexane.

Complexes (49) and (50) reacted slowly with atmospheric oxygen to give the iridium (III) dioxygen adduct (see Scheme 3.36), and, for this reason, they were stored in an inert atmosphere. Complex (51) was found to be preferentially soluble in fluorous solvents, and inert to reaction with atmospheric oxygen. The air-stability of (51), relative to that of (49) and (50), is discussed in more detail in Section 3.7.4.

During the course of this work, the crystal structure of complex (51) was published by Horváth et al.⁹⁰ The structure is very similar to that of _trans-_[RhCl(CO)(P{C₆H₄C₆F₁₃})₃] (30) described here (see Section 3.4.2). Some kinetic data for _trans-_[IrCl(CO)(P{C₆H₄C₆F₁₃})₃] and other, related complexes were also reported, and these are discussed in Sections 1.3.3 and 3.7.5.

Scheme 3.36  Iridium (III) dioxygen adduct

3.7.2 Reactions of PPh₂(C₆H₄-p-C₆F₁₃) (5), PPh(C₆H₄-p-C₆F₁₃)₂ (6) and P(C₆H₄-p-C₆F₁₃)₃ (7) with [IrCl(cod)]₂

Phosphines (5-7) were allowed to react with [IrCl(cod)]₂ using a similar procedure to that used for (1-3). Again, the complexes, _trans-_[IrCl(CO)(PPh₆C₆H₄-p-C₆F₁₃)]₂ (52), _trans-_[IrCl(CO)(PPh{C₆H₄-p-C₆F₁₃})₂] (53) and _trans-_[IrCl(CO)(P{C₆H₄-p-C₆F₁₃})₃] (54) (see Fig. 3.37), were isolated as greenish-yellow powders, after washing with hexane. Complexes (52) and (53) were found to be slightly air sensitive, and were stored in an inert atmosphere to prevent formation of
the iridium (III) oxygen adduct described above. Complex (54) was found to be stable in air and preferentially soluble in perfluorinated solvents.

Fig. 3.37  
trans-[Iridium carbonyl chloride bis(4-perfluorohexylphenyl diphenyl phosphine)] (52), trans-[Iridium carbonyl chloride bis(4-perfluorohexylphenyl) phenyl phosphine)] (53) and trans-[Iridium carbonyl chloride bis(tris{4-perfluorohexylphenyl} phosphine)] (54)

3.7.3 Discussion of IR Spectroscopy Data for the [IrCl(CO)L2] Complexes (49-54)

The metal-carbonyl bond in the family of complexes, trans-[IrCl(CO)L2], is thought to be very similar to that in the complexes, trans-[RhCl(CO)L2] (see Section 3.4.7). Thus, it would be expected that the carbonyl stretching frequencies in the two classes of complex would vary with varying ligand in a similar manner, and, indeed, this is what is observed experimentally (see Table 3.8). Increasing the number of perfluorinated chains on the phosphine leads to a decrease in the electron-density on the iridium centre and a resultant increase in the carbonyl stretching frequency. This trend has been observed previously, and agrees with recent work by Horváth et al. who have also looked at the influence of fluorous tails on Vaska's complex.
Table 3.8  Carbonyl stretching frequencies for complexes (49-54)

<table>
<thead>
<tr>
<th>Complex</th>
<th>v(C=O) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[IrCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (49)</td>
<td>1954</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (50)</td>
<td>1973</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P{C₂H₄C₆F₁₃}₃)₂] (51)</td>
<td>1977</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPh₂C₆H₄-p-C₆F₁₃)₂] (52)</td>
<td>1972</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P{C₂H₄-p-C₆F₁₃}₃)₂] (53)</td>
<td>1979</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P{C₆H₄-p-CF₃}₃)₂] (54)</td>
<td>1953</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P{C₆H₄-p-CF₃}₃)₂] b</td>
<td>1975</td>
</tr>
</tbody>
</table>

a  Spectra run in CHCl₃  b  Synthesised for comparative purposes

analogues. As was noted with the complexes, trans-[RhCl(CO)L₂], the para-C₆F₁₃ chain (on phosphines (5-7)) has a marginally greater effect on v (C=O) than a para-CF₃ group. Comparison of v (C=O) in complexes containing phosphines (1-3) with those containing phosphines (5-7), shows that the electronic influence on the carbonyl group is much the same in both cases, where equal numbers of chains are present. This suggests that, in this type of complex, the C₂H₄ group and the C₆H₄ group shield the metal from the electron-withdrawing effect of the fluorous tails, to a similar degree. This is not, however, in direct agreement with the results of oxidative addition studies which were performed on these complexes (see Section 3.7.4.), and this suggests that the electronic effect of the phosphines on the metal centre, is detected to a differing degree, depending on which indirect observational technique is employed. This is not a major problem, since, by using a variety of analytical techniques, it should be possible to build an accurate picture of chemical behaviour. However, it does serve to highlight the dangers of relying too heavily on one type of analytical data.
3.7.4 Oxidative Addition Studies on Vaska's Complex Analogues

The rate of uptake of dioxygen of Vaska's complex analogues has been used previously as a measure of the electron-density at the metal centre, and it has been shown that the greater the electron-density, the greater the rate of oxidative addition. In order to further examine the electron-withdrawing influence of the phosphines (1-3) and (5-7), it was decided to measure the rates of dioxygen addition of the complexes (49-54). These were each dissolved in chloroform which had been saturated with oxygen, and oxygen was continually bubbled through the solution throughout the experiments. Samples were taken at regular intervals and the areas of the IR peaks in the 1956-80 cm\(^{-1}\) region (arising from \(\nu (C=O)\) in the iridium (I) complex), were compared to that of the peaks in the 2015-30 cm\(^{-1}\) region (arising from \(\nu (C\equiv O)\) in the iridium (III) complex). The relative areas of the peaks was calculated and this allowed the rate of oxidative addition to be deduced. The reaction of the complexes trans-[IrCl(CO)L_2], where L is a tertiary phosphine, with dioxygen (see Scheme 3.38) has been shown to be second order overall, having first order dependence on each of the two reactants. The rate law, therefore, is of the form:

\[
\text{rate} = k_2 [\text{IrCl(CO)L}_2][O_2]
\]

where \(k_2\) is the second order rate constant.

As described above, oxygen was continually bubbled through the solutions in order to maintain a large excess throughout the reactions. It would be expected, therefore, that the oxidative addition reactions would show pseudo-first order kinetics, with respect to the iridium complex, and, indeed, this proved to be the case. A plot of \(\ln(a/(a-x))\) vs. time (\(a = \text{initial conc. of } [\text{IrCl(CO)L}_2], x = \text{no. of mols of } [\text{IrCl(CO)L}_2] \text{ which have reacted at time, t}\) gave a straight line in all cases. The slope of this line for each individual reaction, is equal to \(k_{\text{obs}}\), the observed rate constant under the given conditions. This is not a particularly useful value, as it varies considerably with reaction conditions. However, the slope of the graph can also be used to calculate the half-life of the reaction (time at which half of the trans-[IrCl(CO)L_2] has oxidised, or, \(t\) when \(a = x\)) and this is a more useful parameter which can be used to quantitatively compare the reaction rates. The results of the study are given in Table 3.9.
Scheme 3.38  Oxidative addition of dioxygen to Vaska's complex analogue

![Scheme 3.38](image)

Table 3.9  Half-lives for reactions of complexes (49-54) with dioxygen

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(C=O) of O₂ adduct (cm⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[IrCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (49)</td>
<td>2017</td>
<td>107</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (50)</td>
<td>2022</td>
<td>684</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P(C₂H₄C₆F₁₃)₃)₂] (51)</td>
<td>2024</td>
<td>&gt;2000⁵</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPhC₆H₄-p-C₆F₁₃)₂] (52)</td>
<td>2019</td>
<td>132</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPh(C₂H₄-p-C₆F₁₃)₂] (53)</td>
<td>2023</td>
<td>380</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P(C₂H₄-p-C₆F₁₃)₃)₂] (54)</td>
<td>2025</td>
<td>1395</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(PPh₃)₃] b</td>
<td>2015</td>
<td>62</td>
</tr>
<tr>
<td>trans-[IrCl(CO)(P(C₂H₄-p-CF₃)₃)₂] b</td>
<td>2022</td>
<td>980</td>
</tr>
</tbody>
</table>

b Synthesised for comparative purposes  c The solubility of this complex in chloroform is low and solid particles were seen in the solution, suggesting that not all of the complex was dissolved. For this reason, the calculated half-life is not as accurate as those given for the other complexes, although it is almost certainly greater than 2000 min, which is given as a conservative estimate.

As can be seen from the data in Table 3.9, half-life increases with increasing carbonyl stretching frequency. This correlation is not, however, entirely consistent, since the complexes containing phosphines (2) and (3) have longer half-lives than their carbonyl stretching frequencies might suggest (see Section 3.7.3). Assuming that there are no significant steric effects, this study suggests that the C₂H₄ spacer in phosphines (1-3), is not as effective at shielding the electronic influence of the fluorous tails from the
metal centre as the C₆H₄ group in phosphines (5-7). As expected, triphenylphosphine gives the fastest rate of dioxygen addition, and P(C₆H₄-p-CF₃)₃ gives a slightly shorter half-life than P(C₆H₄-p-C₆F₁₃)₃.

3.7.5 Attempted Calculation of Second Order Rate Constants k₂, for the Reaction of Vaska’s Complex Analogues with Dioxygen

As described above, the second order rate constant k₂, is a measure of rate at a given temperature, and, being independent of reagent concentration, is a useful parameter for the comparison of reaction rates. For a second order reaction, such as the reaction of [IrCl(CO)L₂] with dioxygen, the rate equation can be written as:

\[
\text{rate} = k_2 [\text{IrCl(CO)L}_2][O_2] \quad \text{eq. 1}
\]

If the concentration of one of the reactants is in large excess, (10 mol equivalents or greater is generally the accepted value) then the concentration of this reactant will effectively remain constant throughout the experiment. This will lead to pseudo-first order kinetics being observed (see Section 3.7.4), and a value of kₗₒₗₚ at a specific (large) concentration of the reactant which is in excess, can be calculated. This value can be inserted into the rate equation (eq. 1) thus:

\[
\text{rate} = k_{\text{obs}} [\text{IrCl(CO)L}_2] \quad \text{eq. 2}
\]

Rearranging eq. 1 and 2, it can be seen that:

\[
k_{\text{obs}} = k_2 [O_2] \quad \text{eq. 3}
\]

If a number of values of kₗₒₗₚ are obtained at different concentrations of O₂, then a plot of kₗₒₗₚ vs. [O₂] should give a straight line with a slope equal to the second order rate constant k₂. In this particular case, it was difficult, experimentally, to measure several different values of kₗₒₗₚ, since the concentration of oxygen must be varied by a known amount, and must always be kept at level which is at least 10 times greater than the concentration of the trans-[IrCl(CO)L₂]. The calculation of k₂ was, however, attempted for the complexes (49-54), using known amounts of two chloroform solutions saturated with N₂ and O₂ respectively, in order to control the concentration of the oxygen. The method was first tested using triphenylphosphine, and a value for k₂ of 0.019 mol⁻¹dm³s⁻¹ at 23 °C was calculated. This compares reasonably well with
the literature value of 0.05 moll\(^{-1}\)dm\(^3\)s\(^{-1}\) recorded at 25 °C,\(^{(91)}\) and so it was assumed that the method would give valid, useful results for the other phosphines. When the experiment was repeated using the complexes (49-54), however, no useful data could be obtained. The complexes did not show pseudo-first order kinetics as they had done when oxygen was continually bubbled through the reaction solution, and the overall rate of reaction was much slower than expected. Plots of ln\((a/(a-x))\) vs. time gave curved lines, on which the gradient decreased with time (see Fig. 3.39), and this suggests that the rate of reaction and, hence, \(k_{obs}\) was decreasing with time. This behaviour was not observed with triphenylphosphine. The reason for this progressive reduction in rate is not known, although it is a possibility that it is related to the oxygen affinity of the perfluorinated tails (see Section 3.6.5). It may be that molecules of oxygen in solution are 'trapped' in the fluorous tails and, as a result, are unable to react with the iridium centre. As the reaction progresses, more oxygen is

![Graph of ln\((a/(a-x))\) vs. time for the reactions of (52) and Vaskas complex with O\(_2\)](image)

'\text{trapped}' and the rate of reaction decreases accordingly. This type of behaviour was not observed when oxygen was continuously bubbled through the solution, since any
oxygen which was ‘trapped’ would be immediately replaced. The complexes containing three tails showed a more marked decrease in rate than those containing one or two chains, and this fact supports the above hypothesis. This effect meant that values for $k_2$ could not be calculated for these complexes.

Oxidation studies on Vaskas complex analogues containing perfluorinated chains have also been performed by Horváth et al. The results of these studies are, qualitatively, similar to the work described here, although no direct comparisons can be made, as the experimental techniques used are quite different. An interesting point in Horváth’s work, however, is that $\text{trans-}[\text{IrCl(CO)L}_2]$ where $L$ is (3), reacts with oxygen more quickly in THF than in $\text{CF}_3\text{C}_6\text{F}_{11}$, despite the fact that the solubility of oxygen is considerably higher in the latter, perfluorinated solvent. It is possible that the reason for this is that the oxygen is held firmly in solution by the perfluorinated solvent, hence, it is not available for reaction with the iridium(I) centre to any great extent. This tallies with the observations described here concerning the affinity of perfluorinated moieties towards oxygen.

3.8 Conclusions from Co-ordination Chemistry

It can be concluded, from the work described in this chapter that the chemical behaviour and reactivity of the ligands (1-3) and (5-10) is, broadly speaking, similar to that of more established, protio phosphines. It is possible, in most cases, to synthesise ‘fluorous’ analogues of known complexes, although only in certain cases are these analogues soluble in fluorous media and, hence, of potential use in F.B.S. catalysis. It is also evident that the inclusion of perfluorinated tails in the phosphines has an effect on the chemical and physical properties of complexes into which they are incorporated. These effects can be grouped into three general areas; electronic effects, steric effects and physical effects, and each of these is discussed below.

(i) Electronic effects: The electronic influence of the perfluorinated chains is evident in the NMR and IR spectroscopy data throughout this chapter. Although, in some cases, large effects are not apparent (for example, with the complexes $[\text{RhCp*Cl}_3L]$), on the whole there is a noticeable change in electronic environment of...
both phosphorus and metal centre, relative to the protio analogues of the complexes described. This change is generally manifested as an apparent reduction in electron-density on the metal centre and in the surrounding ligand sphere. The degree of change is governed by the number of fluorous chains present in the molecule and, as would be expected, those complexes which are fluorous soluble (and so have potential for use in F.B.S catalysis) generally experience the largest change in electronic character due to the necessarily high number of chains incorporated into their structure.

(ii) Steric effects: Unsurprisingly, the fluorous tails exert steric influence on many of the complexes into which they are incorporated. The steric bulk of the phosphines does not appear to cause any major problems in terms of actually preventing the formation of any complexes, but the geometry of certain complexes is affected (for example cis/trans-isomerisation of [PtCl₂L₂] complexes).

(iii) Physical effects: The incorporation of exceptionally heavy, fluorinated phosphines into metal complexes inevitably results in changes in their physical properties. The molar masses of the complexes are increased dramatically and, in some cases, the complexes become sticky and difficult to handle. The solubility of the complexes is also modified and this is essential for the F.B.S. concept, although this effect can result in characterisation and experimental difficulties. The affinity of the fluorous tails towards oxygen appears, in some cases, to introduce unexpected effects in some of the complexes (for example in the Wilkinson’s and Vaska’s complex analogues) and this is a property which is both potentially useful, in terms of catalytic oxidations, and harmful, in terms of catalyst/reagent decomposition.

The effects described above would be expected to have some influence on the catalytic potential of the complexes in terms of both chemical activity and practical procedure. A series of catalytic experiments was performed with the intention of investigating the extent of these effects, and these studies are described in Chapter 4.
References for Chapter 3


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Chapter 4

Fluorous Biphase Catalysis

4.1 Introduction

As previously described (see Section 1.3.3), using a fluorous biphasic system allows heterogeneous separation to be applied to homogeneous catalysis. Although several examples of fluorous biphasic catalysis have been reported, few are concerned with the use of truly homogeneous reaction conditions. Some of these reported reactions were conducted at high pressures, using autoclave reactors. Although visual access to these systems is not possible, it is believed that the solvent systems used are monophasic at the high pressures and temperatures employed during the reactions. The majority of F.B.S. experiments reported to date, however, have been performed under conditions in which the organic phase and the fluorous phase remain immiscible. This results in immobilisation of the catalyst in the fluorous phase and, hence, facilitates easy separation of reactants and products from catalysts. However, it is essentially no different to an aqueous/organic biphasic system and, in that sense, does not exploit the real advantages of the fluorous biphase technique.

The extensive co-ordination chemistry which has been carried out with ligands (1-3) and (5-10), has shown that their reactivity and general behaviour is not unlike that displayed by the more established protio phosphines, triphenylphosphine and triethylphosphine, although significant differences, namely in electronic profile, do exist. With this in mind, a series of catalytic experiments was attempted, in order to examine whether the phosphines (1-3) and (5-10) would continue to exhibit behaviour comparable to that of their protio analogues in a catalytic environment. In order to take full advantage of the benefits offered by the fluorous biphase system, the experiments (where possible) were performed under conditions such that the two layers were monophasic at the time of reaction. In addition to testing the ligands, the
catalytic runs also provided an opportunity to investigate the effect that the choice of solvents had on the catalytic process (in terms of rate, separation, etc) and, to this end, several different solvent systems were examined.

4.1.1 Preliminary Catalytic Studies

Many of the protio analogues of complexes whose synthesis is described in the previous chapter, have been used as catalysts. However, for the fluorous biphase concept to be fully exploited, it was necessary that any complexes used as F.B.S catalysts must be preferentially soluble in perfluorinated solvents. The complex, trans-[RhCl(CO)(P{C\textsubscript{2}H\textsubscript{4}C\textsubscript{6}F\textsubscript{13}}\textsubscript{3})\textsubscript{2}] (30) (see Fig. 4.1), fulfils this criterion and is also stable in air and easy to handle and, for these reasons, this complex was selected for use as a catalyst in some simple, preliminary experiments. The analogous complex to

![Fig. 4.1](trans-[RhCl(CO)(P{C\textsubscript{2}H\textsubscript{4}C\textsubscript{6}F\textsubscript{13}}\textsubscript{3})\textsubscript{2}] (30))

(30) where L is triphenylphosphine, is known to be an effective catalyst for several processes, including carboxylation and hydroformylation\textsuperscript{(11)}, although these processes require rather high temperatures and pressures\textsuperscript{(12)}. Since the aim of these experiments was, primarily, to examine the fluorous biphase as a catalytic medium, it was decided to use complex (30) to attempt to hydrogenate cyclohexene under mild conditions. This allowed the reactions to be performed in glass vessels and, hence, the solvent system could be observed throughout the experiments.

The first attempted catalytic reaction was performed in a partially open system (see Fig. 4.2) and hydrogen was bubbled through the solution. The solvent system
consisted of PP3, (perfluoro-1,3-dimethylcyclohexane) toluene and diethyl ether (and cyclohexene to be hydrogenated). This mixture resulted in a two layer system at room temperature, which became monophasic at around 50 °C. The top layer consisted, primarily, of toluene and cyclohexene, whilst the bottom layer (containing the dissolved catalyst) consisted of PP3. The ether was added in order to lower the temperature at which miscibility between the two phases occurred, as it is miscible with all the solvents used (see Section 4.2.4). At room temperature, ether is present in both layers. The reaction was heated and stirred for several hours. However, analysis by $^1$H NMR spectroscopy revealed that no reaction had occurred. Several experimental problems were identified and these included: (i) the continuous bubbling of the hydrogen through the solution resulted in solvent evaporation, and (ii) the temperature at which miscibility was achieved was higher than the boiling point of ether and, so, this ‘mixing agent’ was boiled off after a time.

This initial experience resulted in modification to a closed system and replacement of the ether ‘mixing agent’ with hexane, which is miscible with both organic and perfluoro- solvents, but which has a higher boiling point than ether (69 °C,
Also, the lack of activity of complex (30) prompted a change in the catalytic species used.

4.2 Development of an Experimental System for Performing the Hydrogenation of Styrene Using Complexes of the Type [RhClL₃]

It was decided to replace complex (30) with the Wilkinson’s complex analogue, [RhClL₃], where L is P(C₂H₄C₆F₁₃)₃ (3) (see Fig. 4.3). It is well known that complexes of this type are excellent hydrogenation catalysts and have been shown to be active under mild conditions (25 °C, 1 atm H₂). Although problems with oxidation had previously been observed with complexes of this type, (see Section 3.6) it was decided that, if adequate care was taken in their preparation, they were generally stable in solution for long enough to produce meaningful results. Styrene was used as the substrate in place of cyclohexene. This change was made, primarily, to make characterisation of any hydrogenated product easier, since, if cyclohexene were used, it would be difficult to distinguish both it and its hydrogenated product (cyclohexane) from the hexane ‘mixing agent’. The catalyst, [RhClL₃] where L is P(C₂H₄C₆F₁₃)₃ (3), was prepared by adding the chloride-bridged, dimeric, precursor [RhCl(C₂H₄)₂]₂ (see Section 3.6) to (3) in dichloromethane under scrupulously dry and anaerobic conditions. A stoichiometric amount of phosphine was used (3:1 P to Rh ratio) with a catalyst to styrene ratio of 1:94. This mixture was stirred for five minutes and dry, degassed PP₃ (5ml) was then added. The reddish brown colour quickly moved from the dichloromethane, into the PP₃ layer, and this was then carefully transferred, via a cannular, into a second Schlenk flask where it formed the fluorous layer of the catalytic
biphase. Toluene (2 ml), hexane (4 ml) and styrene (2 ml) (all dry and degassed) were then added to the flask, resulting in a biphasic system (see Fig. 4.4). The flask was then evacuated, attached to a hydrogenation apparatus.

Fig. 4.4 Biphasic solvent system used in catalysis

(see Fig. 4.5) and backfilled with hydrogen to a pressure of 1 atm. The mixture was stirred and heated to around 55 °C, using an oil bath, at which temperature, the two phases became miscible.

Fig. 4.5 Hydrogenation apparatus used for hydrogenation of styrene
After 2 hours, a small sample was taken and analysed using $^1$H NMR spectroscopy, however, no signals due to ethyl benzene were visible. The reaction was left over the weekend (70 hours) and $^1$H NMR analysis after this extended period revealed that around 90% of the styrene had been hydrogenated to ethyl benzene. Although the catalysis was actually successful, efficient separation was not achieved. Upon cooling to room temperature, it could be seen that the organic layer was slightly coloured and this indicated that some of the catalytic species had leached from the fluorous layer. This leaching was thought to be due to decomposition of the catalytic species. The hydrogenation apparatus employed a water reservoir to equalise and maintain the hydrogen pressure, and this undoubtedly allowed water vapour and dissolved oxygen to enter the system. As described previously, (see Section 3.6) $[\text{RhClL}_3]$ where $L$ is (3), is particularly sensitive to oxygen, and oxidation of the phosphine is often observed if any $O_2$ is present in the system. It is likely, therefore, that some of the phosphine (3), was oxidised to $O=\text{P(C}_2\text{H}_4\text{C}_6\text{F}_{13})_3$, thus rendering it incapable of co-ordinating to the rhodium centre, and, hence, allowing the metal to leach into the organic layer. To counter these problems, a dedicated metal apparatus, specifically designed for performing hydrogenation experiments, was built (see Fig. 4.6). This rig was scrupulously leak tested, and kept clean and dry at all times, and this allowed consistent, repeatable results to be obtained. It was decided that it would be advantageous to make the catalyst in situ, again, to reduce possible contamination as much as possible. A further problem with the original method was that the oil bath used to heat the catalytic mixture was very difficult to control accurately, and the temperature varied over a range of several degrees centigrade. In order to overcome
this, a band heater was designed and built with a temperature range of 0-200 °C, and an accuracy of ±1.5 °C (see Fig. 4.7).

Fig. 4.7 Thermostatic heater used to control temperature of catalytic system

This facilitated efficient, accurate heating, and did not interfere with the use of a magnetic stirrer. After implementing the modifications described above, the reaction procedure was as follows:

(i) a stirrer bead and the free phosphine were loaded into a Schlenk flask (under N₂ if necessary).

(ii) dry, degassed solvents and reagents (PP3, hexane, toluene, styrene, etc) were added via a syringe or cannular, under N₂.

(iii) the flask was attached to the hydrogenation line, evacuated and then backfilled with H₂ to 1 atm.

(iv) the flask was heated to the required temperature and stirred for 15 minutes.

(v) an aliquot of toluene solution containing [RhCl(C₂H₄)₂]₂ catalyst precursor was added.

(vi) after reaction, the mixture was cooled in ice and then samples (2 ml) were taken from each layer for GC analysis.

Each reaction was run for 1 hour, the majority of runs being 10-20% complete after this period. In order to check that this conversion was an accurate representation of
the overall rate, one of the reactions (where \( L = (3) \)) was repeated for 0.5 hrs, 1 hr and 2 hrs. This showed that the rate was uniform over this period, and a graph of \% conversion vs. time yielded a straight line (see Fig. 4.8). A 500:1 catalyst to styrene ratio was used, with a phosphine to rhodium ratio of 4:1 (rather than the 3:1, stoichiometric ratio used previously) in an effort to ensure that sufficient phosphine was present to hold the rhodium in the fluorous phase.

4.2.1 Effect of Variation of Phosphine on Catalysis

Having developed a reliable, repeatable, catalytic procedure, it was then possible to test a variety of phosphines under identical conditions in order to evaluate their usefulness in terms of rate of reaction and potential for product/catalyst separation. These initial comparative studies were all performed using an identical solvent system. This consisted of PP3 (10 ml), hexane (6 ml), toluene (2 ml) and styrene (reagent, 1.8 ml). Using these amounts it was found that at room temperature, a biphase existed, with PP3 (probably containing a small amount of dissolved hexane) forming the lower phase, and toluene, styrene and the majority of the hexane, forming the top phase (see Fig. 4.9). The two phases became miscible at about 60 °C, and

![Graph of % conversion vs. time for the hydrogenation of styrene](image-url)
the system was monophasic at the reaction temperature of 63.5 °C. Upon cooling, the phases separated in a matter of minutes, and, although some hexane remained in the PP3 (lower) layer, there appeared to be no significant leaching of catalyst between the phases when fluorous soluble phosphines were used. For comparative purposes, several protio phosphines were also tested under the conditions described, as well as various phosphines containing perfluorinated chains. Table 4.1 shows the results of the catalytic experiments performed. As can be seen from these results, there is generally a decrease in activity when phosphines containing perfluorinated chains are used. It should be noted that triphenylphosphine shows higher activity if the reaction is performed in toluene with no perfluorinated solvent present (see Table 4.3). The generally lower activity of the phosphines containing perfluorinated chains is probably due, in large part, to the electronic influence of the chains. As with most catalytic cycles the hydrogenation cycle\(^{14}\) (see Scheme 4.10) involves several steps, each of which includes the formation or dissociation of a bond at the rhodium centre. The electron density on the rhodium is, therefore, of great importance, since any change of electron density will result in a change in the ability of the rhodium to undergo bond formation or dissociation. Triphenylphosphine is known to be an effective ligand for this process,\(^{13,15}\) and this means that its electronic properties are such that each of the intermediate species are stabilised to just the right degree to ensure rapid continuation of the cycle. As described previously, (see Chapter 3) the effect of adding perfluorinated chains is to decrease the electron density on the phosphorus
Table 4.1  Catalytic rates for the hydrogenation of styrene using Wilkinson’s complex analogues containing various phosphines

<table>
<thead>
<tr>
<th>Run No.</th>
<th>L</th>
<th>Rate (mmoll⁻¹hr⁻¹)</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh₃</td>
<td>155</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>128</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>P(C₆H₄-m-C₆F₁₃)₃ (10)</td>
<td>117</td>
<td>yes</td>
</tr>
<tr>
<td>4</td>
<td>P(C₆H₄-p-CF₃)₃</td>
<td>139</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>P(C₆H₄-m-CF₃)₃</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>PPh₂Et</td>
<td>105</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>PE₃(C₆H₄-p-C₆F₁₃)₂ᵇ</td>
<td>62</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>PE₃</td>
<td>177</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>P(C₂H₄C₆F₁₃)₃ (3)</td>
<td>79</td>
<td>yes</td>
</tr>
<tr>
<td>10</td>
<td>Ph₂PCH₂CH₂PPh₂ᶜ</td>
<td>72</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>R₂PCH₂CH₂PR₂ᵇᶜ, R = C₆H₄-p-C₆F₁₃</td>
<td>66</td>
<td>—</td>
</tr>
</tbody>
</table>

ᵃ Each run was performed three times and the average rate was calculated. Rates ± 4 mmoll⁻¹hr⁻¹ ᵇ Synthesised by Dr Alison Stuart ᶜ Diphosphine-2:1 P:Rh ratio used

and, hence, on the metal centre. It seems likely that this would result in any oxidative addition steps in the cycle becoming slower, since the rhodium will be less stabilised in the +3 oxidation state relative to the +1 oxidation state (see Section 3.7.4). It is also likely that a reduction in the electron-density on the metal will lead to a corresponding reduction in electron-density on the hydride ligands. This means that nucleophilic attack by the hydride on the alkene (the rate determining step) would be expected to occur more slowly when fluorous chains are present on the phosphine. These effects are thought to be the probable cause of the observed reduction in activity.
This is in agreement with the previously reported observation that the substitution of an electron donating group (eg. OMe) in the para-position of the phenyl ring, causes an increase in catalytic rate in this cycle.\textsuperscript{16} Although this electronic effect is probably the major cause of the observed decrease in activity, it may be that steric effects also have an influence on the rate. Phosphine (7) is substituted in the para-position, and so the C\textsubscript{6}F\textsubscript{13} chain points directly away from the phosphorus and the metal centre. It is unlikely, therefore, to obstruct the approach, and subsequent co-ordination, of either the styrene or the hydride. In contrast, Phosphine (10) is substituted in the meta-
position and, so, the chains are more likely to become involved in steric interactions with both approaching molecules and/or other species which are bound to the metal. It seems likely that this would result in lowering of the rate to some degree and, indeed, phosphine (10) is less active than phosphine (7). This difference is unlikely to be caused by electronic differences, since earlier studies (see Chapter 3) suggest that the electronic profile of the two phosphines is very similar. A similar drop in rate is seen with P(C₆H₄-m-CF₃)₃ relative to P(C₆H₄-p-CF₃)₃.

Triethyl phosphine is surprisingly active in this system and this is thought to be due to solubility considerations. Straight-chain, non-aromatic hydrocarbons (e.g. hexane) are generally soluble in perfluorocarbon solvents. It would be expected, therefore, that the ethyl group would be more soluble in the monophasic toluene, hexane and PP3 mixture than the phenyl group. This is reflected in the observation that colouration due to the rhodium complex can be seen in both layers after cooling of the flask if triethylphosphine is used, but only in the top, organic layer when triphenylphosphine is used. This increased solubility means that the rhodium species is more firmly held in solution when triethylphosphine is the ligand. This results in the effective concentration of the catalytic species being increased, hence, the system is more active (see Section 4.2.4). The comparatively low activity shown by phosphine (3), despite its high solubility, is almost certainly due to the large electronic influence of the C₆F₁₃ tails which is shielded relatively ineffectively by the C₂H₄ spacer (see Chapter 3).

4.2.2 Product/Catalyst Separation

As can be seen in Table 4.1, total separation was achieved when phosphines (7), (10) and (3) were used. That is to say, upon completion of reaction, the organic phase was found to contain no rhodium by atomic absorption analysis (accuracy 9 mg L⁻¹). The volume of the fluorous layer was around 2 ml greater upon completion of the reaction than it was before the run was started and this was found to be due to hexane from the organic layer becoming dissolved in the PP3 during the monophasic period. This phenomenon did not prevent total retention of the catalyst in the fluorous
phase (see Section 4.2.5), although small amounts (< 5%) of styrene and ethyl benzene were 'transported' into the fluorous phase by the leached hexane. In order to double check that no catalytic activity was lost due to catalyst leaching, run 2 (using phosphine (7)) was repeated and, upon completion, the layers were carefully separated and a new organic layer was added (with slightly less hexane to keep the overall volume constant). This process was repeated twice and the recorded rates for the three runs were 133, 128 and 128 mmoll\(^{-1}\)hr\(^{-1}\) respectively. This confirmed that the rhodium catalyst remained in the fluorous phase, and these results demonstrate the high degree of separation which this technique can facilitate.

4.2.3 Effect of Variation of Solvent System on Catalysis

It can be seen in Scheme 4.10, that the solvent occupies a vacant co-ordination site in several of the intermediate species formed in the hydrogenation cycle. It has been shown previously\(^{(17)}\) that the catalytic rate is retarded if solvent co-ordination is impaired. The solvent is also important in terms of the solubilities of the catalyst and the reactants. The rate of olefin hydrogenation has been shown to be proportional to the concentrations of both the substrate and the rhodium,\(^{(15)}\) hence, the rate of reaction will drop if the catalyst and/or the styrene are only partially soluble in the solvent system used. It should be remembered that the reaction actually takes place in a monophasic mixture of two (or more) different solvents, at least one of which is perfluorinated. This complicates the situation because the solubilities of the catalyst and the reagents in this monophasic mixture will be different to their solubilities in the individual solvents. Obviously, the ideal situation is one where the catalyst is preferentially soluble in the fluorous phase, and the styrene and ethyl benzene are preferentially soluble in the organic phase in the biphasic state, and all of the species remain soluble in the mixture of solvents in the monophasic state. It can be seen therefore, that the choice of solvent system is of vital importance, and any change in solvent would be expected to produce a change in reaction rate, in accordance with the considerations discussed above. Although these aspects must be taken into account, the most important requirement of a fluorous biphasic solvent system, is that the
solvents are immiscible at some specific temperature range (ideally encompassing room temperature for practical purposes) and become miscible when heat is applied. The maximum limit on the temperature at which miscibility occurs is determined by the boiling point of the solvent with the lowest boiling point, (unless high pressure apparatus is used) since if this temperature is exceeded, the composition of the solvent system will change, resulting in a change in all of the solubility and miscibility parameters discussed above.

In order to try to establish which solvent system(s) would fulfil this demanding criteria, a series of simple tests was carried out. Several common organic solvents were mixed with PP3 (PP3 was the only perfluorinated solvent used in the test for reasons of cost and convenience) and then heated. The temperature at which miscibility occurred was recorded, if this point was reached before either solvent boiled. Each test was performed in a test tube using 5 ml PP3 and 5 ml organic solvent. The results are shown in Table 4.2. It should be noted that miscibility of phases can be achieved with any of the solvents if a 'mixing agent', (such as hexane) which is miscible with both phases at room temperature, is added to the system. However, this potentially leads to transfer of reagents, products and catalyst between the phases (see Section 4.2.3), and so is not ideal. The results in Table 4.2 demonstrate that fluorobenzene and xylene are the only two solvents which display miscibility at a reasonable temperature (between room temperature and the boiling point of the lowest boiling solvent in the mixture). Xylene becomes miscible with PP3 at 100 °C, however, PP3 boils at 102 °C, and, so, this results in a useful, monophasic temperature range of only 2 °C. Fluorobenzene shows a monophasic temperature range of 10 °C and, although by no means perfect, this is the solvent with the most potential for the type of fluorous biphasic catalytic experiments described here. Based on these findings, a further series of catalytic hydrogenation experiments was performed. $P(C_6H_4-p-C_6F_{13})_3$ (7) was the ligand of choice in these reactions, since it had proved to be the most promising fluorous soluble phosphine in the previous set of experiments. The temperature was raised in order to accomodate the
Table 4.2 Temperature of miscibility of PP3 with common organic solvents at ambient pressure

<table>
<thead>
<tr>
<th>Solvent</th>
<th>bp. (°C)(^{(18)})</th>
<th>miscibility temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dichloromethane</td>
<td>40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>chloroform</td>
<td>61</td>
<td>&gt;61</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>81</td>
<td>&gt;81</td>
</tr>
<tr>
<td>toluene</td>
<td>110</td>
<td>&gt;110</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>85</td>
<td>75</td>
</tr>
<tr>
<td>α,α,α-trifluorotoluene</td>
<td>102</td>
<td>&lt;RT</td>
</tr>
<tr>
<td>T.H.F</td>
<td>66</td>
<td>&gt;66</td>
</tr>
<tr>
<td>xylenes</td>
<td>137-144</td>
<td>100</td>
</tr>
<tr>
<td>DMSO</td>
<td>189</td>
<td>&gt;102(^{b})</td>
</tr>
<tr>
<td>hexane</td>
<td>69</td>
<td>&lt;RT</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>35</td>
<td>&lt;RT</td>
</tr>
</tbody>
</table>

\(^{b}\) 102 °C is bp of PP3

higher temperature of miscibility of fluorobenzene relative to the hexane/toluene mix used previously, but the general procedure remained identical to that described in Section 4.2. At this stage, several non-monophasic catalytic runs were also performed for comparative purposes. The results of this series of experiments are shown in Table 4.3. Comparison of the different rates allows the following conclusions to be drawn from this series of experiments:

(i) Comparison of runs 15, 16 and 2 suggests that the fluorobenzene/PP3 solvent system is more useful than the toluene/hexane/PP3 solvent system. The rate of reaction in the former is faster, and atomic absorption studies showed that no rhodium was present in the fluorobenzene after phase separation had occurred. It should be noted here that run 16 was identical to run 2, except that the temperature was raised to 77.5 °C so that a direct comparison with run 15 could be made. This meant that the reaction temperature of run 16 was slightly higher than the boiling point of hexane,
Table 4.3 Rates of hydrogenation of styrene in different solvent systems

<table>
<thead>
<tr>
<th>Run No.</th>
<th>L</th>
<th>Solvent system</th>
<th>Temp (°C)</th>
<th>Rate (mmol/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>toluene/PP3ᵇ</td>
<td>63.5</td>
<td>86</td>
</tr>
<tr>
<td>13</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>PP3ᶜ</td>
<td>63.5</td>
<td>115</td>
</tr>
<tr>
<td>14</td>
<td>PPh₃</td>
<td>fluorobenzene/PP3</td>
<td>77.5</td>
<td>160</td>
</tr>
<tr>
<td>15</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>fluorobenzene/PP3</td>
<td>77.5</td>
<td>146</td>
</tr>
<tr>
<td>16</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>toluene/hexane/PP3</td>
<td>77.5</td>
<td>134</td>
</tr>
<tr>
<td>17</td>
<td>PPh₃</td>
<td>tolueneᵈ</td>
<td>63.5</td>
<td>211</td>
</tr>
<tr>
<td>1ᵇ</td>
<td>PPh₃</td>
<td>toluene/hexane/PP3</td>
<td>63.5</td>
<td>155</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>toluene/hexane/PP3</td>
<td>63.5</td>
<td>128</td>
</tr>
</tbody>
</table>

ᵃ Each run was performed three times and the average rate was calculated. Rates ± 4 mmol/hrᵇ Reaction occurred in biphasic mixture. Solvents did not become miscible ᶜ Reaction performed in PP3 with neat styrene forming organic phase. Products were extracted with toluene upon completion ᵈ Reaction performed in toluene with no fluorous layer ᵉ Runs from Table 4.1 included for comparative purposes

however, the reaction vessel contained the pressure, and no loss of miscibility was observed.

(ii) Comparison of run 17, with runs 1 and 14, suggests that the rate of catalysis when triphenylphosphine is the ligand, is significantly impaired by the presence of a perfluorinated solvent. This means that the rate of reaction when P(C₆H₄-p-C₆F₁₃)₃ (7) is used, is not as favourable, relative to triphenylphosphine, as is suggested by runs 1 and 2. It seems probable that this effect is due to either a lowering of the solubility of the catalytic species in the solvent mixture, or a decrease in the ability of the solvent to co-ordinate to the metal, thus stabilising electron deficient intermediate species (see Section 4.2.4). It may also be possible that the perfluorinated solvent ‘holds’ the H₂ gas in solution more strongly than is the case with most organic solvents, thus retarding the rate of formation of the rhodium dihydride species (see Scheme 4.10) and, hence, slowing the reaction. A similar effect is believed to occur with O₂ gas (see

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Chapter 3) and further evidence supporting this postulation is discussed in section 4.3.1.

(iii) Comparison of runs 12, 13 and 2 suggests that the rate is faster when the reaction occurs in a monophasic system as opposed to a biphasic system. This is presumably due to the fact that in the former, the reaction can occur anywhere in the solution, whereas, in the latter, the reaction can only occur at the phase interface.

4.2.4 Solvent Leaching

As described earlier, if a ‘mixing agent’, such as hexane, is added to the solvent system, it is found to be present in both phases at the end of the reaction. This does not appear to cause any leaching of catalyst into the organic layer, however, it can cause ‘transport’ of significant amounts of other organic moieties (reagent or product) into the fluorous phase and this is undesirable in terms of product removal and catalyst poisoning. If fluorobenzene is used as the organic phase, a ‘mixing agent’ is not required and although solvent leaching still occurs, it is dramatically reduced, and there is no significant change in the volume of either layer upon phase separation. In an effort to establish the extent of solvent leaching in these experiments, gas chromatography was used to measure the mutual solubilities of several of the

<table>
<thead>
<tr>
<th>Solvent/reagent</th>
<th>Solubility (mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP3</td>
<td>in PP3</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.16</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>0.66</td>
</tr>
<tr>
<td>hexane</td>
<td>miscible</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>0.06</td>
</tr>
<tr>
<td>styrene</td>
<td>0.05</td>
</tr>
</tbody>
</table>
solvents and reagents (see Table 4.4). It can be seen from the results in Table 4.4 that, although complete separation cannot be achieved with any of the solvent systems, the fluorobenzene/PP3 biphase is the most satisfactory, showing the least amount of solvent leaching.

4.3 Hydroformylation Reactions Using Complexes of the Type [RhH(CO)L₃]

In order to examine how effectively fluorous biphase conditions could be applied to olefin hydroformylation under relatively harsh reaction conditions, several catalytic experiments were performed using a purpose built hydroformylation rig at BP Chemicals' Salt-End site in Hull. The experiments involved the catalytic hydroformylation of 1-hexene, an industrially useful reaction\(^\text{(19)}\) which has been extensively studied.\(^\text{(20)(21)(22)}\) The mechanism for this catalytic cycle is shown in Scheme 4.11. Unfortunately, time was limited, and, since phosphine (7) had proved to be the most successful ligand in the hydrogenation studies, (see Section 4.2) it was decided to concentrate on this ligand in the hydroformylation reactions. The reactions were performed in a high pressure autoclave with a volume of 300 cm\(^3\), which was attached to a metal rig (see Fig 4.12). This relatively large reaction vessel meant that a large amount (~0.4g) of phosphine was required for each run. Hence, it was necessary to perform the majority of the experiments using a 3:1 phosphine to rhodium ratio. This is not ideal, since larger P:Rh ratios often lead to improved selectivities,\(^\text{(23)}\) however, stocks of (7) were limited and using this low ratio meant that several runs could be performed, and the influence of other variables (i.e. solvent) could also be examined. A further drawback was that the hydroformylation rig was not set up for the use of air-sensitive materials, and consequently, completely anaerobic conditions could not be achieved.

The catalyst precursor [RhH(CO)L₃] was made \textit{in situ} via the addition of [Rh(CO)\(_2\)(acac)] to the phosphine (7) (see Scheme 4.13). The reactions were
performed under 30 bar of syn-gas (CO/H$_2$ in a 50:50 mix) at 150 °C, and were allowed to continue until there was no more uptake of syn-gas, at which point the vessel was allowed to cool to room temperature. Typically, the solvent system consisted of a biphasic of 60 cm$^3$ organic solvent and 60 cm$^3$ perfluorinated solvent, however, it is not known whether these became monophasic during the reaction, since no visual access was possible. The results of the catalytic runs are given in Table 4.5, and the individual reaction conditions are given in Table 4.6.
Scheme 4.13 *In situ* formation of hydroformylation catalyst $[\text{RhH(CO)}(\text{PPh}_3)_3]$ 

$$\text{Rh(CO)}_2(\text{acac}) + 3\text{L} \xrightarrow{\text{H}_2:\text{CO}(g)} \text{RhH(CO)L}_3$$

These results suggest that, as was the case in the hydrogenation experiments, there is a general drop in rate when (7) is used as the phosphine, compared to when triphenylphosphine is used (see runs 1 and 2). This decrease in rate was not, however, observed for other hydroformylation studies (see Section 4.3.1), and so it is believed that catalyst decomposition due to the presence of air in the system was probably responsible for this effect.

The n/i (straight chain to branched chain) ratio of the aldehyde product (see Fig. 4.14) is consistently higher when (7) is used. The two isomers are formed because the 1-hexene can add to the rhodium centre via either the $\alpha$- or the $\beta$-carbon to give two different intermediate species (see Fig. 4.15) and the subsequent carbonyl insertion step gives either the branched or straight chain product, depending on which of these intermediates is formed.
Table 4.5 Rates and selectivities of hydroformylation reactions performed at BP's Hull site

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Selectivity to aldehyde (%)</th>
<th>n/i ratio</th>
<th>rate (mmoll⁻¹hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.9</td>
<td>1.8</td>
<td>340</td>
</tr>
<tr>
<td>2</td>
<td>46.2</td>
<td>1.7</td>
<td>590</td>
</tr>
<tr>
<td>3</td>
<td>17.5</td>
<td>2.2</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>34.4</td>
<td>2.2</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>29.0</td>
<td>2.3</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>11.9</td>
<td>2.3</td>
<td>190</td>
</tr>
<tr>
<td>7</td>
<td>15.2</td>
<td>2.4</td>
<td>140</td>
</tr>
<tr>
<td>8</td>
<td>25.2</td>
<td>2.1</td>
<td>230</td>
</tr>
</tbody>
</table>

*a* Rates are based on consumption of syn-gas and so the formation of by-products such as hexane (via hydrogenation) affect the rate measurement. This is the reason for the discrepancies between the selectivity and rate measurements.

Table 4.6 Reaction conditions for hydroformylation reactions

<table>
<thead>
<tr>
<th>Run No.</th>
<th>L</th>
<th>P:Rh ratio</th>
<th>Solvent system</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>3:1</td>
<td>toluene</td>
</tr>
<tr>
<td>2</td>
<td>PPh₃</td>
<td>3:1</td>
<td>toluene</td>
</tr>
<tr>
<td>3</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>3:1</td>
<td>toluene/PP3</td>
</tr>
<tr>
<td>4</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>10:1</td>
<td>toluene</td>
</tr>
<tr>
<td>5</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>10:1</td>
<td>toluene/PP3</td>
</tr>
<tr>
<td>6</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>3:1</td>
<td>toluene/PP1ᵇ</td>
</tr>
<tr>
<td>7</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>3:1</td>
<td>fluorobenzene/PP1ᵇ</td>
</tr>
<tr>
<td>8</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>3:1</td>
<td>fluorobenzene/PP3</td>
</tr>
</tbody>
</table>

ᵇ PP1 = perfluorohexane
Fig. 4.14 Straight (n) and branched (i) aldehyde products of hydroformylation reactions

The increased steric bulk of phosphine (7) is probably responsible for the increased n/i ratio, relative to triphenylphosphine. This is because when a bulky phosphine is used, the olefin is encouraged to bind to the rhodium via the α-carbon, since this results in the hydrocarbon chain pointing away from the phosphine ligands, rather than towards them, as is the case if the olefin binds via the β-carbon (see Fig. 4.15). As expected, the selectivity to aldehyde formation for (7), was improved when a 10:1 phosphine to
rhodium ratio was employed (24) (see runs 4 and 5), however, even at this relatively high phosphine concentration, the selectivity was still significantly lower than that achieved for triphenylphosphine (see run 2). PP1 (perfluorohexane) was used as the fluorous layer in runs 6 and 7, and this was the first time that this solvent had been tested. The results indicate that it is not as useful a solvent as PP3, with runs 6 and 7 showing a significant drop in selectivity compared to runs 3 and 8. As with the hydrogenation experiments described earlier (see Section 4.2), the best solvent system in terms of rate and selectivity appears to be the fluorobenzene/PP3 mixture.

Upon completion of the reaction, the vessel was allowed to cool, and the phases separated. Unlike the hydrogenation reactions, efficient catalyst/product separation was not achieved and slight colouration, due to the rhodium catalyst, was visible in the organic phase in every case. Atomic absorption spectroscopy confirmed that catalyst leaching had occurred, with between 2 and 8% of the rhodium ending up in the organic phase.

It is likely that this inefficient separation was caused by oxygen entering the system and reacting with the phosphine to give phosphine oxide, since, as mentioned previously, the reactions were not performed anaerobically. Obviously, if the phosphine is oxidised, it will not co-coordinate to the rhodium and will not hold it in the fluorous phase. This postulation is given further credence by the fact that similar experiments recently reported by Horváth et al. did produce good separation, (25) and also by the results of further hydroformylation studies described below.

### 4.3.1 Further Hydroformylation Studies

In order to further examine the potential of phosphine (7) for use in the biphasic hydroformylation of alkenes, a quantity of the ligand was taken to St Andrews University and tested on a purpose built hydroformylation rig. This system consisted of a relatively small autoclave (4 cm³), and the reaction was performed using a 3:1 phosphine to rhodium ratio. The results (26) of this test are shown in Table 4.7.
Table 4.7 Selectivities and n/i ratios of hydroformylation reactions performed at St Andrews University

<table>
<thead>
<tr>
<th>Run No.</th>
<th>L</th>
<th>Selectivity to aldehyde (%)</th>
<th>n/i ratio</th>
<th>rate (mmoll⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh₃ᵇ</td>
<td>99.5</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>PPh₃</td>
<td>99.8</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>P(C₆H₄-p-C₆F₁₃)₃ (7)</td>
<td>98.7</td>
<td>3.7</td>
<td>9.9</td>
</tr>
</tbody>
</table>

ᵃ Runs performed in 2 ml toluene and 2 ml PP3 ᵇ Run performed in 4 ml toluene (no PP3 present)

The solvent system used for both runs consisted of 2 ml PP3 and 2 ml toluene, and 1-hexene was the olefin reagent. The catalytic precursor was the same as that described for the previous set of experiments, (see Section 4.3) and the only major differences in the procedure were that the reactions conditions were less harsh (20 bar syn-gas, 70 °C) and, crucially, the experiments were performed anaerobically. Again, it is not known whether the system was monophasic or biphasic at the time of reaction, since no visual access was possible. As can be seen from the results, the selectivity achieved with (7) is comparable to that achieved with triphenylphosphine and the reaction rate is considerably faster when (7) is the phosphine. The slower rate observed for run 1 (where no fluorous layer was present) also suggests that the addition of a perfluorinated solvent can actually increase the rate of hydroformylation, rather than retard it, as was seen for the hydrogenation experiments (see Section 4.2.4). The separation of the catalyst from the products when (7) was used appeared to be good, with all of the colour (due to the rhodium complex) remaining in the fluorous layer after the reaction, although, no formal measurements were taken. These results suggest that (7) can be used effectively to apply the separation benefits of fluorous biphasic catalysis to alkene hydroformylation. Also, the marked improvement in performance, relative to triphenylphosphine, suggests that the results of the previous set of hydroformylation experiments (see Section 4.3) did not reflect the true potential of this ligand, and this is almost certainly due to the fact that these experiments were
not performed anaerobically. The increase in rate of reaction observed when (7) is the phosphine, is surprising and in direct contrast to the decrease in rate seen for the hydrogenation experiments. It would be expected that the rate determining step (see Scheme 4.11) would occur more slowly when the electron-density on the rhodium is decreased, since this step involves the oxidative addition of H_2 to a rhodium(I) acyl species to give a rhodium(III) dihydride species\(^{(24)}\). It has been noted before, however, that electron-rich alkyl phosphines tend to reduce the rate of this reaction,\(^{(28)}\) possibly because the rhodium(III) dihydride formed during the rate determining step is stabilised too much, and the cycle cannot progress efficiently. It may be that the increased rate observed with (7) is due to the destabilisation of this rhodium(III) dihydride species, which, under the conditions used here, may become the rate determining factor in the cycle. The slight increase in rate observed when a perfluorinated solvent is added to the reaction mixture is, again, in direct contrast to the reduction in rate seen for the hydrogenation reactions (see Section 4.2.4). This rate increase may be due to the fact that the solvent does not play a major role in the reaction as is the case in the hydrogenation cycle, and so, the non-coordinating nature of the fluorous solvent prevents any ‘unwanted’ metal-solvent interactions which could slow the reaction progress. It may also be the case that the H_2 gas is held more firmly in solution by the PP3, than by the toluene (see section 4.2.4). This effect causes an impairment in the rate of the hydrogenations because the reactions were performed at relatively low pressure (1 atmosphere). In the hydroformylation experiments, however, the high pressure of syn-gas employed means that there is always a large excess of gas present, and so this effect is not important in determining the rate. These results must be viewed with a certain amount of caution until a more complete study can be performed, however, the implication is that (7) is a particularly useful phosphine which can be successfully used in place of triphenylphosphine in a number of catalytic systems.
4.4 Conclusions from Catalytic Experiments

It is evident from the hydrogenation experiments carried out, that heterogeneous separation can be applied to homogeneous reactions using the fluorous biphasic approach. It is also evident, however, that the application of the technique to existing catalytic cycles is by no means a simple transition. The choice of ligand is very important in any catalytic system, and this is certainly the case in fluorous biphasic catalysis. The experiments performed here have highlighted three major areas which must be considered when a ligand is modified for use in the fluorous biphasic, and these are discussed below:

(i) The solubility of the ligand must be such that it is able to hold metal complexes in the fluorous phase. It should be noted that, in order to do this, the ligand(s) must be co-ordinated to the metal throughout the reaction, and, so, the mechanism of the reaction is also important here.

(ii) The implications of the ligand modification must be considered in terms of the effect on the electronic and steric properties which substitution with perfluorinated chains is likely to have. In the case of the phosphines developed here, there is significant change, particularly in the electronic profile of the phosphorus, and in the ability of the phosphines to stabilise metal centres. This can be seen in NMR and IR spectroscopy data (see Chapter 3) and, more importantly, in the catalytic activity of the complexes containing these ligands. The steric influence of the chains is also evident in the geometry of certain complexes (see Chapter 3) and, again, in the catalytic experiments, where the n/i ratio is affected.

(iii) The effect on the practical implications of performing the catalysis must be considered. Addition of perfluorinated chains causes the ligands to become more air sensitive, and, in the case of P(C\textsubscript{2}H\textsubscript{4}C\textsubscript{8}F\textsubscript{13})\textsubscript{3} (3), results in the phosphine being difficult to handle (see chapter 2). The molecular mass of the phosphines is also greatly increased, hence, a far greater mass is required than is the case with protio phosphines. All of these factors influence the effectiveness of a given ligand, and all three effects must be thoroughly explored and quantified in order for a successful fluorous biphasic process to be developed. Further, it is evident that the solvent system used is of vital importance, more so than is the case in most homogeneous processes. The
rate of catalysis and, more importantly, the efficiency of separation, have been shown here to be directly influenced by the solvents used. It also seems likely that the relative solubilities of gases in the solvent may be a significant factor in determining the rate of reaction. The high affinity of perfluorinated moieties for O\textsubscript{2} gas has been shown to have a significant influence on the behaviour of certain systems (see Sections 3.6 and 3.7), and there is also some evidence to suggest that this effect may extend to H\textsubscript{2} gas to some degree (see Sections 4.2.4 and 4.3.1). The most useful solvent system described here is the fluorobenzene/PP3 mixture, however, this is unlikely to hold true for all reactions, and it is probable that the solvent requirements will vary depending on the reaction conditions employed. Extensive investigation into this aspect of fluorous biphasic catalysis is needed, if the technique is to develop further.

In summary, the results presented in this thesis, suggest that fluorous biphasic catalysis is a realistic method of combining the key advantages of homogeneous and heterogeneous catalysis. It is not, however, a simple method, and much investigation, particularly into the properties of solvent systems, is required if it is to be developed into a commercially viable technique.
References for Chapter 4


18, 325.


[24] C. Masters, *'Homogeneous Transition-Metal Catalysis; A Gentle Art'*,

[25] I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai and

[26] Personal communication by D. Gudmunsen. Experiments performed by

[27] C. Masters, *'Homogeneous Transition-Metal Catalysis; A Gentle Art'*,

Chapter 5

Experimental

5.1 Analytical Methods

5.1.1 NMR Spectroscopy

All $^1$H, $^{19}$F and $^{31}$P NMR spectra were recorded on a Bruker ARX 250 spectrometer at 250.13, 235.34, or 101.26 MHz respectively, or on a Bruker DRX 400 spectrometer at 400.13, 376.50, or 161.98 MHz respectively. Air-sensitive samples were run in a 5 mm NMR tube fitted with a Youngs' tap to allow removal of air. Samples which were insoluble in deuterated solvents were run in a 4 mm tube which was inserted into a 5 mm tube containing D$_2$O as a lock substance. $^1$H, $^{19}$F and $^{31}$P NMR spectra were referenced externally to TMS, CFCl$_3$ and 85% H$_3$PO$_4$ respectively, using the high frequency positive convention.

5.1.2 Infra-Red Spectroscopy

All Infra-Red spectra were recorded on a Digilab FTS-40 FTIR spectrometer. Spectra recorded as Nujol-mulls were compressed between KBr plates. Spectra recorded in chloroform solution were held in an IR solution cell (vol. 0.2 cm$^3$) with KBr windows. Far IR data (< 500 cm$^{-1}$) were recorded on Nujol-mull samples compressed between polythene plates.
5.1.3 Mass Spectrometry

Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Kratos concept 1H, double focusing, forward geometry mass spectrometer. 3-Nitrobenzyl alcohol was used as the matrix for the FAB spectra.

5.1.4 Elemental Analysis

All elemental analyses were performed by Butterworth Laboratories Ltd.

5.1.5 Gas Chromatography

Gas chromatography was performed on a Pye Unicam G.C.D. Chromatograph. Areas of peaks were calculated by photocopying the trace, cutting out the peak with a scalpel, and then weighing the peaks on a 4 fig. balance. Relative intensities of peaks were calculated by externally referencing against a peak containing a known quantity of substrate.

G.C. analysis of samples from hydroformylation experiments carried out at BP’s Hull site (see section 4.3), was performed by BP’s analytical department, using 3-pentanone as an internal standard.

G.C. analysis of samples from hydroformylation experiments carried out at St Andrews University (see section 4.3.1), was performed at St Andrews University, using n-octanol as an internal standard.

5.1.6 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy was performed on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer with an accuracy of 9.0 mg/l for rhodium.
Three 1000 cm³ ethanol solutions containing 5, 10, and 15 ppm Rh (as [Rh(acac)₃]) respectively were used to calibrate the spectrophotometer. 0.5 g samples were taken from each catalytic run, and these were then made up to a volume of 50 cm³ with ethanol. These samples were then analysed for rhodium content on the calibrated spectrophotometer.

Atomic absorption analysis of samples from hydroformylation experiments carried out at BP's Hull site (see section 4.3), was performed by BP's analytical department, and no details are given here.

5.1.7 X-Ray Crystallography

X-Ray crystallographic data was gathered on a Siemens P4 four circle diffractometer, with a Mo Kα radiation source (λ = 0.7107 Å) (see section 5.6 for full crystallographic data).

5.2 Solvents

Where necessary, solvents were prepared as follows:
Dichloromethane: Refluxed over calcium hydride, under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
Chloroform: Refluxed over calcium hydride under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
Hexane: Refluxed over potassium metal, under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
Toluene: Refluxed over sodium metal under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
Diethyl ether: Refluxed over sodium metal under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
THF: Refluxed over potassium metal under nitrogen for 3 days. Stored under nitrogen in closed ampoule over molecular sieves (4A).
PP3 and PP1: Purchased from F2 chemicals Ltd. Refluxed over calcium hydride under nitrogen for 3 days. Freeze/pump/thawed 3 times to remove any dissolved gas. Stored under nitrogen in closed ampoule over molecular sieves (4A).

Styrene: Transferred into Schlenk immediately after purchase. Stored over molecular sieves (4A), under nitrogen. Degassed before use.

5.3 Starting Materials (Including Known Compounds Synthesised for Comparative Purposes)

Starting materials and previously known compounds which were synthesised here for comparative purposes, were prepared as follows:

cis-[PtCl2(MeCN)2]: Synthesised according to literature prep.(4)
trans-[PdCl2(MeCN)2]: Synthesised according to literature prep.(4)

[RhCl(C2H4)2]: Purchased from Aldrich Chemical Co. Used as purchased. Stored at 253K.

[RhCl(CO)2]: Purchased from Aldrich Chemical Co. Used as purchased. Stored at 270K.

[RhCp*Cl2]: Purchased from Aldrich Chemical Co. Used as purchased.

[IrCl2(cod)]: Synthesised according to literature prep.(5)
cis-[PtCl2(PPh3)2]: Synthesised according to literature prep.(7)
trans-[PtCl2(PPh3)2]: Synthesised according to literature prep.(7)
trans-[RhCl(CO)(PPh3)2]: Synthesised according to literature prep.(9)
trans-[IrCl(CO)(PPh3)2]: Synthesised according to literature prep.(10)
trans-[IrCl(CO)(P{C6H4-p-CF3})2]: Synthesised according to literature prep.(10)

[RhCp*Cl2(PPh3)]: Synthesised according to literature prep.(12)

[CuCl(cod)]: Synthesised according to literature prep.(6)
P{C6H4-p-CF3}3: Synthesised according to literature prep.(11)
P{C6H4-m-CF3}3: Synthesised according to literature prep.(11)

PCl3: Purchased from Aldrich Chemical Co. Distilled before use. Stored under N2.
PCl2Ph: Purchased from Aldrich Chemical Co. Distilled before use. Stored under N2.
PClPh2: Purchased from Lancaster Chemicals. Used as purchased.
PPh₃: Purchased from Aldrich Chemical Co. Used as purchased.
PdCl₃: Purchased from Aldrich Chemical Co. Used as purchased.
Mg turnings: Purchased from Aldrich Chemical Co. Dried for several hours at 80 °C before use.
Cu powder: Purchased from Aldrich Chemical Co. Used as purchased.
IC₂H₄C₆F₁₃: Purchased from Aldrich Chemical Co. Distilled before use.
IC₂H₄C₆F₁₇: Purchased from Aldrich Chemical Co. Distilled before use.
IC₆F₁₃: Purchased from Aldrich Chemical Co. Distilled before use.
4-IC₆H₄Br: Purchased from Aldrich Chemical Co. Used as purchased.
3-IC₆H₄Br: Purchased from Aldrich Chemical Co. Used as purchased.
2-IC₆H₄Br: Purchased from Aldrich Chemical Co. Used as purchased.
4-BrC₆H₄Br: Purchased from Aldrich Chemical Co. Used as purchased.
2,2'-Bipyridine: Purchased from Aldrich Chemical Co. Used as purchased.
1,2-Dibromoethane: Purchased from Aldrich Chemical Co. Used as purchased.
MgSO₄: Purchased from Aldrich Chemical Co. Used as purchased.
CaCl₂: Purchased from Aldrich Chemical Co. Used as purchased.
NH₃Cl: Purchased from Aldrich Chemical Co. Used as purchased.
Alumina: Purchased from Aldrich Chemical Co. Used as purchased.
Alumina (de-activated): Alumina was shaken for 30 mins with 6% water (by weight).
CO gas: Purchased from Aldrich Chemical Co. Used as purchased.

5.4 Experimental Procedures

Much of the chemistry discussed in this thesis involved the use of potentially dangerous substances and/or techniques, and rigorous attention to safety should be employed when performing any of the experiments described here. In particular:
Carbon monoxide gas is highly toxic and extremely flammable. The practise of drying solvents over alkali metals poses a potential fire risk, and great care must be taken to ensure that the solvent is adequately dry before adding the alkali metal (for example by preliminary drying over MgSO₄). Phosphorus trichloride and most other species containing P-Cl bonds are generally highly toxic and corrosive. Great care must be
taken when handling these substances, and none of the reactions described in this thesis should be performed without adequate training and without first undertaking a comprehensive risk assessment of the procedures and substances involved.

5.4.1 Schlenk Line Procedures

Synthetic procedures involving air-sensitive reagents were carried out on a Schlenk line. This consisted of a glass, dual-manifold line, one section of which was connected to a nitrogen source, and the other to a vacuum outlet. The vacuum was provided by an NGN PSR/2 rotary pump, which was protected by a liquid nitrogen trap. The vacuum and nitrogen outlets and all other outlets were isolable by ground glass Interkey or Youngs greaseless taps. Neoprene vacuum tubing was used to connect Schlenk flasks and other apparatus to the line.

5.4.2 Inert Atmosphere Dry-box

Manipulation of air-sensitive materials was carried out in a Faircrest auto-recirculating, positive-pressure dry-box, which provided a nitrogen atmosphere with an oxygen content of less than 5 ppm. The quality of the atmosphere was maintained by circulation through columns of molecular sieves and manganese dioxide, which removed water and oxygen respectively. Manipulations were also carried out in a nitrogen flush-box, which was flushed with N₂ for at least 20 minutes before use. The atmosphere was kept dry by circulation through molecular sieves.

5.4.3 Kinetic Studies on Complexes of the Type trans-[IrCl(CO)L₂]

(a). Method used to determine reaction half-lives (see section 3.7). Trans-[IrCl(CO)L₂], where L is (1-3), (5-7), PPh₃ or P(C₆H₄-p-CF₃)₃, was dissolved in dry chloroform (5 cm³) which had been saturated with O₂ (8.52 μmolcm⁻³ at 20 °C) in a

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closed system. The solution was stirred and O$_2$ was continually bubbled through the solution at room temperature. Samples (0.2 cm$^3$) were removed at regular intervals and the relative ratio of product:reactant measured by IR spectroscopy before the sample was returned to the reaction vessel.

(b). Method used to attempt to determine second order rate constants $k_2$ (see section 3.7). Three oxidation experiments were performed at 296 K with 20x, 15x and 10x molar excesses of oxygen respectively. The initial concentrations of O$_2$ were established by mixing appropriate aliquots of saturated (O$_2$ and N$_2$) solutions of chloroform. Trans-[IrCl(CO)L$_2$], where L is (1-3), (5-7) or PPh$_3$, (6.1 $\mu$mol) were each dissolved in 14 cm$^3$ of chloroform solution in a 10 cm$^3$, closed, round bottomed flask, submersed in a thermostatically controlled water bath set at 23 °C.

Product:reactant ratios were measured using the procedure described above.

5.4.4 Catalytic Reactions

(a). Method used for performing hydrogenation reactions (see section 4.2). The reactions were performed on a purpose built, metal line. This consisted of stainless steel, manually operated, Autoclave Engineers valves (AE-30 series, 316SS) connected via stainless steel, Autoclave Engineers connectors (316SS). One end of the line was connected to an H$_2$ cylinder, whilst the other end was connected to an NGN PSR/2 rotary, vacuum pump. Gas pressure was measured on a Budenberg, Monel tube pressure gauge (max. press. 2 atm) connected to the line via an Autoclave Engineers connector (316SS). The band heater used to heat the reaction mixtures was made by Leicester University Chemistry Dept. Workshop, and was controlled by an RS, K-series thermostat.

Free phosphine (0.125 mmol, or 0.062 mmol in the case of bidentate phosphines) was loaded into a Schlenk flask which was promptly sealed, evacuated and backfilled with N$_2$. Where the phosphine was very air-sensitive (i.e. L = (3), PEt$_3$), this loading procedure was performed in an inert atmosphere. Relevant amounts of dry, degassed PP3, styrene, fluorobenzene, hexane and toluene were then added via a cannular or syringe. The Schlenk flask was then evacuated and backfilled with H$_2$ to a pressure of 1 atm. The mixture was stirred and heated for 15 mins, by which time it
had equilibrated at the reaction temperature (63.5 or 77.5 °C). 2 cm$^3$ of [RhCl(C$_2$H$_4$)$_2$]$_2$ solution (in either toluene or fluorobenzene) was then added. These solutions were prepared to a concentration of 7.86x10$^{-3}$ M, hence, a 2 cm$^3$ aliquot contained exactly 0.0157 mmol, (6.1 mg) of [RhCl(C$_2$H$_4$)$_2$]$_2$. The reactions were allowed to progress for 1 hr after the addition of the catalyst precursor, after which time the reaction flask was removed from the heat and cooled in ice. Samples were taken (1 cm$^3$ from each layer), passed through a 1 cm depth of alumina (in a pasteur pipette) in order to remove any metal, and then analysed using gas chromatography.

(b). Method used for performing hydroformylation reactions at BP’s Hull site (see section 4.3). The reactions were performed on a purpose built, metal, hydroformylation rig, designed and constructed by BP’s technical staff.

The relevant organic solvents and reagents (dry, degassed toluene or fluorobenzene, typically 50 cm$^3$, and 1-hexene, typically 13.4 g, 159.5 mmol) were weighed out and loaded into the autoclave. The free phosphine (0.382 g, 0.314 mmol for 3:1 P to Rh ratio, 1.277 g, 1.050 mmol for 10:1 P to Rh ratio) was then added, and the autoclave tightly shut. The autoclave was then fitted onto the rig, and the stirrer and heater attached. The autoclave was filled with N$_2$ gas to a pressure of 30 bar, stirred for 30 secs, and the N$_2$ was then vented. This process was repeated once. The dry, degassed, perfluorinated solvent (PP3 or PP1, typically 60 cm$^3$) was then added via a cannular which was inserted into the autoclave via the catalyst injector. The catalyst precursor [Rh(CO)$_2$(acac)] (27.0 mg, 0.105 mmol) was dissolved in 5 g toluene or fluorobenzene (whichever was being used as the organic solvent) and loaded into the catalyst injector. The autoclave was filled with syn-gas (H$_2$:CO, 50:50) to a pressure of 30 bar and stirred for 30 secs. The syn-gas was then vented. This process was repeated once. The autoclave was then filled with syn-gas to a pressure of 3 bar and stirred and heated. When the autoclave reached 150 °C (internal temp), the catalyst precursor was injected into the autoclave and the pressure of syn-gas was immediately increased to 30 bar. This pressure was maintained throughout the reaction via a computer controlled, pressure sensitive valve. When the reaction was complete (when gas uptake had ceased), the autoclave was cooled to room temperature, vented and then opened. Samples (5 cm$^3$) were taken from each layer for GC and AA analysis.
(c). Method used for performing hydroformylation reactions at St Andrews University (see section 4.3.1). The reactions were performed on a purpose built, metal, hydroformylation rig, designed and constructed by St Andrews University staff. 

[Rh(CO)$_2$(acac)] (0.001 M) was dissolved in a degassed mixture of toluene (2 cm$^3$) and PP3 (2 cm$^3$) in an autoclave, and the phosphine (0.003 M) added, all under an inert atmosphere. The resulting mixture was heated to 70 °C and the pressure of syn-gas (H$_2$:CO, 50:50) was adjusted to ca. 14bar. Once the temperature had stabilised, 1-hexene (1 cm$^3$) was injected and the pressure of syn-gas was immediately raised to 20 bar. The solution was stirred and the pressure maintained throughout the reaction. The reaction was allowed to proceed for 1 hr and the autoclave was then cooled and vented, and samples of each layer were taken for GC analysis.

5.5 Synthesis of Tertiary Phosphines

5.5.1 Synthesis of PPh$_2$(C$_2$H$_4$C$_6$F$_{13}$) (1)

NB. for $^{19}$F characterisation purposes, the fluorines in the C$_6$F$_{13}$ chains are labelled as follows: R-C$^a$F$_2$-C$^b$F$_2$-C$^c$F$_2$-C$^d$F$_2$-C$^e$F$_2$-C$^f$F$_2$-CF$_3$

A solution of F$_{13}$C$_6$C$_2$H$_4$I (23.7 g, 0.05 mol) in diethyl ether (70 cm$^3$) was added dropwise to magnesium turnings (1.44 g, 0.06 mol) suspended in diethyl ether (15 cm$^3$) with two drops of 1,2-dibromoethane. The mixture was refluxed for 2 hrs, and the solution decanted into a second flask under nitrogen. Diphenylchlorophosphine (11.03 g, 0.05 mol) in diethyl ether (75 cm$^3$) was added dropwise to the solution over 2 hrs, and the mixture was hydrolysed with degassed aqueous ammonium chloride. The organic layer was separated, dried over MgSO$_4$ and the solvent removed in vacuo. The resulting brown solid was dissolved in the minimum amount of diethyl ether, passed quickly through a separating funnel half filled with alumina eluting with light petroleum (bp 40-60 °C) and the solvent removed in vacuo. The resulting white solid was heated under dynamic vacuum (0.01 mm Hg) for 2 hrs to remove all traces of fluorinated starting material, to leave the product as a white solid, mp 42-44 °C (13.3 g, 50%) (Found: C, 43.0; H, 2.4; F, 48.8. C$_{29}$H$_{14}$F$_{13}$P requires C, 45.1; H, 2.6; F,
46.4%); m/z (EI) 532 (M⁺, 100%), 513 (17) and 185 (60); δₚ (CDCl₃) -16.0 (s), δₕ (CDCl₃) 7.0-7.7 (10H, um, C₆H₅), 2.3 (2H, br t, 3JₖH.H 10, PCH₂), 2.1 (2H, um, CH₂CF₂); δₚ (CDCl₃) -81.3 (3F, t, 3JₚF.₁₄, CF₃), -115.0 (2F, um, CCF₂), -123.0 (2F, um, CCF₂), -123.4 (2F, um, CCF₂), -123.6 (2F, um, CCF₂), -126.6 (2F, um, CCF₂).

5.5.2 Synthesis of PPh(C₂H₄C₆F₁₃)₂ (2)

This was prepared similarly to (1), using phenyldichlorophosphine (5.07 g, 0.023 mol) affording the product as a white solid, mp 35-37 °C (10 g, 50%) (Found: C, 32.9; H, 1.5; F, 58.4; C₂₂H₁₃F₂₆P requires C, 32.9; H, 1.6; F, 58.7%); m/z (EI) 802 (M⁺, 75%), 783 (29), 733 (5) and 683 (4); δₚ (CDCl₃) -23.0 (s), δₕ (CDCl₃) 6.9-7.7 (5H, um, C₆H₅), 2.3 (4H, br t, 3JₖH.H 10, PCH₂), 2.1 (4H, um, CH₂CF₂); δₚ (CDCl₃) -81.4 (3F, t, 3JₚF.₁₂, CF₃), -114.9 (2F, um, CCF₂), -122.4 (2F, um, CCF₂), -123.4 (2F, um, CCF₂), -123.7 (2F, um, CCF₂), -126.6 (2F, um, CCF₂).

5.5.3 Synthesis of P(C₂H₄C₆F₁₃)₃ (3)

This was prepared similarly to (1), using phosphorus trichloride (2.06 g, 0.015 mol) affording the product as a colourless solid-liquid, mp 24-26 °C (8.6 g, 50%) (Found: C, 26.7; H, 1.1; P, 2.5. C₂₄H₁₂F₃₉P requires C, 26.9; H, 1.1; P, 2.9%); m/z (EI) 1072 (M⁺, 86%), 1053 (67), 953 (4), 803 (4), 739 (21) and 656 (46); δₚ (CDCl₃) -25.0 (s), δₕ (CDCl₃) 2.3 (6H, br t, 3JₖH.H 10, PCH₂), 2.1 (6H, um, CH₂CF₂); δₚ (CDCl₃) -81.0 (3F, t, 3JₚF.₁₄, CF₃), -114.3 (2F, um, CCF₂), -121.7 (2F, um, CCF₂), -123.0 (2F, um, CCF₂), -123.7 (2F, um, CCF₂), -126.1 (2F, um, CCF₂).

5.5.4 Attempted Synthesis of PPh₂(C₂H₄C₆F₁₇) (4)⁵

The attempted synthesis was performed similarly to (1), using F₁₁C₃H₄I (28.7 g, 0.05 mol). No useful products were detected.
5.5.5 Synthesis of BrC₆H₄-p-C₆F₁₃

A solution of C₆F₁₃I (18.78 g, 0.042 mol) in hexafluorobenzene (40 cm³) was added dropwise over 3 hrs to a stirred mixture of 4-bromiodobenzene (11.91 g, 0.042 mol), copper powder (5.88 g, 0.092 mol), 2,2'-bipyridine (0.46 g, 2.95 mmol), DMSO (40 cm³) and C₆F₆ (60 cm³) at 70 °C. The mixture was subsequently stirred at 70 °C for 72 hrs before it was poured into a beaker containing dichloromethane (100 cm³) and water (100 cm³). After filtering, the organic layer was separated, washed with water (3 x 50 cm³) and dried over CaCl₂ and MgSO₄. After concentration in vacuo to ca. 30 cm³, the crude product was extracted into PP₃ (3 x 20 cm³) and the solvent removed in vacuo. Distillation in vacuo using a Kugelröhr apparatus gave the product as a colourless liquid (bp 80-96 °C/0.02 mmHg) (17.0 g, 89%); m/z (EI) 474/6 (M⁺, 18%), 455/7 (5), 205/7 (100), 126 (30), and 69 (9) (HRMS: Found M⁺,473.9288; C, H, F requires M, 473.9288); δH (CDCl₃) 7.5 (2H, d, 3JH₉ 8.5, 3,5-ArH), 7.7 (2H, d, 3JH₉ 9, 2,6-ArH); δF (CDCl₃) -81.3 (3F, t, 3JFF 10, CF₃), -111.4 (2F, t, 3JFF 14, C(OF₂)), -121.9 (2F, um, C(OF₂)), -122.4 (2F, um, C(OF₂)), -123.3 (2F, um, C(OF₂)), -126.6 (2F, um, C(OF₂)).

5.5.6 Synthesis of PPh₂(C₆H₄-p-C₆F₁₃) (5)

n-Butyl-lithium (8.63 cm³ of 1.6 M solution in hexane) in diethyl ether (25 cm³) was added dropwise over 1 hr to BrC₆H₄-p-C₆F₁₃ (6.57 g, 0.014 mol) in diethyl ether (75 cm³) at -78 °C and then stirred at this temperature for a further 1 hr. Diphenylchlorophosphine (3.04 g, 0.014 mol) in diethyl ether (25 cm³) was then added dropwise, at -78 °C, to the reaction mixture over a further hour before the reaction mixture was allowed to warm slowly to room temperature with continuous stirring over a 12 hr period. The mixture was hydrolysed with 10% aqueous NH₄Cl (50 cm³), the organic layer was collected, washed with water (2 x 30 cm³) and dried over MgSO₄. The organic phase was concentrated in vacuo to ca. 15 cm³ and passed quickly through a separating funnel half filled with alumina using light petroleum (bp
40-60 °C) as eluent. After the solvent was removed, the white solid was heated in a Kugelröhr oven (80 °C, 0.02 mmHg) to remove starting material, yielding the product as a white solid, mp 76-78 °C (5.3 g, 65%) (Found: C, 49.8; H, 2.2; F, 42.6).

$\text{C}_{24}\text{H}_{14}\text{F}_{13}\text{P}$ requires C, 49.7; H, 2.4; F, 42.6%; $m/z$ (EI) 580 (M+, 100%), 311 (3), 241 (1), 203 (23) and 183 (32); $\delta_\text{p}$ (CDCl$_3$) -5.0 (s), $\delta_\text{H}$ (CDCl$_3$) 7.2-7.5 (14H, um, C$_6$H$_5$ and C$_6$H$_4$), $\delta_\text{p}$ (CDCl$_3$) -81.2 (3F, tt, $^3J_{\text{HF}}$ 10, $^4J_{\text{HF}}$ 2, CF$_3$), -111.3 (2F, tm, $^3J_{\text{HF}}$ 15, C$_6$F$_2$), -121.9 (2F, um, C$_6$F$_2$), -122.2 (2F, um, C$_6$F$_2$), -123.2 (2F, um, C$_6$F$_2$), -126.6 (2F, um, C$_6$F$_2$).

5.5.7 Synthesis of $\text{PPh(C}_6\text{H}_4$-p-Cl)$_2$ (6)

This was prepared similarly to (5), using phenyldichlorophosphine (1.16 g, 6.50 mmol) affording the product as a white solid (3.8 g, 60%) (Found: C, 40.1; H, 1.4; F, 53.4. $\text{C}_{30}\text{H}_{13}\text{F}_{26}\text{P}$ requires C, 40.1; H, 1.4; F, 55.0%); $m/z$ (FAB) 898 (M+, 100%), 821 (12), 503 (24) and 426 (4); $\delta_\text{p}$ (CDCl$_3$) -5.4 (s), $\delta_\text{H}$ (CDCl$_3$) 7.2-7.6 (13H, um, C$_6$H$_5$ and C$_6$H$_4$), $\delta_\text{p}$ (CDCl$_3$) -81.3 (3F, t, $^3J_{\text{HF}}$ 12, CF$_3$), -111.4 (2F, um, C$_6$F$_2$), -121.9 (2F, um, C$_6$F$_2$), -122.2 (2F, um, C$_6$F$_2$), -123.2 (2F, um, C$_6$F$_2$), -126.6 (2F, um, C$_6$F$_2$).

5.5.8 Synthesis of $\text{P(C}_6\text{H}_4$-p-Cl)$_3$ (7)

This was prepared similarly to (5), using phosphorus trichloride (0.57 g, 4.20 mmol) affording the product as a white solid, mp 65-67 °C (2.9 g, 50%) (Found: C, 35.8; H, 0.9; P, 2.5. $\text{C}_{36}\text{H}_{12}\text{F}_{39}\text{P}$ requires C, 35.5; H, 1.0; P, 2.5%); $m/z$ (FAB) 1216 (M+, 65%), 895 (39), 821 (25), 521 (10) and 252 (30); $\delta_\text{p}$ (CDCl$_3$) -6.0 (s), $\delta_\text{H}$ (CDCl$_3$) 7.5 (6H, d, $^3J_{\text{HH}}$ 7, 3,5-ArH), 7.3 (6H, vt, $^3J_{\text{HH}}$ ~$^3J_{\text{HP}}$ 7, 2,6-ArH), $\delta_\text{p}$ (CDCl$_3$) -81.4 (3F, t, $^3J_{\text{HF}}$ 12, CF$_3$), -111.6 (2F, t, $^3J_{\text{HF}}$ 14, C$_6$F$_2$), -122.0 (2F, um, C$_6$F$_2$), -122.3 (2F, um, C$_6$F$_2$), -123.4 (2F, um, C$_6$F$_2$), -126.6 (2F, um, C$_6$F$_2$).
5.5.9 Synthesis of BrC₆H₄-m-C₆F₁₃

This was prepared similarly to BrC₆H₄-p-C₆F₁₃ using 3-bromooiodobenzene (11.91 g, 0.042 mol), affording the product as a colourless liquid (bp 80-90 °C, 0.02 mmHg) (8.6 g, 0.018 mol, 45%); m/z (EI) 474/6 (M⁺, 27%), 455/7 (6), 205/7 (100), 126 (37), and 69 (15); δH (CDCl₃) 7.2-7.7 (4H, um, C₆H₄), δF (CDCl₃) -111.2 (2F, t, 3JFF 14, C⁶F₂), -122.0 (2F, um, C⁶F₂), -122.2 (2F, um, C⁵F₂), -123.2 (2F, um, C⁵F₂), -126.6 (2F, um, C⁵F₂).

5.5.10 Synthesis of PPh₂(C₆H₄-m-C₆F₁₃) (8)

n-Butyl-lithium (8.63 cm³ of 1.6 M solution in hexane) in diethyl ether (25 cm³) was added dropwise over 1 hr to BrC₆H₄-m-C₆F₁₃ (6.57 g, 0.014 mol) in diethyl ether (75 cm³) at -78 °C and then stirred at this temperature for a further 1 hr. Diphenylchlorophosphine (3.04 g, 0.014 mol) in diethyl ether (25 cm³) was then added dropwise, at -78 °C, to the reaction mixture over a further hour before the reaction mixture was allowed to warm slowly to room temperature with continuous stirring over a 12 hr period. The mixture was hydrolysed with 10% aqueous NH₄Cl (50 cm³), the organic layer was collected, washed with water (2 x 30 cm³) and dried over MgSO₄. The organic phase was concentrated in vacuo to ca. 15 cm³ and passed quickly through a separating funnel half filled with alumina using light petroleum (bp 40-60 °C) as eluent. After the solvent was removed, the white solid was heated in a Kugelröhr oven (180 °C, 0.05 mmHg) to remove starting material, yielding the product as a white solid (5.1 g, 62%) (Found: C, 49.3; H, 2.3; C₂₃H₁₄F₁₃P requires C, 49.7; H, 2.4); m/z (FAB) 580 (M⁺, 100%), 503 (21); δF (CDCl₃) -4.8 (s), δH (CDCl₃) 7.2-7.6 (14H, um, C₆H₅ and C₆H₄), δF (CDCl₃) -111.1 (3F, t, 3JFF 10, CF₃), -122.0 (2F, um, C⁶F₂), -122.2 (2F, um, C⁵F₂), -123.2 (2F, um, C⁵F₂), -126.7 (2F, um, C⁵F₂).
5.5.11 Synthesis of PPh(C₆H₄-m-C₆F₁₃)₂ (9)

This was prepared similarly to (8), using phenyldichlorophosphine (1.16 g, 6.50 mmol) affording the product as a white solid (3.4 g, 54%) (Found: C, 40.4; H, 1.5; P, 4.6; C₃₀H₁₂F₂₆P requires C, 40.1; H, 1.4; P, 3.5%); m/z (FAB) 898 (M⁺, 56%), 915 (100), 821 (6) and 503 (18); δ₂ (CDCl₃) -5.0 (s), δ₈ (CDCl₃) 7.2-7.6 (13H, um, C₆H₅ and C₆H₆), δ₉ (CDCl₃) -81.2 (3F, t, 3J₉F 10, CF₃), -111.2 (2F, t, 3J₉F C²F₂), -122.0 (2F, um, C²F₂), -122.2 (2F, um, C²F₂), -123.3 (2F, um, C²F₂), -126.7 (2F, um, C²F₂).

5.5.12 Synthesis of P(C₆H₄-m-C₆F₁₃)₃ (10)

This was prepared similarly to (8), using phosphorus trichloride (0.57 g, 4.20 mmol) affording the product as a white solid (4.1 g, 71%) (Found: C, 35.4; H, 1.0; P, 4.4; C₃₆H₁₂F₃₉P requires C, 35.5; H, 1.0; P, 2.5%); m/z (FAB) 1216 (M⁺, 97%), 821 (51), 169 (21), and 69 (100); δ₂ (CDCl₃) -6.0 (s), δ₈ (CDCl₃) 7.2-7.8 (12H, um, C₆H₆), δ₉ (CDCl₃) -81.5 (3F, t, 3J₉F 10, CF₃), -111.7 (2F, t, 3J₉F C²F₂), -122.0 (2F, um, C²F₂), -122.5 (2F, um, C²F₂), -123.4 (2F, um, C²F₂), -126.8 (2F, um, C²F₂).

5.5.13 Attempted Synthesis of BrC₆H₄-p-C₂H₄C₆F₁₃ precursor to (11)(2)

A solution of 1,4-dibromobenzene (11.8 g, 0.05 mol) in diethyl ether (50 cm³) was added dropwise to Mg turnings (1.3 g, 0.053 mol) suspended in diethyl ether (15 cm³), under N₂. The mixture was refluxed for 2 hrs, and the solution then decanted into a second flask. To this solution was added dropwise over 2 hrs a mixture of IC₃H₂C₆F₁₃ (9.48 g, 0.02 mol) and [CuCl(cod)] (4.14 g, 0.02 mol) in diethyl ether (40 cm³). The mixture was then hydrolysed with degassed aqueous ammonium chloride. The organic layer was separated, dried over MgSO₄, and the solvent removed in vacuo. The resulting brownish-white solid was found to be a mixture of products, predominantly unwanted side-products (see section 2.4).
5.5.14 Synthesis of BrC₆H₄-o-C₆F₁₃

This was prepared similarly to BrC₆H₄-p-C₆F₁₃ using 2-bromoiodobenzene (11.91 g, 0.042 mol), affording the product as a colourless liquid (bp 135-140 °C, 0.02 mmHg) (4.8 g, 0.010 mol, 25%); m/z (EI) 474/6 (M⁺, 23%), 205/7 (100), 126 (45), and 69 (16); δₜ (CDCl₃) 7.2-7.8 (4H, um, C₆H₄), δᵣ (CDCl₃) -81.3 (3F, t, 3Jₚ₢ 10, CF₃), -107.0 (2F, t, 3Jₚ₢ 14, C⁶F₂), -120.1 (2F, um, C⁶F₂), -122.2 (2F, um, C⁶F₂), -123.2 (2F, um, C⁶F₂), -126.6 (2F, um, C⁶F₂).

5.5.15 Synthesis of PCl(C₆H₄-o-C₆F₁₃)₂ (12)

This was prepared similarly to (7), using BrC₆H₄-o-C₆F₁₃ (6.57 g, 0.014 mol) affording the product as an oily white solid (1.5 g, 1.30 mmol, 41%); m/z (FAB) 856 (M⁺, 48%), 69 (100); δₜ (CDCl₃) 80.1 (um), δᵣ (CDCl₃) 7.3-7.8 (8H, um, C₆H₄), δᵣ (CDCl₃) -81.5 (3F, t, 3Jₚ₢ 10, CF₃), -98 to -104 (um), -107 to -112 (um), -114.9 (um), -122.5 (2F, um, C⁶F₂), -123.4 (2F, um, C⁶F₂), -126.7 (2F, um, C⁶F₂).

5.6 Synthesis of Metal Complexes

5.6.1 Synthesis of cis-[PtCl₂(PPh₂(C₂H₄C₆F₁₃))₂] (13)

cis-[PtCl₂(MeCN)₂] (0.105 g, 0.30 mmol) and PPh₂(C₂H₄C₆F₁₃) (0.346 g, 0.65 mmol) were stirred for 2 hrs in refluxing, dry dichloromethane (60 cm³) under N₂. The solvent was removed in vacuo and the resulting off-white solid was washed with light petroleum (bp 40-60 °C) (10 cm³). Recrystallisation from dichloromethane/hexane resulted in a fine, white powder (0.31 g, 0.23 mmol, 78%); (Found: C, 35.9; H, 2.1; C₄₀H₂₈F₂₆P₂Cl₂Pt requires C, 36.1; H, 2.1%); m/z (FAB) 1330 [M⁺], 1295 [M⁺-Cl]; δₜ (CD₂Cl₂) 5.8 (s, 1Jₚₚ 3630), δᵣ (CD₂Cl₂) 7.3-7.7 (10H, um, C₆H₅), 2.7 (2H, br t, 3Jₚₚ 10, PCH₂), 2.4 (2H, um, CH₂CF₂), δᵣ (CD₂Cl₂) -81.1 (3F, t, 3Jₚₚ 10, CF₃), -114.7 (2F,
5.6.2 Synthesis of cis-[PtCl₂(PPh{C₂H₄C₆F₁₃})₂] (14)

This was prepared similarly to (13), using PPh(C₂H₄C₆F₁₃)₂ (0.521 g, 0.65 mmol) affording the product as a fine, white powder (0.36 g, 0.20 mmol, 65%);
(Found: C, 27.4; H, 1.5; C₄₄H₂₆F₅₂P₂Cl₂Pt requires C, 28.2; H, 1.5%); m/z (FAB) 1870 [M⁺], 1835 [M⁺-Cl]; δₚ (CD₂Cl₂) -0.6 (s, ¹J_Pp 3518), δₜ (CD₂Cl₂) 7.2-7.5 (5H, um, C₆H₅), 2.5 (4H, br t, ³J_HH 8, PCH₂), 2.1 (4H, um, CH₂CF₂), δₚ (CD₂Cl₂) -80.9 (3F, t, ³J_FF 7, CF₃), -114.6 (2F, t, ³J_FF 14, C₆F₁₃), -121.7 (2F, um, C₆F₁₃), -122.7 (2F, um, C₆F₁₃), -123.1 (2F, um, C₆F₁₃), -126.1 (2F, um, C₆F₁₃), IR (Nujol) v(M-Cl) 291, 317.

5.6.3 Synthesis of trans-[PtCl₂(P{C₂H₄C₆F₁₃})₃] (15)

P{C₂H₄C₆F₁₃}₃ (0.697 g, 0.65 mmol) was dissolved in dry, degassed dichloromethane (30 cm³) under N₂ in a Schlenk flask. To this was added, via a cannular, cis-[PtCl₂(MeCN)₂] (0.105 g, 0.30 mmol) in dry, degassed dichloromethane (30 cm³) and the resulting mixture was stirred at RT for 2 hrs. The solvent was removed in vacuo and the resulting yellow solid was washed with light petroleum (bp 40-60 °C) (10 cm³). Recrystallisation from dichloromethane/hexane resulted in a fine, white powder (0.42 g, 0.18 mmol, 60%); (Found: C, 21.7; H, 1.2; F, 44.9; C₄₈H₃₄F₇₈P₂Cl₂Pt requires C, 23.9; H, 1.0; F, 61.5%); m/z (FAB) 2409 [M⁺⁺]; δₚ (d⁶ acetone) 11.8 (s, ¹J_Pp 2491), δₜ (d⁶ acetone) 2.6 (6H, um PCH₂), 2.3 (6H, um, CH₂CF₂), δₚ (d⁶ acetone) -81.0 (3F, t, ³J_FF 8, CF₃), -114.4 (2F, t, ³J_FF 14, C₆F₁₃), -121.6 (2F, um, C₆F₁₃), -122.6 (2F, um, C₆F₁₃), -122.9 (2F, um, C₆F₁₃), -126.0 (2F, um, C₆F₁₃), IR (Nujol) v(M-Cl) 346-362.

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5.6.4 Synthesis of cis-[PtCl₂(PPh₂C₆H₄-p-C₆F₁₃)₂] (16)

This was prepared similarly to (13), using PPh₂(C₆H₄-p-C₆F₁₃) (0.377 g, 0.65 mmol) affording the product as a fine, white powder (0.36 g, 0.25 mmol, 84%);

(Found: C, 40.6; H, 1.7; F, 33.8; C₆H₂₆F₂₆₂Cl₂Pt requires C, 40.4; H, 2.0; F, 34.6%);

m/z (FAB) 1391 [M⁺-Cl]; δ_H (CDCl₃) 14.6 (s, 1_J_Pp 3653), δ_H (CDCl₃) 7.1-7.6 (14H, um, C₆H₅ and C₆H₄), δ_P (CDCl₃) -81.2 (3F, t, 3_J_Pp 12, CF₃), -111.6 (2F, t, 3_J_Pp 14, C₀F₂), -121.9 (2F, um, C⁸F₂), -122.1 (2F, um, C⁸F₂), -123.2 (2F, um, C⁸F₂), -126.5 (2F, um, C⁷F₂), IR (Nujol) v(M-Cl) 303, 323.

5.6.5 Synthesis of cis-[PtCl₂(PPh(C₆H₄-p-C₆F₁₃)₂)] (17)

This was prepared similarly to (13), using PPh(C₆H₄-p-C₆F₁₃)₂ (0.583 g, 0.65 mmol) affording the product as a fine, white powder (0.47 g, 0.23 mmol, 75%);

(Found: C, 34.7; H, 1.1; P, 2.4; C₆H₂₆F₂₆₂Cl₂Pt requires C, 34.9; H, 1.3; P, 3.0%);

m/z (FAB) 2027 [M⁺-Cl], 1992 [M⁺-2Cl]; δ_H (CDCl₃) 21.2 (1P, s, 1_J_Pp 3646, trans), 15.3 (1P, s, 1_J_Pp 3635, cis), 7.4-7.9 (13H, um, C₆H₅ and C₆H₄), δ_P (CDCl₃) -81.3 (3F, t, 3_J_Pp 9, CF₃), -111.8 (2F, t, 3_J_Pp 14, C₀F₂), -122.0 (4F, um, C⁶F₂ and C⁸F₂), -123.3 (2F, um, C⁸F₂), -126.6 (2F, um, C⁷F₂), IR (Nujol) v(M-Cl) 303, 323.

5.6.6 Synthesis of cis/trans-[PtCl₂(PPh₂C₆H₄-m-C₆F₁₃)₂] (19)

This was prepared similarly to (13), using PPh₂(C₆H₄-m-C₆F₁₃) (0.377 g, 0.65 mmol) affording the product as a fine, white powder (0.21 g, 0.22 mmol, 73%);

(Found: C, 39.1; H, 2.0; C₄H₂₆F₂₆₂Cl₂Pt requires C, 40.4; H, 2.0%); m/z (FAB) 1391 [M⁺-Cl], 1356 [M⁺-2Cl]; δ_H (CDCl₃) 21.2 (1P, s, 1_J_Pp 2646, trans), 15.3 (1P, s, 1_J_Pp 3633, cis), 7.2-7.8 (14H, um, C₆H₅ and C₆H₄), δ_P (CDCl₃) -81.3 (3F, t, 3_J_Pp 10, CF₃), -111.5 (2F, t, 3_J_Pp 14, C₀F₂), -121.8 (2F, um, C⁸F₂), -122.3 (2F, um,
C$_6$F$_2$), -123.2 (2F, um, C$_6$F$_2$), -126.6 (2F, um, C$_6$F$_2$), IR (Nujol) v(M-Cl) 345-353 (trans), 303, 328 (cis).

5.6.7 Synthesis of cis/trans-[PtCl$_2$(PPh$_2$C$_6$H$_4$-m-C$_6$F$_{13}$)$_2$]$_2$ (20)

This was prepared similarly to (13), using PPh$_2$C$_6$H$_4$-m-C$_6$F$_{13}$ (0.583 g, 0.65 mmol) affording the product as a fine, white powder (0.33 g, 0.16 mmol, 53%); (Found: C, 34.2; H, 1.3; C$_6$H$_2$F$_2$P$_2$Cl$_2$Pt requires C, 35.0; H, 1.3%); m/z (FAB) 2062 [M$^+$], 2027 [M$^+$-Cl]; $\delta_p$ (CDCl$_3$) 21.8 (1P, s, $^1$J$_{PP}$ 2696, trans), 15.8 (1P, s, $^1$J$_{PP}$ 3602, cis), $\delta_t$ (CDCl$_3$) 7.2-7.8 (13H, um, C$_6$H$_5$ and C$_6$H$_4$), $\delta_F$ (CDCl$_3$) -81.4 (3F, t, $^3$J$_F$ 10, CF$_3$), -111.8 (2F, t, $^3$J$_F$ 14, C$_6$F$_2$), -121.8 (2F, um, C$_6$F$_2$), -122.3 (2F, um, C$_6$F$_2$), -123.2 (2F, um, C$_6$F$_2$), -126.6 (2F, um, C$_6$F$_2$), IR (Nujol) v(M-Cl) 346-353 (trans), 303, 323 (cis).

5.6.8 Synthesis of trans-[PtCl$_2$(P$_2$C$_6$H$_4$-m-C$_6$F$_{13}$)$_3$]$_2$ (21)

This was prepared similarly to (13), using P$_2$C$_6$H$_4$-m-C$_6$F$_{13}$ (0.790 g, 0.65 mmol) affording the product as a fine, white powder (0.62 g, 0.23 mmol, 78%); (Found: C, 31.8; H, 1.0; C$_7$H$_2$F$_7$P$_2$Cl$_2$Pt requires C, 32.0; H, 0.9%); m/z (FAB) 2663 [M$^+$-Cl]; $\delta_p$ (C$_6$H$_5$CF$_3$ with D$_2$O sleeve) 21.8 (s, $^1$J$_{PP}$ 2723), no $^1$H or $^{19}$F NMR data was obtained since C$_6$H$_5$CF$_3$ was the only suitable solvent and this swamped the respective signals due to the complex in both spectra; IR (Nujol) v(M-Cl) 346-352.

5.6.9 Synthesis of trans-[PdCl$_2$(PPh$_2$C$_3$H$_4$C$_6$F$_{13}$)$_2$] (22)

trans-[PdCl$_2$(MeCN)$_2$] (0.078 g, 0.30 mmol) and PPh$_2$C$_3$H$_4$C$_6$F$_{13}$ (0.346 g, 0.65 mmol) were stirred for 2 hrs in refluxing, dry dichloromethane (60 cm$^3$) under N$_2$. The solvent was removed in vacuo and the resulting yellow solid was washed with light petroleum (bp 40-60 $^\circ$C) (10 cm$^3$). Recrystallisation from boiling hexane resulted
in a fine, yellow powder (3.0 g, 0.24 mmol, 81%); (Found: C, 36.0; H, 2.1; P, 4.0; C_{40}H_{28}F_{26}P_{2}Cl_{2}Pd requires C, 38.7; H, 2.3; P, 5.0%); m/z (FAB) 1170 [M^+-2Cl]; δ_ρ (CDCl_3) 15.6 (s), δ_H (CDCl_3) 7.2-7.7 (10H, um, C_6H_5), 2.7 (2H, br t, 3_J_{HH} 10, PCH_2), 2.4 (2H, um, CH_2CF_2), δ_F (CDCl_3) -81.3 (3F, t, 3_J_{FF} 10, CF_3), -114.8 (2F, t, 3_J_{FF} 14, C^6F_2), -122.4 (2F, um, C^6F_2), -123.4 (2F, um, C^8F_2), -123.6 (2F, um, C^8F_2), -126.6 (2F, um, C^8F_2), IR (Nujol) v(M-Cl) 361.

5.6.10 Synthesis of trans-[PdCl_2(PPh{C_2H_4C_6F_{13}}_2)_2] (23)

This was prepared similarly to (22), using PPh(C_2H_4C_6F_{13})_2 (0.521 g, 0.65 mmol) affording the product as a fine, yellow powder (0.34 g, 0.19 mmol, 63%); (Found: C, 30.0; H, 1.3; C_{44}H_{26}F_{32}P_{2}Cl_{2}Pd requires C, 29.6; H, 1.5%); m/z (FAB) no significant peaks; δ_ρ (d^6 acetone) 15.0 (s), δ_H (d^6 acetone) 7.4-7.9 (5H, um, C_6H_5), 2.6 (4H, br t, 3_J_{HH} 10, PCH_2), 2.2 (2H, um, CH_2CF_2), δ_F (d^6 acetone) -80.9 (3F, t, 3_J_{FF} 10, CF_3), -113.9 (2F, t, 3_J_{FF} 14, C^6F_2), -121.6 (2F, um, C^6F_2), -122.6 (2F, um, C^8F_2), -123.2 (2F, um, C^8F_2), -126.0 (2F, um, C^8F_2), IR (Nujol) v(M-Cl) 360-368.

5.6.11 Synthesis of trans-[PdCl_2(P{C_2H_4C_6F_{13}}_3)_2] (24)

This was prepared similarly to (22), using P(C_2H_4C_6F_{13})_3 (0.700 g, 0.65 mmol) affording the product as a fine, yellow powder (0.42 g, 0.18 mmol, 60%); (Found: C, 24.9; H, 1.0; P, 3.3; C_{48}H_{24}F_{78}P_{2}Cl_{2}Pd requires C, 24.8; H, 1.0; P, 2.7%); m/z (FAB) 2286 [M^+-Cl], 2251 [M^+-2Cl]; δ_ρ (d^6 acetone) 15.8 (s), δ_H (d^6 acetone) 2.7 (6H, br t, 3_J_{HH} 10, PCH_2), 2.4 (2H, um, CH_2CF_2), δ_F (d^6 acetone) -80.9 (3F, t, 3_J_{FF} 10, CF_3), -114.3 (2F, t, 3_J_{FF} 14, C^6F_2), -121.6 (2F, um, C^6F_2), -122.6 (2F, um, C^8F_2), -122.9 (2F, um, C^8F_2), -126.0 (2F, um, C^8F_2), IR (Nujol) v(M-Cl) 359-363.
5.6.12 Synthesis of trans-[PdCl₂(PPh₂C₆H₄-p-C₆F₁₃)₂] (25)

This was prepared similarly to (22), using PPh₂(C₆H₄-p-C₆F₁₃) (0.377 g, 0.65 mmol) affording the product as a fine, yellow powder (0.32 g, 0.24 mmol, 81%); (Found: C, 43.3; H, 2.0; P, 6.0; C₄₃H₂₂F₂₆P₂Cl₂Pd requires C, 43.1; H, 2.1; P, 4.6%); m/z (FAB) 1302 [M⁺-Cl], 1267 [M⁺-2Cl]; δₚ (CDCl₃) 23.6 (s), δₜ (CDCl₃) 7.3-7.8 (14H, um, C₆H₅ and C₆H₄), δₚ (CDCl₃) -81.3 (3F, t, 3ₕF 10, CF₃), -111.5 (2F, t, 3ₕF 12, C₆F₂), -122.0 (4F, um, C₆F₂ and C₅F₂), -123.2 (2F, um, C₆F₂), -126.6 (2F, um, C₅F₂), IR (Nujol) ν(M-Cl) 360-370.

5.6.13 Synthesis of trans-[PdCl₂(PPh(C₆H₄-p-C₆F₁₃)₂)₂] (26)

This was prepared similarly to (22), using PPh(C₆H₄-p-C₆F₁₃)₂ (0.583 g, 0.65 mmol) affording the product as a fine, yellow powder (0.49 g, 0.25 mmol, 82%); (Found: C, 36.5; H, 1.3; P, 3.9; C₉₀H₃₂F₂₆P₂Cl₂Pd requires C, 36.5; H, 1.3; P, 3.1%); m/z (FAB) 1902 [M⁺-2Cl]; δₚ (CDCl₃) 23.5 (s), δₜ (CDCl₃) 7.4-7.9 (13H, um, C₆H₅ and C₆H₄), δₚ (CDCl₃) -81.3 (3F, t, 3ₕF 10, CF₃), -111.7 (2F, t, 3ₕF 14, C₆F₂), -123.0 (4F, um, C₆F₂ and C₅F₂), -123.2 (2F, um, C₆F₂), -126.6 (2F, um, C₅F₂), IR (Nujol) ν(M-Cl) 354-376.

5.6.14 Synthesis of trans-[PdCl₂(P(C₆H₄-p-C₆F₁₃)₃)₂] (27)

This was prepared similarly to (22), using P(C₆H₄-p-C₆F₁₃)₃ (0.790 g, 0.65 mmol) affording the product as a fine, yellow powder (0.63 g, 0.24 mmol, 80%); (Found: C, 33.3; H, 0.8; P, 2.0; C₇₂H₃₆F₅₈P₂Cl₂Pd requires C, 33.1; H, 0.9; P, 2.4%); m/z (FAB) 2538 [M⁺-2Cl]; δₚ (CDCl₃) 23.3 (s), δₜ (CDCl₃) 7.6 (6H, d, 3ₕH 8, m-C₆H₄P), 7.8 (6H, dd, 3ₕH 10, 3ₕH 8 o-C₆H₄P), δₚ (CDCl₃) -81.3 (3F, t, 3ₕF 9, CF₃), -111.8 (2F, td, 3ₕF 14, 4ₕF 2 C₆F₂), -122.0 (4F, um, C₆F₂ and C₅F₂), -123.3 (2F, um, C₅F₂), -126.6 (2F, um, C₅F₂), IR (Nujol) ν(M-Cl) 360-369.
5.6.15 Synthesis of trans-[RhCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (28)

[RhCl(CO)₂]₂ (0.044 g, 0.11 mmol) and PPh₂(C₂H₆C₆F₁₃) (0.250 g, 0.47 mmol) were stirred for 2 hrs in refluxing, dry dichloromethane (60 cm³) under N₂. The solvent was removed in vacuo and the resulting yellow solid was washed with light petroleum (bp 40-60 °C) (10 cm³), yielding a fine, yellow powder (0.14 g, 0.11 mmol, 50%); (Found: C, 40.7; H, 2.4; C₄₁H₉₂F₆₆P₁₀ClORh requires C, 41.5; H, 2.4%); m/z (FAB) 1202 [M*-CO], 1167 [M*-(CO+Cl)]; δₚ (CDCl₃) 24.5 (d, 2J₁=125), δₜ (CDCl₃) 7.2-7.7 (10H, um, C₆H₅), 2.7 (2H, br t, 3J₉H 10, PCH₂), 2.4 (2H, um, CH₂CF₂), δₚ (CDCl₃) -81.3 (3F, t, 2J₁=10, CF₃), -114.9 (2F, t, 3J₁=14, C₁F₂), -122.4 (2F, um, C₈F₂), -123.4 (2F, um, C₈F₂), -123.6 (2F, um, C₈F₂), -126.6 (2F, um, C₈F₂), IR (Nujol) ν(C=O) 1981.

5.6.16 Synthesis of trans-[RhCl(CO)(PPh{C₂H₄C₆F₁₃}₂)₂] (29)

This was prepared similarly to (28), using PPh(C₂H₄C₆F₁₃)₂ (0.377 g, 0.47 mmol) affording the product as a slightly sticky, yellow powder (0.33 g, 0.19 mmol, 84%); (Found: C, 30.7; H, 1.5; P, 4.5; C₄₁H₉₂F₆₆P₁₀ClORh requires C, 30.5; H, 1.5; P, 3.5%); m/z (FAB) 1770 [M⁺], 1742 [M⁺-CO]; δₚ (CDCl₃) 22.8 (d, 2J₁=125), δₜ (CDCl₃) 7.4-7.9 (5H, um, C₆H₅), 2.7 (4H, um, PCH₂), 2.3 (4H, um, CH₂CF₂), δₚ (CDCl₃) -81.4 (3F, t, 2J₁=10, CF₃), -114.9 (2F, t, 3J₁=14, C₁F₂), -122.5 (2F, um, C₈F₂), -123.5 (2F, um, C₈F₂), -123.8 (2F, um, C₈F₂), -126.7 (2F, um, C₈F₂); IR (Nujol) ν(C=O) 1983.

5.6.17 Synthesis of trans-[RhCl(CO)(P{C₂H₄C₆F₁₃}₃)₂] (30)

P₃C₆H₄C₆F₁₃)₂ (0.504 g, 0.47 mmol) was dissolved in dry, degassed dichloromethane (30 cm³) under N₂ in a Schlenk flask. To this was added, via a cannular, [RhCl(CO)₂]₂ (0.044 g, 0.11 mmol) in dry, degassed dichloromethane (30
cm$^3$) and the resulting mixture was stirred at RT for 2 hrs. The solvent was removed in vacuo and the resulting brown, sticky solid was triturated in hexane (10 cm$^3$) for 30 mins, resulting in a fine, light brown powder (0.28 g, 0.12 mmol, 55%); (Found: C, 25.4; H, 1.0; F, 63.1; C$_{49}$H$_{24}$F$_{78}$P$_{2}$ClORh requires C, 25.5; H, 1.0; F, 64.1%); m/z (FAB) 2311 [M$^+$]; $\delta_r$ (d$^6$ acetone) 22.8 (d, $^2$J$_{PP}$ 122), $\delta_H$ (d$^6$ acetone) 3.2 (6H, um, PCH$_2$), 2.6 (6H, um, CH$_2$CF$_2$), $\delta_F$ (d$^6$ acetone) -80.4 (3F, t, $^3$J$_{PF}$ 11, CF$_3$), -114.4 (2F, t, $^3$J$_{FF}$ 14, C$_6$F$_2$), -121.7 (2F, um, C$_6$F$_2$), -122.7 (2F, um, C$_5$F$_2$), -123.0 (2F, um, C$_5$F$_2$), -126.1 (2F, um, C$_7$F$_2$); IR (Nujol) v(C=O) 1992.

5.6.18 Synthesis of trans-[RhCl(CO)(PPh$_2$(C$_6$H$_4$-p-C$_6$F$_3$)$_2$)] (31)

This was prepared similarly to (28), using PPh$_2$(C$_6$H$_4$-p-C$_6$F$_3$) (0.273 g, 0.47 mmol) affording the product as a yellow powder (0.19 g, 0.14 mmol, 66%); (Found: C, 44.3; H, 2.0; F, 21.5; C$_{49}$H$_{28}$F$_{26}$P$_2$ClORh requires C, 44.3; H, 2.1; F, 37.2%); m/z (FAB) 1298 [M$^+$-CO], 1263 [M$^+$-(CO+Cl)]; $\delta_r$ (CDCl$_3$) (233K) 30.0 (d, $^2$J$_{RP}$ 127), $\delta_H$ (CDCl$_3$) 7.2-7.8 (14H, um, C$_6$H$_5$ and C$_6$H$_4$), $\delta_F$ (CDCl$_3$) -81.3 (3F, t, $^3$J$_{PF}$ 10, CF$_3$), -111.4 (2F, t, $^3$J$_{FF}$ 14, C$_6$F$_2$), -121.8 (2F, um, C$_6$F$_2$), -122.1 (2F, um, C$_5$F$_2$), -123.2 (2F, um, C$_5$F$_2$), -126.5 (2F, um, C$_7$F$_2$); IR (Nujol) v(C=O) 1982.

5.6.19 Synthesis of trans-[RhCl(CO)(PPh(C$_6$H$_4$-p-C$_6$F$_3$)$_2$)$_2$] (32)

This was prepared similarly to (28), using PPh(C$_6$H$_4$-p-C$_6$F$_3$)$_2$ (0.422 g, 0.47 mmol) affording the product as a yellow powder (0.32 g, 0.17 mmol, 75%); (Found: C, 37.7; H, 1.2; P, 3.4; C$_{61}$H$_{28}$F$_{52}$P$_2$ClORh requires C, 37.3; H, 1.3; P, 3.2%); m/z (FAB) 1934 [M$^+$-CO], 1899 [M$^+$-(CO+Cl)]; $\delta_r$ (CDCl$_3$) 29.9 (d, $^2$J$_{RP}$ 129), $\delta_H$ (CDCl$_3$) 7.3-7.9 (13H, um, C$_6$H$_5$ and C$_6$H$_4$), $\delta_F$ (CDCl$_3$) -81.3 (3F, t, $^3$J$_{PF}$ 11, CF$_3$), -111.6 (2F, t, $^3$J$_{FF}$ 14, C$_6$F$_2$), -121.9 (2F, um, C$_6$F$_2$), -122.1 (2F, um, C$_5$F$_2$), -123.2 (2F, um, C$_5$F$_2$), -126.6 (2F, um, C$_7$F$_2$); IR (Nujol) v(C=O) 1983.

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5.6.20 Synthesis of trans-[RhCl(CO)(P{C₆H₄-p-C₆F₁₃})₂] (33)

This was prepared similarly to (28), using P(C₆H₄-p-C₆F₁₃)₃ (0.571 g, 0.47 mmol) affording the product as a yellow powder (0.42 g, 0.16 mmol, 73%); (Found: C, 33.5; H, 0.9; P, 2.5; C₇₃H₂₆F₁₈P₂ClO₇Rh requires C, 33.7; H, 0.9; P, 2.4%); m/z (FAB) 2535 [M⁺-(CO+Cl)]; δₚ (CDCl₃) 30.0 (d, 2Jₚₚ 131), δₜ (CDCl₃) 7.7 (6H, d, 3Jₜₜ 9, m-C₆H₄P), 7.8 (6H, t, 3Jₜₜ 9 = 3J_{Hₚ} 9, o-C₆H₄P), δₚ (CDCl₃) -81.4 (3F, t, 3J_{FF} 10, CF₃), -111.7 (2F, t, 3J_{FF} 14, C₆F₂), -121.9 (2F, um, C₆F₂), -122.1 (2F, um, C₆F₂), -123.2 (2F, um, C₆F₂), -126.5 (2F, um, C₆F₂); IR (Nujol) ν(C=O) 1993.

5.6.21 Synthesis of trans-[RhCl(CO)(PPh₂C₆H₄-m-C₆F₁₃)] (34)

This was prepared similarly to (28), using PPh₂(C₆H₄-m-C₆F₁₃) (0.273 g, 0.47 mmol) affording the product as a yellow powder (0.23 g, 0.17 mmol, 78%); (Found: C, 45.0; H, 2.1; P, 5.6; C₉₇H₂₈F₂₆P₂ClO₇Rh requires C, 44.3; H, 2.1; P, 4.7%); m/z (FAB) 1298 [M⁺-CO], 1263 [M⁺-(CO+Cl)]; δₚ (CDCl₃) (233K) 29.7 (d, 2Jₚₚ 128), δₜ (CDCl₃) 7.2-7.9 (14H, um, C₆H₅ and C₆F₅), δₚ (CDCl₃) -81.3 (3F, t, 3J_{FF} 10, CF₃), -111.4 (2F, t, 3J_{FF} 14, C₆F₂), -121.8 (2F, um, C₆F₂), -122.4 (2F, um, C₆F₂), -123.2 (2F, um, C₆F₂), -126.6 (2F, um, C₆F₂); IR (Nujol) ν(C=O) 1980.

5.6.22 Synthesis of trans-[RhCl(CO)(PPh{C₆H₄-m-C₆F₁₃})₂] (35)

This was prepared similarly to (28), using PPh(C₆H₄-m-C₆F₁₃)₂ (0.422 g, 0.47 mmol) affording the product as a yellow powder (0.30 g, 0.15 mmol, 69%); (Found: C, 37.6; H, 1.4; P, 3.6; C₉₃H₂₆F₅₂P₂ClO₇Rh requires C, 37.3; H, 1.3; P, 3.2%); m/z (FAB) 1934 [M⁺-CO], 1899 [M⁺-(CO+Cl)]; δₚ (CDCl₃) 29.9 (d, 2Jₚₚ 129), δₜ (CDCl₃) 7.3-7.8 (13H, um, C₆H₅ and C₆H₄), δₚ (CDCl₃) -81.3 (3F, t, 3J_{FF} 11, CF₃), -111.5 (2F, t, 3J_{FF} 14, C₆F₂), -121.9 (2F, um, C₆F₂), -122.2 (2F, um, C₆F₂), -123.3 (2F, um, C₆F₂), -126.7 (2F, um, C₆F₂); IR (Nujol) ν(C=O) 1984.
5.6.23 Synthesis of trans-[RhCl(CO)(P[C₆H₄-m-C₆F₁₃]₃)]₂ (36)

This was prepared similarly to (28), using P(C₆H₄-m-C₆F₁₃)₃ (0.571 g, 0.47 mmol) affording the product as a yellow powder (0.45 g, 0.17 mmol, 78%); (Found: C, 33.8; H, 1.0; P, 2.5; C₇₃H₅₄F₇₈P₂ClO₇Rh requires C, 33.7; H, 0.9; P, 2.4%); m/z (FAB) 2570 [M⁺-CO], 2535 [M⁺-(CO+Cl)]; δₚ (d⁶ acetone) 31.1 (d, 2JHP 132), δₜ (d⁶ acetone) -81.2 (3F, t, 3JFF 10, CF₃), -111.8 (2F, t, 3JFF 14, C⁶F₃), -121.2 (2F, um, C⁶F₃), -121.8 (2F, um, C⁵F₂), -122.8 (2F, um, C⁵F₂), -126.1 (2F, um, C⁴F₂); IR (Nujol) ν(C=O) 1992.

5.6.24 Synthesis of [RhCp*Cl₂(PPh₂C₂H₄C₆F₁₃)] (37)

[RhCp*Cl₂]₂ (0.77 g, 0.12 mmol) and PPh₂(C₂H₄C₆F₁₃) (0.133 g, 0.25 mmol) were stirred in refluxing ethanol (60 cm³) under N₂ for 1 hr. The solvent was removed in vacuo and the resulting reddish solid was washed with hexane (10 cm³) yielding a fine, red/orange powder (0.15 g, 0.18 mmol, 73%); (Found: C, 42.9; H, 3.6; F, 26.1; C₃₀H₂₉F₁₃PCl₂Rh requires C, 42.8; H, 3.4; F, 29.4%); m/z (FAB) 841 [M⁺], 805 [M⁺-Cl]; δₚ (CDCl₃) 27.3 (d, 3JHP 144), δₜ (CDCl₃) 7.2-7.7 (10H, um, C₆H₅), 2.8 (2H, br t, 3JHH 12, PCH₂), 2.3 (2H, um, CH₂CF₂), 1.4 (15H, d, 3JHP 4, Cp*), δₚ (CDCl₃) -81.3 (3F, t, 3JFF 10, CF₃), -115.1 (2F, t, 3JFF 14, C₆F₃), -122.5 (2F, um, C⁶F₃), -123.4 (2F, um, C⁵F₂), -124.0 (2F, um, C⁴F₂), -126.7 (2F, um, C³F₂).

5.6.25 Synthesis of [RhCp*Cl₂(PPh(C₂H₄C₆F₁₃))₂] (38)

This was prepared similarly to (37), using PPh(C₂H₄C₆F₁₃)₂ (0.200 g, 0.25 mmol) affording the product as a red/orange powder (0.23 g, 0.21 mmol, 88%); (Found: C, 35.2; H, 2.4; P, 3.1; C₆₃H₁₁₈F₁₇₂PCl₂Rh requires C, 34.6; H, 2.5; P, 2.8%); m/z (FAB) 1076 [M⁺-Cl]; δₚ (CDCl₃) 18.3 (d, 2JHP 146), δₜ (CDCl₃) 7.5-8.1 (5H, um, C₆H₅), 2.8 (4H, um, PCH₂), 2.2 (4H, um, CH₂CF₂), 1.4 (15H, d, 3JHP 4, Cp*), δₚ
5.6.26 Synthesis of \([\text{Rh}Cp^*\text{Cl}_2(\text{P}[\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}])])\) (39)

\(\text{P}[\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}]\), (0.268 g, 0.25 mmol) was dissolved in degassed ethanol (30 cm\(^3\)) under N\(_2\) in a Schlenk flask. To this was added, via a cannular, \([\text{Rh}Cp^*\text{Cl}_2]\) (0.77 g, 0.12 mmol) in degassed ethanol (30 cm\(^3\)) and the resulting mixture was stirred at RT for 1 hr. The solvent was removed in vacuo and the resulting red solid was recrystallised from dichloromethane/hexane resulting in a fine, red/orange powder (0.25 g, 0.18 mmol, 75%); (Found: C, 30.2; H, 2.0; P, 2.3; \(\text{C}_{34}\text{H}_{27}\text{F}_{39}\)\(\text{PCl}_{2}\)\(\text{Rh}\) requires C, 29.5; H, 2.0; P, 2.3%); \(m/z\) (FAB) 1346 [M\(^+\)-Cl]; \(\delta_{\text{p}}\) (CDCl\(_3\)) 19.4 (d, \(^2J_{\text{RhP}}\) 147), \(\delta_{\text{H}}\) (CDCl\(_3\)) 2.8 (6H, um, PCH\(_2\)), 2.4 (6H, um, \(\text{CH}_2\text{CF}_2\)), 1.5 (15H, d, \(^3J_{\text{HP}}\) 4, \(\text{Cp}^*\)), \(\delta_{\text{F}}\) (CDCl\(_3\)) -81.3 (3F, t, \(^3J_{\text{FF}}\) 10, CF\(_3\)), -115.3 (2F, t, \(^3J_{\text{FF}}\) 14, \(\text{C}^\text{F}_2\)), -122.3 (2F, um, \(\text{C}^\text{F}_2\)), -123.3 (2F, um, \(\text{C}^\text{F}_2\)), -123.6 (2F, um, \(\text{C}^\text{F}_2\)), -126.6 (2F, um, \(\text{C}^\text{F}_2\)).

5.6.27 Synthesis of \([\text{Rh}Cp^*\text{Cl}_2(\text{PPh}_2\text{C}_6\text{H}_4-\text{p-C}_6\text{F}_{13})])\) (40)

This was prepared similarly to (37), using \(\text{PPh}_2\text{C}_6\text{H}_4-\text{p-C}_6\text{F}_{13}\) (0.145 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.16 g, 0.18 mmol, 75%); (Found: C, 45.9; H, 3.3; P, 4.3; \(\text{C}_{34}\text{H}_{27}\text{F}_{39}\)\(\text{PCl}_{2}\)\(\text{Rh}\) requires C, 45.9; H, 3.3; P, 3.5%); \(m/z\) (FAB) 853 [M\(^+\)-Cl], 818 [M\(^+\)-2Cl]; \(\delta_{\text{p}}\) (CDCl\(_3\)) 29.9 (d, \(^2J_{\text{RhP}}\) 146), \(\delta_{\text{H}}\) (CDCl\(_3\)) 7.3-8.0 (14H, um, \(\text{C}_6\text{H}_5\) and \(\text{C}_6\text{H}_4\)), 1.4 (15H, d, \(^3J_{\text{HP}}\) 4.5, \(\text{Cp}^*\)), \(\delta_{\text{F}}\) (CDCl\(_3\)) -81.2 (3F, t, \(^3J_{\text{FF}}\) 10, CF\(_3\)), -111.5 (2F, t, \(^3J_{\text{FF}}\) 14, \(\text{C}^\text{F}_2\)), -121.9 (2F, um, \(\text{C}^\text{F}_2\)), -122.1 (2F, um, \(\text{C}^\text{F}_2\)), -123.2 (2F, um, \(\text{C}^\text{F}_2\)), -126.5 (2F, um, \(\text{C}^\text{F}_2\)).
5.6.28 Synthesis of [RhCp*Cl2(PPh{C6H4-p-C6 F13}2)] (41)

This was prepared similarly to (37), using PPh(C6H4-p-C6F13)2 (0.225 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.22 g, 0.18 mmol, 76%); (Found: C, 40.2; H, 2.2; P, 2.2; C40H26F26PCl2Rh requires C, 39.8; H, 2.3; P, 2.6%); m/z (FAB) 1206 [M+], 1171 [M+-Cl], 1136 [M*-2Cl]; δp (CDCl3) 30.2 (d, JRhP 146), δh (CDCl3) 7.3-8.0 (13H, um, C6H5 and C6H4), 1.4 (15H, d, JHP 4, Cp*), δf (CDCl3) -81.2 (3F, t, JFF 10, CF3), -111.6 (2F, t, JFF 14, C6F2), -121.8 (2F, um, C6F2), -122.0 (2F, um, C5F2), -123.2 (2F, um, C4F2), -126.6 (2F, um, C5F2).

5.6.29 Synthesis of [RhCp*Cl2(P{C6H4-p-C6F13})3] (42)

This was prepared similarly to (37), using P(C6H4-p-C6F13)3 (0.304 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.24 g, 0.16 mmol, 65%); (Found: C, 37.1; H, 1.9; F, 45.5; C48H27F39PCl2Rh requires C, 36.2; H, 1.8; F, 48.5%); m/z (FAB) 1524 [M+], 1489 [M*-Cl], 1454 [M*-2Cl]; δp (CD2Cl2) 29.6 (d, JRhP 147), δh (CD2Cl2) 8.0 (6H, t, JHP = 9, o-C6H4P), 7.6 (6H, um, m-C6H4P), 1.2 (15H, d, JHP 4, Cp*), δf (CD2Cl2) -81.6 (3F, t, JFF 10, CF3), -111.8 (2F, t, JFF 14, C6F2), -122.0 (2F, um, C6F2), -122.3 (2F, um, C5F2), -123.4 (2F, um, C4F2), -126.8 (2F, um, C3F2).

5.6.30 Synthesis of [RhCp*Cl2(PPPh2C6H4-m-C6F13)] (43)

This was prepared similarly to (37), using PPh2C6H4-m-C6F13 (0.145 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.14 g, 0.16 mmol, 67%); (Found: C, 45.7; H, 3.1; C34H25F13PCl2Rh requires C, 45.9; H, 3.3%); m/z (FAB) 853 [M*-Cl], 818 [M*-2Cl]; δp (CDCl3) 30.6 (d, JRhP 144), δh (CDCl3) 7.3-8.0 (14H, um, C6H5 and C6H4),

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1.4 (15H, d, 3J_Hp 4, Cp*), δ_F (CDCl_3) -81.7 (3F, t, 3J_FF 10, CF_3), -111.3 (2F, t, 3J_FF 14, C^aF_2), -122.0 (2F, um, C^bF_2), -122.4 (2F, um, C^cF_2), -123.3 (2F, um, C^dF_2), -126.7 (2F, um, C^eF_2).

5.6.31 Synthesis of [RhCp*Cl_2(PPh(C_6H_4-m-C_6F_13)_2)] (44)

This was prepared similarly to (37), using PPh(C_6H_4-m-C_6F_13)_2 (0.225 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.23 g, 0.18 mmol, 78%); (Found: C, 40.2; H, 2.4; P, 2.2; C_{40}H_{28}F_{26}PCl_2Rh requires C, 39.8; H, 2.3; P, 2.6%); m/z (FAB) 1206 [M^+], 1171 [M^+-Cl], 1136 [M^+-2Cl]; δ_F (CDCl_3) 30.8 (d, 2J_Rhp 147), δ_H (CDCl_3) 7.2-8.0 (13H, um, C_6H_5 and C_6H_4), 1.4 (15H, d, 3J_Hp 4, Cp*), δ_F (CDCl_3) -81.3 (3F, t, 3J_FF 10, CF_3), -111.6 (2F, t, 3J_FF 14, C^aF_2), -121.9 (2F, um, C^bF_2), -122.1 (2F, um, C^cF_2), -123.4 (2F, um, C^dF_2), -126.7 (2F, um, C^eF_2).

5.6.32 Synthesis of [RhCp*Cl_2(P(C_6H_4-m-C_6F_13)_3)] (45)

This was prepared similarly to (37), using P(C_6H_4-m-C_6F_13)_3 (0.304 g, 0.25 mmol) and the resulting red solid was recrystallised from dichloromethane/hexane affording a fine, red/orange powder (0.30 g, 0.20 mmol, 83%); (Found: C, 36.4; H, 1.8; P, 3.3; C_{46}H_{27}F_{39}PCl_2Rh requires C, 36.2; H, 1.8; P, 2.0%); m/z (FAB) 1489 [M^+-Cl], 1454 [M^+-2Cl]; δ_F (CDCl_3) 30.6 (d, 2J_Rhp 147), δ_H (CDCl_3) 7.4-7.9 (12H, um, C_6H_5 and C_6H_4), 1.4 (15H, d, 3J_Hp 4, Cp*), δ_F (CDCl_3) -81.5 (3F, t, 3J_FF 10, CF_3), -111.5 (2F, t, 3J_FF 14, C^aF_2), -122.1 (2F, um, C^bF_2), -122.3 (2F, um, C^cF_2), -123.5 (2F, um, C^dF_2), -126.8 (2F, um, C^eF_2).
5.6.33 General Procedure for the Attempted Synthesis of Complexes of the Type 
[RhClL₃] (L = phosphine)

(a). Initial procedure. When L = (1), (2), (5) or (6): Phosphine (0.80 mmol) was dissolved in dry, degassed CH₂Cl₂ (10 cm³), in a Schlenk flask under N₂. To this was added, via a syringe, [RhCl(C₂H₄)₂]₂ (0.051 g, 0.130 mmol) dissolved in dry, degassed CH₂Cl₂ (10 cm³), all under N₂. The resulting mixture was stirred for 30 mins at RT under N₂, and the solvent was then removed in vacuo, yielding in all cases a brown, sticky solid. ³¹P NMR spectroscopy showed no useful products (see section 3.6). When L = (3), (7) or (10). Exactly as above, but phosphine was dissolved in dry, degassed PP₃, rather than CH₂Cl₂.

(b). Test tube Synthesis. When L = (1), (2), (5), (6), P(C₆H₄-p-CF₃)₃ or P(C₆H₄-m-CF₃)₃: Phosphine (0.16 mmol) was dissolved in dry, degassed CDCl₃ (1 cm³) in a Schlenk flask under N₂. To this was added, via a syringe, [RhCl(C₂H₄)₂]₂ (0.010 g, 0.027 mmol) in dry, degassed CDCl₃ (1 cm³). A sample of the resulting mixture was immediately transferred, under N₂, to an NMR tube fitted with a Youngs tap, and NMR spectra were taken after ca. 10 mins (see Table 3.7 for NMR data). When L = (3), (7) or (10): Phosphine (0.16 mmol) was dissolved in dry, degassed PP₃ (1 cm³) in a Schlenk flask under N₂. To this was added, via a syringe, [RhCl(C₂H₄)₂]₂ (0.010 g, 0.027 mmol) dissolved in dry, degassed CH₂Cl₂ (1 cm³), all under N₂. The resulting mixture was stirred for 2 mins, after which time all of the colour due to the rhodium had transferred into the lower, fluorous phase. A sample of the fluorous phase was transferred, under N₂, to an NMR tube fitted with a Youngs tap, and NMR spectra were taken after ca. 10 mins, using a D₂O sleeve (see section 5.1.1) (see Table 3.7 for NMR data).

(c). Synthesis of [RhCl(P{C₆H₄-p-C₆F₁₃}₃)] using freeze, pump, thaw cycles to degas phosphine: Exactly as above, but phosphine in PP₃ solution was given three freeze, pump, thaw cycles (frozen with liquid nitrogen, pumped for 10 mins each cycle) and [RhCl(C₂H₄)₂]₂ CH₂Cl₂ solution was given one freeze, pump, thaw cycle (same conditions as phosphine), before the solutions were added together. The resulting mixture was given one freeze, pump, thaw cycle (same conditions as phosphine),
before a sample was taken from the fluorous layer for NMR analysis (see section 3.6.5).

5.6.34 Synthesis of trans-[IrCl(CO)(PPh₂C₂H₄C₆F₁₃)₂] (49)

[IrCl(cod)]₂ (0.074 g, 0.11 mmol) and PPh₂C₂H₄C₆F₁₃ (0.234 g, 0.44 mmol) were stirred in dry, degassed THF (20 cm³) under CO gas (1 atm) for 30 mins at RT. The solvent was removed in vacuo. Dry, degassed hexane (5 cm³) was then added, and the resulting yellow slurry was stirred for 5 mins to give a yellow solid which was quickly filtered in air, and dried in vacuo, yielding a fine yellow powder (0.18 g, 0.14 mmol, 63%); (Found: C, 36.2; H, 1.9; P, 5.2; C₄₁H₂₈F₂₆P₂ClIr requires C, 37.3; H, 2.1; P, 4.7%); m/z (FAB) 1320 [MH⁺]; δₚ (CDCl₃) 19.4 (s), δₜ (CDCl₃) 7.3-7.9 (10H, um, C₆H₅), 3.0 (2H, br t, 3JHH 10, PCH₂), 2.5 (2H, um, CH₂CF₂), δₚ (CDCl₃) -81.3 (3F, t, 3JFF 10, CF₃), -114.6 (2F, t, 3JFF 14, C₆F₂), -122.3 (2F, um, C₆F₂), -123.5 (2F, um, C₅F₂), -123.9 (2F, um, C₄F₂), -126.7 (2F, um, C₃F₂), IR (Nujol) v(C=O) 1954.

5.6.35 Synthesis of trans-[IrCl(CO)(PPh(C₂H₄C₆F₁₃)₂)] (50)

This was prepared similarly to (49), using PPh(C₂H₄C₆F₁₃)₂ (0.353 g, 0.44 mmol) affording the product as a fine, yellow powder (0.24 g, 0.13 mmol, 58%); (Found: C, 28.3; H, 1.2; P, 3.3; C₄₅H₂₆F₅₂P₂ClIr requires C, 29.0; H, 1.4; P, 3.3%); m/z (FAB) 1860 [MH⁺]; δₚ (CDCl₃) 18.3 (s), δₜ (CDCl₃) 7.5-7.9 (5H, um, C₆H₅), 2.9 (4H, um, PCH₂), 2.6 (4H, um, CH₂CF₂), δₚ (CDCl₃) -81.3 (3F, t, 3JFF 10, CF₃), -114.9 (2F, t, 3JFF 14, C₆F₂), -122.5 (2F, um, C₅F₂), -123.5 (2F, um, C₄F₂), -123.8 (2F, um, C₃F₂), -126.7 (2F, um, C₂F₂), IR (Nujol) v(C=O) 1973.
5.6.36 Synthesis of trans-[IrCl(CO)(P(C₂H₄C₆F₁₃)₃)] (51)

This was prepared similarly to (49), using P(C₂H₆C₆F₁₃)₃ (0.472 g, 0.44 mmol) affording the product as a fine, yellow powder (0.35 g, 0.15 mmol, 66%); (Found: C, 24.5; H, 0.9; P, 2.5; C₄₀H₂₄F₇₈P₂ClOIr requires C, 24.5; H, 1.0; P, 2.6%); m/z (FAB) 2400 [MH⁺]; δₚ (d⁶ acetone) 18.5 (s), δₚ (d⁶ acetone) 2.7 (6H, um, PCH₂), 2.5 (6H, um, CH₂CF₂), δₚ (d⁶ acetone) -81.0 (3F, t, 3J₉F 10, CF₃), -114.4 (2F, t, 3J₉F 14, C₆F₂), -121.7 (2F, um, C₆F₂), -122.6 (2F, um, C₆F₂), -123.0 (2F, um, C₆F₂), -126.1 (2F, um, C₂F₂), IR (Nujol) ν(C≡O) 1977.

5.6.37 Synthesis of trans-[IrCl(CO)(PPh₂C₆H₄-p-C₆F₁₃)] (52)

This was prepared similarly to (49), using PPh₂C₆H₄-p-C₆F₁₃ (0.255 g, 0.44 mmol) affording the product as a fine, yellow powder (0.22 g, 0.15 mmol, 70%); (Found: C, 40.6; H, 1.9; P, 4.8; C₄₀H₂₈F₉₆P₂ClOIr requires C, 40.6; H, 1.9; P, 4.3%); m/z (FAB) 1416 [MH⁺], 1381 [MH⁺-Cl]; δₚ (CDCl₃) 24.5 (s), δₚ (CDCl₃) 7.2-7.8 (14H, um, C₆H₅ and C₆H₄), δₚ (CDCl₃) -81.2 (3F, t, 3J₉F 10, CF₃), -111.5 (2F, t, 3J₉F 14, C₆F₂), -121.9 (2F, um, C₆F₂), -122.1 (2F, um, C₆F₂), -123.2 (2F, um, C₂F₂), -126.5 (2F, um, C₂F₂), IR (Nujol) ν(C≡O) 1959.

5.6.38 Synthesis of trans-[IrCl(CO)(PPh(C₆H₄-p-C₆F₁₃)] (53)

This was prepared similarly to (49), using PPh(C₆H₄-p-C₆F₁₃) (0.395 g, 0.44 mmol) affording the product as a fine, yellow powder (0.34 g, 0.17 mmol, 76%); (Found: C, 36.3; H, 0.9; P, 3.0; C₆₀H₂₆F₅₂P₂ClOIr requires C, 35.7; H, 1.3; P, 3.0%); m/z (FAB) 1988 [M⁺-(CO+Cl)]; δₚ (CDCl₃) 24.7 (s), δₚ (CDCl₃) 7.3-7.9 (13H, um, C₆H₅ and C₆H₄), δₚ (CDCl₃) -81.2 (3F, t, 3J₉F 10, CF₃), -111.6 (2F, t, 3J₉F 14, C₆F₂), -121.8 (2F, um, C₆F₂), -122.1 (2F, um, C₆F₂), -123.2 (2F, um, C₂F₂), -126.6 (2F, um, C₂F₂), IR (Nujol) ν(C≡O) 1972.
5.6.39 Synthesis of trans-[IrCl(CO)(P\{C_{6}H_{4}-p-C_{6}F_{13}\})_{2}] (54)

This was prepared similarly to (49), using P\{C_{6}H_{4}-p-C_{6}F_{13}\} (0.535 g, 0.44 mmol) affording the product as a fine, yellow powder (0.35 g, 0.13 mmol, 60%); (Found: C, 32.4; H, 0.9; P, 3.8; C_{73}H_{24}F_{78}P_{2}ClOIr requires C, 32.6; H, 0.9; P, 2.3%); m/z (FAB) 2688 [MH^{+}]; δ\(_{r}\) (CDCl\(_{3}\)) 24.7 (s), δ\(_{HH}\) (CDCl\(_{3}\)) 7.8 (6H, dd, \(^{3}J_{HH}\) 9.5, \(^{3}J_{HF}\) 8, o-\(C_{6}H_{4}P\)), 7.6 (6H, d, \(^{3}J_{HH}\) 8, m-\(C_{6}H_{4}P\)), δ\(_{r}\) (CDCl\(_{3}\)) -81.3 (3F, t, \(^{3}J_{FF}\) 10, CF\(_{3}\)), -111.7 (2F, t, \(^{3}J_{FF}\) 14, C\(^{6}\)F\(_{2}\)), -121.9 (2F, um, C\(^{6}\)F\(_{2}\)), -122.1 (2F, um, C\(^{5}\)F\(_{2}\)), -123.3 (2F, um, C\(^{5}\)F\(_{2}\)), -126.6 (2F, um, C\(^{4}\)F\(_{2}\)), IR (Nujol) ν(C=O) 1979.
### 5.7 Crystal Structure Data

Table 5.1 Crystal data and structure refinement for O=P(C₆H₄-m-C₆F₁₃)₃ (oxide of (12)) and Cl-P(C₆H₄-o-C₆F₁₃)₂ (12).

<table>
<thead>
<tr>
<th></th>
<th>O=P(C₆H₄-m-C₆F₁₃)₃</th>
<th>Cl-P(C₆H₄-o-C₆F₁₃)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₁₅H₂₆F₃₉OP</td>
<td>C₂₄H₄ClF₂₆P</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1232.43</td>
<td>856.72</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>190(2) K</td>
<td>190(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/c</td>
<td>P T</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td>(a = 6.318(5) \text{ Å})</td>
<td>(a = 9.275(4) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(b = 14.95(2) \text{ Å})</td>
<td>(b = 11.9448(12) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(c = 45.28(5) \text{ Å})</td>
<td>(c = 13.797(5) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 91.65(2)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(\beta = 92.35(10)^\circ)</td>
<td>(\beta = 108.86(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(\gamma = 90^\circ)</td>
<td>(\gamma = 90.85(3)^\circ)</td>
</tr>
<tr>
<td><strong>Volume, (z)</strong></td>
<td>4274(7) Å³, 4</td>
<td>1445.4(8) Å³, 2</td>
</tr>
<tr>
<td><strong>Density (calculated)</strong></td>
<td>1.916 Mg/m³</td>
<td>1.968 Mg/m³</td>
</tr>
<tr>
<td><strong>Adsorption coefficient</strong></td>
<td>0.269 mm⁻¹</td>
<td>0.375 mm⁻¹</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>2408</td>
<td>836</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.51 x 0.16 x 0.13 mm</td>
<td>0.32 x 0.11 x 0.10 mm</td>
</tr>
<tr>
<td><strong>(\theta) range for data collection</strong></td>
<td>2.63 to 25.03°</td>
<td>2.85 to 25.00°</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>(-1 \leq h \leq 7, -1 \leq k \leq 17, -53 \leq l \leq 53)</td>
<td>(0 \leq h \leq 11, -14 \leq k \leq 14, -16 \leq l \leq 15)</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>8462</td>
<td>5330</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>7094 ((R_{int} = 0.0558))</td>
<td>4995 ((R_{int} = 0.0350))</td>
</tr>
<tr>
<td><strong>Adsorption correction</strong></td>
<td>Not applied</td>
<td>Not applied</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least squares on (F^2)</td>
<td>Full-matrix least squares on (F^2)</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>7086 / 0 / 432</td>
<td>4989 / 30 / 469</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on (F^2)</strong></td>
<td>1.025</td>
<td>1.011</td>
</tr>
<tr>
<td><strong>Final R indices ([I&gt;2\sigma(I)])</strong></td>
<td>(R1 = 0.2443, wR2 = 0.5667)</td>
<td>(R1 = 0.0880, wR2 = 0.2384)</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>(R1 = 0.3906, wR2 = 0.7264)</td>
<td>(R1 = 0.1453, wR2 = 0.3069)</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>2.768 and -2.338 eÅ⁻³</td>
<td>1.491 and -0.736 eÅ⁻³</td>
</tr>
</tbody>
</table>
Table 5.2 Crystal data and structure refinement for cis-[PtCl₂(PPh₂C₂H₄C₆F₁₃)₂] (13) and trans-[RhCl(CO)(P{C₂H₄C₆F₁₃}₃)₂] (30).

<table>
<thead>
<tr>
<th></th>
<th>cis-[PtCl₂(PPh₂C₂H₄C₆F₁₃)₂]</th>
<th>trans-[RhCl(CO)(P{C₂H₄C₆F₁₃}₃)₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄₅H₃₄Cl₂F₂₆OP₂Pt</td>
<td>C₄₉H₅₂ClF₇₈OP₂Rh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1388.63</td>
<td>2310.98</td>
</tr>
<tr>
<td>Temperature</td>
<td>190(2) K</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P 1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.084(2) Å</td>
<td>a = 11.205(9) Å</td>
</tr>
<tr>
<td></td>
<td>b = 10.666(2) Å</td>
<td>b = 15.062(4) Å</td>
</tr>
<tr>
<td></td>
<td>c = 26.487(5) Å</td>
<td>c = 22.506(5) Å</td>
</tr>
<tr>
<td></td>
<td>α = 88.79(1)°</td>
<td>α = 84.70(2)°</td>
</tr>
<tr>
<td></td>
<td>β = 79.25(1)°</td>
<td>β = 86.23(4)°</td>
</tr>
<tr>
<td></td>
<td>γ = 66.28(1)°</td>
<td>γ = 79.93(2)°</td>
</tr>
<tr>
<td>Volume, z</td>
<td>2557.8(8) Å³</td>
<td>3719(3) Å³</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.803 Mg/m³</td>
<td>2.064 Mg/m³</td>
</tr>
<tr>
<td>Adsorption coefficient</td>
<td>3.039 mm⁻¹</td>
<td>0.544 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1352</td>
<td>2240</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.48 × 0.40 × 0.08 mm</td>
<td>0.71 × 0.40 × 0.12 mm</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>2.98 to 24.98°</td>
<td>2.53 to 25.00°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, 0 ≤ l ≤ 31</td>
<td>-1 ≤ h ≤ 12, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>8530</td>
<td>13090</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8530 (Rint = 0.000)</td>
<td>11855 (Rint = 0.0188)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>8530 / 0 / 527</td>
<td>11855 / 0 / 1093</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.065</td>
<td>0.992</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R₁ = 0.0882, W = 0.2423</td>
<td>R₁ = 0.0560, W R² = 0.1287</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1098, W = 0.2717</td>
<td>R₁ = 0.0858, W R² = 0.1486</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>3.149 and -3.533 eÅ⁻³</td>
<td>1.686 and -0.571 eÅ⁻³</td>
</tr>
</tbody>
</table>
References for Chapter 5


Appendix

EXAFS Data For Selected Complexes

Table A.1 contains iridium and platinum L\text{III}-edge and rhodium and palladium K-edge EXAFS data for some of the complexes described in this thesis. Iridium and platinum L\text{III}-edge EXAFS data were collected at the Daresbury synchrotron radiation source operating at 2 GeV (ca. $3.2 \times 10^{10}$ J) with an average ring current of 190 mA on station 7.1 using an order sorting Si(111) monochromator, offset to 50\% of the rocking curve for harmonic rejection. Rhodium and palladium K-edge EXAFS data were collected under the same conditions on station 9.2 using a double crystal Si(220) monochromator, offset to 50\% of the rocking curve for harmonic rejection. The EXAFS data were collected in transmission mode (except where stated) on solid samples diluted with boron nitride and mounted between Sellotape strips in 1 mm aluminium spacers. The EXAFS data treatment utilised the programs EX\textsuperscript{(1)} and EXCURVE 92.\textsuperscript{(2)} Several data sets were collected for each sample, and averaged to improve the signal to noise ratio.

Table A.1  Iridium and platinum L\textsubscript{III}-edge and rhodium and palladium K-edge EXAFS data for selected complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(M-C)</th>
<th>2σ\textsuperscript{2c}</th>
<th>d(M-P)</th>
<th>2σ\textsuperscript{2c}</th>
<th>d(M-Cl)</th>
<th>2σ\textsuperscript{2c}</th>
<th>d(M...O)</th>
<th>2σ\textsuperscript{2c}</th>
<th>EF\textsuperscript{d}</th>
<th>F.I\textsuperscript{e}</th>
<th>R\textsuperscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(16)</td>
<td>—</td>
<td>—</td>
<td>2.281(6)</td>
<td>0.006(1)</td>
<td>2.342(4)</td>
<td>0.008(2)</td>
<td>—</td>
<td>—</td>
<td>-13.95(62)</td>
<td>2.50</td>
<td>19.48</td>
</tr>
<tr>
<td>(24)\textsuperscript{g}</td>
<td>—</td>
<td>—</td>
<td>2.344(9)</td>
<td>0.006(1)</td>
<td>2.275(13)</td>
<td>0.011(2)</td>
<td>—</td>
<td>—</td>
<td>-4.35(76)</td>
<td>3.05</td>
<td>19.74</td>
</tr>
<tr>
<td>(25)</td>
<td>—</td>
<td>—</td>
<td>2.362(5)</td>
<td>0.003(1)</td>
<td>2.270(3)</td>
<td>0.003(1)</td>
<td>—</td>
<td>—</td>
<td>-3.63(32)</td>
<td>0.84</td>
<td>10.90</td>
</tr>
<tr>
<td>(26)</td>
<td>—</td>
<td>—</td>
<td>2.359(4)</td>
<td>0.002(1)</td>
<td>2.261(3)</td>
<td>0.002(1)</td>
<td>—</td>
<td>—</td>
<td>-4.21(33)</td>
<td>0.93</td>
<td>11.47</td>
</tr>
<tr>
<td>(27)</td>
<td>—</td>
<td>—</td>
<td>2.268(5)</td>
<td>0.006(1)</td>
<td>2.350(5)</td>
<td>0.006(1)</td>
<td>—</td>
<td>—</td>
<td>-13.66(44)</td>
<td>3.18</td>
<td>22.87</td>
</tr>
<tr>
<td>(28)</td>
<td>1.788(2)</td>
<td>0.001(1)</td>
<td>2.350(1)\textsuperscript{b}</td>
<td>0.006(1)</td>
<td>—</td>
<td>—</td>
<td>2.936(3)</td>
<td>0.006(1)</td>
<td>0.17(24)</td>
<td>1.46</td>
<td>15.53</td>
</tr>
<tr>
<td>(30)</td>
<td>1.799(3)</td>
<td>0.001(1)</td>
<td>2.326(2)\textsuperscript{b}</td>
<td>0.008(1)</td>
<td>—</td>
<td>—</td>
<td>2.928(4)</td>
<td>0.004(1)</td>
<td>-1.75(32)</td>
<td>3.17</td>
<td>22.11</td>
</tr>
<tr>
<td>(31)</td>
<td>1.806(3)</td>
<td>0.002(1)</td>
<td>2.346(2)\textsuperscript{b}</td>
<td>0.009(1)</td>
<td>—</td>
<td>—</td>
<td>2.932(4)</td>
<td>0.006(1)</td>
<td>-0.42(29)</td>
<td>2.60</td>
<td>18.42</td>
</tr>
<tr>
<td>(32)</td>
<td>1.825(4)</td>
<td>0.002(1)</td>
<td>2.348(2)\textsuperscript{b}</td>
<td>0.005(1)</td>
<td>—</td>
<td>—</td>
<td>2.952(4)</td>
<td>0.006(1)</td>
<td>-1.82(43)</td>
<td>2.91</td>
<td>19.90</td>
</tr>
<tr>
<td>(33)</td>
<td>1.813(3)</td>
<td>0.001(1)</td>
<td>2.343(2)\textsuperscript{b}</td>
<td>0.010(1)</td>
<td>—</td>
<td>—</td>
<td>2.944(14)</td>
<td>0.009(1)</td>
<td>1.32(37)</td>
<td>2.62</td>
<td>17.98</td>
</tr>
<tr>
<td>(36)\textsuperscript{g}</td>
<td>1.804(5)</td>
<td>0.005(1)</td>
<td>2.344(2)\textsuperscript{b}</td>
<td>0.009(1)</td>
<td>—</td>
<td>—</td>
<td>2.932(6)</td>
<td>0.007(1)</td>
<td>0.30(39)</td>
<td>3.93</td>
<td>22.44</td>
</tr>
<tr>
<td>(52)</td>
<td>1.802(6)</td>
<td>0.013(1)</td>
<td>2.343(1)\textsuperscript{b}</td>
<td>0.009(1)</td>
<td>—</td>
<td>—</td>
<td>2.934(2)</td>
<td>0.001(1)</td>
<td>-7.55(24)</td>
<td>2.80</td>
<td>20.45</td>
</tr>
<tr>
<td>(53)</td>
<td>1.820(5)</td>
<td>0.004(1)</td>
<td>2.338(1)\textsuperscript{b}</td>
<td>0.006(1)</td>
<td>—</td>
<td>—</td>
<td>2.944(5)</td>
<td>0.004(1)</td>
<td>-8.76(26)</td>
<td>3.45</td>
<td>22.16</td>
</tr>
<tr>
<td>(54)</td>
<td>1.816(5)</td>
<td>0.002(1)</td>
<td>2.337(2)\textsuperscript{b}</td>
<td>0.006(1)</td>
<td>—</td>
<td>—</td>
<td>2.944(5)</td>
<td>0.004(1)</td>
<td>-9.26(34)</td>
<td>3.31</td>
<td>22.19</td>
</tr>
</tbody>
</table>
Standard deviations in parentheses. The systematic errors in bond distances arising from the data collection and analysis procedures are ca. ± 0.02 Å for the first co-
ordination shells and ca. ± 0.04 Å for subsequent shells. b Rh-P and Rh-Cl bonds could not be distinguished. The fit given here is for a single shell of 3 P atoms. c Debye-
Waller factor d Fermi energy e Fit index = Σᵢ[(χᵢ - χᵢₑ)kᵢ]²
f R-factor = [(χᵢ - χᵢₑ)kᵢdk/χᵢₑkᵢdk] × 100% g Data collected in fluorescence mode